Optics Communications 326 (2014) 74–79

Contents lists available at ScienceDirect

Optics Communications

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

The third-order nonlinear optical susceptibility of gold

Robert W. Boyd [a,b,c,d,*], Zhimin Shi [e], Israel De Leon [c]

[a] The Institute of Optics, University of Rochester, Rochester, NY 14627, USA
[b] Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, USA
[c] Department of Physics and School of Electrical Engineering and Computer Science, University of Ottawa, Ottawa, Canada ON K1N 6N5
[d] Department of Physics and Astronomy, University of Glasgow, SUPA, Glasgow, UK
[e] Department of Physics, University of South Florida, Tampa, FL 33620, USA

A R T I C L E I N F O

Article history:
Received 3 January 2014
Received in revised form
2 March 2014
Accepted 4 March 2014
Available online 13 April 2014

Keywords:
Nonlinear optics
Gold
Plasmonics
Third-order nonlinear susceptibility

A B S T R A C T

We critically analyze reported measured values of the third-order nonlinear optical susceptibility $\chi^{(3)}$ of bulk gold. Reported values of this quantity span a range of more than three orders of magnitude. Much of this variation results from the use of different measurement procedures which are sensitive to different contributions to the nonlinear optical response. For example, values measured through use of third-harmonic generation or non-degenerate four-wave mixing tend to be significantly lower than those obtained from measurements of the intensity-dependent refractive index. We ascribe this behavior to the fact that the first two processes respond only to "instantaneous" nonlinearities, whereas the nonlinear refractive index has a contribution from the much stronger but much slower "hot electron," or "Fermi-smearing" mechanism, which has a response time of the order of picoseconds. The data also reveal that the hot-electron contribution has a strong dependence on laser wavelength, because of the turn-on of the 5d to 6sp transition at about 550 nm. It is hoped that the compilation presented here will prove useful in establishing what value of $\chi^{(3)}$ is most appropriate for adoption under various laboratory conditions.

1. Introduction

As a consequence of recent interest in plasmonics [1,2] and especially in nonlinear interactions in plasmonics [3], it has become increasingly important to possess accurate values of the nonlinear susceptibilities of metals of interest such as gold. In this paper, we summarize some of what is known of the third-order nonlinear optical (NLO) response of gold. We choose to treat only gold in the present paper both for definiteness and because gold is probably the single most important metal of interest to plasmonics.

As will become clear from the ensuing discussion, reported values of $\chi^{(3)}$ for gold span a very large range. While it is of course possible that some of the reported values are simply incorrect, the available data suggests that the measured value of $\chi^{(3)}$ depends sensitively on the laboratory conditions under which it was obtained, such as the laser wavelength, pulse duration, and details of the sample preparation.

Our goal in writing this report is primarily to compile what is known experimentally about the NLO response of gold. It is hoped that a compendium of laboratory results of this sort can help lead to a deeper understanding of the NLO response of material systems, although we emphasize that the development of this enhanced understanding is not the primary intent of the present report.

A notable complication to the present analysis is that the conceptual understanding of nonlinear optics is often based on the use of the nonlinear susceptibility $\chi^{(3)}$, whereas many laboratory measurements yield the complex nonlinear refractive index coefficient n_2 or just the nonlinear absorption coefficient β, which is proportional to the imaginary part of n_2. Formulas for converting between n_2 and $\chi^{(3)}$ are well established (and are summarized in the Appendix of this paper), but the conversion involves the complex refractive index of the material. As a result, the real (and imaginary) part of $\chi^{(3)}$ depends on both the real and imaginary parts of n_2, both of which thus need to be measured. At times, only one of these parts is known with good precision, and the determination of $\chi^{(3)}$ then becomes inaccurate. For this reason, within this review we will at times quote values of β, at other times n_2 values, and at still other times $\chi^{(3)}$ values, depending on which is known most accurately.

2. Theoretical understanding of the NLO response of gold

Our primary interest in writing this paper is to provide a compendium and analysis of laboratory investigations of the

* Corresponding author at: Department of Physics, University of Ottawa, Ottawa, Canada ON K1N 6N5. Tel.: +1 585 217 8681.
E-mail address: boydrw@mac.com (R.W. Boyd).

http://dx.doi.org/10.1016/j.optcom.2014.03.005
0030-4018/© 2014 Published by Elsevier B.V.

third-order NLO response of gold. Nonetheless, to place this discussion in context, in this section we present a brief survey of the theoretical understanding of the NLO response of gold. A very good, early treatment of this topic has been provided by Hache et al. [4].

This paper emphasizes that there are three dominant contributions to the third-order nonlinear optical response of gold, which we next describe.

(1) *The intraband or "free electron" contribution*: This is the contribution from the electrons in the partially filled 6s conduction band of gold [6]. These free electrons contribute to the linear optical properties of gold by means of the well-known dielectric response function which is given in SI units by

$$\varepsilon_{\text{free}} = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_e}, \tag{1}$$

where $\omega_p^2 = Ne^2/\epsilon_0 m$ is the square of the plasma frequency, ε_0 is the permittivity of free space, m and $-e$ are the mass and the charge of the electron, respectively, and γ_e is a damping parameter. It is crucial to note that free electrons do not have contributions to the nonlinear optical response in the electric-dipole approximation. This conclusion follows from the simple reason that, because there is no restoring force, there can be no nonlinearity in the restoring force. Furthermore, the ponderomotive nonlinearity [5] of free electrons, which can be important for Fermi–Dirac metal plasma such as silver, is expected to play a negligible role for gold owing to the presence of strong interband transition. Nonetheless, when electrons are confined, for instance within a spherical metal nanoparticle, they do display a nonlinear response as a consequence of quantum-size effects. Hache et al. [4] have shown that the nonlinear susceptibility of a gold particle of radius a can be expressed (in Gaussian units) as

$$\chi^{(3)}_{\text{intra}} = -i\frac{64}{45\pi^2}T_1T_2\frac{1}{a^3}\frac{e^4}{m^2\hbar^5\omega^7}E_F^4 g_1(1-a/a_0), \tag{2}$$

where T_1 and T_2 are population and dipole lifetimes, respectively, E_F is the Fermi energy, which for gold is 5.5 eV, g_1 is a parameter of order unity, and where a_0 is a characteristic size given by

$$a_0 = T_2(2E_F m)^{1/2} g_4, \tag{3}$$

where g_4 is another parameter of order unity. Note that $\chi^{(3)}_{\text{intra}}$ vanishes as $a \to \infty$. These authors estimate that at a wavelength of 532 nm the parameter a_0 will be of the order of 14 nm and that for spheres of radius 5 nm the nonlinear susceptibility will be of the order of $\chi^{(3)}_{\text{intra}} \approx 10^{-10}$esu $\approx 10^{-18}$ m^2/V^2. These authors also note that this calculation can be repeated for the case of third-harmonic generation, in which case they obtain a prediction about a factor of 1000 times smaller.

(2) *The interband contribution*: This contribution involves transitions from the 5d valence band to the 6sp conduction band, and can be interpreted as the lowest-order contribution to the saturation of the absorption associated with this transition. As a result, this interband contribution is largely imaginary. Hache et al. [4] have shown that the interband contribution of the nonlinear susceptibility can be expressed (in Gaussian units) as

$$\chi^{(3)}_{\text{inter}} = -i\frac{2\pi A}{3}T_1'T_2'\frac{e^4}{\hbar^2 m^4\omega^4}J(\omega)|\mathbf{P}|^4, \tag{4}$$

where A is an angular factor, T_1' and T_2' are, respectively, the energy lifetime and the dephasing time for the two-level system describing the interband transition, $J(\omega)$ is the joint density of states, and $\mathbf{P}$ is a constant associated with the momentum operator between the two states. They estimate that for this mechanism $\chi^{(3)}_{\text{inter}}$ is of the order of $-1.7i \times 10^{-8}$ esu or $-2.4i \times 10^{-16}$ m^2/V^2. They also estimate that $\chi^{(3)}$ for third-harmonic generation will be approximately a factor of 10^4 times smaller. A recent theoretical study also shows that it is possible to suppress the interband transition through the use of ultrashort (<10 fs) π-pulses and consequently to achieve self-induced transparency [8].

(3) *The hot-electron contribution*: This contribution involves electrons that are laser-excited from the 5d valence band to the 6sp conduction band. The energy carried by this excitation process ends up heating the electrons in the conduction band. The change in temperature of the conduction-band electrons modifies the Fermi–Dirac distribution function, leading to an increased population for energies above the Fermi level and a decrease in population for energies below the Fermi level. As a result, the dielectric function of gold is changed in a strongly frequency dependent manner [9,10]. Because of the mechanism just described, the hot-electron contribution is often alternatively referred to as the Fermi-smearing contribution. A typical value of the resulting third-order susceptibility is $\chi^{(3)}_{\text{hot electron}} \approx i \times 10^{-8}$ esu $= 1.4i \times 10^{-16}$ m^2/V^2. Detailed experimental studies of the response time of the hot-electron contribution have been reported by Sun et al. [11]. These authors find that the nonlinear response is not instantaneous but is associated with a turn-on time of approximately 500 fs. This value is determined by the time taken for the energy carried by the excitation process to thermalize and heat the conduction electrons. Furthermore, the nonlinear response decays with a relaxation time of several picoseconds. This is the time required for the temperature of the electrons to equilibrate with that of the lattice. Since the heat capacity of the lattice is much larger than that of the electrons, the hot-electron contribution essentially vanishes once this equilibration has occurred.

A recent theoretical prediction of the wavelength dependence of the hot-electron contribution to the third-order nonlinear optical response of gold is given in Fig. 1.

Finally, we point out that the nonlinear response of metallic systems and especially those associated with composite systems and metamaterials are strongly influenced by local field effects. A discussion of such effects lies outside the scope of the present paper, which is concerned primarily with the third-order susceptibility itself. The influence of local field effects has been discussed extensively in earlier work [4,12–16].

3. Laboratory studies of the third-order NLO response of gold

We next turn to a review of some of the experimental studies of the nonlinear response of gold.

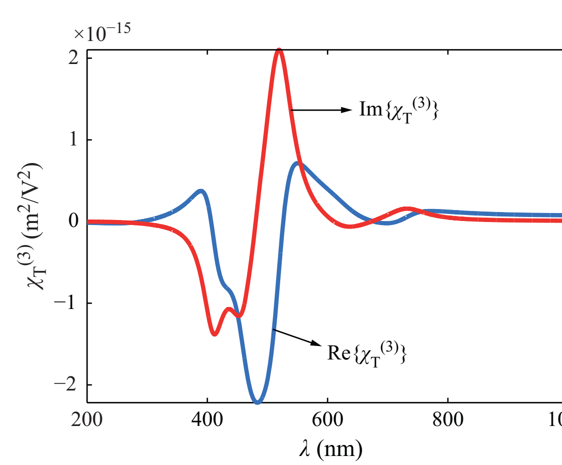

Fig. 1. Theoretically predicted dependence of the hot-electron contribution to $\chi^{(3)}$ on the excitation wavelength. [Reproduced with permission from reference [10].]