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Ultrafast chemical interface scattering as an additional decay channel for nascent nonthermal electrons in small metal nanoparticles

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The use of 4.2 nm gold nanoparticles wrapped in an adsorbates shell and embedded in a TiO_2 metal oxide matrix gives the opportunity to investigate ultrafast electron-electron scattering dynamics in combination with electronic surface phenomena via the surface plasmon lifetimes. These gold nanoparticles (NPs) exhibit a large nonclassical broadening of the surface plasmon band, which is attributed to a chemical interface damping. The acceleration of the loss of surface plasmon phase coherence indicates that the energy and the momentum of the collective electrons can be dissipated into electronic affinity levels of adsorbates. As a result of the preparation process, gold NPs are wrapped in a shell of sulfate compounds that gives rise to a large density of interfacial molecules confined between Au and TiO_2 , as revealed by Fourier-transform-infrared spectroscopy. A detailed analysis of the transient absorption spectra obtained by broadband femtosecond transient absorption spectroscopy allows separating electron-electron and electron-phonon interaction. Internal thermalization times (electron-electron scattering) are determined by probing the decay of nascent nonthermal electrons (NNEs) and the build-up of the Fermi–Dirac electron distribution, giving time constants of 540 to 760 fs at 0.42 and 0.34 eV from the Fermi level, respectively. Comparison with literature data reveals that lifetimes of NNEs measured for these small gold NPs are more than four times longer than for silver NPs with similar sizes. The surprisingly long internal thermalization time is attributed to an additional decay mechanism (besides the classical e-e scattering) for the energy loss of NNEs, identified as the *ultrafast chemical interface scattering* process. NNEs experience an inelastic resonant scattering process into unoccupied electronic states of adsorbates, that directly act as an efficient heat bath, via the excitation of molecular vibrational modes. The two-temperature model is no longer valid for this system because of (i) the temporal overlap between the internal and external thermalization process is very important; (ii) a part of the photonic energy is directly transferred toward the adsorbates (not among "cold" conduction band electrons). These findings have important consequence for femtochemistry on metal surfaces since they show that reactions can be initiated by nascent nonthermal electrons (as photoexcited, out of a Fermi-Dirac distribution) besides of the hot electron gas. © 2004 American Institute of Physics. [DOI: 10.1063/1.1710856]

I. INTRODUCTION

The investigation of the interaction of femtosecond laser pulses with metal nanoparticles (NPs) is a growing field due to the unique possibility of creating a far from equilibrium situation in systems that can exhibit unexpected properties.¹⁻⁴ Indeed, metal NPs are fascinating materials due to their particular electronic, physical and chemical characteristics, which are strongly dependent on size.⁵ The understanding of the dynamics of nonequilibrium electrons in correlation with surface phenomena is important since nonequilibrium hot electrons drive the most basic reactions such as desorption, dissociation^{6,7} or motion of molecules⁸ on surfaces. Therefore, interactions of nonequilibrium hot electron with interfaces control fundamental aspects of surface chemistry and electrochemical processes.⁹ Since small NPs show very high surface-to-volume ratios, they are excellent candidates for the study of ultrafast electronic surface or interface phenomena. Furthermore, the knowledge of the impact of restricted environment or confinement on ultrafast electronic properties of metal nanoparticles is of fundamental importance for the development of nanoscale devices via the tailoring of the properties as a function of size.

Information on the initial stage of ultrafast electron dynamics can be found for clusters of a few atoms.^{10–12} Due to the lack of information on nonthermal electron dynamics in small metal NPs (~5 nm) and in order to improve our knowledge about the role of the interfaces on nonthermal electron dynamics, it is proposed here to make use of 4.2 nm gold NPs (with a very high surface to volume ratio) embedded in a TiO₂ matrix. Upon the absorption of femtosecond pulses by a metal, bulk phenomena such as hot electron transport need to be taken into account while surface effects can be neglected because of the very low surface-to-volume ratio. On the opposite, electron transport phenomena are nonexistent for small NPs but size and surface effects be-

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FIG. 1. (A) Schematic diagram for the different steps of photonic energy redistribution in metal NPs upon the absorption of a femtosecond laser pulse. Nascent nonthermal electrons created quasi-instantaneously redistribute the energy among free electrons via e-e scattering and leads the formation of a hot electron gas with a well-defined electronic temperature, this process (P_I) is called internal thermalization and corresponds to the build-up of a Fermi-Dirac electron distribution. During the external thermalization (P_{II}), the hot electron gas transfers the energy to the lattice through electron-phonon coupling. Finally, the last process includes the heat dissipation toward the surrounding medium via phonon-medium coupling (P_{III}). (B) Simplified picture of the electronic and the lattice temperature change as a function of time according to the two-temperature model (TTM). Within this picture, the build-up of the Fermi electron distribution (P_I) takes place quasi-instantaneously (less than 100 fs). For gold NPs, the energy exchange between the hot electron gas and the lattice occurs in a few ps whereas the heat dissipation process occurs in hundreds of picosecond.

come predominant. Two main parameters are responsible for the interesting properties of NPs: (i) the electron quantum confinement effects, (ii) the surface or interface effects.¹³ The latter factor may dominate the size effect and govern the emergence of novel behaviors for nascent nonthermal electrons when the surface is in close contact with the embedding matrix or is modified by adsorbed molecules. The surface atom to bulk atom ratio is very high for small NPs. Typically, for 4 nm gold NPs about 35% of all the atoms are surface atoms.

The classical picture for the different events of electron relaxation occurring in metal NPs following an external optical energy input involves three main processes which are illustrated in Fig. 1(A): (i) electron–electron scattering (P_I), (ii) electron–phonon interaction (P_{II}), and (iii) phonon–medium interaction (P_{III}).¹⁴ The perturbation of the electron distribution by the absorption of a femtosecond laser pulse by a metal leads to the creation of nascent nonthermal electrons (NNE). In bulk metal, NNEs redistribute the energy by e-e scattering with free "cold" conduction band electrons giving rise to a well-defined temperature for the hot electron

gas (internal thermalization process P_I). The electronic temperature rise varies from hundreds to thousands of Kelvin depending on the laser pump fluence. The hot electron gas transfers the energy into the lattice by electron-phonon interaction until the electronic gas and the lattice are in thermal equilibrium (external thermalization process P_{II}). In the last step, the phonons transfer their energy to the surrounding medium (heat dissipation process P_{III}) within hundreds of picoseconds. Figure 1(B) is a schematic illustration of the two-temperature model (TTM) and shows the electronic (T_{ρ}) and the lattice temperature (T_1) as a function of time. This model,¹⁵ which is commonly employed to describe the energy exchange rate between the hot electron gas and the lattice with two dependent differential equations,¹⁶⁻¹⁹ is based on the assumption that the internal thermalization (P_I) is quasiinstantaneous (less than the duration of the laser pulse).

The combination of femtosecond light pulses with the pump-probe technique is a powerful tool to study nonequilibrium electron dynamics in real time. Investigations on nascent nonthermal electron dynamics performed on bulk metals by two-photon photoemission spectroscopy (2-PPE)^{20,21} or second harmonic generation (SHG)²² with highly excited electrons reported thermalization times of less than 200 fs. Most of the ultrafast transient absorption spectroscopic studies on metal NPs have been dedicated to the electronphonon interaction dynamics and the parameters affecting the energy exchange between the hot electron gas and the lattice have been recently studied in some details.¹⁻³ In contrast, the internal thermalization process has been neglected due to the belief that this process occurs on time scales shorter than the duration of the laser pulse. However, recent studies limited to metal films have shown that the internal thermalization process can be long lived under specific conditions.²³⁻²⁵ Due to the difficulties to investigate the internal thermalization process by femtosecond transient absorption spectroscopy, there are very few reports for e-escattering times using this technique for noble metal NPs despite of the importance of this fundamental phenomenon.²⁶

Ultrafast events that mark the earliest stage in the dynamics of perturbed electrons far from equilibrium, the build-up of a Fermi-Dirac electron distribution, can be classically described as follows: Immediately after the photoexcitation of the metal NPs, the electron distribution corresponds to the spectral shape of the femtosecond laser pulse. In this unique state of matter far from equilibrium, the electron distribution (called nascent nonthermal electron) is different from a Fermi-Dirac distribution. The energetic relaxation of a nascent nonthermal electron occurs by collision with a "cold" conduction band electron of the Fermi sphere creating two secondary hot electrons. Electron-electron scattering is a many-body process in which two electrons collide. During this process the total energy or the number of electrons does not change but individual electron energy is randomized by multiple collision events. On the average, nonthermal electrons will lose more than 50% of their energies after each inelastic collision in exciting electrons below the Fermi level (E_F) into unoccupied states above it.²⁷ Therefore, the hot electron avalanche process leads to the complete thermalization of the electronic gas by filling up the states

close the Fermi level. The whole process typically represents the evolution from an individual to a collective behavior. The main message of this paper is to propose, in addition to the classical mechanism (e-e scattering), which takes place in the bulk, an alternative channel for the energy loss of NNEs.

The originality of the present work lies on five points: (i) the study has been focused on the initial stage of nonequilibrium hot electron thermalization, (ii) the femtosecond transient absorption measurements have been performed within the weak perturbation regime, (iii) the investigation has been undertaken with gold NPs smaller than 5 nm in diameter embedded in a dielectric matrix, (iv) the spectroscopic approach for the determination of the internal thermalization times is different to other studies, (v) an additional mechanism for the energy loss of nonthermal electrons is proposed. The high stability and the sensitivity of the femtosecond setup makes possible to perform measurements under restricted conditions (i.e., low pump fluence and small electronic temperature rise).

The paper is organized as follows: First, steady-state spectroscopy gives information about the influence of surface effects with respect to size effects on collective electrons behavior in gold NPs, an analysis of the differential transient absorption spectra obtained by broadband ultrafast spectroscopy allows to separate the fundamental processes such as the internal and external thermalization (spectral responses from nascent electrons and hot Fermi-Dirac electron distribution have been identified). As a next step, single wavelength pump-probe spectroscopy is employed to determine the rate of internal thermalization by interrogating either the decay of NNEs or the build-up of the hot Fermi-Dirac electron distribution. Then, the implication of the results is briefly discussed based on the TTM and the e-escattering rates obtained here are compared to literature data. Finally, an additional channel (ultrafast chemical interface *scattering*) for nonthermal electrons decay, which consists of an inelastic resonant scattering process into empty electronic states of adsorbates is proposed.

II. EXPERIMENTAL SECTION

Samples preparation: The three dimensions Au/TiO₂ nanoarchitectures composite were prepared by wet-grafting of initial Au NPs of 1.7 nm in diameter derivatized with mercapto succinic acid (MSA) to a TiO₂ mesoporous thin film. The elementary TiO₂ particle size is 15 nm and the thickness of the mesopourous films measured by profilometry is 5 μ m. Before the insertion of gold NPs, the TiO₂ nanocrystalline films exhibit a porosity of 60% with an average size of 20 nm for the pores. Aqueous solution of 1.7 nm gold NPs were synthesized by NaBH₄ reduction of AuCl₄⁻ in a mixture of water and methanol. The synthesis including five consecutive washing and centrifugation steps with pure methanol. This sequence ensures the removal of inorganic ions. The solvent excess was evaporated at temperatures below 40 °C and pressure under 5×10^{-3} Torr for 12 h. The core size of the resulting particles exhibited an average diameter of (1.7 ± 0.4) nm. The final gold NPs used to perform laser spectroscopy measurements was obtained by heat treatment at 723 K for 30 minutes generating gold NPs of (4.2 ± 0.5) nm in diameter. The size of gold NPs has been revealed by transmission electronic microscopy using a Philips CM20. The gold loading in the TiO₂ films is around 20% wt. as revealed by x-ray photoelectron spectroscopy (XPS). The film has a porosity of 60% which leads to an estimation of 2×10^{14} nanoparticles/cm² for TiO₂. The calculations for Au NPs leads to a concentration of about 4×10^{14} nanoparticles/cm² for gold.

Steady-state spectroscopy: UV/visible spectra were recorded on an HP-8353 (Hewlett-Packard) spectrophotometer. Fourier-transform–infrared (FT-IR) spectra were obtained using a Perkin-Elmer 16 PC spectrophotometer with 4 cm⁻¹ resolution and were taken with the "Golden Gate" diamond attenuated total reflection. FT–IR spectra were recorded over an average of 200 scans.

Femtosecond laser setup: Femtosecond transient absorption setup features a compact CPA-2001 Ti:Sa-amplified femtosecond laser (Clark-MXR) with a repetition rate of 1 kHz, a fundamental wavelength at 775 nm, a pulse width of 120 fs and an energy of 1 mJ per pulse. The output beam was split into three parts for pumping two double-stage noncollinear optical parametric amplifiers (NOPA) and to produce a white light continuum in a 2 mm thick sapphire plate. The output pulses of the NOPAs were compressed in SF10-glass prism pair compressors to obtain pulses of 50 fs. Pump and probe beams were directed parallel to each other toward a 60° off-axis parabolic mirror that focused them into the sample. The resulting spot area for the pump pulse is 1.25 $\times 10^{-4}$ cm². The pump-probe cross-correlation measured by Kerr gating in a 0.3 mm thick PBH21 glass window (Ohara, Japan) at the sample position was typically 100–120 fs.

For the monochromatic probing, a DET-110 silicon diode (Thorlabs) was placed directly after the samples to measure the transmitted light intensity. The signal from the detector was connected to a SR-830 lock-in amplifier (Stanford Research Instruments) tuned at 220 Hz by a chopper modulating the pump beam. Time delays between pump and probe pulses were controlled with a linear translation stage (Physic Instrument M511).

Transient absorption spectra were obtained using a white light continuum produced in a 2 mm thick sapphire plate. The white beam was collimated using a 90° off-axis parabolic mirror and steered to the sample using only reflective optics. A smooth monotonic spectral distribution between 470 and 680 nm was obtained by controlling the pump energy with an iris and a variable density filter. A broadband membrane beam splitter was placed before the sample to split the white light beam into signal and reference arms. Both were collected by fiber bundles and sent into a Triax 320 spectrograph (Jobin-Yvon). Reference and signal beams were separated vertically during their travel in the spectrograph and detected individually by diode array detector (A ST116 double Princeton Instrument). Both 1024 elements detector arrays allowed for recording more than 200 nm wide spectra averaging at a time. Chirped pulse duration was 210 fs as measured by Kerr gating in PBH21 glass between 490 (2.53 eV) and 700 nm (1.77 eV). The group velocity disper-



FIG. 2. TEM micrograph of the gold NPs embedded in ${\rm TiO}_2$ matrix. The scale bar represents 20 nm.

sion of the white light continuum was compensated in the transient absorption spectra. The absorbance change was calculated using the ratio between data obtained with and without the pump pulses reaching the samples and corrected for fluctuations in the white light continuum intensity using the reference beam spectra. Estimation of the initial electronic temperature change (ΔT_e) provides values in the range of 25–200 K²⁸ depending on the pump fluence, indicating that the measurements were performed in the weak perturbation regime.

III. RESULTS

A TEM micrograph shows that gold NPs are randomly distributed in the TiO₂ matrix as illustrated in Fig. 2. The gray shapes are TiO₂ NPs whereas the darker disks are Au NPs. The average diameter is 4.2 nm with a standard deviation of 12%. Calculations suggest the existence of about two Au NPs on the average for one TiO₂ nanoparticle. The average distance between neighboring Au NPs is estimated to be around 10 nm. Figure 3 shows the electronic absorption spectrum of gold NPs embedded in TiO₂ nanocrystalline thin films. The measured absorption spectrum (a) contains absorption arising mainly from the band gap of TiO₂ (3.1 eV)



FIG. 3. (a) Experimental and (b) calculated with Eq. (2) UV/visible absorption spectra of the gold NPs embedded in TiO_2 matrix.



FIG. 4. (A) FT–IR spectra of gold NPs embedded in the TiO_2 matrix: (a) Before heat treatmen; (b) after 15 min; and (c) 30 min. (B) Schematic drawing of gold NPs wrapped in oxidic shell of sulfate compounds and embedded in a TiO_2 matrix.

and the electronic interband transitions in gold NPs (2.3 eV) below 390 and 540 nm, respectively. The absorption maximum at 526 nm (2.36 eV) is called the plasmon band and corresponds to the collective oscillations of conduction band electrons across the NPs. The resonance plasmon band is situated very close to the interband transition from the filled d-band to the unoccupied states in the conduction band $(\sim 2.3 \text{ eV})$, this proximity leads to a large absorption to the high energy side band. In the transient absorption experiments, the proximity of the Fermi level and the plasmon band is an advantage for the present study due to the enhancement of the gold NPs response to a femtosecond laser pulse. The spectrum (b) is obtained from calculations and will be compared to the measured absorption spectrum in the Discussion section. In Fig. 4 are shown the FT-IR spectra recording during the heat treatment leading to the final size of the gold NPs. These spectra highlight the chemical transformations in the Au/TiO₂ nanocomposite during the sintering process through the disappearance and the appearance of FT-IR bands from spectra (a) to (c). Figure 5 shows the differential transient absorption spectra recorded at different time delays upon a femtosecond optical pulse excitation at 480 nm (2.58 eV) between -250 fs and 6.5 ps after the laser pulse with steps of 500 fs. A strong bleach around 540 nm (2.30 eV) and a very weak positive absorption for wavelengths longer than 630 nm (1.97 eV) is observed for all transient spectra. The bleach is due to the perturbation of the electron distribution leading to a broadening of the surface plasmon band with a flatter minimum for spectra recorded



FIG. 5. Femtosecond transient absorption spectra after pumping at 480 nm using the broadband light continuum recorded with a delay time step of 500 fs between the pump and the probe pulse from -250 fs to 6.5 ps.

during the early stage. Transient spectra exhibit a positive part for wavelengths longer than 630 nm (1.97 eV) that growths with longer time delays. An interesting feature is the evolution of the spectra profile with delay time, which leads to the absence of an isobestic point before 3 ps. Indeed, a time dependent shift of the crosspoint of the signal with the baseline is observed. The differential absorption spectra are fully developed only after hundreds of femtosecond after the laser pulse. The arrows in Fig. 5 indicate the probe wavelengths used in the two-color pump-probe experiments to separate and extract the time constants for the internal and external thermalization processes. The evolution of the spectra profile with delay time of the transient absorption spectra predict complex kinetics due to the presence of a highly nonequilibrium process. Figure 6 illustrates the transient absorption changes after pumping at 500 nm (2.48 eV) and probing at 530 nm (2.30 eV) with high and low pump fluences. The normalized signals include two steps, a fast decay which is attributed to the external thermalization (electron-phonon interaction) and a slow decay corresponding to the heat dissipation process toward the surrounding medium (phononmedium interaction). The trace profiles are not similar for the different pump fluences. The recovery of the bleach is delayed with respect to the laser pulse for the trace recorded at low pump fluence and the signal is almost flat for several hundreds of femtosecond. Figure 7 shows the transient absorption after pumping at 500 nm (2.48 eV) and probing at



FIG. 7. Transient absorption data after pumping at 500 nm and probing at 625 nm for pump fluence of 500 nJ/pulse for gold NPs. The solid line is the fit of the experimental data according to Eq. (3). The dashed line represents the pump–probe cross correlation of the instrument.

625 nm (1.98 eV). In this spectral region, the empty electronic states are effectively probed²⁹ and the hot electron gas formation is interrogated in real time. As observed in the transient spectra, NNEs give no response at 625 nm. At the opposite, the hot electron gas exhibits an absorption for wavelengths longer than 590 nm for the present system. Therefore, the rise of the signal reflects the formation of the hot electron gas (build-up of the Fermi-Dirac distribution). An important time delay between the laser pulse and the maximum of the signal is observed in accordance with the differential absorption transient spectra. Indeed, as seen in Fig. 5, the transient absorption for wavelengths longer than 600 nm (2.06 eV) does not appear within the instrument response but takes some time to develop. On a longer time scale, the signal decays back to the baseline. The evolution of the transient absorption data recorded at 600 nm (2.06 eV) after pumping at 525 nm (2.30 eV), as displayed in Fig. 8, exhibits a rather different behavior with respect to the previous probe wavelengths. By comparison with the data obtained at 530 nm with the low pump fluence (Fig. 6), the bleach recovery starts immediately at the end of the laser pulse. Furthermore, in contrast to signal recorded at 625 nm (see Fig. 7), the bleach occurs within the instrument response time. This behavior suggests that the signal is linked to electron states that exist quasi-instantaneously upon the absorption of the laser pulse. After 1.3 ps, the signal becomes posi-



FIG. 6. Normalized transient absorption data after pumping at 480 nm and probing at 530 nm with a pump fluence of 400 nJ/pulse (\bigcirc) and 70 nJ/pulse (\bigcirc).



FIG. 8. Transient absorption data after pumping at 525 nm and probing at 600 nm for pump intensity at 675 nJ/pulse. The solid line is a fit of the experimental data according to Eq. (4). The inset shows the pump fluence dependence with the same time scale window for 250, 410, 675, and 940 nJ/pulse.

tive and flattering out for several picoseconds. On a longer time scale, the signal decays slowly back to the baseline indicating that the system remains unchanged after the whole process.

IV. DISCUSSION

A. Origin of the surface plasmon broadening

Let us first discuss the steady-state spectroscopy of the small gold NPs embedded in a TiO₂ matrix studied here. The plasmon band for the present 4 nm Au NPs is much broader than Au NPs in aqueous solution.³⁰ The large linewidth of the plasmon band can have different origins: (i) the quantum size effect (the frequency of electron collision for NPs smaller than 5 nm is enhanced due to the higher rate of scattering at the interface), (ii) a broad size distribution (each NP has an extinction cross section which is dependent on size ($\sim R^3$), this can lead to a slight broadening), (iii) the so-called chemical interface damping.^{31–34} The chemical interface damping is a consequence of the presence of electronic states at the metal/matrix interface. The additional dephasing and the loss of coherence of the surface plasmon is enhanced with the presence of interfacial molecules.

We now attempt to identify the process responsible for the broadening of the plasmon band. First, we concentrate on possibility (i). Due to the quantum size effect, the value of the frequency collision compared to the bulk must be redefined with Eq. (1) because the mean free path is much longer than the size of NPs studied here,^{35–37}

$$\Gamma(R) = \Gamma_{\infty} + A \quad v_F / R. \tag{1}$$

In Eq. (1), $\Gamma(R)$ is the damping constant for the plasmon band, γ_{∞} the bulk damping constant, v_F the Fermi velocity, *R* the nanoparticle radius, and *A* is a constant taken close to unity that describes the size effect.³⁷ A value of 0.52 eV is obtained for $\Gamma(R)$ using 0.08 eV for γ_{∞} , known from a 100 nm gold film.³⁸ The high value for $\Gamma(R)$ indicates that the electron-surface scattering becomes an important process for these small gold NPs. Using the value of $\Gamma(R)$, it is then possible to calculate the spectrum of 4 nm gold NPs embedded in TiO₂ matrix with Eq. (2) where C_{ext} is the extinction cross section for a single spherical particle, ε_m is the dielectric constant of the medium (TiO₂) and λ is the wavelengh.³⁹ The resonance conditions are achieved when $\text{Re}(\varepsilon(\omega))$ $+2\varepsilon_m = 0$,

$$C_{\text{ext}} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\text{Im}(\varepsilon(\omega))}{(\text{Re}(\varepsilon(\omega) + 2\varepsilon_m)^2 + \text{Im}(\varepsilon(\omega))^2)}, \quad (2)$$

where

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{m_e(\omega^2 + \mathrm{i}\omega\Gamma)}$$

and

$$\operatorname{Re}(\varepsilon(\omega)) = \varepsilon_{\infty} - \frac{\omega_p^2}{(\omega^2 + \Gamma^2)}$$

and

$$\operatorname{Im}(\varepsilon(\omega)) = \frac{\omega_p^2}{\omega(\omega^2 + \Gamma^2)}.$$

In the equations above, ω_p is the bulk plasma frequency, ω the frequency of the excitation and ε_{∞} is the high frequency dielectric constant.

The resulting calculated spectrum (b) shown in Fig. 3 exhibits a linewidth of 0.19 eV, which is much narrower that for the measured spectrum (0.68 eV). Therefore, the observed experimental absorption spectrum deviates strongly from Mie's theory prediction.³⁹ That is the broadening cannot be due only to the increase of the frequency collisions, i.e., electron quantum confinement (size effect).

Additionally, the effect of size distribution on the broadening (ii) can be neglected since TEM measurements have revealed a relatively narrow size distribution (12%) that cannot account for the large broadening in the measured spectra because the plasmon band position is weakly dependent on the particle size.^{1,30}

The comparison between the calculated and the measured linewidth of the surface plasmon band indicates a dramatic decrease of the surface collective oscillations lifetime. An additional process needs to be taken into account to explain the drastic change for the surface plasmon lifetime. Thus, the observations lead to the conclusion that the broadening of the plasmon band has to be ascribed to a nonclassical mechanism, i.e., the chemical interface damping (iii).^{31,33} The presence of adsorbates around the gold NPs can accelerate the loss of coherence of the collective excitation. The energy and the momentum of the collective electrons can be dissipated into lowest unoccupied molecular orbitals (LUMO) of the adsorbates or resonant surface states of TiO_2 . It is important to detect the presence of interfacial molecules at the gold/TiO₂ junction that are responsible for collective electrons tunneling into and out interfacial electronic states. The identification of adsorbates resulting from the preparation of Au/TiO₂ nanocomposite is the goal of the next section.

B. Identification of the interface chemical species

It is of great interest to know what happens during the heat treatment to the mercapto succinic acid (MSA) which acts as a stabilizer for Au NPs and is also used as a molecular bridge to build the 3D nanocomposite. The sulfur atom of the thiol group of the stabilizer MSA is covalently bound to the gold surface.⁴⁰ On the other hand, the carboxylic groups are useful to anchor the gold NPs to the TiO₂ surface. Indeed, carboxylic groups can be linked via a bidentate bridging coordination mode to titanium surface atoms.^{41,42} FT-IR spectroscopy was therefore applied to investigate the fate of MSA during the sintering process. Figure 4(A) shows FT-IR spectra of gold NPs attached to the TiO2 nanocrystalline film experiencing the heat treatment. Prior the sintering process, the antisymmetric and the symmetric vibrational stretching mode of carboxylate groups, $\nu_{as}(COO^{-})$ and $\nu_{s}(COO^{-})$, respectively, anchored onto the TiO2 surface are clearly visible in the spectrum (a) at 1580 and 1600 cm^{-1} , respectively. In the intermediate spectrum (b), the intensity of $\nu_{as}(\text{COO}^-)$ and $\nu_s(COO^-)$ decreases whereas new bands appears at

1040 and 1180 cm^{-1} . The heat treatment leads to the vaporization of the gold NPs stabilizer^{43,44} that are not linked to TiO₂ whereas the molecular bridge MSA will be oxidized with the subsequent creation of oxygenated compounds confined between the gold and the TiO₂ NPs. In the final spectrum, the bands attributed to $v_{as}(COO^{-})$ and $v_{s}(COO^{-})$ have completely disappeared whereas the intensity of the bands at 1040 and 1180 cm⁻¹ have increased with time. The interfacial chemical species confined between gold and TiO₂ are identified to be oxygenated compounds, i.e., sulfate and carbonates. Indeed, FT-IR bands at 1040 and 1180 cm⁻¹ are characteristic of sulfate species adsorbed on surfaces.⁴⁵ The broadband at 1640 cm^{-1} is due the vibrational bending mode of adsorbed molecular water whereas the weak band centered at 1350 cm⁻¹ is likely linked to adsorbed carbonates.⁴⁶⁻⁴⁸ X-ray photoemission spectroscopy also revealed a large density of oxygenated sulfur compounds. Thus, gold NPs are wrapped in an oxidic shell of sulfate (carbonates are also present but in a less extent). Figure 4(B) illustrates the structure of the 3D Au/adsorbates/TiO₂ nanocomposite. The detection of adsorbates on Au NPs surface gives further evidence for the nonclassical broadening of the plasmon band. The collective electrons can tunnel back and forth into electronic states of interfacial molecules. The efficiency of this charge transfer process is controlled by the overlap of the metal and adsorbates wave functions. The observation that these gold NPs exhibit a high density of adsorbates may lead to the emergence of novel channels for nonthermal electron relaxation dynamics.

C. Identification and separation of the different electron dynamics processes

The femtosecond data obtained for the gold NPs embedded in a dielectric matrix strongly differs from other ultrafast studies on metal NPs on several aspects: (i) the temporal evolution of the differential absorption spectra profile (inducing a change of sign for certain probe wavelengths), (ii) the delayed recovery when probing at the surface plasmon maximum, (iii) the slow rise when probing the empty electronic states. In the following section, we will show that the origin of these observations are linked to the earliest stage of nonequilibrium nonthermal electrons upon the absorption of a femtosecond pulse, i.e., the build-up of the Fermi–Dirac electron distribution (internal thermalization, e-e scattering).

As seen in Fig. 5, the maximum spectral width is obtained at the earliest stage following the electron perturbation. At this point, a wide range of energies can be exchanged between the electrons, indicating the presence of an uncorrelated state in a situation far from equilibrium due to the broad occupancy changes in the non-Fermi–Dirac electron distribution. In several hundreds of femtosecond, the broad feature considerably narrows indicating the transition from an individual to a collective behavior. As discussed below, this shift is attributed to the build-up of the hot electron gas during the internal thermalization process. It is of interest to compare the measured differential absorption spectra presented here and the numerical simulations available in the literature that demonstrated the spectral distinction between nonthermalized and thermalized electrons.^{24,49,50} It appears from these calculations that nonthermal electrons exhibit spectra with a weak and broad bleach and no positive wings at the lower and higher energy side of the plasmon band. In contrast, the computed transient absorption spectra for the internally thermalized hot electron gas show a narrower bleach with a much stronger amplitude compared to the nonthermal electrons and a positive part on both sides of the bleach (20% to 30% of the bleach amplitude). Upon comparison of the spectra recorded at 250 fs and time longer than 5 ps, a time dependent shift of the crosspoint of the signal with the baseline from 630 to 585 nm is clearly observed between these spectra. The shape of measured transient absorption spectra measured at 250 fs and 5 ps corresponds very well to simulated spectra for nascent electrons and the internally thermalized hot electron gas, respectively. The broadband white light continuum measurements allow to visualize in real time domain the spectral shape evolution of nonthermal electrons to the hot electron gas.

In the following, the separation of e-e and e-ph interaction processes is based on the fact that the spectral responses of NNEs and the hot electron gas are clearly different as demonstrated in the paragraph above. The traces shown in Fig. 6 obtained by probing very close to E_F are very sensitive to the internally thermalized electrons, therefore the external thermalization is expected to be the dominant process for this probe wavelength. At high pump fluence, the recovery can be fitted with a single exponential function and gives a time constant of 3.46 ± 0.04 ps for the external thermalization. However, at low pump fluence, a faster electron-phonon interaction is observed and the experimental data can no longer be reproduced with a single exponential function. The deviation from a singleexponential decay, especially at the early stage of the signal, is an indication of the presence of different processes taking place on similar time scale. This phenomenon is attributed to the noninstantaneous (longer than the laser pulse duration) establishment of the hot Fermi-Dirac electronic temperature and has been previously observed with larger gold NPs in solution.⁴⁹ The deviation is more accentuated with a low pump fluence because the e-e scattering rate is independent on the pump fluence whereas electron-phonon interaction slows down by increasing the initial electronic temperature. Two possible explanations linked to the internal thermalization for the delayed recovery may be proposed: (i) simulated spectra have shown that the cross section for thermalized electrons is higher compared to nonthermal electrons at the maximum of the plasmon bleach. These cross section differences may well explain the origin of the very slow recovery at the early stage due to a mutual compensation of the absorbance changes by the simultaneous recovery of the bleach due to the decay of nascent electrons and the increase of the bleach amplitude linked to the appearance of thermalized electrons. (ii) Another possibility for the delayed bleach recovery comes from the observation that the electron-phonon interaction is very slow when the internal thermalization process is incomplete. 24,25,51 These authors have shown that the rate of electron-phonon coupling increases as long as the internal thermalization is in progress. Indeed, as observed at the early stage of the recovery in Fig. 6, the electron-phonon coupling rate is very close to zero, increasing to reach a constant value when the Fermi-Dirac electron distribution is established. In summary, these data give strong indication on the existence of a finite time for the internal thermalization time but the difficulty is to extract a time constant because of the overlap of the two processes on similar time scale. From this fact, it is proposed to directly interrogate the build-up of the Fermi-Dirac electron distribution. The wavelength at 625 nm used in the experiment shown in Fig. 7 permits to probe in real time the formation of the hot electron gas. To determine the e-e scattering time, Eq. (3) is used. The delayed rise time is introduced by the first term (τ_1) , which describes the noninstantaneous build-up of the electronic temperature.

The second term corresponds to the energy exchange between the hot electron gas and the lattice and the constant B accounts for the slow decay linked to the heat dissipation from gold NPs into the matrix,

$$S(t) = A \exp[1 - \exp(-t/\tau_1)] \exp[-t/\tau_2] + B.$$
(3)

After deconvolution of the pump-probe cross correlation, the solid line obtained with Eq. (3) reproduces well the experimental data (open circles) giving $\tau_1 = 540$ fs (± 30 fs) and $\tau_2 = 3.6$ ps. This signal also contains information about the electron-phonon interaction although they can be separated with a system response function.

In the next part, it will be shown that further evidence for a slow internal thermalization can be taken by interrogating the temporal shift and the narrowing of the transient spectra with the probe wavelength at 600 nm as illustrated in Fig. 8. This spectral region is expected to give a direct and exclusive access to the internal thermalization time with a minimum contribution of the external thermalization. The spectral response of NNEs gives a bleach at 600 nm whereas hot electron gas shows a transient absorption. During the bleach recovery at 600 nm, the signal is modulated due to the superposition of oscillations. The mechanism of generation of these oscillations is beyond the scope of this study and will be discussed in detail in a separate study. The experimental data can be very well fitted in Fig. 8 with the following expression:

$$S(t) = C \exp[-t/\tau_1] + D \cos[2\pi\nu t + \varphi] \exp[-t/\tau_3]$$

+ E, (4)

where τ_1 is the bleach decay time constant, ν the frequency of the oscillations, φ is the phase and τ_3 the damping time constant, *C* and *D* the amplitudes for the exponential decay and the damped cosinus function, respectively and the constant *E* stands for the offset. The excellent fit after convolution of the pump-probe cross correlation of the experimental data confirms the existence of a single recovery process resulting in following time constants: $\tau_1 = 767 \pm 11$ fs, ν = 1.02 THz, $\tau_3 = 720 \pm 55$ fs. Therefore, the bleach recovery recorded at 600 nm is a direct signature of the depopulation of nonthermal electrons via e-e scattering in accordance



FIG. 9. Transient absorption data after pumping at 500 nm and probing at 625 nm for pump fluence of 500 nJ/pulse for gold NPs. The dashed line represents the pump-probe cross correlation of the instrument. The different processes P_I , P_{II} , and P_{III} are depicted in the figure.

with transient absorption spectra. A great advantage with this probe wavelength is the minor contribution of the electron– phonon interaction by probing directly the profile temporal evolution of the differential transient spectra. Another argument toward the observation of e-e scattering process (instead of electron–phonon interaction) is associated to the observed independence of the decay rate on the pump fluence in the range of 210 to 940 nJ/pulse as shown in the inset of Fig. 7. This behavior is a signature of the e-e scattering process as observed for metal films in the weak perturbation regime.⁵²

D. Consequence for the two-temperature model

As stated in the Introduction, the TTM is the widely accepted model to describe the interaction of femtosecond laser pulses with metals. The signal recorded at 625 nm gives an overview of the dynamics of energy redistribution upon the absorption of a laser pulse. Indeed, as observed in the transient absorption spectra, NNEs give no response at 625 nm whereas the hot electron gas exhibits an aborption, as seen in the spectra recorded after 3 ps (when the internal thermalization process is over). Figure 9 depicts the possibility to follow the evolution of the different processes P_I , P_{II} , P_{III} in real time with a single wavelength. The rise of the signal reflects the formation of the hot electron gas, the decay illustrates the electron-phonon and the phonon-medium interactions. The establishment of the electronic temperature, the electronic energy transfer into the lattice as well as the heat dissipation toward the surrounding medium can be directly visualized. By comparison with the schematic picture of Fig. 1, it appears clearly that P_I has a finite time of hundreds of femtosecond. For the system studied here, the twotemperature model illustrated in Fig. 1 appears to be no longer valid. Indeed, this model is based on the assumption that the internal thermalization (e-e scattering, establish-)ment of the Fermi electronic distribution) is quasiinstantaneous (within the laser pulse duration). Internal thermalization can be as long as 800 fs and therefore can take place on the same scale as the electron-phonon interaction. Thus, for the gold nanoparticles studied here, the TTM breaks down within the low-perturbation regime (ΔTe <200 K) where the *e*-*e* and electron-phonon interactions have comparable time constants.

E. Comparison with other studies

In the following, the e-e scattering rates obtained in this work will be compared with published data on noble metal films and nanoparticles. Investigations by two-photon photoemission spectroscopy were conducted with highly energetic electrons (usually between 0.5 to 2 eV above E_F) and therefore, very short lifetimes (in accordance with the Fermi liquid theory) for NNEs on the order of 200 to 10 fs were reported. At the opposite, e-e scattering rates obtained with femtosecond transient absorption spectroscopy are extracted very close to the Fermi level where lifetimes are expected to be the longest. Nascent nonthermal electron lifetimes were also obtained very close to the Fermi level. Thus, we will compare our results with femtosecond data from transient absorption spectroscopy. The measurements performed with 4 nm gold NPs have shown an increase of the lifetime for nonthermal electrons closer to the Fermi surface and surface plasmon position. Surprisingly, the observed internal thermalization times for small gold nanoparticles reported here are significantly longer than those available in the literature for bulk gold. Indeed, previous studies have shown internal thermalization characteristic times of 500 and 350 fs for gold and silver films in the vicinity of the Fermi surface, respectively.^{24,52} Figure 7 has shown that the maximum of the signal is reached after a delay of 1 ps with respect to the pump-probe cross correlation at 0.4 eV above E_F . Concerning works on gold NPs, Link et al. have recently reported e-e-scattering rates for gold particles in solution by extracting the time constants from a signal containing both the e-eand the electron-phonon interaction processes at the plasmon band maximum ($\lambda = 530$ nm, similar to Fig. 6 of this study).⁴⁹ A size independent internal thermalization time of 500 fs was found from traces recorded at 530 nm for gold NPs between 9 and 48 nm. However, the deviation from a single exponential is significantly larger for the gold NPs studied here compared to gold NPs with sizes larger than 9 nm (Ref. 49) (comparison with Fig. 6 of this work). With the probe wavelength at 530 nm, the overlap between the e-eand the e-ph interaction processes is maximum, as a result, it is very difficult to extract the time constants for the internal and external thermalization processes because rate constants are too comparable. As developed above (see paragraph: Identification and separation) other probe wavelengths can avoid this complication. For similar NPs sizes, our results can only be compared with Ag and Cu NPs since no data were found for gold NPs smaller than 9 nm in diameter in the literature. For instance, internal thermalization time of 200 fs has been measured at the Fermi level for silver with the same NPs size²⁶ whereas copper NPs of 10 nm of diameter showed an internal thermalization time of less than 200 fs.²⁹ Therefore, the rate of e - e scattering observed for these small gold NPs is at least four times slower than in silver for similar sizes.²⁶ The fact that e-e scattering rates measured in this work differ significantly from silver with similar particles size may be attributed to an additional mechanism for e-e scattering in the case of small gold NPs modified with a high density of adsorbates.

F. Alternative mechanisms for nonthermal electron energy loss

Classically, e-e scattering process is mainly governed by two main factors: (i) the Pauli exclusion principle, (ii) the Coulombic screening effects.⁵³ The origin of the slow e-escattering rates observed here can be attributed to a decrease of density of states around E_F or to the presence of new channels of electron scattering for these small gold NPs.

1. The appearance of nonmetallic state: Decrease of the available phase space around the Fermi level

The availability of phase space is thought to be the dominant factor controlling the e-e scattering rate due to the Pauli exclusion principle close to E_F . The size regime of the gold NPs is just at the frontier of the appearance of quantum size effects. The discretization of energetic levels can lead to extremely slow e-e scattering rates in Au clusters.⁵⁴ The small NPs size may lead to the creation of a gap around E_F lowering considerably the density of states and thus, the available phase space for e-e scattering. The probability of inelastic scattering is significantly reduced. Recently, nonmetallic properties have been identified by STM/STS for 3 nm gold NPs.⁵⁵ Therefore, the change of the electronic structure caused by electron confinement to a restricted volume could be responsible for the long internal thermalization time. However, the preliminary results from XPS measurements did not give indication of metal to insulator transitions for the gold NPs studied here. The observed low e-e scattering rates should have another origin than the reduction of phase space for electron scattering.

2. The Auger relaxation process

Electronic interband transitions can be excited with the photon energy range used in these experiments. The absorption process in gold NPs for $h\nu > 2$ eV leads the excitation of a *d*-band electron into an empty state of the *sp* band. Therefore, excitation of d-band electrons with $h\nu$ in the range of 2.3-2.5 eV will create hot electron with a small energy excess of 0.3 to 0.5 eV above E_F . A possible relaxation mechanism can occur through the Auger process involving a d-band hole and two sp-band electrons.^{56–59} The Auger process is illustrated in Fig. 10 and can be described as follows: The electronic interband transition leads to the generation of a *d*-band hole and a sp-band electron (a). An electron from the sp band lying slightly below E_F can fill the photogenerated d-band hole (b), and transfer the excess energy to another electron which is excited far above E_F to conserve energy and momentum (c). Finally, the Auger decay process can generate highly energetic electrons ($\sim 2 \text{ eV}$ above E_F) and therefore the resulting energetic distribution of NNEs is in principle equivalent to an intraband transition. However, the Auger generation mechanism is a multistep process for the generation of highly energetic nonthermal electrons com-



FIG. 10. Schematic representation of the Auger decay: Upon absorption of a femtosecond pulse ($h\nu > 2 \text{ eV}$), the interband transition will lead to the generation of a hole in the *d* band and an electron in the *sp* band above E_F (a). A *sp*-band electron can fill the hole (b) with the subsequent excitation of another *sp*-band electron far above E_F (c). This picture shows that, in principle, nascent nonthermal electrons generation via the Auger process (*d*-band electron excitation) is equivalent to an intraband transition (Ref. 57).

pared to the intraband transition excitation. The generation of NNEs through *d*-band holes has been considered for 30 nm gold NPs.⁶⁰ Thus, a reason for the slow e-e scattering rate could be the excitation mechanism (Auger process), which leads to a delayed generation hot electrons. The observation of slower e-e scattering rates close to the plasmon band position can suggest that surface collective excitation plays an important role for nonequilibrium electron dynamics in NPs with diameter of several nanometers.⁶¹ Very recently, a theoretical model was proposed consisting of a dynamical screening induced by the confinement, which strongly modify the classical e-e scattering process.⁶¹⁻⁶³ This mechanism involving the interaction of a nascent electron with a *d*-band hole followed by the emission of a surface plasmon can be viewed as an Auger process. According to this model, a pump energy around 2.3 eV considerably enhances the possibility of *d*-hole scattering into the conduction band by emitting a surface plasmon. The photon energy used in the present experiment ($h\nu \sim 2.4 \text{ eV}$) is very close to the onset of interband transition as well as the surface plasmon band position. A main difference between silver and gold NPs is the proximity of interband transition with the surface plasmon and this could be the origin of the differences in e-e scattering dynamics between these noble metals. The Auger process can hold for bulk metals to explain the differences of behavior for NNEs for Au and Cu with respect to Ag.⁶⁴ Furthermore, an important point is the fact that the e-e scattering time of 200 fs were measured with Ag NPs that exhibit a classical broadening of the surface plasmon.²⁶ Indeed, no chemical interface damping was observed in this case since the absorption spectrum can be well reproduced with Mie's theory (Fig. 2, Ref. 3). Therefore, in view of the very high surface to volume ratio, it is reasonable to privilege surface effects as pointed out by the observations on the surface plasmon damping mechanism at the beginning of the Discussion section.

3. Ultrafast chemical interface scattering (UCIS): inelastic electron resonant scattering process

We shall now discuss the crucial role of the metal/matrix interface on the dynamics of NNEs. Surface effects play a major role in the dynamics of surface plasmon. The comparison between calculated and experimental linewidths of the plasmon band and the detection of a large density of adsorbates have lead to the conclusion that the surface plasmon undergoes a strong chemical interface damping. As demonstrated above, the broadening of the plasmon band can be understood by an additional damping mechanism of the collective oscillations via the electron tunneling into and out adsorbates electronic states. The gold NPs are wrapped in a shell of oxidized molecular species (carbonate and sulfate). It has been shown that the loss of phase coherence is accelerated by the presence of adsorbates that open an additional decay channel for the surface collective oscillations. Both momentum and energy of collective electrons are dissipated via an inelastic scattering.

A gold NP of 4.2 nm in diameter has about 2300 atoms and about 35% of all the gold atoms consist of surface atoms. Because of the high surface atoms to bulk atoms ratio for the gold NPs used here, most of NNEs created upon the absorption of the laser pulse are close contact with adsorbates. Surface effects could be at the origin of the differences for nascent nonthermal electron dynamics in NPs compared to films.

The energetic range of NNEs created via the Auger mechanism is in principle equivalent to an intraband transition excitation as illustrated in Fig. 10. Therefore, the same final picture for the electron distribution changes is obtained for excitation of *d*-band electrons (interband transition) or *sp*-band electrons (intraband transition).⁵⁷ Figure 11 gives an overall energetic diagram illustrating the change of electron distribution in gold, the position of the adsorbates electronic states and the TiO_2 conduction band as a function of energy. The temporal evolution for the redistribution of the photonic energy among the gold, the adsorbates and TiO_2 is illustrated in (A), (B), and (C) of Fig. 11. The ultrafast chemical interface scattering can be described with the following scenario: Immediately after the absorption of the femtosecond pulse, a nonequilibrium distribution of NNEs (as photoexcited) is created with energies E_{ini} in the range $E_F \leq E_{ini} \leq E_F + h\nu$. NNEs experience an inelastic resonance scattering into lowest unoccupied electronic states of adsorbed species closely packed at the interface between Au and TiO₂. Upon colliding at the interface, the electron is temporary transferred into empty electronic level with an energy E_{ini} with the subsequent creation of an intermediate negative ion state. In small NPs, ultrafast heating induces an enhancement of the probability of electron scattering off the NPs.65 Theoretical studies with alkali atoms on metal predict excited state lifetimes of less than 1 fs.⁶⁶⁻⁶⁸ Photoemission linewidths or real-time measurements indicate that the lifetime of the adsorbate resonant states can be as long as 50 fs.⁶⁹⁻⁷² To the best of our knowledge, the excited resonant state lifetimes of adsorbates of few atoms is not known up to now. After a certain resident time, the electron then scatters back with an energy E_{fin} into the gold metal conduction band. The resident time is long



FIG. 11. Schematic drawing of the ultrafast chemical interface scattering (UCIS) process in metal NPs. (A) Change in electron distribution as a function of energy for gold (left-hand side); density of electronic states (LUMO) of interfacial molecules as well as the density of states of the TiO₂ conduction band (right-hand side). The conduction band of TiO₂ and the gold Fermi level lies at about -4.0 eV and -5.4 eV, respectively. (B) Immediately after the absorption of the femtosecond pulse, a nonequilibrium distribution of nascent nonthermal electrons (as photoexcited) is created with energies E_{ini} in the range for intraband transition $E_F \leq E_{ini} < E_F + h\nu$. The corresponding electron distribution change around E_F in gold is shown on the left-hand side. The nascent nonthermal electrons are sufficiently energetic to have access to electronic affinity levels (LUMO) of adsorbed molecules. The electron is temporary transferred into an empty electronic level with an energy E_{ini} with the subsequent creation of an intermediate negative ion state, the lifetime of this state is very short on the order of tens of fs. The electron then scatters back with an energy E_{fin} into the gold metal conduction band. The nascent nonthermal electrons are energy $\Delta E = E_{ini} - E_{fin}$ in the affinity electronic levels of adsorbates and is converted in molecular vibrational energy. The amount of energy loss is directly related to the resident lifetime. (C) This picture illustrates the situation after a few ps, the electron distribution. In view of the energetic range of the hot electron gas, its relative distribution change exhibits a narrower shape in the Fermi–Dirac distribution. In view of the energetic range of the hot electron gas, the LUMO level of adsorbed molecules is not accessible anymore. Note that the scale of electron distribution change in gold is not the same in (B) and (C).

enough to break the phase coherence. NNEs have deposited energy $\Delta E = E_{ini} - E_{fin}$ in the affinity electronic levels of the adsorbates. The amount of energy loss is directly related to the resident time. The broad density of states of the adsorbates^{73,74} make them very efficient nascent nonthermal scavengers. During the inelastic resonant scattering process, the adsorbed molecules receive an impulsive force by experiencing a change in potential and kinetic energies.^{75,76} NNEs transferred back to gold conduction band leave behind "hot" adsorbates that can desorbe from gold surface.^{77,78} The electronic excess energy is converted into heat via the excitation of vibrational modes of the adsorbates.⁷⁹ This process is the so-called desorption induced by electronic transition (DIET) mechanism.⁷⁷ Therefore, the interfacial molecules can directly act as a heat bath in opening a novel channel for the energy and momentum dissipation of NNEs.

The Fermi level of gold and the conduction band edge of TiO₂ lie at 5.4 eV and 4.0 eV below the vacuum level, respectively. However, these values should be taken with precaution since a possible degenerescence of the energetic level can occur at the layer interface. The knowledge of the exact position of the adsorbates electronic states is a real challenge due to the complexity of the interface. Chemical species, sulfate and carbonates, have been detected by FT–IR spectroscopy. Even if the exact nature of the interface and the structure were known, the acquaintance of the physical arrangement of the atoms at the interface would remain

very difficult⁸⁰ and as a consequence the position of corresponding electronic states is far to be obvious. It is possible that closely packed layer of adsorbates at the interface, forming an oxidic shell around Au NPs, has its own electronic structure that gives rise to a broadband of electronic interfacial states. From an energetic point of view, a hot electron transfer into TiO₂ conduction band should be possible since the energy gap is around 1.5 eV. Very recently, an energy transfer from Ag NPs toward strongly reduced TiO₂ has been observed by a combination of STM and photon emission spectroscopy.⁸¹ However, Au NPs deposited on TiO₂ (001) do not exhibit any chemical interface damping, therefore the probability of electron transfer from the metal to electronic affinity levels of TiO₂ is strongly reduced.⁸² Nevertheless, surface states forming a resonant state just below the conduction band edge of TiO₂ can act as affinity levels for NNE.31

Although the charge transfer has occurred between gold and the adsorbates, an "entire" electron is not residing in the interfacial electronic states. The inelastic resonant scattering mechanism should be seen as a dynamical event. Thus, the UCIS process should not be confused with electron transfer into TiO₂ conduction band from the dye excited state, where a long lived charge separated state is created upon light absorption.^{42,83} In our experiments, no long lived injected electrons have been detected by broadband spectroscopy. Yet, very recently an intriguing novel type of solar cells have been reported which consists of dye molecule anchored onto a gold film coated on TiO_2 . The authors report that ballistic electrons can travel through the gold film over 20 to 50 nm to reach the TiO_2 .⁸⁴ In this system, the process is likely assisted by an electrical field in close circuit.

Finally, the slow e-e scattering rates observed for these gold NPs is attributed to the emergence of an additional mechanism of electron scattering, i.e., ultrafast chemical interface scattering (UCIS). The large differences in internal thermalization times between Ag and Au NPs can be understood by the fact that gold NPs employed here exhibit a strong chemical interface damping at the opposite of Ag NPs employed in Voisin et al.²⁶ Indeed, the absorption spectrum for the Ag NPs can be well reproduced using Eq. (2) for 6 nm Ag NPs.³ For gold NPs employed in this work, the overall internal thermalization process of the electronic gas is controlled by surface rather than by size effects. Our proposition for this alternative nonthermal energy loss mechanism is further supported by studies concerning the femtochemistry on Pt(111) where, it was shown that nonthermal electrons are responsible for the triggering of surface chemistry.^{85,86}

G. Relevance to surface femtochemistry

Usually, it is believed that only the hot electron gas drive femtochemistry on metal surface, and based on this assumption, TTM is widely used to describe the surface photochemistry initiated by a fs laser pulse. Here we show that NNEs (out of a Fermi–Dirac distribution) may be transferred toward adsorbates since UCIS is the decay channel to deposit the photonic energy into vibrational modes of adsorbates. Femtosecond spectroscopy showed that the establishment of an electronic temperature can be as long as 800 fs for electrons at 0.4 eV above the Fermi level. NNEs can be long lived and can drive surface chemistry via the inelastic resonant scattering into molecular electronic states. The main difference between NNEs and the hot electron gas is the wide range of energy covered by NNEs, thus a larger range of adsorbates electronic states are accessible to NNE for initiating surface chemistry. Furthermore, the optical energy is not lost via the collision among "cold" conduction band electrons. In other words, empty electronic states of the adsorbates are efficient nascent nonthermal scavengers. For applications involving energy photon conversion, the limit on conversion efficiency can be doubled by harnessing hot electrons instead of thermalized electrons. Therefore, the energy of NNEs can be harnessed to move, to dissociate or to desorbe molecules on surfaces.

V. CONCLUSION

Analysis of the surface plasmon broadening in combination with ultrafast studies of the internal thermalization allowed to identify, in addition to the classical e-e scattering mechanism, an alternative decay channel of nascent nonthermal electrons (as photoexcited) in small gold NPs, i.e., the *ultrafast chemical interface scattering (UCIS)* mechanism.

Analysis of the surface plasmon linewidths showed that surface effects dominates size effects for these 4 nm gold NPs. A pronounced chemical interface damping of the surface plasmon is observed, which indicates the active role of adsorbates allowing electrons tunneling into and out of interfacial electronic states between gold and titanium oxide. These empty resonant electronic states are provided by adsorbates as revealed by FT–IR spectroscopy. The scattering process breaks the phase coherence and dissipates the energy and the momentum of the surface plasmon.

Differential absorption spectra of nonthermal nascent electrons and hot electron gas have been identified by means of broadband white light continuum spectroscopy and are in accordance with previously published simulations.^{9,16} The internal thermalization time has been determined by probing the decay of nonthermal electrons and the build-up of the Fermi–Dirac electron distribution. Even for small gold NPs (4.2 nm in diameter), the internal thermalization is as long as 800 fs at 0.4 eV above E_F . A key issue of this work is the observation of a "slow" e-e scattering process. Indeed, internal thermalization rates are more than four times slower in gold with respect to silver for comparable NPs sizes.²⁶

The slow establishment of an electronic temperature (internal thermalization) is attributed to an alternative mechanism for nonthermal energy loss decay: *ultrafast chemical interface scattering* (UCIS). The nascent nonthermal electrons experience an inelastic resonant scattering process into unoccupied molecular orbitals of adsorbates. The proportion of the different channels still need to be determined, however, we speculate that the ultrafast chemical interface scattering can be the dominant mechanism for nascent nonthermal energy loss for small NPs with chemically modified surfaces. The effect of UCIS process is to retard the build-up of a Fermi–Dirac distribution (e-e scattering). The observation of UCIS process is linked to the fact that these Au NPs exhibit a very high surface atoms to bulk atoms ratio and that they are wrapped in a shell of oxidized species.

The two-temperature model (TTM) is based on the assumptions that the e-e scattering and e-ph interactions rates are well separated and that the whole absorbed photonic energy is transferred into the lattice. Therefore, the twotemperature model is no longer valid for this system because of the temporal overlap between the internal thermalization and the electron-phonon interaction processes. Furthermore, the proposed additional mechanism (UCIS) permits to directly transfer the optical energy toward the surrounding medium without heating up the metal NPs. Thus, a part of the absorbed energy is not transferred into the lattice and even not redistributed among "cold" conduction band electrons. Due to dynamic and energetic reasons, the present system does not fit anymore with the basic assumptions of the TTM. These results suggest that nascent nonthermal electrons (out of a Fermi-Dirac distribution) may play an important role in driving femtochemistry on metal surfaces. The range of adsorbates energetic states accessible to nonthermal electrons is much wider compared to the internally thermalized hot electron gas. The ultrafast study of nascent nonthermal electrons behavior in small NPs is in its infancy. Mathematical models are required to assess the decay proportion via the UCIS process with respect to the classical e-e scattering channel.

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