

Third-order nonlinear optical materials: practical issues and theoretical challenges

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Abstract The renewed interest in all-optical switching has led to more detailed experimental investigations of nonlinear optical properties of materials within wide wavelength ranges. The objectives of these studies are discussed here in the context of the availability of suitable computational data that might be compared with the results of the experimental research. It is concluded that the currently available data are insufficient and should be augmented to provide better guidance for experimental work.

Keywords All-optical switching · Cubic hyperpolarizability · Nonlinear refraction · Third-order optical nonlinearity

Introduction

Calculations of molecular hyperpolarizabilities are a standard feature of many packaged computational chemistry programs. There has been a large number of studies where quantum chemistry tools have been utilized to predict the values of the hyperpolarizabilities, develop structure-property rules of thumb, interpret experimental results. In fact, it may seem like the computation chemistry community has progressed to the point where *in silico* studies may largely replace cumbersome chemical syntheses and tedious experiments directed at finding new materials with optimized nonlinear optical (NLO) properties. This is quite important in view of the current renewal of interest of

experimentalists and theoreticians in molecular materials for all-optical switching (e.g. [1, 2]). However, the computations carried out currently are not sufficient for full characterization of parameters which are crucial for some practical applications of NLO materials. This paper presents an experimentalist's viewpoint and calls for better convergence of computational and experimental studies of cubic NLO properties.

Fundamentals

The NLO properties of molecules are usually discussed in terms of the hyperpolarizabilities β_{ijk} and γ_{ijkl} defined by the power expansion of the Cartesian components of the dipole moment μ_i against the components of the electric field F_j :^{1,2}

$$\mu_i = \mu_i(0) + \alpha_{ij}F_j + \beta_{ijk}F_jF_k + \gamma_{ijkl}F_jF_kF_l + \dots \quad (1)$$

Commonly, it is stated that the linear polarizability α is responsible for the linear optical properties of molecules while the first hyperpolarizability β is responsible for quadratic (second-order) NLO effects and the second hyperpolarizability γ is responsible for cubic (third-order) NLO effects. It may be noted that some authors refer to β as first-order hyperpolarizability and γ as second-order hyperpolarizability. In view of this author, such terminology should be avoided to prevent confusion about the order of relevant NLO effects.

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¹ It should be noted that theoretical and experimental papers often differ in the inclusion or omission of $1/n!$ factors in the power expansion.

² Using Einstein's summation convention.

To convert from microscopic hyperpolarizabilities to macroscopic susceptibilities denoted as $\chi^{(n)}$ and defined through the power dependence of the polarization P_i

$$P_i = P_i(0) + \chi_{ij}^{(1)} F_j + \chi_{ijk}^{(2)} F_j F_k + \chi_{ijkl}^{(3)} F_j F_k F_l + \dots \quad (2)$$

one needs to account for molecular orientations and local field effects. Since optics deals with oscillating fields, Eqs. 1 and 2 need to be modified to account for time dependences, which is conveniently carried out by considering Fourier components of F , μ and P and frequency-dependent hyperpolarizabilities and susceptibilities. For example, consecutive order Fourier components of μ can be presented as

$$\begin{aligned} \mu_i(\omega) &= \alpha_{ij}(\omega) F_j(\omega) \\ \mu_i^{(2)}(\omega_1) &= \beta_{ijk}(\omega_1, \omega_2, \omega_3) F_j(\omega_2) F_k(\omega_3) \\ \mu_i^{(3)}(\omega_1) &= \gamma_{ijkl}(\omega_1, \omega_2, \omega_3, \omega_4) F_j(\omega_2) F_k(\omega_3) F_l(\omega_4) \end{aligned} \quad (3)$$

Different combinations of frequencies in Eq. 3 lead to various NLO effects, each of which can be termed 'frequency mixing' of a certain type. We are concerned here with the cubic NLO effects, which are due to $\mu^{(3)}$. Traditionally, two of these effects are considered sufficiently practically important to be included in quantum chemistry computations of cubic NLO properties of molecules: third harmonic generation (THG) and intensity dependent refractive index (IDRI). However, because of practical difficulties in implementing THG for generation of new frequencies of laser light (usually a cascade of two frequency mixing processes, $\omega + \omega \rightarrow 2\omega$ and $2\omega + \omega \rightarrow 3\omega$ is simply used instead in commercial frequency triplers) the actual interest in this process is not as high as in that of IDRI. The latter process is due to the degenerate cubic hyperpolarizability $\gamma(-\omega; \omega, -\omega, \omega)$ and its macroscopic counterpart $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$. In technical language, IDRI is usually referred to as nonlinear refraction and is described by a value of the nonlinear refractive index n_2 defined by $\Delta n = n_2 I$ where I is the light intensity. It can be shown that n_2 is proportional to the real part of $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$. On the other hand, the imaginary part of $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ describes another important NLO process: nonlinear absorption, usually characterized by the value of the nonlinear absorption coefficient α_2 or the molecular parameter, two photon absorption cross section σ_2 . It follows that, on a microscopic scale, it is important to know both the real and the imaginary components of the complex hyperpolarizability $\gamma(-\omega; \omega, -\omega, \omega)$ of an NLO molecule since their values are decisive for the applicability of a NLO material built of such molecules.

All-optical switching

Both nonlinear refraction and nonlinear absorption have potentially many applications. Nonlinear absorption [3] is

well known to lead to two-photon fluorescence which finds application in two-photon microscopy. The natural spatial selectivity of the two-photon absorption process, which, for a focused laser beam is essentially confined to the area very close to the focus only, can be also used in 3D lithography and 3D optical memory devices. Other applications of nonlinear absorption include power limiting: a process which can be used to protect optical sensors from high power laser pulses. When talking about applications of nonlinear refraction, one usually has in mind the Holy Grail of modern photonics: all-optical switching (AOS) of telecommunication signals. This remains elusive due to the difficulties of obtaining nonlinear materials with the right values of suitable material parameters [4]. Figure 1 shows an example of a device that is capable of all-optical switching: the nonlinear waveguide coupler originally suggested by Jensen [5]. The principle of the operation of such a device is that a light pulse of low intensity is normally transferred from one arm of the coupler to the other by coupling of the two identical waveguide channels. A strong light pulse, however, will always stay in the original channel: the reason being that a high intensity light pulse causes modification of the refractive index inside the channel it travels, causing the loss of coupling with the other waveguide channel. What follows is the possibility of controlling light by light: if only a weak light pulse (signal) is introduced into the device in Fig. 1, it will exit the device through the second channel, however, in the simultaneous presence of another strong pulse (control), it will exit together with it through the first channel.

For the coupler (and many similar concept devices performing all-optical switching) to operate properly, it is necessary that the control laser pulse is able to acquire a nonlinear phase shift $\Delta\phi = 2\pi\Delta n \frac{L}{\lambda} = 2\pi n_2 I \frac{L}{\lambda}$ on the order of π as it traverses the length of the device. Obviously, an obstacle in that would be the presence of either nonlinear or

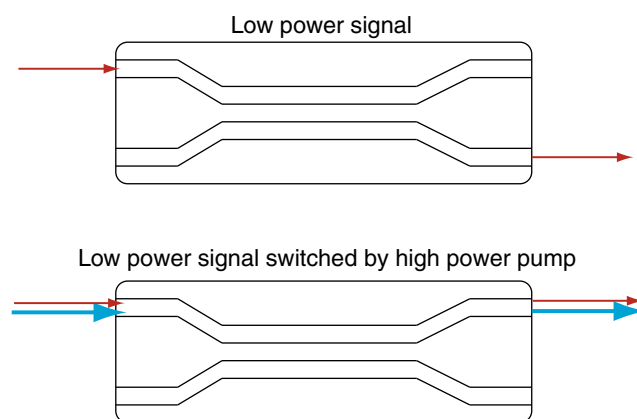


Fig. 1 Principle of all-optical switching in Jensen's half-beat directional coupler. The thin arrow is the signal, the thick arrow is the controlling pulse

linear absorption of light. The requirements for a material to be used in a nonlinear coupler are therefore the following: high $\text{Re}(\chi^{(3)})$, low $\text{Im}(\chi^{(3)})$, low linear absorption. Stegeman and coworkers [6, 7] have shown that it is impossible to obtain AOS at all, if the ratio of $\text{Im}(\chi^{(3)})/\text{Re}(\chi^{(3)})$ is too high. They introduced a merit factor T which is defined as $T = \frac{\alpha_2 \lambda}{n_2} = 4\pi \frac{\text{Im}(\chi^{(3)})}{\text{Re}(\chi^{(3)})}$. For the all-optical switching to be feasible it is necessary that $T < 1$. It should be noted that, for a material which is built of molecules of only one kind, having the cubic hyperpolarizability γ , the T factor will be equal $T = 4\pi \frac{\text{Im}(\gamma)}{\text{Re}(\gamma)}$. Therefore, in principle, the value of this crucial parameter should be accessible both from experimental measurements and from computational chemistry calculations performed on the molecule of interest.

Another factor is W , one-photon merit factor, $W = \frac{n_2 I_{\text{max}}}{\alpha_1 \lambda} > 1$. This condition is framed in terms of the maximum light intensity that can be used to drive the all-optical switch I_{max} . Obviously, a material with strong one-photon absorption, characterized by the one-photon absorption coefficient α_1 , is not able to perform well in an all-optical switch unless its nonlinearity is very high. The condition of low one-photon absorption can be inverted to demonstrate the wide range of parameters exhibited by today's nonlinear optical materials. Figure 2 shows mapping of the materials nonlinearity given by n_2 in cm^2/W and one-photon absorption represented by the loss coefficient α_1 expressed in dB/km to the design parameters of a conceptual AOS device: the minimum light intensity I_{min} needed to operate it and the maximum optical pathlength of a device. The maximum path length of a device can be approximated as the "absorption length", i.e., α_1^{-1} whereas the minimum intensity needed to operate the

device is the result of assuming that the all-optical device needs to acquire a nonlinear phase shift $\Delta\phi$ equal to π .

Datapoints included in the plot are representative values attainable in some of the nonlinear optical materials considered for AOS applications. It is interesting to find that the most important optical material: fused silica glass (SiO_2 glass) is in some respects superior to all other currently considered NLO materials. A very low value of α_1 (on the order of $0.1 \text{ dB}/\text{km}$) means that a device made of this material can be several tens of kilometers long. This allows for AOS with relatively low light intensity of the order of MW/cm^2 even though n_2 of silica is only on the order of $10^{-16} \text{ cm}^2/\text{W}$ [8]. Glasses containing heavier atoms, eg. intensely investigated chalcogenide glasses [9, 10] may have nonlinear optical properties that, in the telecommunication wavelength ranges, are two-three orders of magnitude better than that of silica. However, their performance is limited by their one-photon absorption (and other loss mechanisms like scattering) which is on the order of dB/m . Therefore, their overall suitability for AOS characterized by the minimum light intensity needed to operate the switch is inadequate. A similar limitation is present for materials such as conjugated polymers far from their material resonances. An example here may be substituted poly(p-phenylenevinylene)s which exhibit relatively high optical nonlinearities [11] but the losses of both two-photon and one-photon type are substantial. The highest n_2 for PPV-like materials was measured in unsubstituted PPV [12, 13] which is, however, a difficult material to handle and implement because of its insolubility and because of the high scattering losses due to tendency of the polymer chains to order.

It is also necessary to consider the case of the use of materials that possess very high refractive nonlinearity in the wavelength range corresponding to their strong one-photon absorption. Obviously, such nonlinearity may be much higher than that available away from material resonances. However, as seen in Fig. 2, for a hypothetical case of very strong on-resonance nonlinearity, the high value of n_2 would be accompanied by a high value of α_1 and in result, no improvement in the light intensity needed to operate the device can be obtained.

The value of the merit factor W , or the value of the critical intensity I_{min} is difficult to predict from theoretical computations. In principle, the absorption coefficient α_1 at a given wavelength is available from a routine quantum chemistry computation on a molecule of an NLO chromophore, which should provide the oscillator strengths and energies of absorption transitions, which, together with some assumptions about the electron-phonon coupling and other absorption band broadening mechanisms, should lead to reasonable prediction of an absorption spectrum of a material. Coupling that with a prediction of the value of n_2

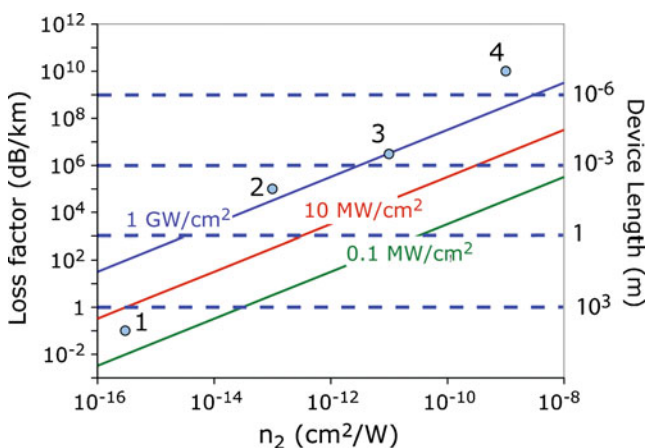


Fig. 2 Illustration of the material parameters achievable in NLO materials and resulting device performance. 1 – fused silica, 2- typical conjugated polymer (e.g. soluble PPVs) far from one-photon absorption. Similar values are achievable in chalcogenide glasses. 3- precursor-route PPV at 800 nm. 4- strong nonlinear chromophore under one-photon resonant conditions. The straight lines denote the minimum light intensity required to obtain the all-optical switching

should, in principle, lead to the evaluation of W , if I_{\max} is known from device design conditions, or to the calculation of I_{\min} . To this author's knowledge, such theoretical predictions have not been attempted yet.

Experimental results

As indicated above, to evaluate suitability of a cubic nonlinear material for real life applications one needs to know full dispersion of the complex $\chi^{(3)}$. For materials with molecular chromophores this translates into determination of the dispersion of the complex γ .

The experimental methods that can be used to evaluate full spectra of γ can be divided into two groups: methods using discrete wavelength measurements which can be combined to provide $\text{Re}(\gamma)$ and $\text{Im}(\gamma)$ spectra and methods using white light supercontinuum to probe a wide range of wavelengths at the same time. The most common technique that allows for the determination of the cubic nonlinearity is that of Z-scan [14] performed with a monochromatic laser beam (but it should be noted that short pulses are relatively spectrally broad: typically on the order of 10nm for fs pulses). Z-scan allows for the simultaneous determination of the refractive and absorptive component of the cubic nonlinearity: usually in terms of the nonlinear refractive index n_2 and the two-photon absorption coefficient α_2 . For commonly performed solution measurements the concentration dependences of the macroscopic nonlinearity parameters allow one to determine the complex hyperpolarizability γ of the solute [15]. The disadvantage of Z-scan compared to time-resolved techniques of measurements is that it does not provide any info on the mechanisms of NLO responses. The known caveats are

that one needs to use low repetition rate to avoid cumulative effects [16, 17] and to watch for signs of photochemical instability.

The advent of the self-mode-locked femtosecond-pulse Ti:sapphire lasers and of efficient optical parametric amplifiers has led to relatively easy availability of high power tunable sources of light, suitable for the investigations of nonlinear optical properties of materials by Z-scan within wide wavelength ranges. Such studies, are however, relatively rare. One of the reasons is the tediousness of the process of obtaining such data. The author of this contribution has been active in the field of experimental studies of cubic nonlinear optical properties of molecules and materials for over two decades and has been concentrating, among others, on providing data on dispersion of cubic hyperpolarizabilities of molecules (especially organometallic molecules) [18].

Systematic studies of the complex cubic hyperpolarizability carried out using the Z-scan technique with high-power low repetition rate femtosecond laser pulses have led to the determination of the dispersion curves for a number of interesting structures, see eg [19–22]. However, the understanding of the obtained relationships remains far from satisfactory. Since both the real and imaginary part of the hyperpolarizability are determined in Z-scan, it is tempting to treat them in a unified manner, as components of some model complex expression [18, 23], or in terms of the nonlinear Kramers-Kronig relation [24]. These approaches lead, however, to a number of conceptual and practical difficulties [25, 26].

In principle it is possible to express the experimentally determined complex γ as a combination of some complex terms resembling those appearing in the sum-over-states (SOS) expression [27] for γ which has been modified to include damping factors Γ_i , eg.:

$$\gamma_{ijkl}(\omega_1; \omega_2, \omega_3, \omega_4) \propto \varphi \sum_{p,q,r} \left[\frac{\mu_{0p}^i (\mu_{pq}^j - \delta_{pq} \mu_{00}^j) (\mu_{qr}^k - \delta_{qr} \mu_{00}^k) \mu_{r0}^l}{(\omega_{p0} + \omega_1 - i\Gamma_p)(\omega_{q0} - \omega_3 - \omega_4 - i\Gamma_q)(\omega_{r0} - \omega_4 - i\Gamma_r)} - \frac{\mu_{0p}^j \mu_{p0}^i \mu_{0q}^k \mu_{q0}^l}{(\omega_{p0} + \omega_1 - i\Gamma_p)(\omega_{p0} - \omega_2 - i\Gamma_p)(\omega_{q0} + \omega_3 - i\Gamma_q)} \right] \quad (4)$$

where φ stands for the permutation operator exchanging the frequencies. It may be noted that for the degenerate hyperpolarizability $\gamma(-\omega; \omega, -\omega, \omega)$ this leads to terms that exhibit both one-photon and two-photon resonances. For example, a term of the form $\frac{A}{(\omega_{v0} - \omega - i\Gamma_v)(\omega_{n0} - i\Gamma_n)(\omega_{m0} - \omega - i\Gamma_m)}$ would give a resonance (and γ enhancement) at frequencies ω close to those of one-photon transitions, ie ω_{v0} or ω_{m0} , but the permutation of frequencies leads also to two-photon terms as eg the term of the form

$\frac{A}{(\omega_{v0} - \omega - i\Gamma_v)(\omega_{n0} - 2\omega - i\Gamma_n)(\omega_{m0} - \omega - i\Gamma_m)}$ which gives a resonance when $\omega = \omega_{n0}/2$.

As described in [18, 25, 26] it may be sometimes possible to guess the form of a suitable simplified expression that can be used to approximate the experimental data. In general, however, the number of terms that may be of importance in the SOS expression is simply too big for this approach to be useful in numerical fitting of the experimental data.

It is not clear if it is practical to search for "dominating" terms in expressions like Eq. 4. In some simple cases like that of Coumarine 307 [26] it may be even possible to describe the dispersion by a single term. This approach is not likely to be general. Figure 3 shows the case of the dispersion of the hyperpolarizability in Rhodamine B chloride [26]. The two-photon absorption spectrum can be treated as two overlapping bands that can be approximated as a sum of two Lorentzians of the form

$$\gamma = \sum \frac{A_i}{\nu_i - \nu - i\Gamma_i} \tag{5}$$

The parameters giving a reasonable fit for the imaginary part of the hyperpolarizability provided in [26] are $A_1 = 4.6 \times 10^{-31}$, $\nu_1 = 24600 \text{ cm}^{-1}$ and $\Gamma_1 = 1480 \text{ cm}^{-1}$, $A_2 = 5.0 \times 10^{-31}$, $\nu_2 = 28350 \text{ cm}^{-1}$ and $\Gamma_2 = 1100 \text{ cm}^{-1}$. The dashed line in Fig. 3 denotes the real part of this complex expression. We have concluded in [26] that the experimentally determined real part of γ must contain contributions additional to those due to the two-photon resonances. Apart from the possibilities that arise from the multitude of terms in Eq. 4 there are also other factors that may need to be taken into account. One of such factors may be due to the presence of excited state molecules that may contribute to the measured nonlinear response. Following the discussion eg in [28], if the concentration of excited state molecules is equal to N_e , the polarization may in such a case be presented as

$$P = \chi_g^{(1)} E + \chi_g^{(3)} EEE + \frac{N_e}{N} (\chi_e^{(1)} - \chi_g^{(1)}) E + \dots \tag{6}$$

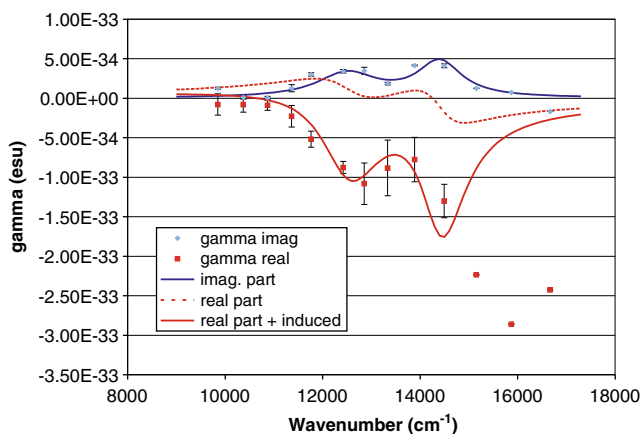


Fig. 3 Rhodamine B data fitted as two Lorentzians. Dispersion of the complex hyperpolarizability of Rhodamine B chloride was determined from Z-scan measurements on ethanol solution containing 1.0 % of the dye. The blue full line is the fit by the imaginary part of a sum of two complex Lorentzians as described in the text and the dashed line is the real part of the same sum of Lorentzians. The red full line is the result of assuming the presence of an additional induced part of the nonlinearity

where the index e relates to excited states and N is the total concentration of nonlinear chromophore molecules.

Depending on whether the excited states are generated by the one-photon or the two-photon absorption processes, the steady-state excited state density N_e can be considered proportional to E^2 (i.e., linearly proportional to the intensity) or to E^4 (square of the intensity) and the effective hyperpolarizability can therefore contain a term that may be proportional to the imaginary part of α or to the imaginary part of γ . In the case of Rhodamine it may be expected that the dominant contribution in the wavelength range of interest comes from two-photon absorption. We attempted therefore to interpret the experimental data by assuming that

$$\text{Re}(\gamma)_{\text{eff}} = \text{Re}(\gamma) + C\text{Im}(\gamma) \tag{7}$$

where the constant C accounts for the change of the refractive properties of the chromophore molecules upon excitation, more explicitly, one can assume that $C \propto (\alpha_e - \alpha_g)$. However, the actual mechanism of the refractive index change upon excitation does not have to be related to the change of the molecule polarizability only. One cannot exclude effects due to molecular orientation, photochemical changes and even thermo-optic effects.

Figure 3 shows the result of the calculation based on the above assumption as a full line. A relatively good fit (obtained by taking $A_1 = 4.6 \times 10^{-31}$, $\nu_1 = 25000 \text{ cm}^{-1}$ and $\Gamma_1 = 1480 \text{ cm}^{-1}$, $A_2 = 5.0 \times 10^{-31}$, $\nu_2 = 28800 \text{ cm}^{-1}$ and $\Gamma_2 = 1100 \text{ cm}^{-1}$) for the range $<14000 \text{ cm}^{-1}$ indicates that the experimental results for $\text{Re}(\gamma)$ for Rhodamine B chloride may be considered tainted by the presence of two-photon generated excited states. Careful intensity dependence studies should be carried out to confirm or reject this possibility: in fact, the C factor should be found proportional to the light intensity used for the determination of the effective γ values.

Looking at this case from the point of view of the possibility of predicting NLO behavior of molecules based on quantum chemical computations, we note that theoretical prediction of the effective nonlinearity would require, among others, the knowledge of the frequency dependences of the linear polarizabilities of the ground state and excited state molecules. Such information is not typically included in the datasets obtained from theoretical computations, although it should be, in principle, relatively easily obtained, possibly with the help of the Kramers-Kronig transform which is discussed below in the context of its nonlinear optics applications.

Kramers-Kronig transforms

In the domain of linear optics one often takes advantage of the fact that the real and imaginary parts of the linear

susceptibility $\chi^{(1)}$ are related through the Kramers-Kronig transform. It would be very useful if this kind of a relation could be used for discussing nonlinear refraction: simply because of the fact that measurements of nonlinear absorption are easier than those of nonlinear refraction, e.g., because the measurements of two-photon absorption of a dye in a solvent usually involve only absorption of a dye while the solvent shows no nonlinear absorption, the same being not true for nonlinear refraction where both components of a solution do contribute to the nonlinear refraction coefficient. Also, the two-photon absorption cross sections can often be conveniently determined through measurements of two-photon induced fluorescence [29, 30]. There has been much discussion of the use of the Kramers-Kronig transform in nonlinear optics (eg [24, 31–33]), however there is confusion concerning even the basic issue whether this transform can be used at all in the case of nonlinear refraction. Indeed, Boyd states in his "Nonlinear Optics" book [34] that "... Probably the most important process for which it is not possible to form a Kramers-Kronig relation is for the self-induced change in refractive index ... Moreover, one can show by explicit calculation ... that for specific model systems the real and imaginary parts of $\chi^{(3)}$ are not related in the proper manner to satisfy the Kramers-Kronig relations". Despite that, a number of papers has been written where the nonlinear refraction and nonlinear absorption were considered related through a relation of the form

$$\text{Re}[\gamma(-\omega; \omega, -\omega, \omega)] = \frac{2}{\pi} \int_0^{\infty} \frac{\text{Im}[\gamma(-\omega'; \omega', -\omega, \omega)]}{\omega'^2 - \omega^2} \omega' d\omega' \quad (8)$$

It should be noted that the imaginary part of γ under the integral is not the same γ which is related to the ordinary (degenerate) two-photon absorption because of the two different arguments ω and ω' . Instead, this hyperpolarizability describes the process of non-degenerate two-photon absorption, *i.e.*, absorbing two photons at once, one of them at ω , the other at ω' and the resulting excited state being at $\omega + \omega'$. It might be noted that non-degenerate two-photon absorption spectra may be obtained experimentally in a relatively straightforward manner by using pump-probe experiments, especially ones in which the pump is a laser beam at ω and the probe is white light supercontinuum, allowing one to obtain the whole spectrum of the two-photon absorption cross section $\sigma_2(\omega, \omega')$ for fixed ω . Unfortunately, a single experiment of this kind, *i.e.*, obtaining results for a single value of ω , does not suffice, a full two-dimensional spectrum of σ_2 would be needed to be able to perform the Kramers-Kronig transform. In the same way, a theoretical computation of two-dimensional two-photon absorption spectra is needed if one plans to use

the computed nonlinear absorption data for evaluation of the theoretical dispersion of the nonlinear refraction. Although it may be possible in some simple cases to roughly approximate the values of the non-degenerate nonlinear absorption [25, 26], this is not a good idea in the case of molecules with a multitude of excited states and possible two-photon resonances.

Conclusions

There has been some renewal of interest of experimentalists and theoreticians in molecular materials for all-optical switching. However, the typical quantum chemistry approaches do not provide a complete picture of relevant parameters that could be compared with the parameters obtainable from experiments and could be used for designing better molecules and materials. While it is common to compute the spectra of the degenerate two-photon absorption, what is really needed by the experimentalists is the full hyperpolarizability dispersion curves. From the point of view of the application potential, it would be optimal if the computations could provide wavelength dependences of the merit factors T and W which could be used to identify wavelength ranges of potential applications.

The presence of additional mechanisms giving rise to nonlinear refraction and absorption is also of importance and additional data such as frequency dependences of excited state polarizability may be useful for predicting the experimental behavior of NLO materials.

It remains crucial to assess the suitability of the Kramers-Kronig approaches to the analysis of experimental and theoretical data. More widespread computations of non-degenerate two-photon absorption spectra may be helpful in such analyses.

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References

1. Hales JM, Zheng S, Barlow S, Marder SR, Perry JW (2006) Bisdioxaborine polymethines with large third-order nonlinearities for all-optical signal processing. *J Am Chem Soc* 128:11362–11363
2. Hales JM, Matichak J, Barlow S, Ohira S, Yesudas K, Bredas JL, Perry JW, Marder SR (2010) Design of polymethine dyes with large third-order optical nonlinearities and loss figures of merit. *Science* 327:1485–1488
3. He GS, Tan LS, Zheng Q, Prasad PN (2008) Multiphoton absorbing materials: Molecular designs, characterizations, and applications. *Chem Rev* 108:1245–1330

4. Christodoulides DN, Khoo IC, Salamo GJ, Stegeman GI, van Stryland EW (2010) Nonlinear refraction and absorption: Mechanisms and magnitudes. *Adv Opt Photon* 2:60–200
5. Jensen SM (1982) The non-linear coherent coupler. *IEEE J Quantum Electron* 18:1580–1583
6. Mizrahi V, DeLong KW, Stegeman GI, Saifi MA, Andrejco MJ (1989) 2-photon absorption as a limitation to all-optical switching. *Opt Lett* 14:1140–1142
7. Stegeman GI, Torruellas WE (1996) Nonlinear materials for information processing and communications. *Philos Trans R Soc Lond Phys Sci Eng*:745–756
8. Milam D (1998) Review and assessment of measured values of the nonlinear refractive-index coefficient of fused silica. *Appl Opt* 37:546–550
9. Zakery A, Ruan Y, Rode AV, Samoc M, Luther-Davies B (2003) Low-loss waveguides in ultrafast laser-deposited As_2S_3 chalcogenide films. *J Opt Soc Am B: Opt Phys* 20:1844–1852
10. Ta'eed VG, Baker NJ, Fu LB, Finsterbusch K, Lamont MRE, Moss DJ, Nguyen HC, Eggleton BJ, Choi DY, Madden S, Luther-Davies B (2007) Ultrafast all-optical chalcogenide glass photonic circuits. *Opt Expr* 15:9205–9221
11. Gabler T, Brauer A, Waldhausl R, Bartuch U, Horhold HH, Michelotti F (1998) Nonresonant n_2 and TPA coefficient measurement in polymer waveguides by different measurement techniques. *Pure Appl Opt* 7:159–168
12. Samoc A, Samoc M, Woodruff M, Luther-Davies B (1995) Tuning the properties of poly(p-phenylenevinylene) for use in all-optical switching. *Opt Lett* 20:1241–1243
13. Samoc A, Samoc M, Woodruff M, Luther-Davies B (1998) Poly (p-phenylenevinylene): An attractive material for photonic applications. In: Wise DL, Wnek GE, Trantolo DJ, Cooper TM, Gresser JD (eds) *Photonic polymer systems: Fundamentals, methods and applications*, vol 49, *Plastics engineering*. Marcel Dekker Inc, New York, Basel, Hong Kong, pp 373–436
14. Sheikh-bahae M, Said AA, Wei T, Hagan DJ, Van Stryland EW (1990) Sensitive measurement of optical nonlinearities using a single beam. *IEEE J Quantum Electr* 26:760–769
15. Samoc M, Samoc A, Luther-Davies B, Bao Z, Yu L, Hsieh B, Scherf U (1998) Femtosecond z-scan and degenerate four-wave mixing measurements of real and imaginary parts of the third-order nonlinearity of soluble conjugated polymers. *J Opt Soc Am B: Opt Phys* 15:817–825
16. Kamada K, Matsunaga K, Yoshino A, Ohta K (2003) Two-photon-absorption-induced accumulated thermal effect on femtosecond Z-scan experiments studied with time-resolved thermal-lens spectrometry and its simulation. *J Opt Soc Am B: Opt Phys* 20:529–537
17. Samoc M, Samoc A, Luther-Davies B, Humphrey MG, Wong M-S (2003) Third-order optical nonlinearities of oligomers, dendrimers and polymers derived from solution Z-scan studies. *Opt Mat* 21:485–488
18. Powell CE, Morrall JP, Ward SA, Cifuentes MP, Notaras EGA, Samoc M, Humphrey MG (2004) Dispersion of the third-order nonlinear optical properties of an organometallic dendrimer. *J Am Chem Soc* 126:12234–12235
19. Samoc M, Dalton GT, Gladysz JA, Zheng Q, Velkov Y, Aagren H, Norman P, Humphrey MG (2008) Cubic nonlinear optical properties of platinum-terminated polyynediyl chains. *Inorg Chem* 47:9946–9957
20. Dalton GT, Cifuentes MP, Watson LA, Petrie S, Stranger R, Samoc M, Humphrey MG (2009) Organometallic complexes for nonlinear optics. 42. Syntheses, linear, and nonlinear optical properties of ligated metal-functionalized oligo(p-phenyleneethynylene)s. *Inorg Chem* 48:6534–6547
21. Babgi B, Rigamonti L, Cifuentes MP, Corkery TC, Randles MD, Schwich T, Petrie S, Stranger R, Teshome A, Asselberghs I, Clays K, Samoc M, Humphrey MG (2009) Length-dependent convergence and saturation behavior of electrochemical, linear optical, quadratic nonlinear optical, and cubic nonlinear optical properties of dipolar alkynylruthenium complexes with oligo(phenyleneethynylene) bridges. *J Am Chem Soc* 131:10293–10307
22. Roberts RL, Schwich T, Corkery TC, Cifuentes MP, Green KA, Farmer JD, Low PJ, Marder TB, Samoc M, Humphrey MG (2009) Organometallic complexes for nonlinear optics. 45. Dispersion of the third-order nonlinear optical properties of triphenylamine-cored alkynylruthenium dendrimers. *Adv Mat* 21:2318
23. Samoc M, Samoc A, Grote JG (2006) Complex nonlinear refractive index of DNA. *Chem Phys Lett* 431:132–134
24. Sheik-Bahae M (2005) Nonlinear optics basics. Kramers-Kronig relations in nonlinear optics. In: Guenther RD (ed) *Encyclopedia of modern optics*. Academic Press, Amsterdam
25. Samoc M, Samoc A, Dalton GT, Cifuentes MP, Humphrey MG, Fleitz PA (2008) Dispersion of the complex cubic nonlinearity in two-photon absorbing organic and organometallic chromophores. *Proc SPIE-Int Soc Opt Eng* 6801:68011O-68011-68016
26. Samoc M, Samoc A, Humphrey MG, Cifuentes MP, Luther-Davies B, Fleitz PA (2008) Z-scan studies of dispersion of the complex third-order nonlinearity of nonlinear absorbing chromophores. *Mol Cryst Liq Cryst* 485:894–902
27. Orr BJ, Ward JF (1971) Perturbation theory of non-linear optical polarization of an isolated system. *Mol Phys* 20:513–&
28. Pang Y, Samoc M, Prasad PN (1991) Third-order nonlinearity and two-photon-induced molecular dynamics: Femtosecond time-resolved transient absorption, Kerr gate and degenerate four-wave mixing studies in poly(p-phenylenevinylene)/sol-gel silica film. *J Chem Phys* 94:5282–5290
29. Xu C, Webb WW (1996) Measurement of two-photon excitation cross sections of molecular fluorophores with data from 690 to 1050 nm. *J Opt Soc Am B: Opt Phys* 13:481–491
30. Makarov NS, Drobizhev M, Rebane A (2008) Two-photon absorption standards in the 550–1600 nm excitation wavelength range. *Opt Expr* 16:4029–4047
31. Hutchings DC, Sheik-bahae M, Hagan DJ, Van Stryland EW (1992) Kramers-Kronig relations in nonlinear optics. *Opt Quant Electr* 24:1–30
32. Lucarini V, Saarinen JJ, Peiponen KE (2003) Multiply subtractive Kramers-Kronig relations for arbitrary-order harmonic generation susceptibilities. *Opt Commun* 218:409–414
33. Peiponen KE, Lucarini V, Saarinen JJ, Vartiainen E (2004) Kramers-Kronig relations and sum rules in nonlinear optical spectroscopy. *Appl Spectrosc* 58:499–509
34. Boyd RW (2008) *Nonlinear optics*, 3rd edn. Academic, Amsterdam