

Nonlinear birefringence due to non-resonant, higher-order Kerr effect in isotropic media

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Abstract: The recent interpretation of experiments on the nonlinear non-resonant birefringence induced in a weak probe beam by a high intensity pump beam in air and its constituents has stimulated interest in the non-resonant birefringence due to higher-order Kerr nonlinearities. Here a simple formalism is invoked to determine the non-resonant birefringence for higher-order Kerr coefficients. Some general relations between nonlinear coefficients with arbitrary frequency inputs are also derived for isotropic media. It is shown that the previous linear extrapolations for higher-order birefringence (based on literature values of n_2 and n_4) are not strictly valid, although the errors introduced in the values of the reported higher-order Kerr coefficients are a few percent.

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1. Introduction

There has been a growing interest in higher-order nonlinear coefficients $\chi^{(2m+1)}$ of odd order where $m = 2, 3, 4$ in Kerr media [1–5]. Earlier work on higher-order nonlinearities in semiconductors were related to charge carrier excitation either due to cascaded effects, saturation effects such as band filling *etc.* [6,7]. To the best of our knowledge, the first direct measurement of the fifth order Kerr nonlinearity is the work of Arabat and Etchepare who measured the non-resonant $\chi^{(5)}$ for a WG630 Schott glass at intensities of 100's GW/cm² [3]. More recently, fifth order nonlinearities have been measured in a number of glasses and organic materials [1,4,5]. Chen and associates at Cornell also verified that there is resonant enhancement of the fifth order nonlinearity for wavelengths approaching the absorption edge of a glass and were even able to use this to estimate the seventh order susceptibility in a chalcogenide glass [4].

The fact that an intense beam induces a nonlinear birefringence $\Delta n_{bir}^{(2)}(I)$, (I – local intensity), in any medium is well-known since the early days of nonlinear optics [8]. Such a birefringence is usually formulated in terms of the third order susceptibility $\chi^{(3)}$ for Kerr nonlinearities involving electronic states in a medium. For isotropic Kerr media, $\Delta n_{bir}^{(2)}(I) \propto n_2 I$ and the proportionality constant depends on how many unique eigenmodes are present. For example, the numerical factor is 1/3 for a single intense beam where-as it is 2/3 for a strong pump, weak probe geometry.

The general formulation of the nonlinear birefringence problem requires calculating the nonlinear index changes produced by a strong pump beam either for the pump itself, or for a second beam, usually a weak probe beam, with different frequency, propagation direction and/or polarization properties from those of the pump. In isotropic media this normally requires knowledge of the ratio of at least two nonlinear susceptibilities and their dispersion with frequency [8]. This can be a daunting problem since the number of different susceptibility terms increases rapidly with the order of the nonlinearity, i.e. with " m " in $\chi^{(m)}$. The situation simplifies considerably for isotropic media in the non-resonant regime for the susceptibilities since there is only one independent nonlinear susceptibility for each value of m [3,9,10]. The formulation of the nonlinear birefringence problem described here relies strongly on this fact and a formula is derived for arbitrary order nonlinearities.

The most recent interest in nonlinear birefringence due to higher-order Kerr coefficients was stimulated by experiments at ~800nm on filaments which form in air at high (>10 TW/cm²) laser intensities [1,11]. In order to explain their birefringence measurements, Loriot *et al.* assumed non-resonant nonlinear index coefficients up to n_{10} (involving $\chi^{(11)}$). There is some controversy in the filamentation community concerning the interpretation of the measured birefringence but in this paper we simply focus on their analytical expression for the birefringence due to higher-order Kerr effects [12]. They obtained their contributions to the birefringence from the well-known relations between the tensor coefficients for $\chi^{(3)}$ and that obtained for $\chi^{(5)}$ by Arabat and Etchepare based on an anharmonic oscillator model, and then linear extrapolation to higher-orders [3]. Although this nonlinear oscillator model fails to reproduce accurately the frequency dispersion of the third (and presumably higher-order) nonlinearities obtained from quantum mechanics, it does give non-resonant ($\omega \rightarrow 0$) results for $\chi^{(3)}$, $\chi^{(5)}$ and $\chi^{(7)}$, albeit not in terms of physically measurable parameters [2,9,10]. We are not aware of any extension to yet higher-order nonlinearities.

The most frequently cited nonlinear index coefficient n_2 in isotropic media is defined for a single intense beam (x -polarized, for example) as [8]:

$$n_2(-\omega; \omega) = \frac{1}{4n_x^2 \epsilon_0 c} \Re\{\chi_{xxxx}^{(3)}(-\omega; \omega, -\omega, \omega) + \chi_{xxxx}^{(3)}(-\omega; \omega, \omega, -\omega) + \chi_{xxxx}^{(3)}(-\omega; -\omega, \omega, \omega)\} \quad (1)$$

Note that we have introduced a notation $(-\omega; \omega)$ for n_2 in which the beam which induces the nonlinear index change is the second (+) ω argument and the first argument ($-\omega$) identifies the eigenmode in which the index change occurs. If another eigenmode is present such as a weak “probe” beam of the same or different frequency ω_p , also x -polarized but travelling at a small angle to the “pump” beam, the appropriate nonlinearity in this case is defined as

$$n_2(-\omega_p; \omega) = \frac{1}{4n_0^2 \epsilon_0 c} \Re\{\chi_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) + \chi_{xxxx}^{(3)}(-\omega_p; \omega_p, \omega, -\omega) + \chi_{xxxx}^{(3)}(-\omega; -\omega, \omega_p, \omega) + \chi_{xxxx}^{(3)}(-\omega_p; \omega, \omega_p, -\omega) + \chi_{xxxx}^{(3)}(-\omega_p; -\omega, \omega, \omega_p) + \chi_{xxxx}^{(3)}(-\omega_p; \omega, -\omega, \omega_p)\} \quad (2)$$

In this paper we derive from first principles the nonlinear birefringence introduced by higher-order Kerr coefficients in the non-resonant limit in an isotropic medium. We start by reformulating the well-known relations for $\chi^{(3)}$ in terms of combinatorial expressions which then provide a simple procedure for dealing with the higher-order Kerr nonlinearities. We find that the extrapolation used by Loriot *et al.* is not correct for the pump-probe geometry they considered [1].

The procedure followed here is a three-step process:

1. The nonlinear polarizations $P_{xp}^{NL}(\omega_p)$ and $P_{yp}^{NL}(\omega_p)$ are calculated in terms of the nonlinear susceptibilities by permuting the input eigenmodes via their *frequencies* for an isotropic medium.
2. The relation between the $\chi_{ijkl}^{(3)}(-\omega_p; \omega, -\omega, \omega_p)$ susceptibilities is found for an isotropic medium by permuting the *polarizations*. This utilizes the concept that the nonlinear polarization in an isotropic medium *must* be independent of the choice of axes.
3. The square of the refractive indices, i.e. n_x^2 and n_y^2 are calculated from the respective polarizations and the square root of each is taken to give the nonlinear birefringence $\Delta n_{bir}^{NL} = n_x^{NL} - n_y^{NL}$.

2. Pump-probe geometry

Here we consider the specific geometry of the Loriot *et al.* experiment shown in Fig. 1 [1]. An intense plane wave of the form

$$\vec{E}(\vec{r}, t) = \frac{1}{2} E_x(\omega) e^{-i\omega t} + c.c. \quad (3)$$

is assumed to propagate along the z -axis in an isotropic material, i.e. the x -axis is chosen parallel to the polarization of the intense beam. A second probe beam (subscript “ p ”) of frequency $\omega_p = \omega$ is also present but propagating at a small angle from the z -axis in the y - z plane (making it a different eigenmode from the pump beam). Its polarization has equal x and y -components written as

$$E_{xp}(\vec{r}, t) = \frac{1}{2} E_{xp}(\omega_p) e^{-i\omega_p t} + c.c.; \quad E_{yp}(\vec{r}, t) = \frac{1}{2} E_{yp}(\omega_p) e^{-i\omega_p t} + c.c. \quad (4a)$$

and the nonlinear polarization induced in the probe beam is written as

$$P_{xp}^{NL}(\vec{r}, t) = \frac{1}{2} P_{xp}^{NL}(\omega_p) e^{-i\omega_p t} + c.c.; \quad P_{yp}^{NL}(\vec{r}, t) = \frac{1}{2} P_{yp}^{NL}(\omega_p) e^{-i\omega_p t} + c.c. \quad (4b)$$

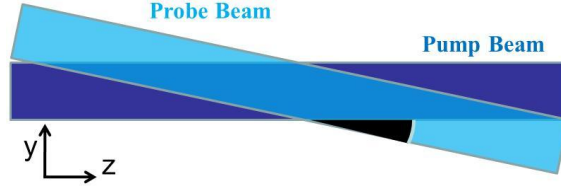


Fig. 1. The pump-probe interaction geometry in reference 1. The angle between the beams was 4°.

3. Nonlinear polarizabilities

The third order nonlinear polarization induced by the pump beam in the molecules of the air, as experienced by the probe beam, is

$$\begin{aligned} P_{xp}^{(3)}(\omega_p) = & \frac{1}{4} \varepsilon_0 \{ \bar{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) + \bar{\chi}_{xxxx}^{(3)}(-\omega_p; \omega, -\omega, \omega_p) \\ & + \bar{\chi}_{xxxx}^{(3)}(-\omega_p; -\omega, \omega_p, \omega) + \bar{\chi}_{xxxx}^{(3)}(-\omega_p; -\omega, \omega, \omega_p) \\ & + \bar{\chi}_{xxxx}^{(3)}(-\omega_p; \omega, \omega_p, -\omega) + \bar{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, \omega, -\omega) \} E_{xp}(\omega_p) E_x^*(\omega) E_x(\omega). \end{aligned} \quad (5)$$

The susceptibilities $\bar{\chi}_{xxxx}^{(3)}(-\omega_p)$ are values of the coefficient averaged over the constituent air molecules, i.e.

$$\bar{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) = \sum_q w_q \chi_{xxxx,q}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) \text{ etc.} \quad (6)$$

here w_q is the fraction of the number density corresponding to species q , i.e. nitrogen, oxygen etc. In the non-resonant limit (identified by the superscript $\tilde{\sim}$), the imaginary part of the susceptibility is negligibly small, zero for $\omega = 0$, and [8]

$$\begin{aligned} \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) &= \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; -\omega, \omega_p, \omega) = \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, \omega, -\omega) \\ &= \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega, -\omega, \omega_p) = \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; -\omega, \omega, \omega_p) = \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega, \omega_p, -\omega). \end{aligned} \quad (7)$$

are all real. Therefore,

$$P_{xp}^{(3)}(\omega_p) = \frac{6}{4} \varepsilon_0 \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) E_{xp}(\omega_p) E_x^*(\omega) E_x(\omega). \quad (8)$$

A different way to arrive at this result is to note that there are three separate input positions for frequency in the expression for $\chi^{(3)}$ giving 3! (= 3x2x1) different possibilities when they are permuted over the three input fields. (In nonlinear optics $E_x^*(\omega)$ and $E_x(\omega)$ can be treated as separate eigenmodes because they have different frequencies in a mixing process, i.e. $+\omega$ and $-\omega$.) Thus there are three separate NLO (nonlinear optics) eigenmodes, each of which appears just once, so that the total number of unique terms is given by 3!/1!1!1!, i.e.

$$\mathbf{P}_{xp}^{(3)}(\omega_p) = \frac{1}{4} \frac{3!}{1!1!1!} \varepsilon_0 \tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) \mathbf{E}_{xp}(\omega_p) |\mathbf{E}_x(\omega)|^2. \quad (9)$$

Similarly, for the polarization nonlinearly induced along the y-axis by the strong x-polarized field,

$$\begin{aligned} \mathbf{P}_{yp}^{(3)}(\omega_p) &= \frac{1}{4} \varepsilon_0 \{ \tilde{\chi}_{yyxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) + \tilde{\chi}_{yyxx}^{(3)}(-\omega_p; \omega_p, \omega, -\omega) \\ &+ \tilde{\chi}_{yyxx}^{(3)}(-\omega_p; \omega, \omega_p, -\omega) + \tilde{\chi}_{yyxx}^{(3)}(-\omega_p; -\omega, \omega_p, \omega) \\ &+ \tilde{\chi}_{yyxy}^{(3)}(-\omega_p; -\omega, \omega, \omega_p) + \tilde{\chi}_{yyxy}^{(3)}(-\omega_p; \omega, -\omega, \omega_p) \} \mathbf{E}_{yp}(\omega) \mathbf{E}_x^*(\omega) \mathbf{E}_x(\omega). \end{aligned} \quad (10)$$

In the non-resonant limit all six $\tilde{\chi}^{(3)}$ s are equal so that with 3 independent eigenmodes each of which appears only once,

$$\mathbf{P}_{yp}^{(3)}(\omega_p) = \frac{1}{4} \frac{3!}{1!1!1!} \varepsilon_0 \tilde{\chi}_{yyxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega) \mathbf{E}_{yp}(\omega_p) |\mathbf{E}_x(\omega)|^2. \quad (11)$$

The nonlinear susceptibilities are now abbreviated so that $\tilde{\chi}_{xxxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega)$ and $\tilde{\chi}_{yyxx}^{(3)}(-\omega_p; \omega_p, -\omega, \omega)$ are written as $\tilde{\chi}_{xxxx}^{(3)}(-\omega_p)$ and $\tilde{\chi}_{yyxx}^{(3)}(-\omega_p)$ respectively. (This will also subsequently be extended to higher-order susceptibilities.) Furthermore, since the labeling of the axes in isotropic media is arbitrary, $\tilde{\chi}_{yyxx}^{(3)}(-\omega_p) = \tilde{\chi}_{xyxy}^{(3)}(-\omega_p)$. Applying the same arguments as for the probe case but with two equal co-polarized fields at $+\omega$ for $\mathbf{P}_x^{(3)}(\omega)$ but not for $\mathbf{P}_y^{(3)}(\omega)$, the nonlinear polarizations experienced by the pump beam are

$$\mathbf{P}_x^{(3)}(\omega) = \frac{1}{4} \frac{3!}{2!1!} \varepsilon_0 \tilde{\chi}_{xxxx}^{(3)}(-\omega) \mathbf{E}_x(\omega) |\mathbf{E}_x(\omega)|^2 = \frac{1}{2} \mathbf{P}_{xp}^{(3)}(\omega_p), \quad (12a)$$

$$\mathbf{P}_y^{(3)}(\omega) = \frac{1}{4} \frac{3!}{1!1!1!} \varepsilon_0 \tilde{\chi}_{yyxx}^{(3)}(-\omega) \mathbf{E}_y(\omega) |\mathbf{E}_x(\omega)|^2 = \mathbf{P}_{yp}^{(3)}(\omega_p). \quad (12b)$$

Generalizing these results to the $2m + 1$ case [4],

$$\mathbf{P}_{xp}^{(2m+1)}(\omega_p) = \left[\frac{1}{4^m} \frac{(2m+1)!}{m!m!} \varepsilon_0 \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p) |\mathbf{E}_x(\omega)|^{2m} \right] \mathbf{E}_{xp}(\omega_p) = (m+1) \mathbf{P}_x^{(2m+1)}(\omega), \quad (13)$$

$$\mathbf{P}_{yp}^{(2m+1)}(\omega_p) = \left[\frac{1}{4^m} \frac{(2m+1)!}{m!m!} \varepsilon_0 \tilde{\chi}_{(2)y,(2m)x}^{(2m+1)}(-\omega_p) |\mathbf{E}_x(\omega)|^{2m} \right] \mathbf{E}_{yp}(\omega_p) = \mathbf{P}_y^{(2m+1)}(\omega). \quad (14)$$

Here the co-ordinate subscripts $(2m+2)x$ mean that there is a total of $2m+2$ “x co-ordinates,” one referring to the output polarization of the probe, and one of the remaining $2m+1$ refers to the input probe polarization, interspersed amongst the $2m$ others associated with $\pm\omega$ of the pump beam. The $(2)y,(2m)x$ means that there are 2 “y” co-ordinates, one always being the first co-ordinate which refers to the output probe polarization, and the second to the input probe beam polarization interspersed amongst the $2m \pm \omega$ x-polarizations associated with the pump beam.

Therefore the total polarization for the probe beam is given by

$$\begin{aligned} \mathbf{P}_{xp}^{(1)}(\omega_p) + \mathbf{P}_{xp}^{NL}(\omega_p) &= \varepsilon_0[n_x^2(\omega_p) - 1]E_{xp}(\omega_p) = \varepsilon_0[(n_0^2 - 1) \\ &+ \sum_{m=1} \frac{1}{4^m} \frac{(2m+1)!}{m!m!} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p) |E_x(\omega)|^{2m}]E_{xp}(\omega_p); \end{aligned} \quad (15)$$

$$\begin{aligned} \mathbf{P}_{yp}^{(1)}(\omega_p) + \mathbf{P}_{yp}^{NL}(\omega_p) \varepsilon_0[n_y^2(\omega_p) - 1]E_{yp}(\omega_p) &= \varepsilon_0[(n_0^2 - 1) \\ &+ \sum_{m=1} \frac{1}{4^m} \frac{(2m+1)!}{m!m!} \tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega_p) |E_x(\omega)|^{2m}]E_{yp}(\omega_p). \end{aligned} \quad (16)$$

For the pump beam, the ω_p on the input side is replaced by another ω and hence there are $m + 1 + \omega$'s but still $m - \omega$'s so that

$$\begin{aligned} \mathbf{P}_x^{(1)}(\omega) + \mathbf{P}_x^{NL}(\omega) &= \varepsilon_0[n_x^2(\omega) - 1]E_x(\omega) = \varepsilon_0[(n_0^2 - 1) \\ &+ \sum_{m=1} \frac{1}{4^m} \frac{(2m+1)!}{(m+1)!m!} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega) |E_x(\omega)|^{2m}]E_x(\omega). \end{aligned} \quad (17)$$

For $\mathbf{P}_y^{NL}(\omega)$, the first 2 y 's belong to the probe beam and there are still $m \omega$'s and $m - \omega$'s, just like in $\mathbf{P}_{yp}^{NL}(\omega_p)$ so that

$$\begin{aligned} \mathbf{P}_y^{(1)}(\omega) + \mathbf{P}_y^{(NL)}(\omega) &= \varepsilon_0[n_y^2(\omega) - 1]E_y(\omega) = \varepsilon_0[(n_0^2 - 1) \\ &+ \sum_{m=1} \frac{1}{4^m} \frac{(2m+1)!}{m!m!} \tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega) |E_x(\omega)|^{2m}]E_y(\omega). \end{aligned} \quad (18)$$

4. Total nonlinear birefringence

It is clear from Eqs. (15)–(18), that in order to find the birefringence, the relationship between the nonlinear susceptibilities $\tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega)$ and $\tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega)$ must be found. This depends on the symmetry properties of the medium. Even for isotropic media these are relatively complicated calculations and hence they are summarized in the Appendix along with some general results valid for all frequencies. Making the results specific to the non-resonant, isotropic medium case, Eq. (A17) is

$$\begin{aligned} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p) &= (2^m + 1) \tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega_p); \\ \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega) &= (2^m + 1) \tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega). \end{aligned} \quad (19)$$

For the pump-probe geometry in the non-resonant limit, Eq. (19) is inserted into Eqs. (16) and (18) to give

$$\begin{aligned} \mathbf{P}_{yp}^{(1)}(\omega_p) + \mathbf{P}_{yp}^{NL}(\omega_p) &= \varepsilon_0[n_y^2(\omega_p) - 1]E_{yp}(\omega_p) = \varepsilon_0[(n_0^2 - 1) \\ &+ \sum_{m=1} \frac{1}{4^m} \frac{(2m+1)!}{(2^m + 1)m!m!} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p) |E_x(\omega)|^{2m}]E_{yp}(\omega_p), \end{aligned} \quad (20)$$

$$\begin{aligned} \mathbf{P}_y^{(1)}(\omega) + \mathbf{P}_y^{(NL)}(\omega) &= \varepsilon_0[n_y^2(\omega) - 1]E_y(\omega) = \varepsilon_0[(n_0^2 - 1) \\ &+ \sum_{m=1} \frac{1}{4^m} \frac{(2m+1)!}{(2^m + 1)m!m!} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega) |E_x(\omega)|^{2m}]E_y(\omega), \end{aligned} \quad (21)$$

so that both the x - and y -components of the nonlinear polarization are given in terms of the same susceptibilities. Noting that $n_{2m}(-\omega_p; \omega) = (m+1)n_{2m}(-\omega; \omega)$ from Eq. (13) and combining Eqs. (15), (17), (20), and (21) now leads directly to

$$\begin{aligned} n_x^2(\omega_p) &= n_0^2 \{1 + [\sum_{m=1} \bar{A}_m I^m]\}; & n_y^2(\omega_p) &= n_0^2 \{1 + [\sum_{m=1} \frac{1}{(2^m+1)} \bar{A}_m I^m]\}, \\ n_x^2(\omega) &= n_0^2 \{1 + [\sum_{m=1} \frac{1}{m+1} \bar{A}_m I^m]\}; & n_y^2(\omega) &= n_0^2 \{1 + [\sum_{m=1} \frac{1}{(2^m+1)} \bar{A}_m I^m]\}, \end{aligned} \quad (22)$$

in which the coefficient \bar{A}_m is given by

$$\begin{aligned} \bar{A}_m &= 2 \frac{\bar{n}_{2m}(-\omega_p; \omega)}{n_0}, \\ \bar{A}_m &= \frac{1}{2n_0} \frac{1}{2^m n_0^m c^m \epsilon_0^m} \frac{(2m+1)!}{m!m!!} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p) = \frac{1}{2n_0} \frac{(m+1)}{2^m n_0^m c^m \epsilon_0^m} \frac{(2m+1)!}{m!m!!} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega). \end{aligned} \quad (23)$$

This form was chosen so that for the individual nonlinearities m

$$\Delta \bar{n}_x^{(m)}(\omega_p) = \bar{n}_{2m}(-\omega_p; \omega) I^m. \quad (24)$$

In order to make contact with the experimental data in reference 1 we focus on the nonlinear refractive indices for the pump-probe case so that the nonlinear birefringence is given by

$$\begin{aligned} \bar{n}_x(\omega_p) &= n_0 \sqrt{1 + [\sum_{m=1} \bar{A}_m I^m]}; & \bar{n}_y(\omega_p) &= n_0 \sqrt{1 + [\sum_{m=1} \frac{1}{(2^m+1)} \bar{A}_m I^m]}; \\ \Delta n_{bir}^{NL}(\omega_p) &= n_x(\omega_p) - n_y(\omega_p). \end{aligned} \quad (25)$$

The expansion of $\sqrt{1+b}$ for small b is well known from textbooks [13], to be:

$$\sqrt{1+b} = \sum_{s=0}^{\infty} \frac{(-1)^s (2s)!}{(1-2s)(s!)^2 4^s} b^s = 1 + \frac{1}{2}b - \frac{1}{8}b^2 + \frac{1}{16}b^3 - \frac{5}{128}b^4 + \frac{7}{256}b^5 - \dots \quad (26)$$

Therefore

$$\Delta \bar{n}_{bir}^{NL}(\omega_p) = n_0 \sum_{s=0}^{\infty} \frac{(-1)^s (2s)!}{(1-2s)(s!)^2 4^s} ([\sum_{m=1} \bar{A}_m I^m]^s - [\sum_{m=1} \frac{\bar{A}_m}{2^m+1} I^m]^s). \quad (27)$$

The leading term ($s=1$), expanded up to n_{10} (largest term reported in reference 1), is

$$\begin{aligned} \Delta \bar{n}_{bir}^{s=1}(\omega_p) &= n_0 \left\{ \frac{1}{3} \bar{A}_1 I + \frac{2}{5} \bar{A}_2 I^2 + \frac{4}{9} \bar{A}_3 I^3 + \frac{8}{17} \bar{A}_4 I^4 + \frac{16}{33} \bar{A}_4 I^4 + \frac{32}{65} \bar{A}_5 I^5 \right. \\ &= \frac{2}{3} \bar{n}_2(-\omega_p; \omega) I + \frac{4}{5} \bar{n}_4(-\omega_p; \omega) I^2 + \frac{8}{9} \bar{n}_6(-\omega_p; \omega) I^3 \\ &\quad \left. + \frac{16}{17} \bar{n}_8(-\omega_p; \omega) I^4 + \frac{32}{33} \bar{n}_{10}(-\omega_p; \omega) I^5 \right. \end{aligned} \quad (28)$$

Terms with $s \geq 2$ contain products of the nonlinear coefficients. Including all of the terms up to I^5 ,

$$\begin{aligned}
\Delta \bar{n}_{bir}^{NL} = & \frac{2}{3} \bar{n}_2(-\omega_p; \omega) I + \left[\frac{4}{5} \bar{n}_4(-\omega_p; \omega) - \frac{4}{9n_0} \bar{n}_2^2(-\omega_p; \omega) \right] I^2 \\
& + \left[\frac{8}{9} \bar{n}_6(-\omega_p; \omega) - \frac{14}{15n_0} \bar{n}_2(-\omega_p; \omega) \bar{n}_4(-\omega_p; \omega) + \frac{13}{27n_0^2} \bar{n}_2^3(-\omega_p; \omega) \right] I^3 \\
& + \left[\frac{16}{17} \bar{n}_8(-\omega_p; \omega) - \frac{26}{27n_0} \bar{n}_2(-\omega_p; \omega) \bar{n}_6(-\omega_p; \omega) - \frac{12}{25n_0} \bar{n}_2^2(-\omega_p; \omega) \right. \\
& \left. + \frac{22}{15n_0^2} \bar{n}_2^2(-\omega_p; \omega) \bar{n}_4(-\omega_p; \omega) - \frac{50}{81n_0^3} \bar{n}_2^4(-\omega_p; \omega) \right] I^4 \\
& + \left[\frac{32}{33} \bar{n}_{10}(-\omega_p; \omega) - \frac{50}{51n_0} \bar{n}_2(-\omega_p; \omega) \bar{n}_8(-\omega_p; \omega) - \frac{44}{45n_0} \bar{n}_4(-\omega_p; \omega) \bar{n}_6(-\omega_p; \omega) \right. \\
& \left. + \frac{40}{27n_0^2} \bar{n}_2^2(-\omega_p; \omega) \bar{n}_6(-\omega_p; \omega) + \frac{37}{25n_0^2} \bar{n}_2(-\omega_p; \omega) \bar{n}_4^2(-\omega_p; \omega) \right. \\
& \left. - \frac{67}{27n_0^3} \bar{n}_2^3(-\omega_p; \omega) \bar{n}_4(-\omega_p; \omega) + \frac{847}{972n_0^4} \bar{n}_2^5(-\omega_p; \omega) \right] I^5.
\end{aligned} \tag{29}$$

Note that all the numerical pre-factors in this case are all less than 2.5. The products of different nonlinear coefficients are limited to 2 here. However, products of more than two nonlinear coefficients occur for higher-orders in intensity, the first one being $\bar{n}_2 \bar{n}_4 \bar{n}_6 I^6$. From Eq. (29) it is evident that in a strict mathematical sense the nonlinear birefringence cannot be used as a means to measure the nonlinear coefficients higher than \bar{n}_2 . There is no direct correlation between the coefficient \bar{n}_{2m} and the corresponding power of the intensity I^m for $m > 1$ due to the existence of the product terms. However, it makes sense to use the simplified notation of Eq. (29) if the relation $\bar{n}_{2m} \gg \bar{n}_{2k_1} \bar{n}_{2k_2} \dots \bar{n}_{2k_n}$, $m = k_1 + k_2 + \dots k_n$ holds.

5. Comparison with experiments on air

Reference 1 contains data measured in air and its constituents for $n_2(-\omega_p; \omega) \rightarrow n_8(-\omega_p; \omega)$ and also $n_{10}(-\omega_p; \omega)$ for argon. Based on their values, $\bar{n}_{2m}(-\omega_p; \omega) \gg \bar{n}_{2q}^r(-\omega_p; \omega) \bar{n}_{2u}^v(-\omega_p; \omega)$ with $m = rq + vu$ and $m \leq 5$ is always satisfied in air. Assuming that the only nonlinear mechanism present is the Kerr effect, the nonlinear birefringence is given by the leading term, Eq. (28), which can be expressed as the series

$$\Delta \bar{n}_{bir}^{NL}(\omega_p) = \sum_{m=1} \frac{2^m}{2^m + 1} \bar{n}_{2m}(-\omega_p; \omega) I^m. \tag{30}$$

This result should be compared with the expansion used by Loriot et al. [1]. Based on a linear extrapolation from the first two terms which Loriot *et al.* obtained from the literature [3,8] they assumed the series

$$\Delta \bar{n}_{bir}^{NL}(\omega_p) = \sum_{m=1} \frac{2m}{2m+1} \bar{n}_{2m}(-\omega_p; \omega) I^m \tag{31}$$

in their analysis of their data. Note that in both series the numerical pre-factors $2^m/(2^m + 1)$ and $2m/(2m + 1)$ respectively converge to unity for large m . A graphical comparison of the two expansions is given in Fig. 2. In Fig. 2(a) we compare the expansion terms as deduced from Eq. (30), $2^m/(2^m + 1)$, to the ones derived by Loriot et al. $2m/(2m+1)$. As m is increased their difference is maximized for $m = 11$. The relative deviation of Loriot *et al.*'s

expansion terms as compared to the analytically derived factors is depicted in Fig. 2(b). For $m = 11$ the relative error peaks at 6.25%. Furthermore, the Loriot *et al.* formulation systematically underestimates the expansion term coefficients and thus leads to an overestimation of the corresponding $\bar{n}_{2m}(-\omega_p; \omega)$ coefficient for $m > 2$.

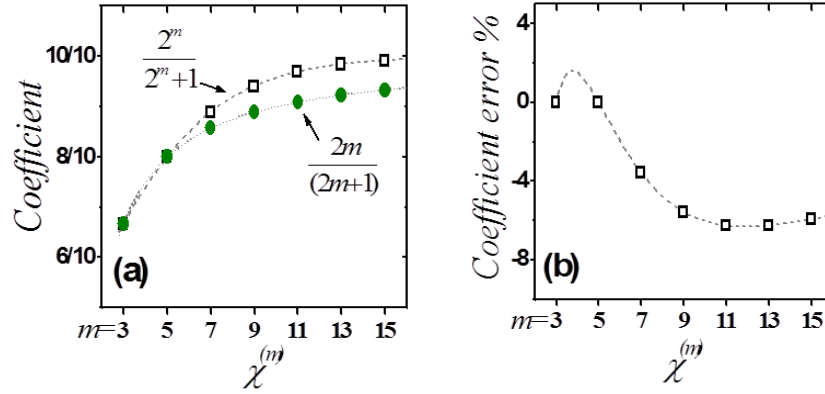


Fig. 2. Comparison between the expansion coefficients estimated by the two models. (a) Coefficients corresponding to $\chi^{(m)}$ terms. (\square) analytical model, (\bullet) Loriot et al. estimation, dotted/dashed lines are a guide to the eye. (b) Relative error for the various coefficients of the $\chi^{(m)}$ terms. (Dotted lines are guides to the eye).

6. Conclusions

Expressions for the non-resonant, nonlinear birefringence induced in a probe beam (frequency ω_p) by a strong pump beam of the same frequency in an isotropic medium have been derived for nonlinear Kerr indices $n_{2m}(-\omega_p; \omega)$ for arbitrary m . This was made possible by using combinatorial approaches and by assuming that in isotropic media there is only one unique value for $\chi^{(2m+1)}(-\omega_p)$ for each value of m which was verified previously in the literature for $m = 1, 2$. Some general relations for arbitrary frequency inputs were also derived.

Because the polarization, linear and nonlinear, induced in a material depends on the square of the refractive index, the nonlinear birefringence was found to depend not only on the intensity-dependent refractive index coefficients $n_{2m}(-\omega_p; \omega)$ but also on the products of the various nonlinear index coefficients. Comparison with existing experiments in air and its constituents showed that the product terms were negligible in that case.

An analytical series was found to describe the nonlinear birefringence. This series was different from that assumed by Loriot et. al based on a linear extrapolation of two points. Since in both cases the individual numerical factors for $n_{2m}(-\omega_p; \omega)$ converged to unity for increasing m , the errors introduced into the analysis of the data were relatively small.

Appendix A. Relationships between the nonlinear susceptibilities

In this Appendix the relations between the $\tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p)$ and $\tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega)$ are derived, some for arbitrary frequency inputs. Isotropy requires that each coordinate (x and y) comes in pairs. It also requires that the nonlinear polarization should be independent of the orientation of any axis system used. Consider first the *general case* (unrelated to the previous discussion) of three, parallel, co-polarized (along the x -axis) input fields E_1 , E_2 and E_3 with different frequencies ω_1 , ω_2 and ω_3 producing the field ω_4 via $\chi_{xxx}^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3)$. The third order nonlinear polarization (along the x -axis) is

$$\mathbf{P}_x^{(3)}(\omega_4) = \frac{1}{4} \varepsilon_0 \chi_{xxxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \mathbf{E}_1 \mathbf{E}_2 \mathbf{E}_3. \quad (\text{A1})$$

Now consider the axis system (x' , y') rotated 45° from the original x -axis [8]. The three fields have the following components along the x' -axis and y' -axis

$$\mathbf{E}_{1x'} = \frac{1}{\sqrt{2}} \mathbf{E}_1; \mathbf{E}_{2x'} = \frac{1}{\sqrt{2}} \mathbf{E}_2; \mathbf{E}_{3x'} = \frac{1}{\sqrt{2}} \mathbf{E}_3; \mathbf{E}_{1y'} = \frac{1}{\sqrt{2}} \mathbf{E}_1; \mathbf{E}_{2y'} = \frac{1}{\sqrt{2}} \mathbf{E}_2; \mathbf{E}_{3y'} = \frac{1}{\sqrt{2}} \mathbf{E}_3. \quad (\text{A2})$$

For isotropic media, $\chi_{x'x'x'x'}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) = \chi_{xxxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1)$, $\chi_{x'xyy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) = \chi_{x'x'y'y'}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) = \chi_{yyxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1)$ etc., and hence the nonlinear polarization induced along the x' -axis is given by

$$\begin{aligned} \mathbf{P}_{x'}^{(3)}(\omega_4) &= \frac{1}{4} \varepsilon_0 [\chi_{xxxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \mathbf{E}_{1x'} \mathbf{E}_{2x'} \mathbf{E}_{3x'} + \chi_{x'xyy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \mathbf{E}_{1y'} \mathbf{E}_{2y'} \mathbf{E}_{3x'} \\ &\quad + \chi_{xyyx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \mathbf{E}_{1x'} \mathbf{E}_{2y'} \mathbf{E}_{3y'} + \chi_{xyxy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \mathbf{E}_{1y'} \mathbf{E}_{2x'} \mathbf{E}_{3y'}] \\ \rightarrow \mathbf{P}_{x'}^{(3)}(\omega_4) &= \frac{1}{4} \varepsilon_0 \frac{1}{2\sqrt{2}} [\chi_{xxxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) + \chi_{x'xyy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \\ &\quad + \chi_{xyyx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) + \chi_{xyxy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1)] \mathbf{E}_1 \mathbf{E}_2 \mathbf{E}_3. \end{aligned} \quad (\text{A3})$$

The nonlinear polarization $\mathbf{P}_{x'}^{(3)}(\omega_4)$ in Eq. (A3) can also be obtained by projecting the nonlinear polarization given by Eq. (A1) onto the x' -axis to give

$$\mathbf{P}_{x'}^{(3)}(\omega_4) = \frac{1}{4} \varepsilon_0 \frac{1}{\sqrt{2}} \chi_{xxxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \mathbf{E}_1 \mathbf{E}_2 \mathbf{E}_3. \quad (\text{A4})$$

Since Eqs. (A3) and (A4) *must* give the same result which is valid for any frequencies,

$$\begin{aligned} \chi_{xxxx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) &= \chi_{x'xyy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) + \chi_{xyyx}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1) \\ &\quad + \chi_{xyxy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1). \end{aligned} \quad (\text{A5})$$

Note that *any* isotropic material, for example a mature electron plasma, which exhibits third order effects such as third harmonic generation [14,15] *must* have all of these coefficients non-zero and related as given by Eq. (A5). In the non-resonant limit it can easily be shown that

$$\tilde{\chi}_{x'xyy}^{(3)}(-\omega_p) = \tilde{\chi}_{xyyx}^{(3)}(-\omega_p) = \tilde{\chi}_{xyxy}^{(3)}(-\omega_p) \rightarrow \tilde{\chi}_{xxxx}^{(3)}(-\omega_p) = 3\tilde{\chi}_{x'xyy}^{(3)}(-\omega_p). \quad (\text{A6})$$

The same result holds for pump beam, i.e. $\tilde{\chi}_{xxxx}^{(3)}(-\omega) = 3\tilde{\chi}_{x'xyy}^{(3)}(-\omega)$. Although this result is valid for a single medium, extension to multi-component air is trivial giving

$$\tilde{\chi}_{xxxx}^{(3)}(-\omega_p) = 3\tilde{\chi}_{x'xyy}^{(3)}(-\omega_p) \quad \tilde{\chi}_{xxxx}^{(3)}(-\omega) = 3\tilde{\chi}_{x'xyy}^{(3)}(-\omega). \quad (\text{A7})$$

An alternate and more compact approach for arriving at the same result is to again resort to combinatorial mathematics. Since there are three input polarization components, two y' -polarized and one x' -polarized, which can be permuted among the three input eigenmodes (frequencies), there are $3!$ possibilities for permuting the corresponding polarization components in $\tilde{\chi}_{x'xyy}^{(3)}(-\omega_4; \omega_3, \omega_2, \omega_1)$. Because there must be two identical polarization

components (y') and only one x', there are 3!/2!1! unique possibilities and Eq. (A5) can be re-written in the non-resonant limit as

$$\tilde{\chi}_{xxx}^{(3)}(-\omega_p) = \frac{3!}{2!1!} \tilde{\chi}_{xyy}^{(3)}(-\omega_p); \quad \tilde{\chi}_{xxx}^{(3)}(-\omega) = \frac{3!}{2!1!} \tilde{\chi}_{xyy}^{(3)}(-\omega) \quad (\text{A8})$$

The evaluation of the relation between $\tilde{\chi}_{xxxxx}^{(5)}(-\omega_p)$ and $\tilde{\chi}_{yyxxx}^{(5)}(-\omega_p)$ (and subsequently the yet higher-order susceptibilities) has additional aspects (relative to the $\chi^{(3)}$ case) associated with the $\tilde{\chi}_{yyxxx}^{(5)}(-\omega_p) = \tilde{\chi}_{xyyxx}^{(5)}(-\omega_p) = \tilde{\chi}_{xyyyy}^{(5)}(-\omega_p)$ etc. terms. Again assuming the general case of five, parallel, co-polarized (along the x-axis) input fields namely $E_1, E_2, E_3, E_4,$ and E_5 with different frequencies $\omega_1, \omega_2, \omega_3, \omega_4$ and ω_5 producing the field ω_6 via $\chi_{xxxxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$. This produces the nonlinear polarization (along the x-axis)

$$P_x^{(5)}(\omega_6) = \frac{1}{16} \varepsilon_0 \chi_{xxxxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1) E_1 E_2 E_3 E_4 E_5. \quad (\text{A9})$$

Now consider again the axis system (x', y') rotated 45° from the original x-axis. The five input x-polarized fields again have components along the x'-axis and y'-axis. Note that both mixed polarization terms like $\chi_{xyyxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$ as well as $\chi_{xyyyy}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$ contribute to the nonlinear polarization induced along the x'-axis, $P_{x'}^{NL}(\omega_6)$. For the first one, there are 5! input slots for the polarization of which 3 are identical (x') and the two others are also identical (y') and, for the second one, there are 4 (y') identical slots and only the x' is a single slot. Hence the number of unique combinations are 5!/3!2! and 5!/4!1! respectively for $\tilde{\chi}_{xyyxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$ and for $\tilde{\chi}_{xyyyy}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$. There are further simplifications in the *non-resonant limit* $\tilde{\chi}_{xyyxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1) = \tilde{\chi}_{xyyxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$ etc. so that

$$P_{x'}^{(5)}(\omega_6) = \frac{1}{16} \varepsilon_0 \frac{1}{4\sqrt{2}} [\tilde{\chi}_{xxxxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1) + \frac{5!}{3!2!} \tilde{\chi}_{xyyxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1) + \frac{5!}{4!1!} \tilde{\chi}_{xyyyy}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)] E_1 E_2 E_3 E_4 E_5. \quad (\text{A10})$$

The nonlinear polarization $P_{x'}^{(5)}(\omega_6)$ in Eq. A10 can also be obtained by projecting the nonlinear polarization given by Eq. (A9) onto the x'-axis to give

$$P_{x'}^{NL}(\omega_6) = \frac{1}{16} \varepsilon_0 \frac{1}{\sqrt{2}} \tilde{\chi}_{xxxxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1) E_1 E_2 E_3 E_4 E_5. \quad (\text{A11})$$

Again Eqs. (A10) and (A11) must yield identical results and noting again from references 2 and 8 that $\tilde{\chi}_{xyyxx}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1) = \tilde{\chi}_{xyyyy}^{(5)}(-\omega_6; \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$ etc. yields for the cases of interest here in the non-resonant limit

$$\tilde{\chi}_{xxxxx}^{(5)}(-\omega_p) = 5 \tilde{\chi}_{yyxxx}^{(5)}(-\omega_p); \quad \tilde{\chi}_{xxxxx}^{(5)}(-\omega) = 5 \tilde{\chi}_{yyxxx}^{(5)}(-\omega). \quad (\text{A12})$$

Consider briefly the 7th and 9th order susceptibilities. The same procedures as for the 3rd and 5th order cases are used. In order to derive the relationship between the different $\tilde{\chi}_{xxxxxxx}^{(7)}(-\omega_p), \tilde{\chi}_{yyxxxxx}^{(7)}(-\omega_p)$, etc. seven co-polarized input fields are considered, first in the x,

y, z coordinate system and then in an axis system rotated 45° in the x-y plane. In this case, the mixed polarization terms

$$\chi_{xyyxxx}^{(7)}(-\omega_8; \omega_7, \omega_6, \omega_5, \omega_4, \omega_3, \omega_2, \omega_1), \chi_{xyyyxxx}^{(7)}(-\omega_8; \omega_7, \omega_6, \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$$

$\chi_{xyyyyy}^{(7)}(-\omega_8; \omega_7, \omega_6, \omega_5, \omega_4, \omega_3, \omega_2, \omega_1)$ all contribute to the nonlinear polarizations induced along the x'-axis, $P_x^{(7)}(\omega_8)$. The number of unique combinations are 7!/5!2!, 7!/4!3! and 7!/6!1! respectively for the three cases. Thus again in the non-resonant limit

$$\begin{aligned} P_x^{NL}(\omega_8) &= \frac{1}{64} \varepsilon_0 \frac{1}{8\sqrt{2}} [\tilde{\chi}_{xxxxx}^{(7)}(-\omega_8) + \frac{7!}{5!2!} \tilde{\chi}_{xyyxxx}^{(7)}(-\omega_8) \\ &\quad + \frac{7!}{4!3!} \tilde{\chi}_{xyyyxxx}^{(7)}(-\omega_8) + \frac{7!}{6!1!} \tilde{\chi}_{xyyyyy}^{(7)}(-\omega_8)] E_1 E_2 E_3 E_4 E_5 E_6 E_7 \\ &= \frac{1}{64} \varepsilon_0 \frac{1}{\sqrt{2}} \tilde{\chi}_{xxxxx}^{(7)}(-\omega_8) E_1 E_2 E_3 E_4 E_5 E_6 E_7 \end{aligned} \quad (A13)$$

Based on the preceding results, only one, unique, nonlinear susceptibility is expected for an isotropic material in the non-resonant limit for each order “2m+1” of $\chi^{(2m+1)}$. Therefore all the mixed polarization susceptibilities are equal which gives

$$\tilde{\chi}_{xxxxxx}^{(7)}(-\omega_p) = 9 \tilde{\chi}_{yyxxxx}^{(7)}(-\omega_p); \quad \tilde{\chi}_{xxxxxx}^{(7)}(-\omega) = 9 \tilde{\chi}_{yyxxxx}^{(7)}(-\omega). \quad (A14)$$

Again using the same approach, for the 9th order susceptibility,

$$\begin{aligned} P_x^{(9)}(\omega_{10}) &= \frac{1}{256} \varepsilon_0 \frac{1}{16\sqrt{2}} [\tilde{\chi}_{xxxxxxx}^{(9)}(-\omega_{10}) + \frac{9!}{7!2!} \tilde{\chi}_{xyyxxxxx}^{(9)}(-\omega_{10}) + \frac{9!}{5!4!} \tilde{\chi}_{xyyyxxxx}^{(9)}(-\omega_{10}) \\ &\quad + \frac{9!}{3!6!} \tilde{\chi}_{xyyyyyxxx}^{(9)}(-\omega_{10}) + \frac{9!}{1!8!} \tilde{\chi}_{xyyyyyyy}^{(9)}(-\omega_{10})] E_1 E_2 E_3 E_4 E_5 E_6 E_7 E_8 E_9 \\ &= \frac{1}{256} \varepsilon_0 \frac{1}{\sqrt{2}} \tilde{\chi}_{xxxxxxx}^{(9)}(-\omega_{10}) E_1 E_2 E_3 E_4 E_5 E_6 E_7 E_8 E_9. \end{aligned} \quad (A15)$$

In the non-resonant limit

$$\tilde{\chi}_{xxxxxxx}^{(9)}(-\omega_{10}) = 17 \tilde{\chi}_{yyxxxxxx}^{(9)}(-\omega_{10}) \quad (A16)$$

These results suggest simple relations governing the relationship between the susceptibilities, namely

$$\begin{aligned} \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_p) &= (2^m + 1) \tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega_p); \\ \tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega) &= (2^m + 1) \tilde{\chi}_{yy,(2m)x}^{(2m+1)}(-\omega). \end{aligned} \quad (A17)$$

For frequency inputs $\omega_1, \omega_2, \omega_3, \dots, \omega_{2m+1}$ giving an output frequency ω_{2m+2} for isotropic media, the above formulas suggest the following general result:

$$\begin{aligned}
\tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_{2m+2}) &= \frac{1}{2^m} \left[\tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_{2m+2}) + \frac{(2m+1)!}{(2m)!1!} \tilde{\chi}_{(2)y,(2m)x}^{(2m+1)}(-\omega_{2m+2}) \right. \\
&+ \frac{(2m+1)!}{(2m-2)!3!} \tilde{\chi}_{(4)y,(2m-2)x}^{(2m+1)}(-\omega_{2m+2}) + \frac{(2m+1)!}{(2m-4)!5!} \tilde{\chi}_{(6)y,(2m-4)x}^{(2m+1)}(-\omega_{2m+2}) \dots \\
&\left. + \frac{(2m+1)!}{2!(2m-1)!} \tilde{\chi}_{(2m-1)y,(2)x}^{(2m+1)}(-\omega_{2m+2}) \right].
\end{aligned}
\tag{A18}$$

which gives

$$\begin{aligned}
\tilde{\chi}_{(2m+2)x}^{(2m+1)}(-\omega_{2m+2}) &= \frac{1}{2^m - 1} \left[\frac{(2m+1)!}{(2m)!1!} \tilde{\chi}_{(2)y,(2m)x}^{(2m+1)}(-\omega_{2m+2}) \right. \\
&+ \frac{(2m+1)!}{(2m-2)!3!} \tilde{\chi}_{(4)y,(2m-2)x}^{(2m+1)}(-\omega_{2m+2}) + \frac{(2m+1)!}{(2m-4)!5!} \tilde{\chi}_{(6)y,(2m-4)x}^{(2m+1)}(-\omega_{2m+2}) \dots \\
&\left. + \frac{(2m+1)!}{2!(2m-1)!} \tilde{\chi}_{(2m-1)y,(2)x}^{(2m+1)}(-\omega_{2m+2}) \right].
\end{aligned}
\tag{A19}$$

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