Cross-propagating Beam-Deflection measurements of third-order nonlinear optical susceptibility

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ABSTRACT

We extend our recently developed Beam-Deflection (BD) method which we used to determine the sign, magnitude, and ultrafast dynamics of bound electronic and nuclear nonlinear optical responses, to measure elements of the third-order nonlinear optical susceptibility tensor with longitudinal field components. In these measurements, in contrast to the conventional BD technique where excitation and probe beams are nearly collinear, the interaction geometry involves orthogonal propagation of excitation and probe beams. This cross-propagating BD method enables probing with the electric field polarized parallel to the wavevector of the excitation beam as well as conventional parallel and perpendicular polarizations as in most other experimental methods. This technique may be of use in detecting possible magneto-electric contributions to the nonlinear susceptibility. The ratio between parallel and perpendicular bound-electronic responses in this method is shown to be larger than the factor of 3 predicted by theory and measured in the conventional configuration.

Keywords: Ultrafast Nonlinear Optics; Nonlinear Optical Materials; Ultrafast Phenomena; Kerr Effect

1. INTRODUCTION

Nonlinear refraction (NLR) and absorption (NLA) cause changes in the optical properties of a material as the irradiance of light increases. These phenomena open a variety of applications such as generation of ultrashort pulses, all-optical signal processing, and ultrafast switching [1]. The ever-increasing role of nonlinear optics has created a pressing demand for the characterization of the nonlinear optical susceptibility of various materials. The nonlinear susceptibility tensor is controlled by symmetry restrictions which are imposed by the spatial symmetry of the nonlinear medium. These limitations may reduce the number of independent coefficients or tensor elements for a given nonlinear susceptibility tensor. The lowest-order nonlinear response with non-vanishing terms is the third-order nonlinearity. Various experimental techniques are devoted to measuring the nonlinear optical (NLO) response. For example, Z-scan [2] measures the magnitude and sign of the NLR and NLA. Also, different time-resolved and polarization dependent techniques have been reported for measuring the third-order nonlinear properties of materials such as the optical Kerr effect (OKE) [3-6], degenerate four-wave mixing (DWFM) [7], as well as nonlinear interferometry [8]. However, the polarization combinations are often limited because of the interaction geometry. To fully exploit the third-order nonlinear optical properties of materials, we modified our Beam-Deflection (BD) technique [9] to study the elements of the third-order susceptibility tensor with field components along the propagation direction.

BD is a recently developed technique for measuring the sign, magnitude, and ultrafast dynamics of the third-order NLO response of a material [9]. Nonlinear refraction occurs at any wavelength in different phases of matter, e.g. liquids, gases, and solids, and may exhibit non-instantaneous responses [10-12]. The NLO response of materials includes both bound-electronic and nuclear contributions. The great sensitivity of the BD method (demonstrated sensitivity to nonlinearly-induced phase distortion of $\lambda/20{,}000$) allows such measurements [9]. Here we present an extension of the BD technique which involves a crossed-beam interaction geometry for excitation and probe beams. Here we use femtosecond laser pulses. This cross-propagating beam geometry was first used for characterizing the change in the refractive index induced by absorption due to thermal nonlinearities in the case of small thermal diffusion lengths compared to the excitation beam radius [13, 14]. In this geometry, the optical interaction length is determined by a combination of the beam sizes and shapes along with the pulsewidths. The cross-propagating geometry allows measurements of the nonlinear susceptibility tensor elements with longitudinal field components in addition to those available with the standard geometries. The control of polarization combinations helps to measure the ratio between different third-order susceptibility tensor elements. This may be of particular interest for the detection of the recently proposed magneto-electric (ME)

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susceptibility, where a nonlinear magnetic dipole is induced parallel to the magnetic optical field direction [15-17]. As we shall show, the crossed-beam method allows us to separately look at cases where the magnetic vectors in pump and probe are parallel, but the electric fields are perpendicular, and vice versa, perhaps allowing identification of magneto-electric contributions to the nonlinear susceptibility. In this work, we present polarization resolved cross-propagating BD measurements of a few selected organic solvents (CCl_4, $SnCl_4$, and Anisaldehyde) to study the third-order susceptibility tensor elements and responses of these materials.

2. CROSS-PROPAGATING BEAM-DEFLECTION TECHNIQUE

Beam-Deflection is a time-resolved and polarization-dependent technique for measuring the magnitude, sign, and dynamics of NLR and NLA. The principle of the BD method is similar to transient absorption spectroscopy with some modifications for measuring NLR. This method can measure the dynamics of NLR and NLA as opposed to techniques such as Z-scan [2] which only measures the magnitude and sign of the temporally and spatially averaged nonlinearities. Different polarization combinations between excitation and probe beams reveal information about both the instantaneous bound-electronic response and non-instantaneous nuclear motions. Three useful polarization combinations are co-polarized (parallel), cross-polarized (perpendicular), and magic angle (54.7°). At the magic angle, nuclear reorientation does not contribute to the detected signal, thus, in many situations, only the collision-induced and instantaneous bound electron response is detected. For highly symmetric molecules such as carbon tetrachloride, the reorientational response from nuclear reorientation vanishes [18]. When a strong excitation pulse interacts with a Kerr medium, it creates an index gradient that follows the Gaussian spatial profile of the irradiance of the beam, $I_e(\boldsymbol{r};t)$, in both transverse and longitudinal planes. The induced phase gradient appears as a refractive index gradient in its wings and acts as a thin prism. When the probe beam is focused to a spot size ~ 3-5× smaller than that of the excitation beam and displaced to the wings of the induced phase gradient, it experiences a linear index gradient. This deflects the probe beam by a small angle which is measured using a position sensitive segmented detector in the far-field. The nearly collinearly interaction scheme, requires the polarization of the excitation and probe beams to be in the transverse plane and, thus, it limits the polarization combinations to a single plane. By modifying this method to the cross-propagating geometry, we can measure the induced index change for polarization combinations which are not permitted by the collinear geometry, allowing the detection of suspected magneto-electric [15-17] susceptibility contributions to the nonlinear refractive index along the wavevector of the excitation beam.

In the present configuration, the experimental geometry entails a complex interaction scheme between excitation and probe beams and restricts the interaction length to the temporal and spatial dimensions of the two pulses, see Fig. 1(a). In other words, the detected signal is not directly proportional to the thickness of the sample and the effective interaction length is determined by the beam pulsewidths (τ_e, and τ_p) as well as spot sizes (w_e, and w_p) of both the excitation and probe beams, respectively. This can also help to extract the pulsewidth and spot size of the excitation beam from the cross-correlation signal. The effective interaction length is less than the spatial extent of the pulse; therefore, the spatial overlap of two pulses is relatively small within the interval of temporal overlap, and the deflection signal is significantly smaller than in the collinear case. To eliminate the need for tight focusing along the deflection axis, a cylindrical lens is used to tightly focus the excitation beam in one axis. When using two different wavelengths for the excitation and probe beams, the effects of group velocity mismatch is reduced due to the smaller interaction length comparing to the collinear case. Also, in the case of measurements on liquids, the cuvette walls do not contribute to the detected signal because the excitation and probe beams are interacting inside the liquid sample and do not spatially overlap on the cuvette walls. Since excitation and probe beams have perpendicular propagation vectors, it is possible to vary the polarization of the two beams to measure configurations different from the collinear case. In addition to the two standard parallel and perpendicular cases, another two perpendicular polarization configurations as well as magic angle configurations are measurable, see Fig. 1(b, c). This method enables the possibility of measuring two combinations where the magnetic optical fields of excitation and probe beams are parallel ($\chi^{(3)}_{zyyz}$) or perpendicular ($\chi^{(3)}_{xyyx}$) but the electric fields are perpendicular. This may help to measure the effect of nonlinear magnetic dipole moments which are along the magnetic field of the excitation beam [15-17]. The induced irradiance-dependent refractive index in different configurations, is given by:

$$n_j(I) \cong n_0 + \frac{3}{4n_0}\chi^{(3)}_{jiij}\left|E_{i,e}\right|^2 \qquad (i,j = x,y,z), \tag{1}$$

where n_0 is the linear index of refraction, $\chi^{(3)}_{jiij}$ is the corresponding tensor element, and $E_{i,e}$ is the amplitude of the excitation field polarized along i. The deflection angle, θ, is also proportional to the change in the refractive index and is given by

$$\theta \cong \int \nabla[\Delta n(\boldsymbol{r},t)]ds, \tag{2}$$

where *ds* is an infinitesimal displacement along the beam path [9].

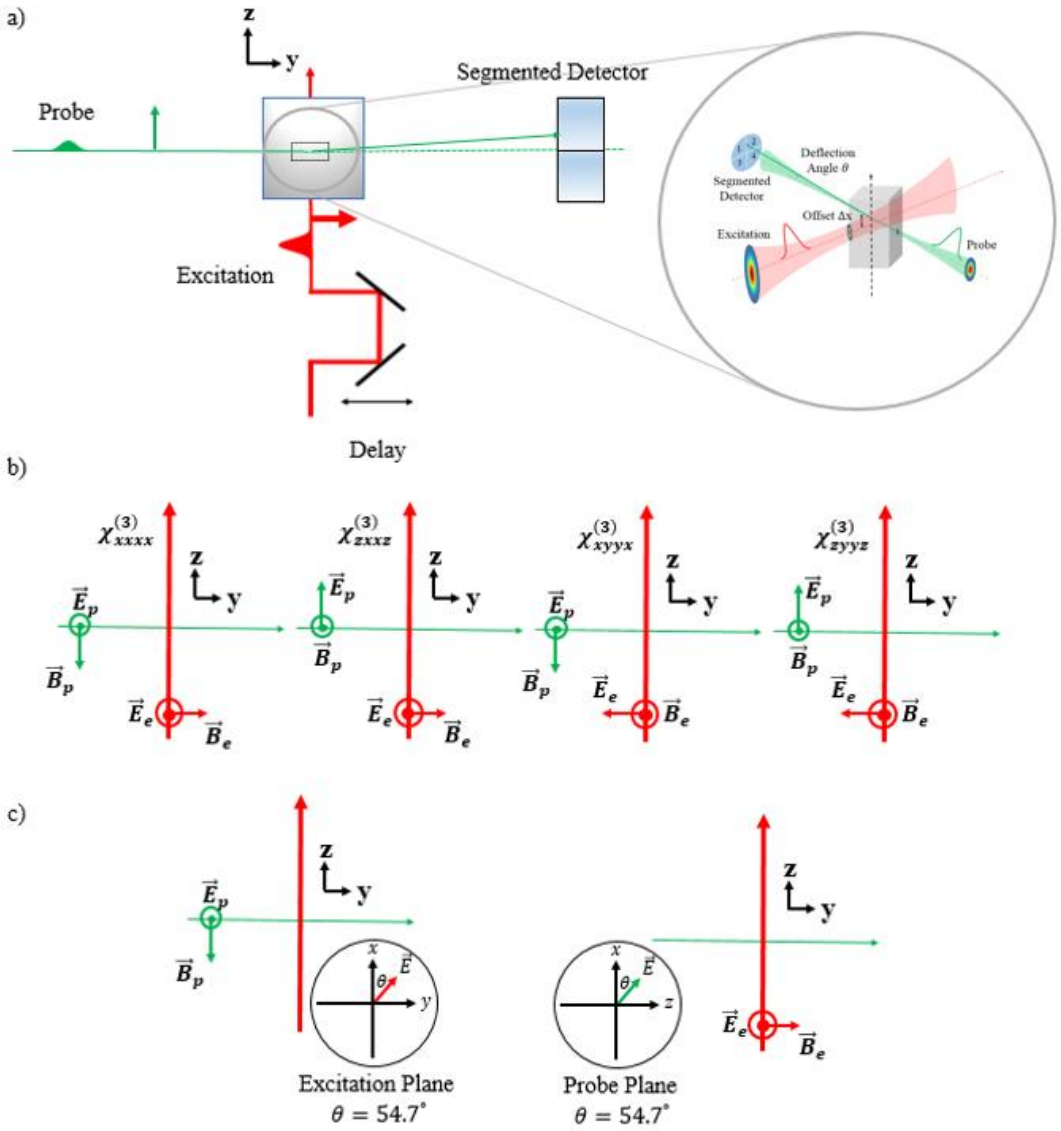

Fig. 1. (a) Schematic diagram of cross-propagating Beam-Deflection experiment and the interaction of excitation and probe beams. The probe is spatially displaced to the wings of the Gaussian profile of the excitation beam. (b) Different polarization configurations for parallel, perpendicular, and (c) magic angle between excitation (E_e, B_e) and probe (E_p, B_p). Case (b) offers opportunities to study the cases where electric fields of the excitation and probe beams are perpendicular but the magnetic fields are parallel, or vice-versa, or where both are perpendicular.

A regeneratively-amplified femtosecond laser (Clark-MXR) with 775 nm output pulse, 1 kHz repetition rate, 1 mJ pulse energy, and ~150 fs (FWHM) pulsewidth is used. A portion of the beam is focused into a 1 cm quartz cuvette filled with water to generate a white-light continuum, and then spectrally filtered by a narrow band-pass filter ($\Delta\lambda$~10 nm) at 650 nm to be used as the probe. A combination of half-wave plate, and polarizer is used to control the energy, and another half-wave plate is used to rotate the polarization of the probe (similarly for the excitation). The probe beam is focused in the sample and propagated to the far field and collected by a quad-segmented Silicon photodiode (OSI QD5-0-SD). To increase the signal-to-noise ratio we modulate the 1 kHz repetition rate excitation beam at 285 Hz for lock-in detection. The excitation beam is also filtered at 775 nm by using a narrow band-pass filter (~ 10 nm) and temporally delayed to measure the dynamics.

3. RESULTS AND DISCUSSION

Cross-propagating Beam-Deflection measurements are performed on a few symmetric molecules such as carbon tetrachloride (CCl_4) and tin tetrachloride ($SnCl_4$). In the non-resonant limit, the magnitude of the bound-electronic nonlinearity in isotropic molecules is predicted to be a factor of 3 smaller for crossed polarizations than for parallel polarizations. This theoretical prediction for isotropic tensor symmetry was verified by collinear BD geometry measurements in previous works [9-12]. Here, Gaussian fits to the results for carbon tetrachloride and tin tetrachloride are used to find the ratio between parallel and perpendicular polarization contributions, as shown in Fig. 2(a, b). It is intriguing to see a ratio of 4 compared to the collinear geometry, where our experiments and theory show that the ratio is 3 [9]. Measurements on isotropic liquids have not shown any difference between the different off-diagonal cases, $(\chi^{(3)}_{zyyz})$ or $(\chi^{(3)}_{xyyx})$ which indicates that the magnetic optical field direction does not seem to affect the result. This technique is also used in measuring dynamics of NLR of meta-Anisaldehyde and para-Anisaldehyde organic liquids for parallel, perpendicular, and magic angle configurations as shown in Fig. 2(c, d). In this case, the non-instantaneous contributions to the BD signal are a result of nuclear rotations [9-12]. The polarization dependence of the non-instantaneous response can be observed at longer delay, where for parallel polarization the signal is positive, and for perpendicular polarization it is negative. At the magic angle the nuclear rotations are completely eliminated and the signal is only due to mechanisms with isotropic symmetry which we attribute to the instantaneous bound-electronic response and collision-induced mechanisms [9-12].

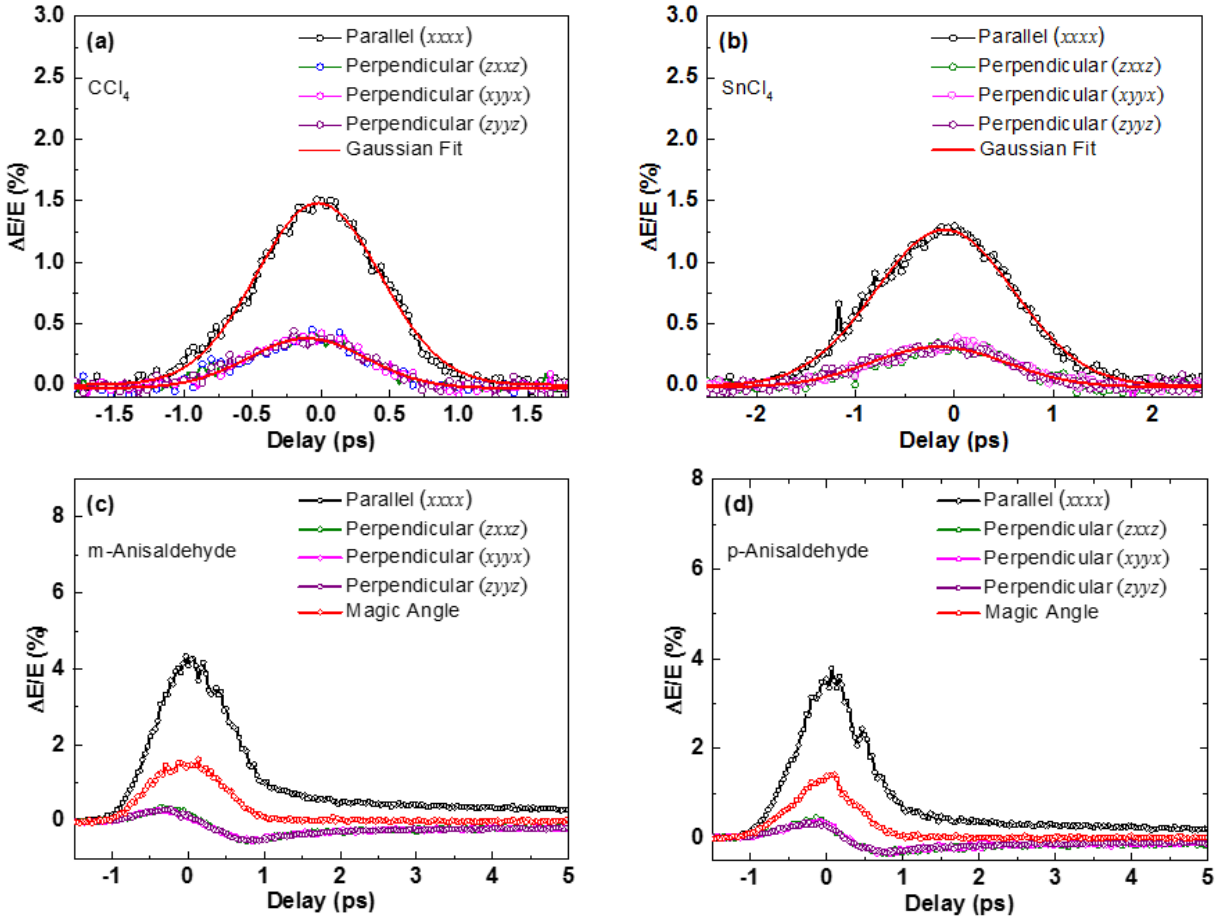

Fig. 2. Beam-Deflection measurements of isotropic organic molecules in liquid form in different polarization configurations, for (a) carbon tetrachloride (CCl_4), (b) Tin tetrachloride ($SnCl_4$), (c) 3-Methoxybenzaldehyde (m-Anisaldehyde), and (d) 4-Methoxybenzaldehyde (p-Anisaldehyde).

4. CONCLUSION

We extended our recently developed Beam-Deflection method, which allowed bound-electronic and each nuclear contribution to be explicitly separated, to a geometry where the excitation and probe propagate at 90^0 with respect to each other. Both geometries time-resolve the nonlinear response, allowing various elements of the bound-electronic and nuclear third-order nonlinear optical susceptibility tensor to be measured. In addition to being able to measure the usual tensor components available in the collinear propagation geometry, this cross-propagating BD method is able to measure the deflection signal with probe beam polarized along the wavevector of the excitation beam. This combination of geometries allows all tensor elements to contribute to the NLR and NLA depending on polarization combinations, and will, therefore, help in separately determining their contributions to the overall nonlinearity. The possibility of measuring tensor elements with different orientations of magnetic fields with respect to electric field, helps to investigate the possible contribution of magneto-electric effects in the third-order nonlinear optical susceptibility which is under further study. The ratio of 4 between parallel and perpendicular polarization rather than the predicted 3 as measured in the collinear geometry, is not yet understood and is the subject of ongoing investigation.

5. ACKNOWLEDGEMENT

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