

Microscopic cascading of second-order molecular nonlinearity: new design principles for enhancing third-order nonlinearity

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Abstract: Herein, we develop a phenomenological model for microscopic cascading and substantiate it with *ab initio* calculations. It is shown that the concept of local microscopic cascading of a second-order nonlinearity can lead to a third-order nonlinearity, without introducing any new loss mechanisms that could limit the usefulness of our approach. This approach provides a new molecular design protocol, in which the current great successes achieved in producing molecules with extremely large second-order nonlinearity can be used in a supra molecular organization in a preferred orientation to generate very large third-order response magnitudes. The results of density functional calculations for a well-known second-order molecule, (*para*)nitroaniline, show that a head-to-tail dimer configuration exhibits enhanced third-order nonlinearity, in agreement with the phenomenological model which suggests that such an arrangement will produce cascading due to local field effects.

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OCIS codes: (190.4380) Nonlinear optics, four-wave mixing; (190.4710) Optical nonlinearities in organic materials; (000.1570) Chemistry.

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1. Introduction

π -Conjugated organic systems have long been of particular interest for all-optical switching applications, because they exhibit large non-resonant optical nonlinear response due to the delocalized nature of the molecular electronic structure [1]. To date, a number of approaches have been proposed to further enhance the third-order nonlinear response of these systems, for example multidimensional electronic delocalization in multi-branched dendritic structures [2] resulting in cooperative enhancement of nonlinearities. Another approach to the enhancement of second- and third-order nonlinear response of linear conjugated organics is optimizing of their Bond Length Alternation (BLA) by varying the ground-state polarization [3,4]. Such a variation is usually achieved by means of adjusting solvent polarity. However, the static fields attainable even in the most polar solvents are not sufficient to produce substantial variations of BLA [4].

In these and many other approaches conventional power series expansion of the induced dipole moment which in the static-field limit reads

$$\mu_i = \alpha_{ij} E_j + \frac{1}{2!} \beta_{ijk} E_j E_k + \frac{1}{3!} \gamma_{ijkl} E_j E_k E_l + \dots, \quad (1)$$

is used to describe the local response of a molecule to the (local) field, and considers the intrinsic nonlinearities of molecules in the gas phase, where local intermolecular interactions are neglected. Here, α_{ij} is microscopic molecular polarizability, β_{ijk} is molecular first hyperpolarizability, and γ_{ijkl} is molecular second hyperpolarizability. The local field factors are introduced when transitioning from microscopic properties to macroscopic linear, $\chi^{(1)}$, second-

order, $\chi^{(2)}$, and third-order, $\chi^{(3)}$, response of the medium. In this work we refer to β or $\chi^{(2)}$ as second-order nonlinearity, and to γ or $\chi^{(3)}$ as the third-order nonlinearity. Hence, all known approaches to enhance molecular nonlinearities rely on structural changes of molecular moieties, resulting in corresponding changes of (hyper)polarizabilities in each given order. New, radically different approaches are needed to create a major advancement in this field.

In this contribution we propose one such conceptually different approach to attain large values of third-order nonlinearities. This approach is based on microscopic cascading of second-order nonlinearities. Cascading is a procedure for generating a high-order optical nonlinearity by repeated use of a lower-order nonlinearity. Since low-order nonlinearities tend to be intrinsically stronger than corresponding high-order nonlinearities, cascading has the potential to produce a larger high-order response than what can be obtained directly (i.e. from intrinsic high-order nonlinear response). In this paper, we report results from *ab initio* computations, using time-dependent density functional theory (TDDFT), along with a phenomenological model. In particular, we demonstrate the numerical observation of strongly enhanced second hyperpolarizabilities, γ (the microscopic counterpart of $\chi^{(3)}$) generated by means of cascading processes quadratic in the first hyperpolarizability, β (the microscopic counterpart of $\chi^{(2)}$).

It is useful to distinguish microscopic cascading from macroscopic cascading. Macroscopic cascading [5] achieves an effective $\chi^{(3)}$ nonlinear response from a $\chi^{(2)}$ material by means of propagation effects, and therefore requires stringent phase-matching conditions. Microscopic cascading makes use of local field effects and dipole-dipole interactions to allow neighboring molecules to mimic a gamma-type response [6,7] beyond their 'intrinsic' third-order nonlinearities. Both macroscopic and microscopic cascading can effectively induce large third-order nonlinear responses. In this work, we will concentrate on microscopic cascading, since this procedure is more generally useful as it fully mimics a true, local, gamma-type molecular response.

The theory of microscopic cascading was proposed as early as in 1973 by Bedeaux and Bloembergen [8]. Their result when written in modern notation and in the scalar approximation becomes

$$\chi^{(3)} = L^4 N \gamma + \frac{2}{3} L^5 N^2 \beta^2, \quad (2)$$

where the local field factor is given by $L = (\epsilon + 2)/3$. Here, the first term represents the usual direct contribution to $\chi^{(3)}$ and the second term yields the cascaded contribution. Note that the cascading term scales quadratically with the molecular number density N . For number densities approaching those of condensed matter, the cascading term can yield the dominant contribution to the nonlinear susceptibility, as was recently demonstrated [7] for the case of $\chi^{(5)}$.

Although several groups have worked on cascaded nonlinearities over the years [9–13], we feel that there has not been an adequate concerted effort to explore the microscopic cascading concept for γ in conjunction with a molecular system. In this work we present the first detailed theoretical modeling of microscopic cascading for a molecular aggregate system using TDDFT response-theory, a first-principles quantum-theoretical approach. We emphasize that Eq. (2) constitutes a very simple model for cascading. This result is based on the validity of the Lorentz local field model and assumes that the locations of the molecules are distributed randomly within the material. By means of our model and the *ab-initio* computations, we determine how large the cascaded contribution can become by studying different relative orientations of the molecules, and by locating the molecules at the optimum separation within a material. We note that ordered collections of molecules can alternatively be thought of as constituting supermolecules and other types of supramolecular complexes. This way of looking at local field effects and cascaded processes may provide a complementary procedure for understanding the properties of these structures and of optimizing their performance for specific tasks in the field of photonics.

2. Theory

We assume that two beta-type chromophores are separated by the directed distance $\hat{n}D$, where \hat{n} is a unit vector pointing from chromophore 1 to chromophore 2, as shown in Fig. 1. We also assume that each chromophore responds only to the component of the electric field along its primary axis and that it develops a dipole moment pointing in this direction. Thus, if the applied electric field is E_0 , the dipole moment induced in chromophore 1 can be written as

$$p_1 = \beta_1(E_0 \cdot \hat{\beta}_1)^2 \hat{\beta}_1, \quad (3)$$

where β_1 is the first hyperpolarizability of chromophore 1 and $\hat{\beta}_1$ is a unit vector along its primary axis. This dipole creates an electric field at the location of the second chromophore that is given by the standard dipole formula

$$E_2 = \frac{3\hat{n}(p_1 \cdot \hat{n}) - p_1}{4\pi\epsilon_0 D^3}. \quad (4)$$

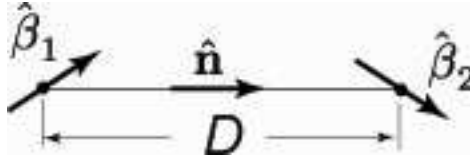


Fig. 1. Geometry of two beta-type chromophores interacting by means of near-field dipole-dipole mechanism.

This field, in concert with the applied field, then creates a third-order response in chromophore 2 given by

$$p_2 = \beta_2(E_0 \cdot \hat{\beta}_2)(E_2 \cdot \hat{\beta}_2)\hat{\beta}_2, \quad (5)$$

where β_2 is the first hyperpolarizability of chromophore 2 and $\hat{\beta}_2$ is a unit vector along its primary axis. We can then define an effective value of the second hyperpolarizability for this geometry by means of the expression

$$p_2 = \gamma_{eff} E_0^3, \quad (6)$$

where p_2 is the modulus of p_2 and E_0 is the modulus of E_0 .

It is useful to study some limiting cases of these formulas. First let us assume that the vectors E_0 , \hat{n} , $\hat{\beta}_1$, and $\hat{\beta}_2$ all point in the same direction. We then find that

$$p_2 = 2\gamma_{iso} E_0^3 + \frac{2\beta_1\beta_2 E_0^3}{4\pi\epsilon_0 D^3}, \quad (7)$$

so that

$$\gamma_{eff} = 2\gamma_{iso} + \frac{2\beta_1\beta_2}{4\pi\epsilon_0 D^3}, \quad (8)$$

where γ_{iso} is the second hyperpolarizability of the isolated chromophore. The second term in Eq. (8) is the pure cascading contribution and its sign depends on mutual orientation of the molecules in the dimer. Let us now assume that the two chromophores have identical chemical composition, i.e. $\beta_1 = \beta_2 = \beta$. If they are oriented parallel to each other, we find that

$$\gamma_{eff} = 2\gamma_{iso} + \frac{2\beta^2}{4\pi\epsilon_0 D^3}, \quad (9)$$

whereas if they are antiparallel to each other we obtain

$$\gamma_{eff} = 2\gamma_{iso} - \frac{2\beta^2}{4\pi\epsilon_0 D^3}. \quad (10)$$

As a different special case, let us now assume that $\hat{\beta}_1$ and $\hat{\beta}_2$ are parallel to each other but are orthogonal to \hat{n} . If E_0 is parallel to $\hat{\beta}_1$ and $\hat{\beta}_2$, and if we again assume that the two chromophores have identical composition, we find that

$$\gamma_{eff} = 2\gamma_{iso} - \frac{\beta^2}{4\pi\epsilon_0 D^3}. \quad (11)$$

If instead $\hat{\beta}_1$ and $\hat{\beta}_2$ are antiparallel to each other, we find that

$$\gamma_{eff} = 2\gamma_{iso} + \frac{\beta^2}{4\pi\epsilon_0 D^3}. \quad (12)$$

Still assuming that $\hat{\beta}_1$ and $\hat{\beta}_2$ are parallel to each other but are orthogonal to \hat{n} , we now assume that E_0 is orthogonal to $\hat{\beta}_1$ and $\hat{\beta}_2$. We find that in this case p_2 vanishes. More general situations can be modeled by means of direct numerical evaluation of Eqs. (3) through (5).

3. Computations

For our density functional study of microscopic cascading we chose (*para*)nitroaniline (PNA) “push-pull” molecule as it is known to have relatively large β and has been a convenient benchmarking system for many studies [14]. Moreover, due to its short pi-bridge it is known to be a robust system for computations with approximate density functionals [15,16]. The computations were performed with the Amsterdam Density Functional package (ADF) [17], employing the PBE [18] non-hybrid generalized gradient approximation (GGA) functional, a hybrid version of PBE with 25% Hartree-Fock (HF) exchange (PBE0) [19], and a 50% HF PBE hybrid functional [20] that we label PBE-H/H (for “Half-Half”). For calculations of hyperpolarizability tensors, the ‘aeresponse’ module of ADF, described in Refs [15,16], was used. In this code, molecular polarizability and hyperpolarizability tensors are computed directly from analytical time-dependent DFT (TDDFT) response theory for a given set of frequencies, without recourse to a truncated sum over excited states. A triple-zeta Slater-type atomic orbital basis set with polarization functions for all atoms (TZP) from the ADF basis set library was employed, along with its default set of density-fitting functions. For PNA, a basis set of this flexibility, and functionals used here, have previously been shown to yield good agreement of computations with experiment for first and second order nonlinear response tensors [15,16,21]. An optimized geometry for PNA was taken from Ref. 15. Computations were performed for the degenerate $\gamma(\omega; \omega, -\omega, \omega)$ at telecommunication wavelengths. Our interest in degenerate second hyperpolarizability is motivated by a particular application – all-optical switching – where the real part of the non-resonant degenerate third-order susceptibility determines the Intensity Dependent Refractive Index (IDRI) of a medium.

Two PNA molecules in the dimer were stacked as shown in Fig. 2 with \hat{n} perpendicular to the molecular plane (x,y). The distance, D , between PNA molecules was initially set to 3 Angstroms. We did not further optimize the geometry of the dimer, keeping both PNA molecules planar. For both non-hybrid and hybrid TDDFT computations on PNA dimer in an

anti-parallel (head-to-tail, HT) configuration (Fig. 2), we found a substantial enhancement of the degenerate $\gamma(\omega; \omega, -\omega, \omega)$ at the telecommunication wavelength of 1300 nm - to about three times the monomer value for the hybrid DFT computations, indicating a significant contribution from microscopic cascading (see Table 1). In a parallel (head-to-head, HH) arrangement, a significant suppression of γ was found, confirming the expectations from our model and validating the sign of the cascading term in Eqs. (11) and 12.

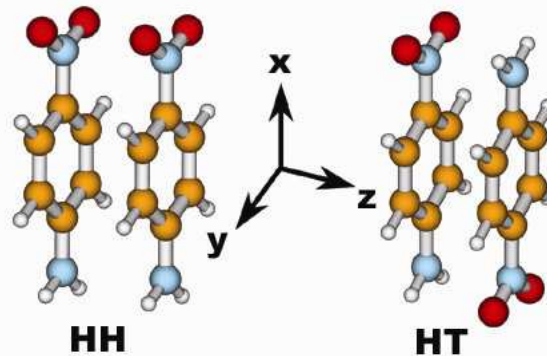


Fig. 2. Head-to-head (HH) and head-to-tail (HT) configurations of (*para*)nitroaniline (PNA) dimer.

Moreover, the simple phenomenological model for cascading yields a similar magnitude for the enhancement when we use the β tensor components, computed for an isolated PNA molecule to estimate the cascading term in Eq. (12) (the results are collected in Table 1). This means that in order to investigate cascading mechanisms, relatively cheaper computations of the β tensors of monomers, instead of computing $\gamma(\omega; \omega, -\omega, \omega)$ for a compound system, might already point one's efforts in the right direction. For example, recently synthesized large β twisted chromophores [22] would be particularly promising targets to search for experimental signatures of microscopic cascading resulting in enhanced $\chi^{(3)}$.

Table 1. Orientationally Averaged Degenerate First and Second Hyperpolarizabilities of Isolated PNA Molecule and the Dimer, and Second Hyperpolarizability Estimated by Means of Eqs. (11) and 12

System	β_{av} (10^3 au)	γ_{av} (10^3 au)	$2\gamma_{iso} \pm \beta_{av}^2/D^3$ (10^3 au) [model]
Isolated (PBE)	1.97	23.29	
Isolated (PBE0)	1.81	21.96	
Isolated (PBE-H/H)	1.57	21.57	
Dimer HH (PBE)	1.89	71.61	25.28
Dimer HH (PBE0)	1.84	33.97	25.97
Dimer HH (PBE-H/H)	1.66	28.76	29.59
Dimer HT (PBE)	0.03	152.16	67.90
Dimer HT (PBE0)	0.03	63.91	61.88
Dimer HT (PBE-H/H)	0.02	60.27	56.67

Overall, the hybrid TDDFT computations (PBE0 and PBE-H/H functionals) agree well with each other, and they agree well with the predictions from our phenomenological model of microscopic cascading. A stronger enhancement for the PNA dimer obtained with a non-hybrid generalized gradient approximation (GGA) functional, compared to the hybrid DFT results, indicates that the significantly less computational resource consuming GGA computations will be able to indicate if an enhancement occurs, but likely lead to an

overestimation of the effect. Nonetheless, these computations might be useful for an initial, quick, screening of possible molecular candidates and relative orientations, for example. We tentatively attribute the overestimation to known problems of non-hybrid TDDFT to treat excitations involving a substantial charge-transfer [23–25].

In order to analyze the cascading mechanism further, an analysis of the computed $\gamma(\omega; \omega, -\omega, \omega)$ of the PNA head-to-tail dimer in terms of localized molecular orbitals was performed [15]. So-called natural Localized Molecular orbitals (NLMOs) were employed for the analysis [26]. The NLMO analysis showed that a single pair of π orbitals can be associated with very nearly the complete overall enhancement of γ . This pair of orbitals is shown in Fig. 3. Their contribution to the averaged γ mostly stems from the $zzzz$ component of the tensor (i.e. along the normal vector \hat{n}), a tensor component which is virtually absent in the response of the isolated PNA molecule.

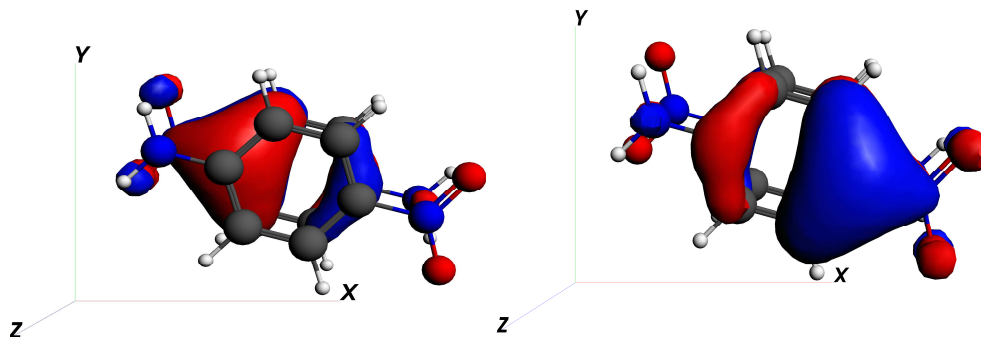


Fig. 3. Field-Free NLMOs whose contribution amounts for the enhancement of the averaged value of the second hyperpolarizability.

The orbitals displayed in Fig. 3 are rather strongly delocalized π NLMOs of the conjugated bridge that connects the donor and acceptor groups. For further discussion of the NLMOs of PNA, and their contributions to β and γ in the monomer we refer the reader to Refs [15,16]. The predominant role of the π -bridge orbitals in the cascading effect suggests that (i) the enhancement mechanism of γ is related to an orbital-overlap component of π stacking, which should be amenable to distance tuning, and (ii) that chemical modifications of the π -bridge between the donor and the acceptor moieties can potentially have a strong impact on the magnitude of the cascading effect which might allow for chemical tuning. The π orbitals of the aryl bridge were previously shown to play a secondary role for the magnitude of γ in PNA [15]; the more dominant contributors to the single-molecule response are the nitrogen lone pair orbital and the extent of its delocalization, and the orbitals in the acceptor group (which is consistent with the push-pull NLO mechanism). The cascading contributions calculated for these orbitals include their response to the presence of the electric field [15]. A partial charge-transfer between the monomers is hinted at by the significant overestimation of the non-hybrid TDDFT cascading contribution for the HT dimer which was already discussed above. At present, the analysis program module is restricted to providing contributions in terms of field-free orbitals, and therefore obtaining additional information about the mechanism would entail the development of a more refined analysis technique. It is clear from the present analysis, however, that the π -overlap between the PNA monomers is a defining feature of this mechanism at π -stacking distances. We would like to emphasize that π -delocalization is confined within PNA monomers. We do not want to insinuate that there is π -delocalization between the moieties that results in the enhancement of γ .

To verify the inverse cube dependence of the cascading term on the distance, D , between the chromophores predicted by the model, we calculated γ of the HT dimer and of the isolated PNA molecule as a function of D . The cascading term, γ_{cascade} , was computed by subtracting two times the orientationally averaged γ of the isolated PNA molecule from γ calculated for the dimer at corresponding values of D . The results are presented in Fig. 4. A fit over the

range of distances studied here shows that γ_{cascade} is roughly inversely proportional to the power 2.5 of the distance between the molecules. This slight disagreement with the model, which affords an exact inverse cube behavior (Eq. (12)), can be attributed to a number of reasons. First, TDDFT with exchange-correlation potentials as used in this work is not expected to describe correctly the behavior at large distances due to a rapid decay of the local exchange contributions with D . On the other hand, the model does not take into account effects that arise when the orbitals of the monomers begin to overlap in the dimer at shorter distances; a regime where TDDFT on the other hand is expected to generate accurate results. Taking these factors into consideration, the rapid decay of the cascading effect calculated from $\gamma(\omega; \omega, -\omega, \omega)$ for the dimer at larger separations is consistent with the predictions from the phenomenological model.

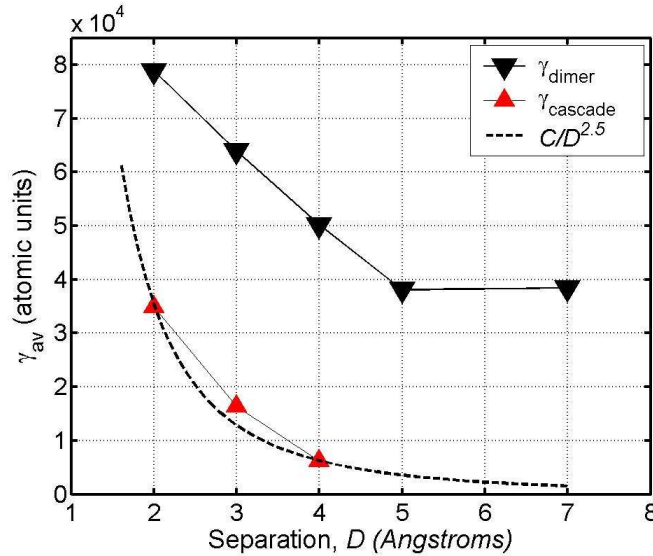


Fig. 4. Orientationally averaged degenerate second hyperpolarizability of HT PNA dimer vs the distance, D , between the molecular planes computed with hybrid PBE0 functional.

Table 2. Dispersion of Orientationally Averaged Degenerate First and Second Hyperpolarizabilities of the HT Dimer (Hybrid TDDFT)

Wavelength (nm)	β_{av} (au)	γ_{av} (10^3 au)
800	33	-175.14
1064	28	78.53
1300	26	63.91
1550	25	58.45

The dispersion data for the first and second hyperpolarizabilities computed with hybrid PBE0 functional are collected in Table 2. Figure 5 shows the computed orientationally averaged degenerate second hyperpolarizability of an isolated PNA molecule, the HT dimer, and the cascading contribution (difference between the dimer value and two times the monomer) versus the wavelength. The computations predict that the cascading contribution to the total effective γ of the dimer grows faster than γ of isolated PNA molecule as the wavelength decreases. Below 1064 nm the cascading contribution becomes larger than γ of the isolated PNA molecule, and below about 900 nm an anomalous dispersion indicates that the influence of electronic excitations becomes dominating. This trend suggests that the cascaded γ of the dimer is spectrally red shifted. The reason for the red shift is most likely

attributable to the enhanced π -delocalization, which further supports the results of NMLO analysis.

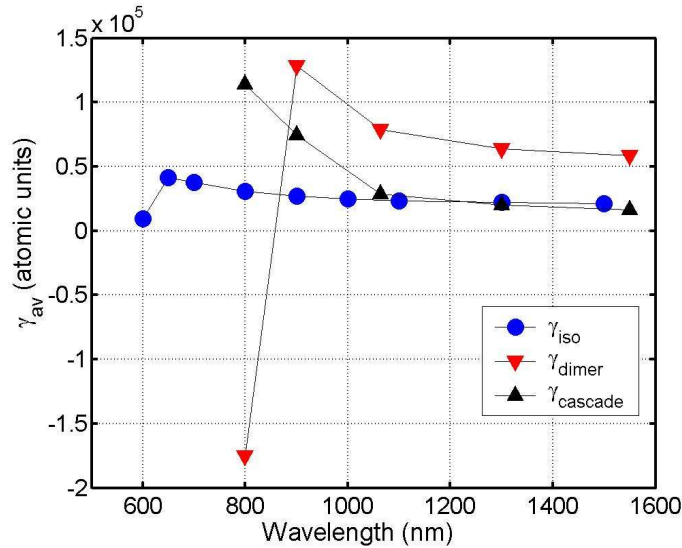


Fig. 5. Dispersion plots of γ_{av} .

It is worthwhile to also note that preliminary non-hybrid all-electron relativistic TDDFT computations on (*para*)nitroaniline molecules linked to a tetrahedral Au_{20} cluster delivered up to two orders of magnitude enhancement of the second hyperpolarizability. Although this enhancement is possibly overestimated in these computations, these results suggest that a combination of microscopic cascading with electromagnetic and chemical enhancement from a metal cluster has the potential to push $\chi^{(3)}$ to magnitudes far exceeding current limits. These computations are on-going; the results will be published elsewhere [27].

4. Conclusion

To conclude, we developed a simple phenomenological model of microscopic cascading based on local dipole-dipole interaction of neighboring molecules. *Ab initio* computations of first and second hyperpolarizabilities of *para*-nitroaniline and dimers thereof substantiated the model and suggest a design protocol for obtaining materials with particularly large values of the real part of third-order nonlinearity. The most obvious way to increase the real part of the direct (as opposed to cascaded) contribution to the second polarizability, γ , is to use resonant enhancement. Unfortunately, the imaginary part will inevitably grow as one approaches one- or two-photon resonance of a molecule. Our design protocol allows for using molecules with a large real part of the first hyperpolarizability, β , to generate a large real part of second hyperpolarizability, γ , without introducing extra loss, because molecular resonances, in particular two-photon resonance, are not involved.

Acknowledgments

This work was supported by a seed grant from the Office of Vice President for Research at the University at Buffalo. The authors are grateful to Prof. Hans Ågren of KTH, Stockholm for valuable discussion. R. W. Boyd acknowledges support by a MURI grant from the U. S. Army Research Office (USARO). J. Autschbach acknowledges support from the National Science Foundation (NSF) (grant CHE 447321).