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The third-order nonlinear optical susceptibility of gold

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ABSTRACT

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.

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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

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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 $\omega_p^2 = Ne^2/\varepsilon_0 m$ 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

$$\chi^{(3)}_{\text{intra}} = -i\frac{64}{45\pi^2} T_1 T_2 \frac{1}{a^3} \frac{e^4}{m^2\hbar^5\omega^7} E_F^4 g_1 (1 - a/a_0), \tag{2}$$

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 $\chi^{(3)}_{\text{intra}} \approx 10^{-10}\text{esu} \approx 10^{-18}\ \text{m}^2/\text{V}^2$. 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 $-2.4i \times 10^{-16}\ \text{m}^2/\text{V}^2$. 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 $\chi^{(3)}_{\text{hot electron}} \approx i \times 10^{-8}\ \text{esu} = 1.4i \times 10^{-16}\ \text{m}^2/\text{V}^2$. 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.

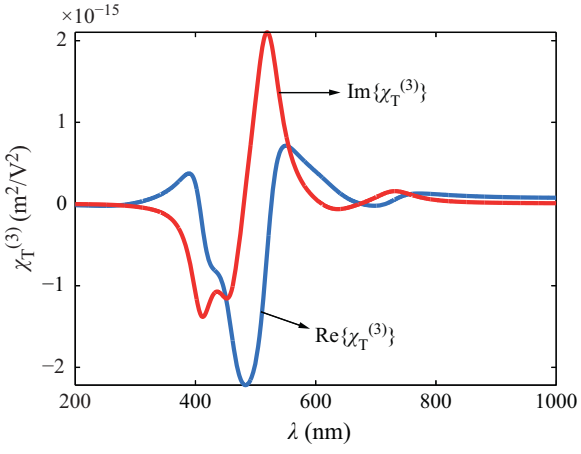

Fig. 1. Theoretically predicted dependence of the hot-electron contribution to $\chi^{(3)}$ on the excitation wavelength. [Reproduced with permission from reference [10].]

3.1. Bloembergen et al. [17,19]

The first reported study of the third-order nonlinear optical response of gold was that of Bloembergen and coworkers [17]. This measurement was performed through use of third-harmonic generation (THG). It thus includes only the "instantaneous" contributions to $\chi^{(3)}$ and specifically does not include the hot-electron contribution. Furthermore, the measurement provides only the complex modulus of $\chi^{(3)}$. This paper quotes a nonlinear coefficient for gold in terms of that of silicon, which they take as a calibration standard. They quote a value of $C_{1111}(\mathrm{Au}) = (0.27 \pm 0.131) C_{1111}(\mathrm{Si})$ where elsewhere in this paper they state that $C_{1111}(\mathrm{Si}) = 5.1 \times 10^{-11}$ esu. Here C_{1111} is the Maker–Terhune coefficient [18] which denotes the x-component of $\chi^{(3)}$ in response to electric fields in the x direction. We thus find that $C_{1111}(\mathrm{Au}) = 0.27 \times 5.1 \times 10^{-11}$ esu $= 1.38 \times 10^{-11}$ esu. These authors were presumably using the then-common convention that $\chi^{(3)} = 4C_{1111}$. We thus find that $\chi^{(3)}(\mathrm{Au}) = 4C_{1111}(\mathrm{Au}) = 5.51 \times 10^{-11}$ esu. We can convert this value to SI units using the formulas from the Appendix to obtain

$$\chi^{(3)}(\mathrm{MKS}) = 1.40 \times 10^{-8} \chi^{(3)} \text{ esu} = 7.71 \times 10^{-19} \text{ m}^2/\text{V}^2. \quad (5)$$

A related study was published 2 years later by the same group [19]. Here the authors note that they are studying a polycrystalline material, and thus are measuring an orientational average of the $\chi^{(3)}$ tensor. $\chi^{(3)}$ values are given relative to those of silicon, but the value of silicon seems to be not given. (More precisely, the value for silicon is stated to be $6.9 \times 10^4 \pm 30\%$ relative to that of LiF, but the value for LiF is not given.) In any case, the quoted result is

$$|\chi^{(3)}(\mathrm{Au})| = (0.086 \pm 0.030) |\chi^{(3)}(\mathrm{Si})| \quad (6)$$

The vertical bars were included presumably to indicate explicitly that only the modulus of $\chi^{(3)}$ had been determined. There seems to be no discussion as to why the ratio of the two $\chi^{(3)}$ values is so much different as in the earlier study. Assuming the same value of $|\chi^{(3)}(\mathrm{Si})|$ as in their first paper, we obtain for gold the value

$$\begin{aligned}\chi^{(3)}(\mathrm{MKS}) &= 7.71 \times 10^{-19} \text{ m}^2/\text{V}^2 \times (0.086/0.27) \\ &= 2.45 \times 10^{-19} \text{ m}^2/\text{V}^2 \end{aligned} \quad (7)$$

3.2. Smith et al. [15,20]

Smith et al. present the results of a z-scan [21] investigation of the nonlinear absorption of gold composite media [15,20] and a thin gold film [20]. Measurements were performed using 30-ps pulses at a wavelength of 532 nm. These measurements thus are sensitive to both the "instantaneous" and the hot-electron contributions to $\chi^{(3)}$. They report (for instance, in the abstract) a nonlinear absorption coefficient ranging from $\beta = 1.9 \times 10^{-3}$ to 5.3×10^{-3} cm/W (or 1.9 to 5.3×10^{-5} m/W) for different regions of the nominally uniform thin gold film. Conversion to a value of $\chi^{(3)}$ was complicated by the fact that they could not detect any nonlinear response in their closed-aperture z-scan measurements and thus could determine only an upper bound on the real part of n_2. However, we can make an estimate of the value of $\chi^{(3)}$ by assuming that the real part of n_2 vanishes and thus take n_2 to be purely imaginary. We determine the imaginary part of n_2 through use of Eq. (A.4) in the Appendix and subsequently determine $\chi^{(3)}$ through use of Eq. (A.2) in the Appendix. We take the complex refractive index of gold at a wavelength of 532 nm from the data of Johnson and Christy [25]. We find that $\varepsilon = -4.5498 + 2.3919i$ and that $n = 0.5433 + 2.2011i$. We thus find that $\chi^{(3)} = (-3.4 + 0.84i) \times 10^{-15}$ m^2/V^2 for the smaller of the reported values of β and that $\chi^{(3)} = (-9.5 + 2.3i) \times 10^{-15}$ m^2/V^2 for the larger value of β.

The authors of this work also pointed out that the lack of the experimental data of the nonlinear refraction parameter γ for a continuous gold film could lead to substantial errors in deducing the value of $\chi^{(3)}$. To overcome such difficulty, they further studied a gold doped composite glass with a gold concentration of 10^{-5}, whose both γ and β were measurable. By using generalized Maxwell–Garnett theory, they concluded that the nonlinear susceptibility of bulk gold should be $\chi^{(3)} = (-1 + 5i) \times 10^{-8}$ esu or $\chi^{(3)} = (-1.4 + 7i) \times 10^{-16}$ V^2/m^2.

3.3. Wang et al. [22]

This group [22] performed z-scan measurements on a roughened gold film at a wavelength of 532 nm and reports an enhanced value of $\chi^{(3)}$. They report a large positive real part of $\chi^{(3)}$ of 1.3×10^{-7} esu and a large negative imaginary part of -5.2×10^{-8} esu. A negative imaginary part is a characteristic of absorption saturation. When converted to SI units, these values become

$$\mathrm{Re}\,\chi^{(3)} = 1.3 \times 10^{-7} \times 1.40 \times 10^{-8} \text{ m}^2/\text{V}^2 = 1.82 \times 10^{-15} \text{ m}^2/\text{V}^2$$

$$\mathrm{Im}\,\chi^{(3)} = -5.2 \times 10^{-8} \times 1.40 \times 10^{-8} \text{ m}^2/\text{V}^2 = -7.3 \times 10^{-16} \text{ m}^2/\text{V}^2$$

However, we believe that the authors used an incorrect conversion formula in converting β to $\chi^{(3)}$ during which the real part of the linear refractive index of gold was used instead of the complex value. If we use the correct formula, their experimental results lead to $\chi^{(3)} = (3.7 + 5.0i) \times 10^{-14}$ m^2/V^2. The authors speculate that this large value of $\chi^{(3)}$ is due to surface plasmon polaritions. In the view of the present authors, it is not clear that it is correct to describe this enhanced response in terms of a change in the value of $\chi^{(3)}$, which is meant to be a material property. The experiments were conducted using laser light at 532 nm in 0.71 ns pulses at a repetition rate of 15 kHz. It is likely that considerable heating of the sample occurred as a result of the long pulse duration and the large repetition rate.

3.4. van Driel group [23,24]

Lee et al. [23] report a value of the nonlinear absorption coefficient of $\beta_{\mathrm{eff}} = 1.2 \times 10^{-5}$ cm/W at a wavelength of 600 nm, which is approximately two orders of magnitude smaller than the value obtained by Smith et al. [20]. However, this experiment was conducted with a pulse duration of 200 fs, whereas Smith et al. used 30 ps pulses and a wavelength of 532 nm. Subsequent work (see below) served to confirm that the differing results are largely a consequence of the different pulse durations.

Rotenberg et al. [24], in the same research group, performed z-scan measurements of the effective nonlinear optical absorption coefficient β_{eff} of 20-nm-thick Au films at 630 nm as a function of pulse duration. Their measurements show that β_{eff} increases from 6.8×10^{-7} to 6.7×10^{-5} cm/W (6.8×10^{-9} to 6.7×10^{-7} m/W) as the pulse width is varied from 0.1 to 5.8 ps.

These authors did not quote a value of $\chi^{(3)}$, and indeed one can only perform an estimate of the value of $\chi^{(3)}$ as the value of the real part of n_2 is not known. However, it is known that the real part of n_2 is much smaller than the imaginary part, and thus as an approximation we set the real part equal to zero. We determine the imaginary part of n_2 through use of Eq. (A.4) and subsequently determine $\chi^{(3)}$ through use of Eq. (A.2). We determine the complex refractive index at a wavelength of 630 nm from the data of Johnson and Christy [25]. We find that $\varepsilon = -11.4 + 1.27i$ and that $n = 0.188 + 3.38i$. We thus find that $\chi^{(3)} = (-76.8 + 4.28i) \times 10^{-20}$ m^2/V^2 and $\chi^{(3)} = (-75.7 + 4.21i) \times 10^{-18}$ m^2/V^2 for the two limiting values of β.

3.5. Xenogiannopoulou et al. [26]

Xenogiannopoulou et al. [26] present both optical Kerr effect (OKE) [27] and z-scan [21] measurements of the nonlinear optical response of gold. Using OKE methods, they report that the real part of $\chi^{(3)}$ is 2.8, 0.9, and 0.6×10^{-9} esu (or 3.9, 1.3, and 0.84×10^{-17} m^2/V^2) for films of 5, 22, and 52 nm thicknesses, respectively. Using the z-scan method, they report a value of $\beta=1\times10^{-3}$ cm/W for a film of 52 nm thickness. They conclude that the corresponding value of $\chi^{(3)}$ is $(-0.28+1.6i)\times10^{-8}$ esu, or $(-0.39+2.2i)\times10^{-16}$ m^2/V^2, which they state is in very good agreement with the results of Smith et al. [20].

3.6. Renger et al. [28]

Renger et al. [28] performed four-wave mixing studies using a variety of well-separated wavelengths in the near infrared to determine the modulus of $\chi^{(3)}$. They determined a value of $|\chi^{(3)}|=0.2$ $nm^2/V^2=2.0\times10^{-19}$ m^2/V^2. It should be noted that this result is close to the value of the Bloembergen group from 1971 [19] but not that of 1969 [17].

4. Summary and discussion

4.1. Reported values of the nonlinear coefficients

Here we summarize the analysis presented in the previous section. Reported values of the nonlinear absorption coefficient β are summarized in Fig. 2. Here the measured values of the nonlinear absorption coefficient β are plotted against the duration of the laser pulse used to perform the measurement. Note the overall trend that β tends to increase with increasing pulse duration, presumably as a consequence of a strong hot-electron contribution to the nonlinear response. For the data of Rotenberg et al., collected at 630 nm, there is a nearly linear dependence on pulse duration. Note also that the data collected at 532 and 600 nm tends to show larger response than the data collected at 630 nm. These results are consistent with the strong wavelength dependence of the nonlinear response near 550 nm as predicted in Fig. 1. The converted values of the third-order response are summarized in Table 1, and the results converted from z-scan experiments are also plotted in Fig. 3. The real part of $\chi^{(3)}$ is associated with the nonlinear phase shift experienced by the optical field upon propagation inside the material, and can be related to nonlinear processes such as Raman and Kerr effects. On the other hand, the imaginary part of $\chi^{(3)}$ is associated with nonlinear absorption. As a reference, a commonly quoted value of χ^3 for carbon disulfide is 3.1×10^{-20} m^2/V^2 [30]. The value of $\chi^{(3)}$ again shows an increase with laser pulse duration as a consequence of the mechanism of the nonlinearity. Such an increase is mainly due to the hot-electron contribution, which is not instantaneous but takes approximately 500 fs to turn on. Note that the nonlinear refraction coefficient γ, directly proportional to the real part of n_2, is much smaller than the value of β and hence suffers poor signal-to-noise ratio in z-scan experiments. For that reason, the value of γ is often taken to be zero when converting z-scan results to obtain the value of $\chi^{(3)}$. While such an assumption is reasonable in estimating the magnitude of $\chi^{(3)}$, it could potentially lead to inaccuracies in the value and even the sign of the real part of $\chi^{(3)}$.

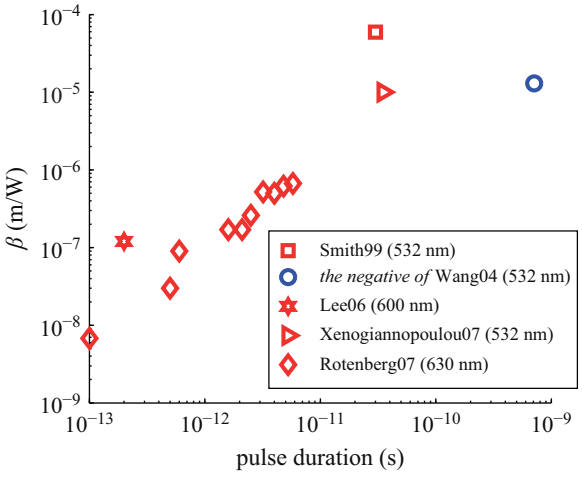

Fig. 2. Measured values of the nonlinear absorption coefficient β plotted against the duration of the laser pulse used to perform the measurement. Note the overall trend that β tends to increase with increasing pulse duration, presumably as a consequence of a strong hot-electron contribution to the nonlinear response. For the data of Rotenberg et al. collected at 630 nm, there is a nearly linear dependence on pulse duration. Note also that the data collected at 532 and 600 nm tends to show larger response then the data collected at 630 nm. These results are consistent with the strong wavelength dependence of the nonlinear response near 550 nm as predicted in Fig. 1.

Table 1
Compilation of the values of the third-order nonlinear optical response as described in this review. For reference, commonly quoted values of $\chi^{(3)}$ and n_2 for CS_2 are 3.1×10^{-20} m^2/V^2 and 3.2×10^{-18} m^2/W, respectively, at 2 ps excitation [30].

$\chi^{(3)}$ (m^2/V^2)	Method	τ_{pulse} (ps)	λ (nm)	n_2 (m^2/W)	Ref.
7.71×10^{-19}	THG	30	1064		[17]
2.45×10^{-19}	THG	30	1064		[19]
$(-1.4+7i)\times10^{-16}$	z-scan	30	532	$(14.8+7.0i)\times10^{-14}$	[20]
$(-9.5+2.3i)\times10^{-15}$	z-scan	30	532	$2.2i\times10^{-12}$	[20]
$(3.7+5.0i)\times10^{-14}$	z-scan	710	532	$(13.2-5.5i)\times10^{-13}$	[22]
$(-15.4+1.3i)\times10^{-18}$	z-scan	0.2	600	$5.73i\times10^{-15}$	[23]
$(-76.8+4.3i)\times10^{-20}$	z-scan	0.1	630	$3.41i\times10^{-16}$	[24]
$(-75.7+4.2i)\times10^{-18}$	z-scan	5.8	630	$3.36i\times10^{-14}$	[24]
$(-0.39+2.2i)\times10^{-16}$	z-scan	35	532	$(4.69+2.08i)\times10^{-14}$	[26]
2.0×10^{-19}	FWM	0.2	800		[28]

4.2. Comments

It is useful to review the values of $\chi^{(3)}$ that other researchers have used in their theoretical work. In their theoretical paper, Conforti et al. [9] provide an estimate of the value of $\chi^{(3)}$ for a four-wave mixing geometry with a pump wavelength of 950 nm and a probe wavelength of 500 nm. They adopt the value $\chi^{(3)}=(-8.4+11i)\times10^{-8}$ esu $=(-1.2+1.5i)\times10^{-15}$ m^2/V^2, and they note that this huge value, six orders of magnitude greater than that of fused silica, is due to the resonance of the probe with the interband transitions of gold.

In a separate paper, Samson et al. [29] consider the propagation of ultrashort pulses at a wavelength of 640 nm in a gold-clad waveguide. They adopt a value for the nonlinear response of gold of $\chi^{(3)}=7.6\times10^{-19}$ m^2/V^2. Note that this is the "earlier" (1969) result of Bloembergen.

In conclusion, in this work we have presented a summary of experimental measurements of the nonlinear response of gold. Although there is considerable variation in the reported values, the data also shows a strong trend regarding its dependence on wavelength and on laser pulse duration.

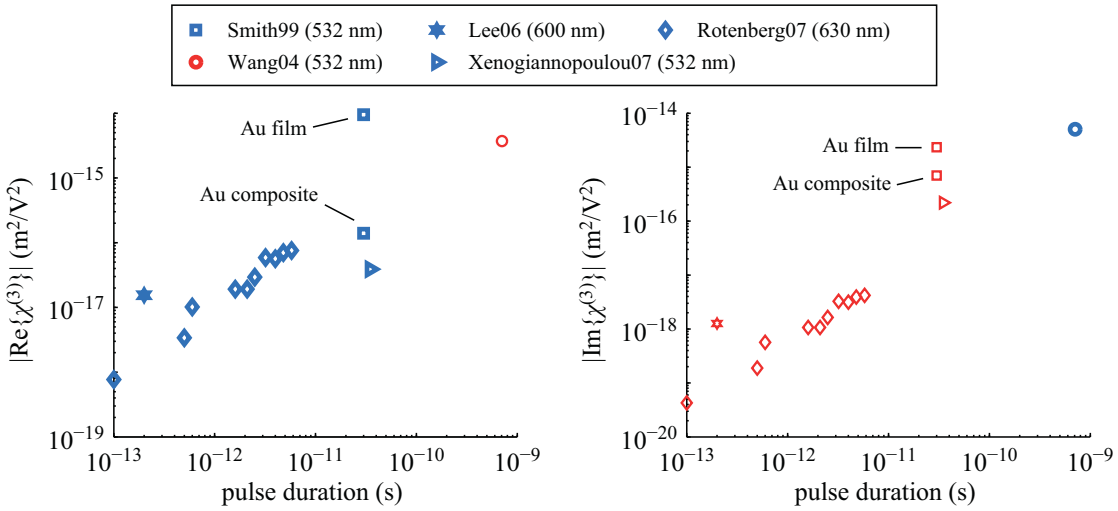

Fig. 3. Converted values of the third order nonlinear susceptibility $\chi^{(3)}$ plotted against the duration of the laser pulse from reported z-scan measurements. The thick blue and thin red markers indicate that the original values are negative and positive, respectively. Note that the correctly converted values are plotted from Wang-04, and that the Smith-99 paper reported results obtained from both a continuous Au film and Au-doped composite glass.

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Appendix

In this appendix we summarize procedures for converting between the Gaussian (esu) system of units and the SI system of units. We also review the relationships among the nonlinear susceptibility, the intensity-dependent refractive index, and the intensity-dependent absorption coefficient. Many of these results can also be found with derivation in the book written by one of us [30]. While an equivalent equation can be found in this reference, its equation number is included in parenthesis in the present discussion.

Conversion of the third-order susceptibility between the SI and Gaussian systems is performed using (C.12)[1]:

$$\chi^{(3)}\ (\mathrm{m}^2/\mathrm{V}^2) = [4\pi/(3\times 10^4)^2]\,\chi^{(3)}\ \text{esu} = 1.40\times 10^{-8}\chi^{(3)}\ \text{esu}. \tag{A.1}$$

The coefficient n_2 of the intensity-dependent refractive index is implicitly defined by the expression $n = n_0 + n_2 I$ for the refractive index n in the presence of an optical beam of intensity I. The relation between n_2 and $\chi^{(3)}$ is given in the SI system of units by (4.1.19-20)[2]:

$$n_2\ (\mathrm{m}^2/\mathrm{W}) = \frac{3}{4n_0 n_0' \epsilon_0 c}\chi^{(3)}\ (\mathrm{m}^2/\mathrm{V}^2) = \frac{283}{n_0 n_0'}\chi^{(3)}\ (\mathrm{m}^2/\mathrm{V}^2) \tag{A.2}$$

where n_0' denotes the real part of the linear refractive index n_0. Alternatively, the coefficient n_2 can be expressed in terms of the nonlinear susceptibility as given in Gaussian units as (4.1.21):

$$n_2\ (\mathrm{cm}^2/\mathrm{W}) = \frac{12\pi^2}{n_0 n_0' c}10^7\chi^{(3)}\ (\mathrm{esu}) = \frac{0.0395}{n_0 n_0'}\chi^{(3)}\ (\mathrm{esu}). \tag{A.3}$$

Another quantity of interest is the coefficient β of the intensity-dependent absorption coefficient, defined implicitly through the relation $\alpha = \alpha_0 + \beta I$. Here α is the familiar intensity absorption coefficient, defined through $dI/dz = \alpha I$. The quantities β and n_2 are related through

$$\beta = (2\omega/c)\mathrm{Im}\ n_2 \tag{A.4}$$

in any system of units.

It is crucial to note that a measurement of β determines only the imaginary part of n_2. Because the relationship between n_2 and $\chi^{(3)}$ involves the linear refractive index n_0, which for a metal is a complex quantity, a measurement of β cannot by itself be used to determine even the imaginary part of $\chi^{(3)}$. This fact leads to some of the ambiguity noted in the body of this paper in estimating accurate values for $\chi^{(3)}$.

[1] (C.12) refers to Eq. (12) in Appendix C of Nonlinear Optics, R. W. Boyd, Third Edition, Academic Press, Amsterdam (2008).

[2] (4.1.19-20) refers to Eqs. (19) and (20) in Section 1 of Chapter 4 of Nonlinear Optics, R.W. Boyd, Third Edition, Academic Press, Amsterdam (2008).

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