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A toy model for the nonlinear optical response of molecules with modulated conjugation

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ABSTRACT

In organic molecules, the optical response originates from the motion of the pi-electrons, which are constrained to move along the molecule's conjugated path. As an electron moves through the conjugated path, it interacts with the rest of the charges such that its motion is very dependent on the shape of the molecule. In this paper we introduce a simple model for that allows us to determine how the shape of the conjugated path affects the nonlinear optical response of the molecule. Our results apply to typical second-order dipolar structures: we have determined how the symmetry of the conjugated path affects the optical response, and we have found potential new strategies for making better molecules.

Keywords: Electro-optic modulators, Nonlinear Optics, Nonlinear Optical chromophores, modulated conjugation, first hyperpolarizability, molecular Nonlinear Optics

1. INTRODUCTION

Materials with good nonlinear optical (NLO) properties are needed for applications in all-optical information transmission, storage and retrieval, and manipulation.[1-3] The purely electronic response of organic photonic materials would provide higher modulation frequencies, such as wider bandwidths could be used in modulator devices, that would surpass the performance of the inorganic piezoelectric single crystals, such as LiNiO₃, that are used presently in conjunction with laser diode sources to provide electro-optic amplitude modulation for long-haul optical data transmission systems, [4] One potential advantage of organic nonlinear optical materials with respect to semiconductors is that the response at the macroscopic level can be related to the response at the molecular level by simple addition rules. This means that the optimization of the macroscopic nonlinear response is based on the optimization of the response at the molecular level. Due to the great versatility of organic chemistry, the number of organic molecules that could be potentially synthesized for the incorporation into optoelectronic devices has been estimated to be of the order of Avogadro's number.[5-7]

Accurate and exact expressions for the (frequency dependent) for the linear and nonlinear molecular polarizabilities can be obtained through quantum perturbation theory methods.[8] However, the exact evaluation of the exact quantum expressions for medium sized structures is quite difficult, since it requires knowledge of the relevant properties of ground and all the excited states of the structure. In principle these quantities can be evaluated using quantum chemistry methods, but the level of accuracy of such calculations is yet not good enough to reproduce the experimental results quantitatively.[9,10]

To avoid the complexity involved with sums over an infinite number of states, most experimental and phenomenological approaches have traditionally replaced the exact expressions for the molecular linear and nonlinear molecular polarizabilities within the "two-level model" approximation. Within the two-level model approximation, the molecular optical response around a resonant peak is assumed to be dominated by the contribution of only two states (the ground and the first excited state). Such an approximation was shown to yield qualitative results (in agreement with the experimental characterization) for relatively small compounds with only one charge transfer band in the linear absorption spectrum, such as nitroanilines,[11] but clearly is insufficient to describe properly the behavior of medium sized molecules with more than one single transfer band peak. Furthermore, Zyss and collaborators have shown that the two-level model is unphysical for structures with non-dipolar symmetries.[12-14] Nevertheless, the two-level model is employed regularly by the experimentalist to extrapolate the resonance-enhanced measured values of the nonlinear

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response to the off-resonance regime, and similarly, the theoreticians have widely used the two-level model to qualitatively investigate the effects of different structural properties upon the nonlinear response.

In order to look for general relationships between the fundamental properties of the molecules and its linear and nonlinear optical response, an alternative approach based in the application of the Thomas-Kuhn sum rules has been proposed. Such an approach is possible because, the generalized Thomas-Kuhn sum rules impose general relationships between the quantum properties that determine the optical response of the molecule. This kind of methodology was pioneered by Prof. Mark G. Kuzyk, who used the Thomas-Kuhn sum-rules to prove that the molecular response is bounded and calculated the quantum limit in terms of fundamental properties such as the number of delocalized electrons of the molecule and the wavelength of maximum absorption. The methodology has been successfully applied and extended to guide the search for optimal structures, and to investigate the underlying physical principles behind the nonlinear optical response of molecular systems.[14-28]

Previous research indicated that to improve the first hyperpolarizability it is best to use different kinds of spacers along the conjugated path.[24,26,28] In this paper we introduce a simple toy model that can help us to find out if there is an optimal way of arranging the spacers for the optimization of the first hyperpolarizability in typical organic molecules.

2. THEORY

In Nonlinear Optics, the polarization of the material, \bar{P} , defined as the electric dipole moment per unit of volume, is not directly proportional to the amplitude of the applied electric field, \bar{E} . Hence, the polarization of the medium is expanded as a series in the electric field:

$$\bar{P} = \chi^{(1)}\bar{E} + \chi^{(2)}(\bar{E})^2 + \chi^{(3)}(\bar{E})^3 + \chi^{(4)}(\bar{E})^4 \dots \quad (1)$$

a short hand notation used to express the dependence of the polarization in different powers of the amplitude of the electric field.

A more rigorous definition is provided taking into account the tensor nature of the fields, as follows. The *ith* component of the polarization \bar{P} is related with the components of the electric field amplitude through:

$$P_i = \chi_{ij}^{(1)}E_j + \chi_{ijk}^{(2)}E_jE_k + \chi_{ijkl}^{(3)}E_jE_kE_l + \dots \quad (2)$$

where Einstein's summation convention is implied.

In general, it is more convenient to express nonlinear quantities in the frequency domain. If $E_i^{\omega_k}$ represents the amplitude of the electric field oscillating with frequency ω_k and $P_i^{\omega_1}$ represents the amplitude of the polarization of the medium oscillating with frequency ω_1 , the equivalent to Eq. (2) in the frequency domain is given by:

$$P_i^{\omega_\sigma} = \chi_{ij}^{(1)}(-\omega_\sigma; \omega_\sigma)E_j^{\omega_\sigma} + \chi_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2)E_j^{\omega_1}E_k^{\omega_2} + \chi_{ijkl}^{(3)}(-\omega_\sigma; \omega_1, \omega_2, \omega_3)E_j^{\omega_1}E_k^{\omega_2}E_l^{\omega_3} + \dots \quad (3)$$

where $\chi_{i\alpha_1\dots\alpha_n}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n)$ are the tensor components of the *n*th-order electric susceptibility. Notice that conservation of energy implies that for any order, the electric susceptibilities must zero unless: ($\omega_\sigma = \omega_1 + \omega_2 \dots + \omega_n$). The *n*th-order electric susceptibility is an optical property of the material that serves to evaluate the *n*th-order (non)linear efficiency of the material. For example, in the case of the generation of second harmonic (where the incident

beam at frequency ω produces nonlinearly an output at frequency 2ω), a second-order nonlinear effect, the i th-component of the nonlinear polarization is related to the amplitude of the fields through:

$$P_i^{2\omega} = \chi_{ijk}^{(2)}(-2\omega; \omega, \omega) E_j^\omega E_k^\omega. \quad (4)$$

By inspecting Eq. 4, it is clear that the efficiency of a material for the generation of second-harmonic (from ω to 2ω) will directly related to the value of $\chi_{ijk}^{(2)}(-2\omega; \omega, \omega)$, since, a bigger susceptibility would imply a stronger polarization of the medium oscillating at frequency 2ω . Therefore, at the macroscopic level, the nonlinear electric susceptibilities quantify the nonlinear efficiency of the medium.

2.1 The molecular hyperpolarizabilities

Following the same approach as with the macroscopic polarization (Eq. 3), the induced dipole of a molecule \vec{p} , is expanded in powers of the electric field:

$$p_i^{\omega_\sigma} = \alpha_{ij}^{(1)}(-\omega_\sigma; \omega_\sigma) E_j^{\omega_\sigma} + \beta_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) E_j^{\omega_1} E_k^{\omega_2} + \gamma_{ijkl}^{(3)}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) E_j^{\omega_1} E_k^{\omega_2} E_l^{\omega_3} + \dots \quad (5)$$

where $\alpha_{ij}^{(1)}(-\omega_\sigma; \omega_\sigma)$ is the molecular linear polarizability, $\beta_{ijk}^{(2)}(-\omega_\sigma; \omega_1, \omega_2)$ is the *first hyperpolarizability*, $\gamma_{ijkl}^{(3)}(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$ is the *second hyperpolarizability*, and so on. The first and second hyperpolarizabilities are properties of the molecule and depend on its structure, in the same manner as the electric susceptibilities are a property of the material. For example, in the same manner as a second order nonlinear process is forbidden in systems with a center of symmetry,[10] a molecule must also lack a center of symmetry in order to have a non zero first hyperpolarizability. The investigation, study and characterization of nonlinear optical behavior at the molecular level is then related to the investigation and study and characterization of the hyperpolarizabilities.

2.2 Quantum-mechanical expressions for the hyperpolarizabilities

The molecular polarizabilities depend on fundamental properties of the structure, and can be derived in terms of some fundamental properties of the unperturbed states of the molecule (or any other quantum system), using quantum perturbation theory.[8] These fundamental properties are:

- The energy difference between the ground state, $|g\rangle = |0\rangle$, and the n th excited state, $|n\rangle$, defined as E_{n0} .
- The line widths of the excited states, Γ_{n0} , inversely proportional to the lifetime of the excited states.
- The transition dipole moments, x_{nm} , defined as $x_{nm} = \langle n | \hat{x} | m \rangle$, where \hat{x} is the position operator along the x -direction (in the molecular coordinates).

The diagonal component of the first hyperpolarizability (along the x -direction), $\beta_{xxx}^{(2)}(-\omega_\sigma; \omega_1, \omega_2)$ is then given by:[8]

$$\beta_{xxx}^{(2)}(-\omega_\sigma; \omega_1, \omega_2) = (-e)^3 \sum'_{n,m} x_{gm} \bar{x}_{mn} x_{ng} \cdot D_{nm}(\omega_1, \omega_2), \quad (6)$$

where the prime sign in the sum indicates that the sum is to be carried over all the excited states, but does not include the ground state; $(-e)$ is the charge of the electron, and the bar operator has been defined such as:

$$\bar{x}_{mn} = \begin{cases} x_{nm} & \text{if } n \neq m, \\ x_{nn} - x_{gg} \equiv \Delta x_{ng} & \text{if } n = m. \end{cases} \quad (7)$$

The dispersion factors, $D_{nm}(\omega_1, \omega_2)$, are given by:

$$D_{nm}(\omega_1, \omega_2) = I_{1,2} \left\{ \frac{1}{(E_{mg} - i\Gamma_m - \hbar\omega_1 - \hbar\omega_2)(E_{ng} - i\Gamma_n - \hbar\omega_1)} + \frac{1}{(E_{mg} + i\Gamma_m + \hbar\omega_2)(E_{ng} - i\Gamma_n - \hbar\omega_1)} + \frac{1}{(E_{mg} + i\Gamma_m + \hbar\omega_2)(E_{ng} + i\Gamma_n + \hbar\omega_1 + \hbar\omega_2)} \right\}, \quad (8)$$

where \hbar is the reduced Planck constant, such as $\hbar\omega$ is the energy of the photons associated with a monochromatic beam oscillating at frequency ω , and the operator $I_{1,2}$ is mean to perform an average over all the possible permutations of $(\omega_1 \leftrightarrow \omega_2)$. A similar expression can be obtained for the second hyperpolarizability,[8,27]

However, in this paper we will focus only on the off-resonance limit, where the energy of the incoming photons is negligible in comparison with the energy differences on the unperturbed molecule. In his case the dispersion factor (Eq. 8) does not depend on the incoming frequencies and reduces to:

$$D_{nm} = \frac{3}{E_{mg} E_{ng}} \quad (9)$$

3. GOAL

As previously explained, the strength of the second-order nonlinear response is determined through the first hyperpolarizability (β). A molecule with a high β value has a better optical performance in the regime of interest for our study.

Typically, molecules with second-order nonlinear optical response consist of a conjugated path between a donor and an acceptor. The conjugated path consists on a series of one or more conjugated spacers. Figure 1 shows some typical conjugated spacers.

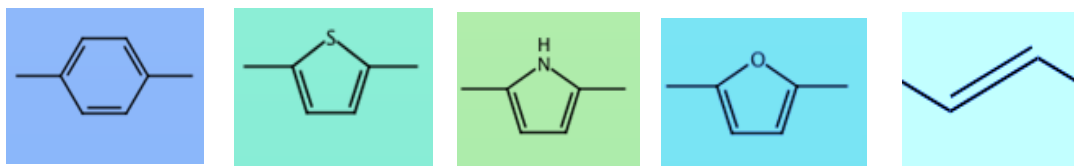


Figure 1: Typical conjugated spacers

As an electron moves through the conjugated path, it interacts with the rest of the charges in the molecule, such as its motion is very dependent on the shape of the molecule. We want to find out if there is an optimal way of arranging the spacers for the optimization of β in typical organic molecules.

Every kind of spacer has a unique value of the aromatic stabilization energy (ASE). Thus, the presence of a spacer along the conjugated path produces a “bump” in the potential function $V(x)$ along the conjugated path. These “bumps” can help to improve the second order nonlinear response (β).[24,26,28] Our goal is to understand the influence of these

“bumps” on the potential of the molecule along its conjugated path in order to design better optically responsive molecules.

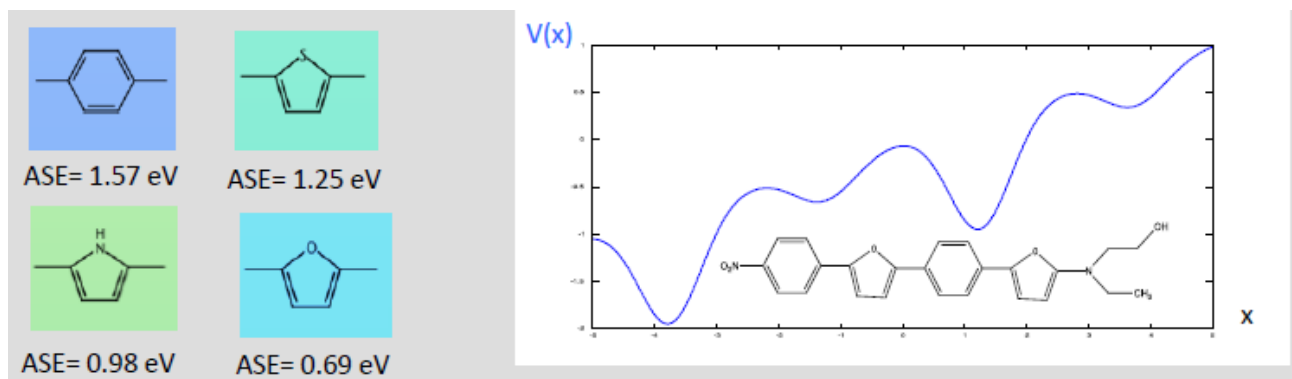


Figure 2: Aromatic Stabilization Energies (ASE) of different conjugated spacers (left), and the resulting potential that comes by combining different spacers according to our model (right)

4. METHODS

The potential energy along the conjugated path, $V(x)=V(\text{DA})+V(\text{bumps})$, is made up from 0-2 spacers located between the donor and the acceptor. The effect of donor and acceptor is modeled as $V(\text{DA})= k.x/\text{latL}$, where k is a constant and latL is the length of the molecule.

Each spacer creates a bump in the conjugated path. The bumps are modeled as negative Gaussian functions, The depth and width of the bump were determined through two parameters, ac and σ , respectively. As the values of ac and σ for each spacer are changed, a new potential trial is generated. Figure 3 shows a sample potential made out of 4 spacers, and the relationship between ac and σ for the negative Gaussian function.

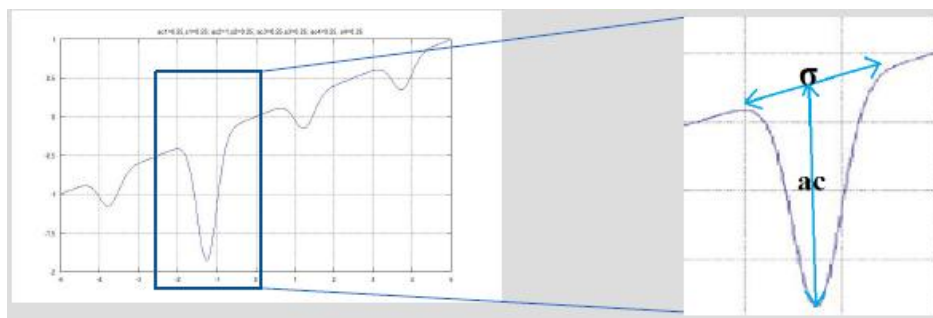


Figure 3: A sample potential made out of 4 spacers. The inset shows how the two parameters determine the shape of our negative Gaussian function.

For each potential trial, we then solved the Schrodinger Equation to compute the corresponding first hyperpolarizability, β . This was done using finite difference methods via MatLab.

5. RESULTS

Four different sets of simulations were tried.

First, we tested 84 different simulations with donor and acceptor only ($V(x)=k.x/\text{latL}$), with k and latL as independent variables. It was found that as the length of the conjugated path (latL) increases, β increases. However, as k increases, β increases first, and then goes to zero. The results are summarized in Figure 4.

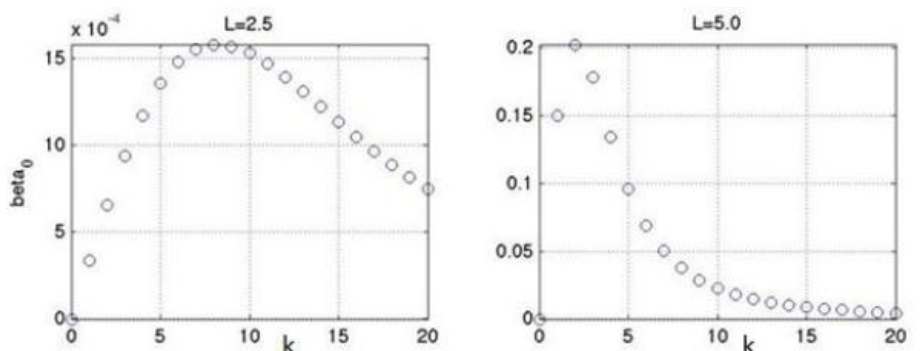


Figure 4: β values for two different latL (2.5, 5.0), as a function of k for molecules with only donor and acceptor components (no bumps along the conjugated path).

In the second set of simulations, we introduced a bump along the conjugated path. We tested three positions for the bump ($1/3 \text{ latL}$, $1/2 \text{ latL}$, $2/3 \text{ latL}$). We performed a total of 480 simulations with different values of \mathbf{ac} , σ , k , and latL . Our results show that if the bump is at the center of the molecule, as σ increases, so does β , such as the best molecules should have no bumps at all. However, if the bump is placed at an asymmetric positions it can help to improve β . More importantly, it is possible to have significant β values without the need of using Donor and Acceptor units.

In our third set of simulations, we simulated structures with two bumps along the conjugated path ($\text{latL}=5$), for different values \mathbf{ac} , σ and k . It was found that the best values of β were achieved when the two bumps were sharp/deep ($\sigma=0.1$).

6. CONCLUSIONS

Our study confirms that the symmetry of conjugated path has very strong influence on the second-order molecular nonlinear response (β). Interestingly, the presence of one bump along the conjugated path improves β , as long as the bump is not in a center position. This is in agreement with the symmetry constraints upon β .

Generally, molecules with an even number of bumps will generate higher values of β since the associated potential is less centrosymmetric. Although the presence of donor and acceptor caps helps to break the centrosymmetry, it was found that as the difference of potential between donor and acceptor increases, the electrons get trapped on one side of the molecule and the β value decreases.

In the case where the conjugated path has two spacers, it was found that the best β was generated when the presence of the spacers results in sharp/deep bumps along the conjugated path.

Finally, we extended the calculations to molecules with four spacers along the conjugated path. We have found that the best strategy for making more efficient molecules by combining 4 spacers with different aromatic stabilization energy (ase) should follow the following pattern: Donor – low ase spacer – low ase spacer – high ase spacer – high ase spacer – Acceptor. We also confirmed that it is best to use different kinds of spacers along the conjugated path in order to improve the response. However, we have found that the order in which the different spacers are aligned is very important.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

- [1] Prasad, P. N. and Williams, D. J., [Introduction to Nonlinear Optical Effects in Molecules and Polymers], Wiley, New York, (1991).
- [2] Williams, D. J., [Nonlinear Optical Properties of Organic and Polymeric Materials], ACS, Washington D.C., Vol. 233 (1983).
- [3] Williams, D. J., "Organic Polymeric and Non-polymeric Materials with Large Optical Nonlinearities," *Angew. Chem. Int. Ed. Engl.*, 23, 690-703 (1984).
- [4] Dalton, L. R., [Nonlinear Optical Materials: From chromophore design to commercial applications], *Advances in Polymer Science*, Vol 158., Springer-Verlag, Berlin Heidelberg, (2002).
- [5] Lipinski, C. and Hopkins, C., "Navigating chemical space for biology and medicine," *Nature*, 432, 855-861 (2004).
- [6] Ertl, P., "Cheminformatics Analysis of Organic Substituents: Identification of the Most Common Substituents, Calculation of Substituent Properties, and Automatic Identification of Drug-like Bioisosteric Groups," *J. Chem. Inf. Comput. Sci.*, 43(2), 374-380 (2003).
- [7] Wang, M., Hu, X., Beratan, D., and Yang, W., "Designing Molecules by Optimizing Potentials," *J. Am. Chem. Soc.*, 128, 3228-3232 (2006).
- [8] Orr, B. J., and Ward, J. F., "Perturbation theory of the non-linear optical polarization of an isolated system," *Mol. Phys.*, 20, 513-526 (1971).
- [9] Hu, X., Xiao, D., Keinan, S., Asselberghs, I., Therien, M. J., Clays, K., Yang, W. and Beratan, D. N., "Predicting the Frequency Dispersion of Electronic Hyperpolarizabilities on the Basis of Absorption Data and Thomas-Kuhn Sum Rules," *J. Phys. Chem. C.*, 114 (5), 2349-2359 (2010).
- [10] Miura, M., Aoki, Y. and Champagne, B. J., "Assessment of time-dependent density functional schemes for computing the oscillator strengths of benzene, phenol, aniline, and fluorobenzene," *J. Chem. Phys.*, 127, 084103 (2007).
- [11] Oudar, J. L. and Chemla, D. S., "Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment," *J. Chem. Phys.*, 66, 2664-2668 (1977).
- [12] Bidault, S., Brasselet, S., Zyss, J., Maury, O., and Le Bozec, H., "Role of spatial distortions on the quadratic nonlinear optical properties of octupolar organic and metallo-organic molecules," *J. Chem. Phys.* 126, 034312 (2007).
- [13] Brasselet, S. and Zyss, J., "Relation between quantum and geometric dimensionalities in molecular nonlinear optics: Beyond the two-level model for anisotropic systems," *Journal of Nonlinear Optical Physics and Materials* 5, 671-694 (1996).
- [14] Kuzyk, M. G., "Fundamental Material Limitations on Optical Devices," *Circuits and Devices*, 19, 8-17 (2003).
- [15] Kuzyk, M. G., "Fundamental Limits of Nonlinear Susceptibilities," *Optics and Photonics News*, 14(12), 26 (2003).
- [16] Tripathy, K., Perez-Moreno, J., Kuzyk, M. G., Coe, B. J., Clays, K. and Kelley, A. M. "Why Hyperpolarizabilities Fall Short of the Fundamental Quantum Limit," *J. Chem. Phys.*, 121, 7932-7945 (2004).
- [17] Kuzyk, M. G., "Physical Limits on Electronic Nonlinear Molecular Susceptibilities" *Phys. Rev. Lett.*, 85, 1218-1221 (2000).
- [18] Kuzyk, M. G., "Fundamental limits on third-order molecular susceptibilities," *Opt. Lett.*, 25, 1183-1185 (2000).
- [19] Kuzyk, M. G., "Quantum limits of the hyper-Rayleigh scattering susceptibility," *IEEE J. Select. Topics Quantum Electron.*, 7, 774-780 (2001).
- [20] Kuzyk, M. G., "Erratum: Physical Limits on Electronic Nonlinear Molecular Susceptibilities," *Phys. Rev. Lett.*, 90, 039902 (2003).

- [21] Kuzyk, M. G., "Fundamental limits on third-order molecular susceptibilities: erratum," *Opt. Lett.*, 28, 135 (2003).
- [22] Kuzyk, M. G. "Compact sum-over-states expression without dipolar terms for calculating nonlinear susceptibilities," *Phys. Rev. A*, 72, 053819 (2005).
- [23] Kuzyk, M. G., and Watkins, D. S.; "The effects of geometry on the hyperpolarizability", *J. Chem. Phys.*, 124, 244104 (2006).
- [24] Perez-Moreno, J., Zhao, Y., Clays, K., and Kuzyk, M. G., "Modulated conjugation as a means for attaining a record high intrinsic hyperpolarizability," *Opt. Lett.*, 32, 59 (2007).
- [25] Perez-Moreno, J., et al. "Combined molecular and supramolecular bottom-up nanoengineering for enhanced nonlinear optical response: Experiments, modeling, and approaching the fundamental limit," *J. Chem. Phys.*, 126, 740705 (2007).
- [26] Zhou, J., Kuzyk, M. G. and Watkins, D. S., "Pushing the hyperpolarizability to the limit", *Opt. Lett.*, 31, 2891 (2006).
- [27] Perez-Moreno, J., Clays and K., Kuzyk, M. G., "A new dipole-free sum-over-states expression for the second hyperpolarizability," *J. Chem. Phys.*, 128, 084109 (2008).
- [28] Perez-Moreno, J. Zhao, Y. X., Clays, K. Kuzyk, M. G. , Shen, Y. Q., Qui, L., Hao, J. M. and Guo, K. P., "Modulated conjugation as a means of improving the intrinsic hyperpolarizability," *J. Am. Chem. Soc.*, 131, 5084 (2009).