Nonlinearity measurements of thin films by third-harmonic-generation microscopy

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We show that the electronic part of the nonlinear susceptibility χ^3 of thin films can be easily measured by third harmonic microscopy. The phenomenon of third harmonic generation (THG) is excited by a femtosecond laser beam focused at the interface between the thin film and a reference layer. The value of χ^3 is deduced from the THG intensity measurements with the help of a classical model. The validity of this simple and alternative method is established by testing reference liquid films.

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There is a growing use of nonlinear thin films. This leads to an increasing interest in their studies. However, the problem of analyzing these thin films arises from their weak thickness that avoids conventional methods already used for the characterization of bulk media. An alternative microscopy technique, taking advantage of the discontinuity of the third order nonlinear susceptibility χ^3 and/or of the linear refractive index at the material interfaces, has been developed recently: when an exciting beam at the wavelength λ is focused on an interface, a coherent wave is built in the forward direction at the wavelength $\lambda/3$ by the third harmonic generation (THG) process [1,2]. This phenomenon has been used for microscopic observations of biological samples [3–5] and has been extended to homogeneous wide band gap semiconductor thin films [6]. Recently, it has been proposed for the determination of material properties [7] and for the determination of the transverse structure of photonic band gap fibers composed of Bragg structures [8].

We use this THG technique to measure the third order nonlinear susceptibility χ^3 of nonlinear thin films. We prove the efficiency of this method by testing classical nonlinear liquids inserted between two microscope coverslips. The study could be generalized to any nonlinear thin films.

The laser source used in the experimental setup is a synchronously pumped OPO (Spectra-physics Tsunami-Opal system). The system provides stable 130 fs pulses at a wavelength of 1.5 μm. The repetition rate is 80 MHz. The laser beam is focused at the material interface by a microscope objective (LOMO Achromat 40×/0.65, Newport 20×/0.2), as shown in Fig. 1. The third harmonic light (emitted at 0.5 μm in the forward direction through the sample) is collected with a condenser (aperture NA=0.4), filtered from the fundamental wavelength using an interference filter (λ_o =500 nm, $\Delta\lambda$=40 nm) and measured by a photomultiplier tube (PMT, Hammamatsu R5700). The condenser has a working distance of 3 cm. The photocurrent from the PMT is

synchronously detected via a lock-in amplifier, digitized and sent to a computer, which synchronizes the scanning process and the data collection.

The THG intensity I is measured as a function of the position of the focus of the microscope objective in the coverslip. It presents two maxima I_1 and I_2 obtained, respectively, when the focus is at the input interface (silica/air) and at the output interface (silica/nonlinear liquid) of the silica coverslip (Fig. 2).

I_1 and I_2 obey [9–11]

$$I_1 = H(I_L)^3 |\chi_{\mathrm{Si}} J(b, \Delta k_{\mathrm{Si}})|^2,$$

$$I_2 = H(I_L)^3 |\chi_{\mathrm{Si}} J(b, \Delta k_{\mathrm{Si}}) - \chi_{\mathrm{mat}} J(b, \Delta k_{\mathrm{mat}})|^2, \tag{1}$$

where I_L is the laser intensity; the subscripts Si and mat designate, respectively, the silica and the nonlinear material to measure. We have neglected the intensity changes due to reflection losses at the interfaces and supposed $\chi_{\mathrm{air}}=0$. H is a numerical parameter not made explicit here. $J(b, \Delta k)$ is defined by

$$J(b, \Delta k) = \int_0^\infty \frac{e^{i\Delta k z}}{\left(1 + 2i\dfrac{z}{b}\right)^2} \, dz, \tag{2}$$

b being the confocal parameter (smaller than the silica thickness) and Δk the wave vector mismatch defined by

$$\Delta k = 3k_1 - k_3 = \frac{6\pi}{\lambda}(n_1 - n_3), \tag{3}$$

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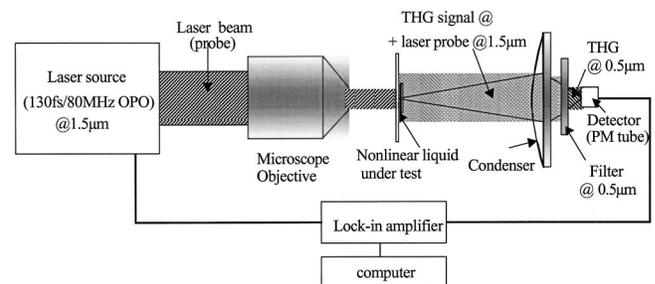
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FIG. 1. Experimental setup.

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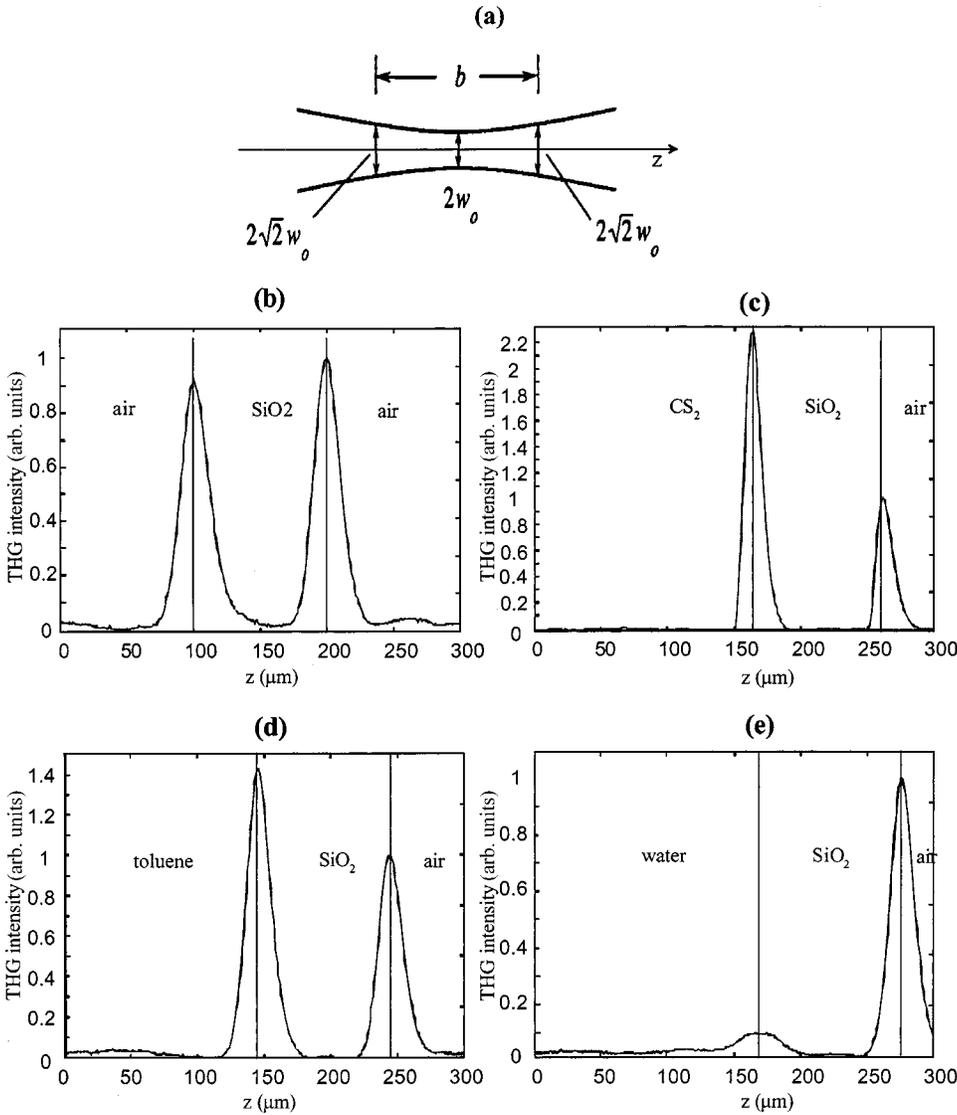
FIG. 2. THG intensity for different liquids embedded between two silica coverslips as a function of the position of the focus on the z axis (a) scheme of the focused beam, (b) reference for the silica slide, (c) CS_2, (d) toluene, and (e) water.

where n_1 and n_3 are, respectively, the refraction indices at wavelengths λ and $\lambda/3$.

In order to deduce χ_{mat}/χ_{Si} from the measurements of I_1 and I_2 using Eq. (1), it is necessary to know the values of the parameter $J(b,\Delta k)$. This parameter has been calculated [11]. J/b depends only on the product $b\Delta k$. The curve representing J as a function of Δk is shown in Fig. 3.

The validity of the numerical estimation of J has been controlled experimentally using the interfaces between air and reference nonlinear glasses for which χ and Δk have been measured separately [12]. Table I presents the results obtained. They confirm the validity of the model and allow the determination of b. For the microscope objective ($\times 40$, NA$=0.65$) used in the main part of our measure-

TABLE I. Measurements on Schott silicate glasses.

Material	$n_2 \times 10^{20}$ (m^2/W) [12][a]	$\|\Delta k_{mat}\|$ [12] (μm^{-1})	I_2 (arb. units)	J/b (arb. units)[b]	J/b absolute[c]
SF1	15	0.6	1.6	1.8	0.32
SF2	9	0.49	1	1.9	0.36
SF58	34	1.03	2.7	1	0.19
SF59	38	1.07	2.8	0.9	0.17

[a]n_2 is proportional to χ^3. It is measured at $I=1.5$ μm. Δk is measured between 1.5 and 0.5 μm.
[b]A relative value of J/b is calculated using formula (2) and taking arbitrary units for measured values of I_2.
[c]The absolute value of J/b is deduced from a comparison between the curve in Fig. 3 and the relative values of J/b (column 5 of this table).
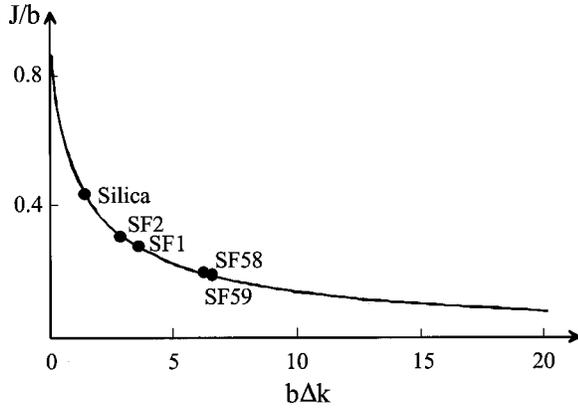
FIG. 3. Values of $J/b(b,\Delta k)=J$ as a function of $b\Delta k$ (from Ref. [11]). The solid circles are measurement points for different Schott nonlinear glasses.

ments, we measure $b=6\ \mu$m.

Our setup now being controlled and calibrated, we use it to measure the third order nonlinear susceptibility of nearly transparent liquids (at both wavelengths λ and $\lambda/3$). We verify that the liquid thickness is larger than b. We measure the THG intensities I_1 and I_2 [see Fig. 2 and formula (1)]. The ratio $R=I_2/I_1$ obeys the following relation:

$$1-\frac{\chi_{\text{mat}}}{\chi_{\text{Si}}}\frac{J(b,\Delta k_{\text{mat}})}{J(b,\Delta k_{\text{Si}})}=\pm\sqrt{R}. \qquad (4)$$

If the dispersion of the liquid is known, the values of J are obtained from Fig. 3, and $\chi_{\text{mat}}/\chi_{\text{Si}}$ can be deduced from Eq. (4). However, two values of $\chi_{\text{mat}}/\chi_{\text{Si}}$ are possible according to the choice of the sign in Eq. (4). A complementary observation is necessary in order to choose the right sign. We have made here a rough estimation of the relative values of χ_{mat} measuring the THG intensity at the interface liquid/air with a long working distance microscope objective, a very small volume of nonlinear liquid being placed in a simple petri

dish. The measurements and results are presented in Table II.

We remark that the value of the parameter $b\Delta k$ remains situated between the two values 3 and 6 for the fairly dispersive materials studied. Thus, the value of J/b remains in the range 0.22 to 0.31 for such materials: if the uncertainty on the dispersion is large—typically in the range of 30%—the uncertainty obtained on the ratio $\chi_{\text{mat}}/\chi_{\text{Si}}$ will be of the same order. The precision obtained can be sufficient if the setup is used to test thin films of new materials and to get in a short time the value of χ without measuring the dispersion. We notice that the choice of the confocal parameter is important: too small a value of b yields a larger uncertainty in the determination of J, while too large a value limits the THG intensity. The choice made here of $b=6\ \mu$m ($\times 40/0.65$) is a good compromise.

We can compare the results shown in Table II to those obtained on the same liquids by different measurement techniques and for different durations of the laser excitation, in the nanosecond, picosecond, and femtosecond range of excitation. We first restate some general features concerning the nonlinear susceptibility of liquids.

(i) Two main phenomena, displaying very different relaxation times, contribute to the nonlinear susceptibility of liquids: electronic processes, with relaxation times in the femtosecond range, and molecular movements, especially rotations, with relaxation times in the picosecond range. Molecular rotations are absent in the case of isotropic molecules, while they can have a large contribution to stationary values of χ in the case of anisotropic molecules. For instance, in the case of CS_2, the part of the electronic contribution to the stationary value of χ, measured by a time resolved phase grating method [14], is only 11%. We thus expect a decrease of χ for anisotropic molecules when the laser pulse duration goes from some picoseconds to some femtoseconds, while we expect a conservation of χ for isotropic molecules.

(ii) In third harmonic generation, only the electronic part of χ is active. Thus, the measurements of χ by THG methods are expected to give the same value χ_e whether the pulse

TABLE II. Measurements of the nonlinear susceptibility of liquids.

Nonlinear material	Δk (μm^{-1})[a]	$b\Delta k$ with $b=6\ \mu$m	$J/b(b,\Delta k_{\text{mat}})$ from Fig. 3	$R=I_1/I_2$ (measured)	$\chi_{\text{mat}}/\chi_{\text{Si}}$ (This work[b])	$\chi_{\text{mat}}/\chi_{\text{Si}}$ (Ref. [15])
Reference Silica	0.23[a]	1.4	0.45	1	1	1
Water	0.25[a]	1.5	0.44	0.1	1.3	
Methanol	0.31	1.9	0.42	0	1	1
Carbon tetrachloride	0.5	3	0.31	1	3	2.4
Toluol	0.5	3	0.31	1.2	3.5	3.5
Carbon disulfide	1.6	9.6	0.14	2	8	8
Cyclohexane	0.3–0.8	1.8–4.8	0.4–0.22	1	2–4	2.1
Nitrobenzene	0.5–1	3–6	0.31–0.2	1.4	3.3–4.5	4.9
Chloroform	0.5	3	0.31	0.3	2.2	2.1

[a]The values of Δk are taken either from direct measurements at 0.5 and 1.5 μm (silica, water), or from dispersion measurements made in the visible and near infrared spectrums, and extrapolated by the Briot formula [13] to the working wavelengths 0.5 and 1.5 μm.
[b]$\chi_{\text{mat}}/\chi_{\text{Si}}$ is calculated from Eq. (4).

duration used for THG excitation has nanosecond or femtosecond values. All the other methods used, such as four wave mixing, Z scan, the optical Kerr effect, self-rotation of the polarization ellipse, etc., are connected with the propagation of the waves and serve to measure the total susceptibility χ, i.e., the sum of the electronic and molecular components, this last one being more or less active according to the duration of the excitation.

Our experimental results agree totally with these considerations:

(1) We obtain the same values of χ as Meredith *et al.* [15] who use THG excited by a Q-switch laser (see Table II).

(2) The value of χ for isotropic materials remains the same in the present measurements as in all the previous measurements made by diverse methods, in the nanosecond and picosecond range of excitation [15–17].

(3) The ratio $\chi_{\text{THG}}/\chi_{\text{total pico}}$ of the susceptibility measured by THG to the susceptibility measured by propagation methods in picosecond excitation takes the values 0.08, 0.2, 0.5, respectively, for CS_2, $C_6H_5NO_2$, $C_6H_5CH_3$. In the case of CS_2, there is a reasonable agreement between the ratio $\chi_e/\chi_{\text{total}}$ of 11% mentioned above [14] and our measurement.

In conclusion, the THG microscopy method proves to be simple and efficient for the nonlinear characterization of materials, and particularly of thin films. Our experiments confirm that the THG signal measured is consistent with the classical bulk model near interfaces, as already observed by Baral *et al.* [2]. The values of χ remain the same in our measurements as in the other THG measurements taken, whatever the pulse duration in isotropic materials, confirming that only the electronic part of χ is active in THG.

[1] T. Y. F. Tsang, Phys. Rev. A **52**, 4116 (1995).

[2] Y. Barad, H. Eisenberg, M. Horowitz, and S. Silberberg, Appl. Phys. Lett. **70**, 922 (1997).

[3] L. Canioni, S. Rivet, L. Sarger, R. Barille, P. Vacher, and P. Voisin, Opt. Lett. **26**, 515 (2001).

[4] D. Yelin and Y. Silberberg, Opt. Express **5**, 169 (1999).

[5] J. A. Squier, M. Muller, G. J. Brakenhoff, and K. R. Wilson, Opt. Express **3**, 315 (1998).

[6] C. K. Sun, S. W. Shu, S. P. Tai, S. Keller, U. K. Mishra, and S. P. DenBaars, Appl. Phys. Lett. **77**, 2331 (2000).

[7] J. M. Schins, T. Schrama, J. Squier, G. J. Brakenhoff, and M. Müller, J. Opt. Soc. Am. B **19**, 1627 (2002).

[8] R. Barille, L. Canioni, L. Sarger, S. Rivet, F. Brechet, P. Roy, and D. Pagnoux, Opt. Lett. (to be published).

[9] R. W. Boyd, *Nonlinear Optics* (Academic Press, New York, 1992).

[10] G. C. Bjorklund, IEEE J. Quantum Electron. **11**, 287 (1975).

[11] A. N. Naumov, D. A. Sidorov-Biryukov, A. B. Fedotov, and A. M. Zheltikov, Opt. Spectrosc. **90**, 778 (2001).

[12] S. Montant, Ph.D. thesis, University of Bordeaux I, 1999.

[13] G. Bruhat, *Optique* (Masson, Paris, 1992).

[14] E. Etchepare, G. Grillon, J. P. Chambaret, G. Hamoniaux, and A. Orszag, Opt. Commun. **63**, 329 (1987).

[15] G. R. Meredith, B. P. Buchalter, and C. Hanzilk, J. Chem. Phys. **78**, 1543 (1983).

[16] P. P. Ho and R. R. Alfano, Phys. Rev. A **20**, 2170 (1979).

[17] N. P. Xuan, J. L. Fourier, J. Gazengel, and G. Rivoire, Opt. Commun. **51**, 433 (1984).