Gold nanoparticle assemblies: interplay between thermal effects and optical response

Yannick Guillet,^a Majid Rashidi-Huyeh,^{a,b} Dominique Prot^{a,c} and Bruno Palpant^a

^a Université Pierre et Marie Curie – Paris 6, CNRS UMR 7588, INSP, Campus Boucicaut, 140 rue de Lourmel, Paris, F-75015 France

^b Department of Physics, University of Sistan and Baluchestan, 98135-674 Zahedan, Iran

^c Université Paris Sorbonne – Paris 4, France

E-mail: bruno.palpant@upmc.fr

Abstract

Gold nanoparticle assemblies present an optical response which is very sensitive to different phenomena of thermal origin. In a recent paper, we have described how the interaction of light with matrix-embedded gold nanoparticles can result in the generation of thermal excitations. Here we show how thermal processes can affect the optical response of a nanoparticle assembly. We then connect both aspects and finally point out their involvement in the nonlinear optical response of nanocomposite media. This allows us to tackle two key issues in the field of third-order nonlinear properties of gold nanoparticles: The influence of the generalized thermal lens in the long laser pulse regime and the hot electron contribution to the gold particle intrinsic third-order susceptibility, including its spectral dispersion and intensity-dependence.

1 Introduction

In a recent paper published in this review, we have presented theoretical approaches allowing to describe the thermal behaviour of a gold nanoparticle assembly under pulsed optical excitation [1]. Beyond, the modification of the linear and nonlinear optical response of nanocomposite materials by thermal effects represents also an interesting issue to address. Indeed, due to the local electric field enhancement associated with the surface plasmon resonance, gold nanoparticle assemblies have been extensively studied for their optical Kerr effect [2]. In these studies, the influence of thermal phenomena has often been invoked. However, such assessments are most of the time limited to qualitative considerations. Here, we will first provide the basic notions about nonlinear optical properties of gold nanoparticle assemblies. Then, the influence of thermal effects on their linear and nonlinear optical responses will be emphasized. The main results will be exemplified throughout the paper. Two important practical points will be addressed: The influence of the generalized thermal lens on the third-order nonlinear response, and the hot electron contribution to the gold particle intrinsic third-order susceptibility, including its spectral dispersion and intensity-dependence.

2 Third-order nonlinear optical response of gold nanoparticles

2.1 The optical Kerr effect

We just give here some elements regarding the third-order nonlinear optical properties of nanocomposite materials, so as to present the issue of our investigations. A more complete analysis of both theoretical approaches and experimental findings has been published in Ref. [3]. We refer to the notations and concepts already presented in Ref. [1]. The local electric field enhancement in the vicinity of the SPR makes noble metal nanoparticles attractive for their nonlinear optical response. Indeed, as the latter varies as an integer power of the electric field experienced by matter, the enhancement of the local field E_L results in the amplification of the metal nonlinear response as compared to the bulk phase one. The n^{th} -order nonlinearity is characterized by the n^{th} -order susceptibility, which links the n^{th} -order polarization to the n^{th} power of the field [4,5]. In centrosymmetric media the even-order susceptibilities from electric dipole origin vanish. The first non-zero nonlinear susceptibility is then the third-order one, $\chi^{(3)} = \chi_1^{(3)} + i\chi_2^{(3)}$. Disregarding the third-harmonic generation process, the third-order polarization then writes:

$$P^{(3)}(\omega) = 3\epsilon_0 \chi^{(3)}(\omega) |E(\omega)|^2 E(\omega), \quad (1)$$

where ϵ_0 is the permittivity of vacuum and $E(\omega)$ is the electric field complex amplitude at circular frequency ω . The

simplified notation $\chi^{(3)}(\omega)$ for the susceptibility usually denotes the 4th-rank tensor $\chi_{xxxx}^{(3)}(\omega; \omega, \omega, -\omega)$ if the field is polarized along the x axis. Eq. (1) corresponds to a phenomenon known as the optical Kerr effect, by analogy with the magneto-optic or electro-optic Kerr effects. One can show that it amounts at first order to write the complex optical index as the sum of the linear one (subscript “0”) and a term proportional to the wave intensity, I , as:

$$\begin{cases} n = n_0 + \gamma I, \\ \alpha = \alpha_0 + \beta I. \end{cases} \quad (2)$$

γ and β are the nonlinear refraction and absorption coefficients, respectively. They are linked to the complex third-order nonlinear susceptibility through [6–8]:

$$\begin{cases} \chi_1^{(3)}(\text{esu}) = \frac{cn_0}{240\pi^2} \left(2n_0\gamma - \frac{\alpha_0\beta}{2k^2} \right), \\ \chi_2^{(3)}(\text{esu}) = \frac{cn_0}{240\pi^2} \left(\frac{n_0\beta}{k} + \frac{\alpha_0\gamma}{k} \right), \end{cases} \quad (3)$$

where k denotes the modulus of the wave vector and c the speed of light in vacuum. The components of $\chi^{(3)}$ in Eq. (3) are expressed in the usual electrostatic units (esu), linked with the SI units by:

$$\chi^{(3)}(\text{esu}) = 10^{-8} (c^2/4\pi) \chi^{(3)}(\text{SI}). \quad (4)$$

2.2 Influence of dielectric confinement

Let us now examine the optical Kerr effect in nanocomposite materials. As said before, the local electromagnetic field enhancement at the SPR results in the large amplification of the metal nonlinear response which can then be several orders of magnitude higher than the one of the bulk phase [9,10]. This is a direct consequence of the dielectric confinement already evoked in Ref. [1] in the case of the linear response. Metal nonlinear properties are also affected by electronic confinement: the intrinsic nonlinear susceptibility of a gold nanoparticle is certainly different from that of bulk gold due to finite size effects. We will come back to this point later.

The concept of effective medium can be generalized to the nonlinear optical response of a nanocomposite material [11–13]. Most of the time, such materials contain nanoparticles the nonlinear susceptibility modulus of which is much larger than the dielectric host one. Hence, $|\chi^{(3)}|$ values of the order of 10^{-8} esu and 10^{-14} esu have been reported, respectively, for bulk gold [6] (or gold particles [10]) and different transparent dielectric media in the visible or near-infrared [14–16]. Now assuming that the metal susceptibility, $\chi_m^{(3)}$, is identical for all particles and homogeneous inside each (decoupling approximation) the following relation can be obtained [12,13]:

$$\chi_{\text{eff}}^{(3)} = p \left\langle f_\ell^2(\mathbf{r}) \right\rangle_m \left\langle |f_\ell(\mathbf{r})|^2 \right\rangle_m \chi_m^{(3)}, \quad (5)$$

$f_\ell(\mathbf{r})$ is the local field factor at point $\mathbf{r}$ and the brackets denote the average value in all the metal particles contained in the volume considered. This equation underlines the relevance of the calculation of the local field topography in a nanocomposite medium, as the one presented in Ref. [1], for analyzing its nonlinear optical response. Equation (5) can further be reduced to a simple analytical expression in the limit case of a dilute medium (low p value) since in this case the local field factor is identical for all particles and is given by Eq. (6) of Ref. [1]. One then obtains [9,11,13,17]:

$$\chi_{\text{eff}}^{(3)} = p f_\ell^2 |f_\ell|^2 \chi_m^{(3)}. \quad (6)$$

This expression, together with Eq. (6) of Ref. [1], is abundantly used in the literature devoted to the optical Kerr effect in nanocomposite media. From Eq. (5) or (6) it is obvious that dielectric confinement induces a local field correction to the nonlinear response of metal nanoparticles, which has several significant consequences [6,18,19]. Since both f_ℓ and $\chi_m^{(3)}$ are complex quantities, the medium third-order nonlinear response may present unexpected values. Moreover, the real and imaginary parts of $\chi_{\text{eff}}^{(3)}$ may experience strong sign and magnitude variations in the SPR spectral range. Finally, as $|f_\ell|$ exhibits a resonant behaviour at the SPR frequency, $|\chi_{\text{eff}}^{(3)}| \sim |f_\ell|^4$ is greatly enhanced. This explains both the interest raised by gold nanoparticles for nonlinear optical materials and the high sensitivity of their nonlinear response to every morphological parameter acting on the local field.

2.3 Intrinsic third-order susceptibility of gold nanoparticles

After focusing on the effect of dielectric confinement on the third-order nonlinear optical response, let us glance at the intrinsic nanoparticle susceptibility. Surprisingly, very few theoretical works have been devoted to the value of $\chi_m^{(3)}$ in noble metal nanoparticles [19,20] after the pioneering studies of Flytzanis' group who identified and evaluated the different electronic contributions [9,10,18,21]. They first distinguished two pure nonlinear origins corresponding to intraband and interband transitions as in the linear case. The intraband contribution, $\chi_{\text{intra}}^{(3)}$, due to a quantum size effect and varying with particle radius R_p , is absent in the bulk phase. It is estimated to be negligible as compared with the interband contribution, $\chi_{\text{inter}}^{(3)}$. The latter is thought to be mainly imaginary and negative since it corresponds to the saturation of resonant two-level transitions. However, the validity of this argument may be ensured for photon energies larger than the interband transition threshold only. Moreover, the calculations of Hache *et al.* have been carried out in a specific spectral domain, close to this IB threshold in the vicinity of point X of the Brillouin zone and to the SPR of gold particles [18]. This actually means that the imaginary character of $\chi_{\text{inter}}^{(3)}$ as well as, more generally, the sign and modulus of both electronic contributions, are expected to undergo spectral variations, which is rarely considered in the literature.

As soon as the incident wave intensity is sufficiently high, the modification of the conduction electron distribution induced by photon absorption may result in a significant modification of the optical transition spectrum [22,23]. This is the *Fermi smearing*, which is not a pure electronic nonlinear effect but was demonstrated by Hache and co-workers to amount to an optical Kerr effect contribution [18], that they characterized by the *hot electron* susceptibility, $\chi_{hot\ electrons}^{(3)}$. However, their calculation was restricted to both a specific energy range close to the SPR and a specific excitation pulsewidth (picosecond), a parameter on which the induced electron distribution modification is highly dependent. Thanks to very recent calculations, we will show below that $\chi_{hot\ electrons}^{(3)}$ in fact exhibits strong variations with pulse duration, photon energy and even laser intensity.

It appears then that Flytzanis' group findings should not be taken for granted in being generalized whatever light excitation wavelength, intensity and temporal regime. However, within their restricted applicability domain, they provide a good idea of the nature and order of magnitude of the different contributions to $\chi_m^{(3)}$. Let us summarize their main results: At the SPR frequency of gold nanoparticles the intraband contribution is found to be negligible against the interband one. The latter is mainly imaginary and has a negative sign: $\text{Im } \chi_{inter}^{(3)} \sim -1.7 \times 10^{-8}$ esu. For picosecond pulse excitation at the SPR, the hot electron contribution is also mainly imaginary but has a positive sign. Its magnitude is higher than the one of $\chi_{inter}^{(3)}$: $\text{Im } \chi_{hot\ electrons}^{(3)} \sim 1.1 \times 10^{-7}$ esu. A compilation and an analysis of several results regarding the value of $\chi_m^{(3)}$, extracted from experimental data obtained on weakly concentrated nanocomposites and reported in the literature, can be found in Ref. [3].

3 Influence of thermal exchanges on the nonlinear optical response

The fast energy input in the electron gas drives the latter out of equilibrium and induces the modification of the transition spectrum implying energy states close to the Fermi level and then the modification of the optical response close to the interband transition threshold. The return of the global medium back to thermodynamic equilibrium via all other processes goes along with the variation of the optical properties due to electron gas cooling down, lattice temperature change, host medium heating and thermal exchange between neighbouring particles. Hence, the mechanisms involved in the optical response dynamics mainly originate from thermal effects, at a broad meaning. In this last part, we will describe how temperature variations can be related to the induced variations of the optical response. It amounts in fact to model the mechanisms involved and to evaluate their influence. Depending on the situation (excitation and observation timescales considered, spectral domain, input power,...) it may be possible to focus on a few

Figure 1

Linear absorption coefficient of the virtual thin Au:SiO₂ film (thickness: 140 nm, $p=8\%$) which will be further considered for the calculation of its nonlinear optical response. The collision factor Γ in the Drude model has been set to 1.1 eV to account partially for finite size effects in gold nanoparticles.

of them, either the most significant ones, or those the effects of which are to be specifically studied, or treat them in a global manner. We will present here two usual cases, defined relatively to the establishment of the thermodynamic equilibrium between electrons, metal lattice and local environment at the nanoscale. For this, a thin Au:SiO₂ film with concentration $p = 8\%$ and thickness $L = 140$ nm will be considered. Particle diameter is fixed at 2.6 nm. In order to partially account for finite size effects on the optical response (broadening and quenching of the SPR absorption band due to electron mean free path limitation [24]) the value of the collision factor Γ has been set to 1.1 eV. Let us stress that such a phenomenological way to describe finite size effects in gold nanoparticles would not be sufficient to explain the actual observations for the optical response. Indeed, a realistic interpretation should include the influence of both the free electron spill-out and the skin of reduced polarizability for the core d electrons [25]. The absorption spectrum of our virtual sample, deduced from Maxwell-Garnett theory (MGT), is shown on Fig. 1 where the effects of both SPR and interband transitions are clearly identified.

3.1 Stationary regime

The stationary thermo-optical regime has been recently studied in our group from both theoretical and experimental points of view [26,27]. Let us here synthesize the key principles and issues in order to apply the findings to one specific aspect of the nonlinear optical response of gold nanoparticles. This regime is rather easy to deal with regarding the thermal aspect since the only knowledge of one temperature is sufficient to describe the thermodynamic

state of a particle and its close neighborhood. It is encountered when applying a continuous laser or a pulsed laser the pulsewidth of which is large as compared with the characteristic time of nanoscale heat exchanges. Beyond the issue of overheating by light absorption, this situation corresponds also to thermo-modulation experiments or more simply to cases where the global medium temperature varies macroscopically.

3.1.1 Thermo-optical response of gold

The origins of the thermo-optical response of noble metals are multiple and were the subject of numerous investigations in the 1970s, particularly for gold [28–33]. Various mechanisms lead to the modification of the interband and intraband transitions following a temperature variation, by affecting either directly the electron distribution, or the properties related to the lattice via the increase of the interatomic distance, or the collision processes.

The complex index variation of a material can be linearly linked, to first order, with the temperature variation through the thermo-optical coefficients $d_T n = \delta n / \delta T$ and $d_T \kappa = \delta \kappa / \delta T$:

$$\Delta \tilde{n}(t) = (d_T n + i d_T \kappa) \Delta T(t). \quad (7)$$

The thermo-optical coefficients of gold, averaged in the range 295–670 K, have thus been determined by a precise analysis of the literature, notably by cross-checking different experimental data from thermo-modulation spectroscopy [26].

3.1.2 The case of nanocomposite media

The thermo-optical response of a nanocomposite medium depends naturally on that of its constituents. In the manner of the third-order nonlinear optical response of nanocomposite materials (see § 2.2), their thermo-optical response does not amount to the simple volume average of the responses of each of their constituents. Indeed, the local field factor the complex value of which undergoes strong variations around the SPR plays an essential role. As far as the optical properties of an inhomogeneous material can be, under certain hypotheses, described by an effective medium approach like MGT, the latter can be extended to the case of the dependence on temperature. For that purpose, we identify the parameters depending on T (metal and matrix indices, metal concentration) in the expression of the effective susceptibility which we differentiate then. We have thus shown that the effective thermo-optical response in the SPR spectral domain presents a resonant character. The condition of such a resonance appears to be exactly similar to that of the optical response at the SPR. Metal particles present their own thermo-optical response, possibly affected by the interactions with their neighbours. The local field plays then the role of a “complex magnifying glass” by amplifying and warping this intrinsic spectral response in the vicinity of the plasmon resonance. This is particularly perceptible for gold nanospheres where the SPR and the interband transition threshold, at the origin of the main modifications of the optical response, are

located at very close photon energies. The consequences are surprising at first sight: The effective thermo-optical coefficients of the global medium are amplified by the effect of local field enhancement, and presents spectral variations in both sign and magnitude very different from those observed for the constituents taken separately. Stationary ellipsometry measurements at different temperatures have confirmed these findings [27]. Additionally, we have been able to infer that the thermal expansion of metal nanoparticles is quenched when embedded in a solid matrix.

3.1.3 Application to the nonlinear response: Thermal lens contribution

The principle of thermal lens is as follows. The inhomogeneous intensity distribution in the transverse section of a laser beam induces the heating of the material with a spatial profile correlated to the beam one through optical absorption and energy conversion mechanisms. Due to the material thermo-optical response, the inhomogeneous heating induces an index gradient in the transverse plane. The medium then acts on the beam as a lens, converging or diverging depending on the sign of $d_T n$. Moreover, the beam absorption by the medium may be modulated following the value of $d_T \kappa$. The thermo-optical coefficients then tend to play a role equivalent to that of the nonlinear coefficients for the Kerr effect. This has already been highlighted in various experimental works. By applying the z-scan technique in the time-resolved off-axis scheme Ganeev *et al.* have demonstrated the presence of a thermal lens effect in the third-order nonlinear response of metal nanoparticles in the nanosecond pulse regime and its absence in the picosecond regime [34]. Liao *et al.* have also invoked thermal effects to explain the discrepancies observed between different pulse temporal regimes [35]. Furthermore, several authors have demonstrated the involvement of thermal lens in the value of $\chi^{(3)}$, stemming from cumulative thermal effects generated at high pulse repetition rates [36–39]. We are thus led to define the thermo-optical contribution to the nonlinear refraction and absorption coefficients, γ_{th} and β_{th} .

We have applied the three-temperature model (3TM) together with the results concerning the thermo-optical properties of nanocomposite materials in order to evaluate the contribution of the thermal lens phenomenon to the third-order nonlinear optical response of our virtual Au:SiO₂ film in the nanosecond pulse regime. At this timescale the problem is simplified since (i) heat diffusion at the macroscale (laser beam waist, about a few tens micrometers) takes several milliseconds to be significant and can thus be neglected during the pulse passage; (ii) laser intensity at the beam centre is homogeneous within a hundred nanometer scale, which means that all nanoparticles receive the same input energy; (iii) at the spatial mesoscale (one particle and its environment) the temperature field can be considered as homogeneous [26]; (iv) at the mesoscale the heat conduction characteristic time is worth a few picoseconds, which implies that at the pulse timescale the local medium follows the energy input

instantaneously. From the lattice and matrix temperature dynamics calculated in the nanosecond regime by using the 3TM (§ 3.1.2 of Ref. [1]) with typical experimental conditions [3] (pulsewidth: 7.5 ns, absorbed peak power: $P_{abs0} = 5 \times 10^{17}$ W m⁻³) we have deduced the effective medium temperature increase during the pulse passage, $\Delta\bar{T}$. This parameter is defined as the average temperature increase experienced by the pulse along its passage across the medium, weighted by the pulse intensity profile corresponding to the actual light flux measured in a nonlinear optical experiment [40]:

$$\Delta\bar{T} = \frac{\int_{-\infty}^{+\infty} [T(t) - T_0] P_{abs}(t) dt}{\int_{-\infty}^{+\infty} P_{abs}(t) dt}. \quad (8)$$

The effective thermo-refractive and thermo-absorptive coefficients, $d_T n$ and $d_T \alpha$, of the Au:SiO₂ medium for a given gold concentration are determined as explained in § 3.1.2. The corresponding equivalent thermal nonlinear coefficients are then deduced from:

$$\begin{cases} \gamma_{th} = d_T n \Delta\bar{T} / I_{00} \\ \beta_{th} = d_T \alpha \Delta\bar{T} / I_{00} \end{cases} \quad (9)$$

where I_{00} is the laser pulse peak energy, calculated from the value of P_{abs0} by using the medium linear absorption coefficient, air-film transmission, film thickness and metal concentration. In this pulse temporal regime, $\Delta\bar{T}$ is proportional to intensity [40]. Consequently, γ_{th} and β_{th} do not depend on the I_{00} value. The result of this calculation is presented on Fig. 2 where γ_{th} and β_{th} are reported as a function of photon energy for the virtual sample described

above. Let us describe the main features revealed by these curves. First, the overall order of magnitude of the thermal contribution is fully comparable to that of experimental data obtained in similar conditions. The thermal effect is then likely to compete with the pure nonlinear optical Kerr effect from electronic origin. Secondly, the thermo-optical effect contributes significantly to nonlinear absorption around the SPR, whereas this effect is always disregarded in the literature unlike the refractive part. This leads us to talk rather about a generalized thermal lens contribution. Finally, γ_{th} and β_{th} undergo strong magnitude and sign variations in the plasmon resonance spectral domain. This has interesting consequences as for instance on the thermal lens effect, as illustrated in a schematic manner on Fig. 3: Depending on the incident light wavelength, the same material can behave, either as a converging, or as a diverging lens.

Figure 3

Schematic illustration of the spectral dispersion of the thermal lens phenomenon in a nanocomposite medium.

Figure 2

Calculated spectral dispersion of the thermal contribution to the nonlinear refraction (red) and absorption (violet) coefficients of the virtual thin Au:SiO₂ film under 7.5 ns laser pulses.

3.2 Transient regime

This regime corresponds in particular to the case where the medium is exposed to ultrashort light pulses, as in a pump-probe experiment or in certain nonlinear optical investigations. Whereas in the stationary regime the mechanisms responsible for the thermo-optical response can be treated in a global manner, they need to be explicitly described in the transient regime as each acts in a different way and follows its own dynamics.

3.2.1 Calculation of the optical response dynamics

The optical response of a metal in the visible, near UV or near IR domain is driven by the properties of quasi-free conduction electrons and bound core electrons. The intraband and interband transition spectrum is determined by the knowledge of the conduction electron distribution around the Fermi level, $f(E, t)$, that is the occupation probability of an electron state of energy E at time t . f appears then as the relevant parameter to link the metal microscopic behaviour to its optical response. When the electron gas is at internal equilibrium (i.e. as soon as f can be given by the Fermi-Dirac

Figure 4

Spectral dispersion of the differential transmission (color level) as a function of pump-probe delay for the virtual thin Au:SiO₂ film corresponding to Fig. 5, calculated by solving Boltzmann equation in the athermal regime. Pump photon energy: 1.55 eV; energy absorbed from the laser pulse: $1.4 \times 10^{19} \text{ W m}^{-3}$; pulse duration: 250 fs. The thin horizontal line at $t=0$ denotes the instant of pump-probe superimposition.

statistics) the electron temperature T_e can be employed instead. We have already described in [1] the usual approach to describe the electron distribution dynamics (or that of T_e). Once the time evolution of f is determined by this model, and provided several data (as pulse energy and width, wavelength, linear absorption coefficient, initial temperature, particle size, host medium thermal conductivity, metal concentration,...) are known, the Drude (§ 2.1.1 of [1]) and Rosei (§ 2.1.2 of [1]) models are used to evaluate the modification of the metal dielectric function. Finally, an electromagnetic calculation method suited to inhomogeneous media – as for instance an effective medium theory or the multiple-scattering approach that we have presented in [1] – is carried out to obtain the response of the whole nanocomposite material. One can thus simulate the differential transmission or reflection of a sample in a pump-probe experiment or determine its nonlinear susceptibility.

As an example, the time evolution of the differential transmission $\Delta T/T$ (denoting the relative variation of the sample optical transmittance induced by the pump pulse and measured by the probe one) of the virtual Au:SiO₂ film is presented in colour levels on Fig. 4 as a function of probe photon energy. The pump pulse duration is 250 fs and its photon energy is 1.55 eV, corresponding to the fundamental frequency of a usual Ti:sapphire femtosecond laser. This result has been obtained by solving Boltzmann equation in the athermal regime as described previously (cf. § 3.1.1 of [1]), including the modification of the e - e and e - ph characteristic relaxation times due to finite size effects by using the values reported in Ref. [41] for $R_p=1.3 \text{ nm}$. One can notice on Fig. 4 the specific signature of gold around the

interband transition threshold at $\sim 2.4 \text{ eV}$, corresponding to the change in the conduction electron occupation probability around E_f induced by the pump pulse, amplified and warped by the local field factor at the SPR. As notified in Ref. [1], the influence of the thermal transport mechanism and particularly the importance of the ballistic regime for heat conduction in the matrix [42] is not effective at this short timescale and does not need to be considered in the calculation.

3.2.2 Application to the nonlinear response: Hot electron contribution

The hot electron phenomenon is likely to contribute significantly to the gold nanoparticle intrinsic susceptibility, $\chi_m^{(3)}$, as discussed previously. Let us recall that the only theoretical work devoted to the evaluation of the hot electron susceptibility is the one of Hache *et al.* as discussed in § 2.3. We have used our own approach based on Boltzmann equation or 3TM, depending on pulse duration, to determine the complex value of $\chi_{hot\ electrons}^{(3)}$. From the dynamics of the gold nanoparticle dielectric function provided by the procedure discussed just above it is possible to calculate the effective dielectric function variation during the pulse passage, $\Delta \bar{\epsilon}(\omega)$, exactly in the same manner as we did in the case of temperature for the thermal lens contribution (cf. § 3.1.3). Indeed, in a conventional nonlinear optical experiment the laser pulse acts as both the pump and probe pulses. $\Delta \bar{\epsilon}(\omega)$ then writes:

$$\Delta \bar{\epsilon}(\omega) = \frac{\int_{-\infty}^{+\infty} [\epsilon(\omega, t) - \epsilon_0(\omega)] P_{abs}(t) dt}{\int_{-\infty}^{+\infty} P_{abs}(t) dt}. \quad (10)$$

The complex index variation, $\Delta \bar{n}(\omega)$, is then deduced.

The nonlinear optical coefficients are obtained by dividing $\Delta \bar{n}$ by the peak intensity I_{00} , and the nonlinear susceptibility is deduced from Eqs. (3). This procedure has been applied to the virtual Au:SiO₂ material previously defined, in the case of 2 ps pulses and with varying incident laser power. Fig. 5 presents with a logarithmic scale the result of the calculations for the modulus of $\chi_{hot\ electrons}^{(3)}$, reported as a function of I_{00} and for selected photon energies. Two important features have to be pointed out on this figure. First, $|\chi_{hot\ electrons}^{(3)}|$ exhibits very large spectral variations. This stems from two reasons: (i) $\Delta \bar{\epsilon}$ undergoes spectral dispersion at fixed P_{abs0} , directly linked with the dispersion of the electron distribution, and (ii) P_{abs0} itself strongly varies with $\hbar\omega$ at fixed I_{00} , mainly because of the medium linear absorption dispersion (Fig. 1). This second reason – which somehow is of weak physical interest – is nevertheless crucial from a practical point of view: As the energy injected in gold nanoparticles strongly depends on α_0 and then on wavelength, the only knowledge of the laser beam power (or pulse peak intensity) is far from being sufficient in nonlinear optical measurements on nanocomposite materials. The peak power absorbed by metal volume units, P_{abs0} , appears to be a more relevant parameter. The second feature to be underlined on Fig. 5 is

that $|\chi_{\text{hot electrons}}^{(3)}|$ presents variations with intensity at given photon energy as soon as I_{00} reaches about 10 MW cm^{-2} , whereas one should expect a constant value, which is true at low energy only. In the intensity range of usual picosecond lasers (including amplified ones), the hot electron contribution to the gold nanoparticle intrinsic susceptibility is not constant: It is then not a pure third-order nonlinear effect. These findings confirm the care which needs to be taken regarding the generalization of results obtained in the frame of restricted conditions, as already pointed out in § 2.3. Nonetheless, by carrying out similar calculations (not shown here) on another virtual sample free of finite size effect and in a similar temporal pulse regime as to match the model assumptions of Hache *et al.* for the hot electron susceptibility, we obtain a value of $|\chi_{\text{hot electrons}}^{(3)}|$ at low intensity and at the SPR frequency close to the one they estimated (1.1×10^{-7} esu) [18]. Moreover, the investigation of the complex value of $\chi_{\text{hot electrons}}^{(3)}$ reveals that it is purely imaginary and positive at SPR, which was also reported in Ref. [18].

4 Conclusion

In a previous paper, we showed how the interaction of light with matrix-embedded gold nanoparticles can result in the generation of thermal excitations through different energy exchange mechanisms. Here, after having summarized the basic formalism and characteristics of the third-order

nonlinear optical properties of metal nanoparticle assemblies, we have presented how thermal processes can affect their optical response. We have then connected both aspects and pointed out their involvement in the nonlinear optical response of nanocomposite media. This has allowed us to take up the challenge of tackling two key issues in the field of third-order nonlinear properties of gold nanoparticles, which had never been carefully addressed until now: The influence of the generalized thermal lens in the long pulse regime and the hot electron contribution to the gold particle intrinsic third-order susceptibility, including its spectral dispersion and intensity-dependence. Numerous fields need further investigations from the theoretical point of view. Furthermore, the application of these approaches to the analysis of experimental data requires very well defined materials, with a high control level of the morphological parameters, as well as the ability to tune one experimental parameter value only while keeping the others constant. This may represent the adult age of the nonlinear optical investigations on gold nanoparticles.

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About the authors

Yannick Guillet got his PhD in Université Pierre et Marie Curie – Paris 6 in 2007, on the ultrafast dynamics of the nonlinear response of gold nanoparticle assemblies. He now develops femtosecond laser experiments as a post-doctoral researcher.

Majid Rashidi-Huyeh is associate professor at University of Sistan and Baluchestan, Zahedan (Iran). He achieved his PhD in 2006 about the influence of thermal effects on the optical response of metal-dielectric nanocomposite materials.

Dominique Prot is associate professor of physics at the Université Paris Sorbonne – Paris IV. His research is conducted in the Institut des Nanosciences de Paris (Université Pierre et Marie Curie – Paris 6) on electromagnetic properties of nanocomposite materials and is mainly focused on electric field calculation in matrix-embedded metal nanoparticles.

Figure 5

Variation of $|\chi_{\text{hot electrons}}^{(3)}|$ with incident pulse peak intensity (pulse duration: 2 ps) and at selected photon energies in the virtual $\text{Au}:\text{SiO}_2$ thin film corresponding to Fig. 1.

Bruno Palpant is associate professor at the Université Pierre et Marie Curie – Paris 6. He conducts his research activities in the Institut des NanoSciences de Paris where he is in charge of the group for nonlinear optics and thermal effects in metal nanoparticles. He got his PhD in 1998 from University of Lyon (France) about quantum size effects in matrix-embedded noble metal clusters, before joining Keio University (Japan) for one year. He has been interested in the linear and nonlinear optical response of noble metal nanoparticles and more recently in their link with thermal conduction at small space and time scales.

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