Dispersion of the Third-Order Nonlinear Optical Response of Organics Using a Few State Model

Joel M. Hales, Jochen Campo, Nikolay Makarov, Yanrong Shi, Stephen Barlow, Seth R. Marder, Joseph W.

Perry[†]

School of Chemistry and Biochemistry, Center for Organic Photonic and Electronics, Georgia Institute of Technology, Atlanta, Georgia [†]Corresponding author: joe.perry@gatech.edu

Abstract: Dispersion of the third-order nonlinear optical response can be predicted using a perturbative few-state model approach with knowledge of the linear and two-photon absorption spectra. This approach has been applied toward polymethines and squaraines. ©2012 Optical Society of America

OCIS codes: (190.0190) Nonlinear optics; (190.4400) Nonlinear optics, materials; (190.4710) Optical nonlinearities in organic materials; (070.6020) Signal processing.

1. Introduction

Conjugated organic materials with large third-order nonlinear optical (NLO) responses are of renewed interest for all-optical switching (AOS) [1,2]. Conventional phase-based switching requires materials which simultaneously possess very large nonlinear refractive indices and very small two-photon absorption (2PA) coefficients. At the molecular level, this requires an accurate understanding of the dispersion of the Re(γ) and Im(γ), where γ is the third-order polarizability. Unfortunately, organic molecules can possess a number of low-lying electronic states leading to strong dispersion of γ , even in the near-IR spectral region. Therefore, mapping out this dispersion typically requires broadband NLO characterization of Re(γ) and Im(γ) with reasonable spectral resolution using a technique such as femtosecond-pulsed Z-scan. This can prove to be quite time-consuming particularly when a series of promising molecules are under investigation. Here we show that knowledge of the linear and 2PA spectra can, in conjunction with a well-known few state model derived from perturbation theory, allow for an accurate prediction of the dispersion of γ . Since these broadband spectroscopic techniques can be performed rapidly and with high resolution, even complicated spectral dispersion can be mapped.

2. Perturbative Few State Model

It has long been known that a simplified few state model derived from the perturbation theory expression for γ can be extremely useful for rationalizing the NLO response of organic molecules [3,4]. A typical representation of the few model as a function of excitation frequency ω is given by the following equation:

$$\gamma(\omega) \propto -\frac{M_{ge}^4}{\left(\Omega_{ge} - \hbar\omega\right)^3} + \frac{M_{ge}^2 \Delta \mu_{ge}^2}{\left(\Omega_{ge} - \hbar\omega\right)^3} + \sum_{e'} \frac{M_{ge}^2 M_{ee'}^2}{\left(\Omega_{ge} - \hbar\omega\right)^2 \left(\Omega_{ge'} - 2\hbar\omega\right)}$$

Here, $\Omega = E - i\Gamma$ where E is the energy and Γ is the linewidth of the transition, M is the transition dipole moment, and $\Delta\mu$ is the change in state dipole moment, and the subscripts represent the ground, first excited, and higher-lying excited states (denoted by g, e, and e' subscripts, respectively). It is clear that accurate prediction of complex NLO response using this model requires knowledge of numerous dipole moments and their associated transition energies. While this could, in principle, be accomplished through broadband linear and pump-probe excited-state spectroscopies, certain excited-states would likely be inaccessible due to their small transition energies and vibronically-allowed transitions would also be difficult to quantify. Fortunately, transitions associated with the last two terms in the equation can be identified using high-resolution broadband 2PA spectroscopy while the first term, known as the negative or N term, can be fully characterized by the lowest lying excited state transition evident from linear absorption spectroscopy.

3. Polymethines and Squaraines

Polymethine molecules have been recently proposed as promising candidates for AOS due to their large, preresonantly enhanced $\text{Re}(\gamma)$ values and appropriately spaced 2PA resonances leading to small $\text{Im}(\gamma)$ values in the spectral region-of-interest [5]. The mapping of the dispersion of $\text{Re}(\gamma)$ and the molecular 2PA figure-of-merit (i.e. $|\text{Re}(\gamma)/\text{Im}(\gamma)|$) of particular chalcogenopyrylium-based polymethines was accomplished using linear and nondegenerate 2PA spectroscopies to extract the pertinent transition dipole moments and energies and applying the perturbative few state model [5]. This predicted dispersion was found to give good agreement with experimentally derived values from femtosecond Z-scan measurements. Such systems were found to be well described using two electronically-allowed states and one vibronically-allowed one.

In addition to the spectroscopically simple polymethine molecules, extended squaraine systems were also studied. These systems were structurally similar to molecules reported previously which exhibited extremely large 2PA cross-sections in the near-IR [6]. Broadband, high resolution 2PA spectroscopy showed that such squaraines possess a much richer distribution of strongly-allowed two-photon transitions than the polymethines leading to a more complicated dispersion of the NLO response. Four electronically-allowed excited states and one vibronically-allowed state were required to properly fit the 2PA spectra using the few state model (see Fig. 1, left). Consequently, the dispersion of Re(γ) was found to be quite strong and even exhibited a pronounced sign change toward higher excitation frequencies (see Fig. 1, right). All of these observations were confirmed through direction measurements of Re(γ) using femtosecond Z-scans.



Figure 1. (Left) Linear absorption and 2PA spectra of the squaraine. The 1PA spectrum is shown in solid black; the experimentally measured 2PA data points (squares) were obtained using femtosecond Z-scans and the 2PA spectrum derived from the few-state model is shown as a dotted line. (Right) Dispersion of $Re(\gamma)$ measured by femtosecond Z-scan (squares) and predicted using the few-state model (dotted lines).

In conclusion, using broadband linear and nonlinear absorption spectroscopies and a simple perturbation theory model permitted mapping of the dispersion of $\text{Re}(\gamma)$ and $|\text{Re}(\gamma)/\text{Im}(\gamma)|$ for a number of organic molecules. Such an approach gave results that agreed well with experimentally-determined values from pulsed Z-scan measurements even for squaraine molecules that were found to have quite strong dispersion in the near-IR spectral region. Given the importance of these parameters in AOS applications, this relatively straight-forward approach for predicting the NLO response of potential organic systems could prove quite valuable.

This work was funded in part by the DARPA ZOE program (Grant No. W31P4Q-09-1-0012), by NSF through the CMDITR STC (DMR-0120967), and through the MURI-COMAS (Grant No. FA9550-10-1-0558).

3. References

- [1] M. Hochberg et al., Nat. Mater. 5, 703-709 (2006).
- [2] C. Koos et al., Nat. Photonics 3, 216 (2009).
- [3] Kuzyk, M. G.; Dirk, C. W. Phys. Rev. A 41, 5098 (1990).
- [4] Dirk, C. W.; Cheng, L. T.; Kuzyk, M. G. Int. J. Quantum Chem 43, 27 (1992).
- [5] J. M. Hales et al., Science, **327**, 1485 1488 (2010)
- [6] S.-J. Chung, et al., J. Am. Chem. Soc., 128, 14444-14445 (2006).