

Optical heterodyning of the phase-tuned femtosecond optical Kerr gate signal for the determination of complex third-order susceptibilities

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We show that ultrafast optically stimulated birefringence and dichroism may be conveniently investigated by combining polarization sensitive optically heterodyned detection with phase tune-up between the optical Kerr gate signal and the local oscillator. The real and the imaginary parts of complex third-order optical nonlinearity can be effectively separated and their values and signs determined. 60 fs pulses at 620 nm were used in experiments carried on tetrahydrofuran solutions of canthaxanthin, a carotenoid important for photobiology. The values of both parts of the complex second hyperpolarizability γ as well as the sign of its real part determined by this method compare well with that obtained from the concentration dependence method employing the homodyne-detection optical Kerr gate technique.

Third-order nonlinear properties of optical media remain a subject of considerable theoretical and experimental effort¹ stimulated by the promise of attaining large values of the nonlinear susceptibility $\chi^{(3)}$ needed for practical applications in photonic devices. A reliable and convenient method of determination of the complex third-order susceptibility, $\chi^{(3)}$, i.e., the determination of the magnitudes and signs of both the *real* and the *imaginary* parts of the nonlinear susceptibility of photonic materials is thus of particular interest. Various sophisticated interferometric approaches^{2,3} can be used to determine the complex $\chi^{(3)}$, one of them being recently adapted for the case of strongly absorbing materials.⁴ For molecules of soluble compounds one can also determine the complex microscopic nonlinearity, i.e., the real and the imaginary parts of the molecular third-order hyperpolarizability γ by studying concentration dependence of the signal.¹

We present here a simple method designed for independent determination of both the real and the imaginary components of $\chi^{(3)}$, which is based on optically heterodyned detection of phase-tuned optical Kerr gate (OKG) signal. In general, both the birefringence and the dichroism (related to the real and the imaginary parts of the susceptibility, respectively) give their contributions to the detected OKG signal intensity. It is shown here that the optical phase adjustment between the local oscillator beam and the nonlinear response of the sample may be used for selective enhancement of the contribution from either the real or the imaginary part of third-order nonlinear optical susceptibility. This approach resembles schemes developed for nondegenerate wave mixing in coherent Raman spectroscopy where heterodyne detection has been successfully incorporated.⁵⁻⁷

In this study we apply the new method for the investigation of 4,4'-dioxo- β -carotene, known as canthaxanthin. This all-trans carotenoid, known for its wide distribution in nature as a pigment and important in photobiology, exhib-

its an extensive π -electronic conjugation which substantially enhances its third-order nonlinear optical properties. The compound was kindly supplied by Hoffmann-LaRoche Ltd. All the measurements were carried out on solutions of canthaxanthin in tetrahydrofuran (THF) at room temperature.

For two-wave mixing experiments we have used 60 fs pulses at 620 nm obtained from an amplified CPM oscillator, described in detail elsewhere.^{8,9} The laser system is able to deliver as much as 50 μ J/pulse at 8 kHz rate. The two-wave mixing experimental arrangement is shown schematically in Fig. 1. The laser beam is properly attenuated and split into two portions at 30:1 ratio. The stronger beam is used as a pump beam I_2 and the weaker beam, after passing through a variable delay line, RR, is used as a probe beam I_1 . The pump beam passes through a chopper to facilitate lock-in detection. Polarizers P_1 and P_2 are placed in the paths of the probe and the pump beams, respectively, before the sample. Both beams are polarized at 45° with respect to each other. Another polarizer P_3 is placed in the path of the probe beam after the sample in front of the detector TD. A quarter-wave plate, QP, can also be optionally inserted in front of P_3 in order to provide a $\pi/2$ phase bias for one of the signal beam components.

The detailed theoretical analysis of the method will be presented elsewhere. Here, we focus our attention on a very brief description of the method. We assume that the spatial coordinate system is positioned in such a way that the probe beam is initially x polarized, and the pump beam has both x and y components of equal amplitudes. Assuming a four-wave mixing formalism for the description of the OKG effect (interaction between x and y components of the pump beam and the probe beam) one can use slowly varying envelope approximation to derive expressions for the x and y components of the probe beam. These expressions will depend on the physical mechanism responsible for the interaction, which can involve, e.g., electronic nonlinearity, molecular reorientation, or induced changes of susceptibility due to presence of excited states. Here, however, we are only concerned with the prompt part of the third-order nonlinear response. Thus, all the measurements

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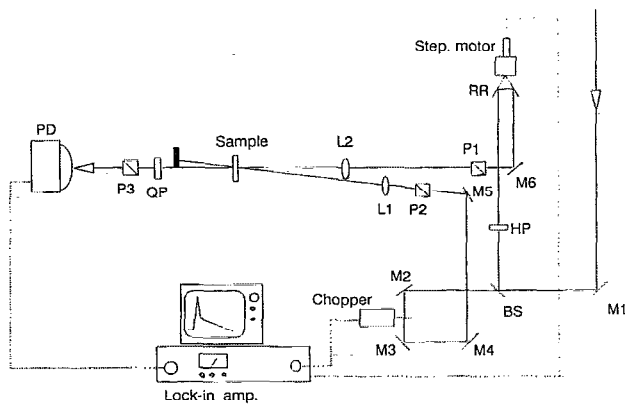


FIG. 1. Experimental arrangement employed for phase-tuned optically heterodyned two-wave mixing (the symbols are defined in the text).

referred to below were performed at the delay between the gate (pump) pulse and the probe pulse equal to zero, i.e., taking the advantage of the ultrafast femtosecond pulses employed, we measure mostly the electronic part of the nonlinearity. In this case the expression for the y component of the probe beam of frequency ω and wave vector k_1 is⁹

$$\frac{d\mathcal{E}_{1,y}(z)}{dz} = i \frac{2\pi\omega^2}{k_1 c^2} (\chi_{yx}^{(3)} \mathcal{E}_{2,x} \mathcal{E}_{2,y}^* \mathcal{E}_{1,x} + \chi_{yyxx}^{(3)} \mathcal{E}_{2,y} \mathcal{E}_{2,x}^* \mathcal{E}_{1,x}), \quad (1)$$

where the boundary condition is $\mathcal{E}_{1,y}(0) = 0$. In general, $\chi^{(3)}$ is complex, therefore, Eq. (1) will contain both real and imaginary terms. The relevant component of the generated field, $\mathcal{E}_{1,y}(L)$, due to the imaginary part of $\chi^{(3)}$ is in-phase with the local oscillator, $\mathcal{E}_{1,x}$, whereas the component due to the real part of $\chi^{(3)}$ is $\pi/2$ out-of-phase. Hence, the amplitude of the y component of the Kerr signal at the sample exit can be presented as $\mathcal{E}_{1,y}(L) = i\mathcal{G}_r(L) - \mathcal{G}_{im}(L)$, where \mathcal{G} is a function which, in the simplest case, will contain field amplitudes and components of $\chi^{(3)}$, and L stands for the beams interaction path. The indices r and im indicate the real and the imaginary parts of the function \mathcal{G} .

In homodyne-detection OKG one simply measures the y component of \mathcal{E}_1 by crossing the polarizer P_1 , and analyzer P_3 ; the measured intensity contains then contributions from both \mathcal{G}_r and \mathcal{G}_{im} . Heterodyne detection involves mixing of the OKG signal with a given fraction of a local oscillator signal (which may be the transmitted portion of the original probe itself).⁵ In our case the analyzer is rotated by some angle, ϕ , to admit a small contribution from the x component of the field. This component, practically equal to $\mathcal{E}_{1,x}(0)$ (neglecting small Kerr-induced contribution), constitutes a local oscillator field. In the presented technique, the phase relation between the response signal and the local oscillator beam is established by the presence or absence of a phase retardation element (a properly oriented quarter-wave plate with one principal axis parallel to the probe polarization \mathbf{x}) in the probe beam in front of the analyzer. The quarter-wave plate imposes a

fixed $\pi/2$ phase bias between the x component (local oscillator) and the y component (Kerr signal) of the field. Thus, without the quarter-wave plate the field after the analyzer is

$$\mathcal{E}_1(L) \propto \mathcal{E}_{1,x}(0) \sin \phi + \mathcal{E}_{1,y}(L) \cos \phi, \quad (2a)$$

and in the presence of the quarter-wave plate

$$\mathcal{E}_1(L) \propto \mathcal{E}_{1,x}(0) \sin \phi + i\mathcal{E}_{1,y}(L) \cos \phi. \quad (2b)$$

The lock-in detected intensity at the chopping frequency, $I = (nc/2\pi) \mathcal{E}_1(L) \mathcal{E}_1^*(L)$ (n standing for the refractive index of the sample), contains, therefore, terms proportional to $\cos^2 \phi$, $\sin^2 \phi$, and $\sin \phi \cos \phi$. For small angles up to first order in ϕ we arrive at

$$I = \frac{nc}{2\pi} (\mathcal{G}_r^2(L) + \mathcal{G}_{im}^2(L) - 2\mathcal{E}_{1,x}(0) \mathcal{G}_{im}(L) \phi), \quad (3a)$$

and

$$I = \frac{nc}{2\pi} (\mathcal{G}_r^2(L) + \mathcal{G}_{im}^2(L) - 2\mathcal{E}_{1,x}(0) \mathcal{G}_r(L) \phi), \quad (3b)$$

without and with a $\pi/2$ phase bias imposed, respectively. In the former case the detection favors the imaginary component of the signal (\mathcal{G}_{im}), while in the latter case the real component (\mathcal{G}_r) is favored.

Now, carrying out the measurements as a function of the angle ϕ and making use of the Eqs. (3), one can fit the dependence of the heterodyned OKG signal with the form $I = z_1 + z_2 \phi$. The coefficient z_2 is either proportional to the imaginary component, $\mathcal{G}_{im}(L)$, or proportional to the real component, $\mathcal{G}_r(L)$. The $\mathcal{G}_{r(im)}(L)$ can be substituted with an effective third-order nonlinearity $(\chi_K^{(3)})_{r(im)}$ and the proper beam intensities. Hence we obtain

$$z_{2,r(im)} = -\mathcal{C} \mathcal{R}_2 n^{-1/2} (\chi_K^{(3)})_{r(im)} I_2 I_1, \quad (4)$$

where $\mathcal{C} = 4\pi^2 \omega^2 L / k_1 c^3$, I_1 and I_2 stand for the pump and the probe beams intensities, respectively, and \mathcal{R}_2 represents a correction factor for attenuation of the beams in the sample due to linear absorption.

Figure 2 shows the dependence of the OKG signal on the analyzer angle, ϕ , for the solution of canthaxanthin in THF as well for pure THF. It is worthwhile to emphasize at this point that the signs of slopes of the lines in the figure render the signs of the corresponding nonlinearities $\chi_K^{(3)}$ according to Eq. (4). Moreover, the ratio of the z_2 coefficients obtained from the least-square fit to the results, like the ones presented in Fig. 2, will determine the real and the imaginary parts of $\chi^{(3)}$ of the investigated sample from the equation

$$(\chi_K^{(3)})_{r(im)}^s = \frac{z_{2,r(im)}^s (\chi_K^{(3)})_r^{\text{THF}}}{z_{2,r}^s \mathcal{R}_2^s}. \quad (5)$$

The superscripts s and THF denote the sample and the reference (tetrahydrofuran), respectively. For nonabsorbing reference we put $\mathcal{R}_2^{\text{THF}} = 1$ and due to a very low concentration of canthaxanthin in the solution we can safely assume the index of refraction for the solution to be the same as for the solvent.

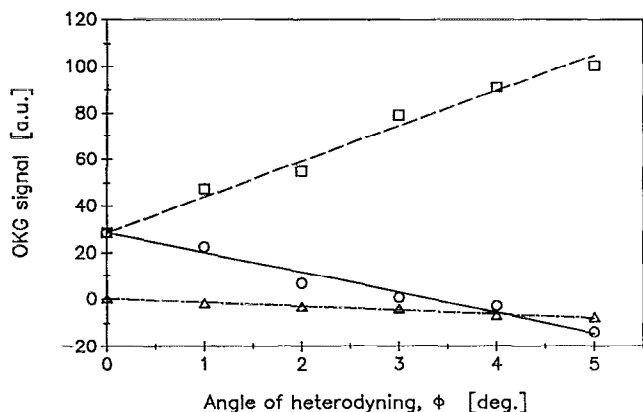


FIG. 2. Dependence of the OKG signal on the angle of heterodyning. The squares represent the data points taken using the quarter-wave plate, i.e., measuring the real part of nonlinearity, in the solution of canthaxanthin. The circles represent the data points for the solution collected without the insertion of the quarter-wave plate (imaginary part of nonlinearity). The triangles represent the data points for pure THF with the use of the quarter-wave plate. No heterodyne enhancement of the signal is observed for pure THF without the quarter-wave plate confirming that the imaginary component of $\chi^{(3)}$ for THF at 620 nm is negligible.

The effective $(\chi_K^{(3)})_{r(im)}$ calculated from Eq. (5) contains contributions from both the solute and the solvent. Therefore, for a dilute solution we have

$$(\chi_K^{(3)})_{r(im)}^s \cong (\chi_K^{(3)})_{r(im)}^{THF} + \mathcal{L}^4 N_c \gamma_{c,r(im)}, \quad (6)$$

where $\gamma_{c,r}$ and $\gamma_{c,im}$ stand for the real and the imaginary parts of the second hyperpolarizability of the solute (canthaxanthin), and N_c denotes the number density of canthaxanthin molecules. $(\chi_K^{(3)})_{r(im)}^{THF}$ is the effective third-order susceptibility of THF for which we assume no imaginary part. \mathcal{L} is the local field correction factor approximated by the Lorentz expression¹ $\mathcal{L} = (n^2 + 2)/3$, where n is the refractive index of the solution at 620 nm. In our calculations we employed the $\chi_{xxxx}^{(3)}$ value for THF equal to 3.7×10^{-14} esu, $n = 1.4070$ and the concentration of canthaxanthin in THF $N_s = 7.80 \times 10^{17} \text{ cm}^{-3}$. Deriving $(\chi_K^{(3)})_r^s$ and $(\chi_K^{(3)})_{im}^s$ from Eq. (5) and then using Eq. (6) we obtained the values of second hyperpolarizabilities of canthaxanthin $\gamma_{c,r} = -1.1 \times 10^{-31}$ esu and $\gamma_{c,im} = 1.6 \times 10^{-31}$ esu. For comparison, we also performed concentration-dependence measurements of the homodyne-detected OKG signal in a series of solutions of different concentrations of canthaxanthin in THF. For a more detailed description of this method see, e.g., Refs. 1 and 10. The obtained values are $\gamma_{c,r} = -1.5 \times 10^{-31}$ esu and $|\gamma_{c,im}| = 2.1 \times 10^{-31}$ esu, which are very close to those derived above by means of the method of phase-tuned optically heterodyned OKG.

In conclusion, the method presented in this letter gives results which are well compatible with those obtained by an "inner reference" method of concentration dependence studies. The new method has the advantage that it can readily be applied to solid samples. The method also yields signs of the real and imaginary parts of second hyperpolarizability by simply performing optically heterodyned OKG experiment as a function of the angle of the analyzer. The sign of slope in a plot of the detected signal vs the angle of the analyzer is opposite to the sign of the measured nonlinearity. Therefore, even a qualitative observation of the magnitude of the signal when the angle of the analyzer is increased readily indicates the sign for the measured nonlinearity (the imaginary part in absence of the quarter-wave plate and the real part in the presence of the quarter-wave plate). Furthermore, the absence of the heterodyne enhancement of a signal without the quarter-wave plate indicates that $\chi^{(3)}$ at the wavelength of measurement is real. Recently, Pfeffer *et al.*¹¹ have also used pulsed polarization-sensitive two-wave mixing in the picosecond time domain to investigate the real and the imaginary components of the third-order nonlinear optical susceptibility. Although basic principles of the two approaches are similar, the theoretical analysis and the experimental method of our work are different. We show that with the use of a phase-sensitive (lock-in) detection one can conveniently obtain the signs and the magnitudes of both the real and the imaginary components of γ and $\chi^{(3)}$. Also, our work focuses on an important conjugated and biologically active material.

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