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Citation: The Journal of Chemical Physics **125**, 044101 (2006); doi: 10.1063/1.2216699
View online: https://doi.org/10.1063/1.2216699
View Table of Contents: http://aip.scitation.org/toc/jcp/125/4
Published by the American Institute of Physics

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Lingyun Zhu, Yuanping Yi, and Zhigang Shuai[a)]
Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, 100080 Beijing, People's Republic of China

Jean-Luc Brédas
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; and Centre de Recherche en Electroniques et Photoniques Moléculaires, Service de Chimie de Matériaux Nouveaux, Université de Mons-Hainaut, B-7000 Mons, Belgium

David Beljonne
Centre de Recherche en Electroniques et Photoniques Moléculaires, Service de Chimie de Matériaux Nouveaux, Université de Mons-Hainaut, B-7000 Mons, Belgium; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Egbert Zojer[b)]
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; and Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

(Received 23 November 2005; accepted 25 May 2006; published online 24 July 2006)

Based on essential-state models for three-photon absorption (3PA), we have investigated the structure-property relationships for stilbene-based dipolar and quadrupolar chromophores. The emphasis lies on the evolution of the 3PA cross section with the degree of ground-state polarization. For dipolar systems, we find a dominant role played by $\Delta\mu$, which expresses the change in dipole moment between the ground state and the 3PA active excited state. Thus, the strategies usually applied to maximize the second-order polarizability β are also applicable to optimize the 3PA cross section. For quadrupolar systems, the 3PA response is dominated by contributions from channels including various low-lying two-photon allowed states, which limits the applicability of essential-state models. Optimization strategies can be proposed but vary for different ranges of ground-state polarization. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2216699]

I. INTRODUCTION

Two-photon absorption (2PA) is based on the simultaneous absorption of two photons[1] and is important in numerous applications that exploit the nonlinear intensity dependence of the absorption probability. These applications include two-photon laser scanning microscopy,[2–4] photodynamic therapy,[5] optical power limiting,[6,7] three-dimensional microfabrication,[8–11] and optical data storage.[12–15] In several instances, three-photon absorption (3PA), which presents an even higher order of the optical nonlinearity, can be beneficial as the possibility of using even longer wavelengths would lead to a further improvement in penetration depth [when considering the transparency window of living organisms in the near-IR (Ref. 16)] and to a minimization of scattering losses. Moreover, when exploiting 3PA processes at shorter wavelengths, one can expect an enhancement of the spatial resolution.[17]

To design materials for such applications, a better understanding of the relationship between the chemical structure of a chromophore and its 3PA cross section is essential. Reliable theoretical prediction of structure-property relations[18] has become very useful to provide design strategies in the light of costly and time-consuming synthesis. In this contribution, we focus on prototypical donor- and acceptor-substituted dipolar and quadrupolar systems and test design concepts frequently used for 2PA chromophores. We focus on the applicability of essential-state models for 3PA (Ref. 19) and study the evolution of the 3PA cross section as a function of the degree of ground-state polarization.

II. EVALUATION OF THE 3PA CROSS SECTION

A. Describing the 3PA response

The three-photon absorption cross section σ_3 is related to the fifth-order molecular susceptibility. It is also accessible via evaluation of the third-order transition matrix elements,[18(b),18(c)]

[a)]Electronic mail: zgshuai@iccas.ac.cn
[b)]Electronic mail: egbert.zojer@tugraz.at

$$T_{g\to f}^{ijk} = \sum P_{ijk} \sum_{m,n} \frac{\langle g|\mu_i|m\rangle\langle m|\mu_j|n\rangle\langle n|\mu_k|f\rangle}{(E_{gm} - \hbar\omega - i\Gamma)(E_{gn} - 2\hbar\omega - i\Gamma)}, \quad (1)$$

where P_{ijk} denotes a complete permutation of the indices i, j, and k; E_{gm} corresponds to the excitation energy from the ground state $|g\rangle$ to excited state $|m\rangle$; μ_i is the component of the electric dipole operator along molecular axis i; $\hbar\omega$ is the photon energy of the incident light (a degenerate 3PA process is assumed); Γ describes a Lorentzian broadening related to the dephasing time, and it is set in the calculations to 0.1 eV.[20] The 3PA cross section, when averaged over molecular orientations assuming an isotropic sample, can be written as[18(b),18(c)] (assuming linearly polarized light)

$$\sigma_3(\omega) = \frac{4\pi^3(\hbar\omega)^3 L^6}{3n^3c^3\hbar 35} \sum_f \left| 2\sum_{ijk} T_{g\to f}^{ijk} T_{g\to f}^{ijk*} + 3\sum_{ijk} T_{g\to f}^{iij} T_{g\to f}^{kkj*} \right| \left\{ \frac{\Gamma}{(E_{gf} - 3\hbar\omega)^2 + \Gamma^2} \right\}, \quad (2)$$

where c is the speed of light in vacuum, L denotes a local-field correction, and n the refractive index of the medium (both set to 1 for vacuum).

B. Essential-state model for 3PA

In order to relate the nonlinear optical response of chromophores to a small number of microscopic parameters, essential-state models[20,21] have been widely used in the field of nonlinear optics. To derive essential-state models for the 3PA cross section, we start from the corresponding T-tensor expression (1) (assuming that all state and transition dipoles are parallel).

1. Dipolar molecules

For dipolar molecules with a dominant one-photon allowed state $|e\rangle$, the essential quantities entering into (1) are the transition dipole between the ground state and that state, M_{ge}, as well as the change in state dipole moment upon excitation, $\Delta\mu_{ge}$. Equation (1) then becomes for resonant 3PA into state $|e\rangle$ (i.e., $\hbar\omega \to E_{ge}/3$),

$$T_{g\to e} = 6\left(\frac{9}{2}\frac{M_{ge}\Delta\mu_{ge}^2}{E_{ge}^2} - \frac{9}{4}\frac{M_{ge}^3}{E_{ge}^2} \right). \quad (3)$$

The numerical forefactor 6 is related to the permutation for the longitudinal components. Note that this expression corresponds to the two-state model proposed by Cronstrand *et al.* in Ref. 19.

From expression (3), we can draw the following conclusions

(i) There are two channels contributing to the 3PA response that are both purely "one-photon" (i.e., related only to the one-photon allowed state $|e\rangle$). The first channel, denoted as the N' term (where the prime is used to avoid confusion with the similar but not identical terms occurring in the three-state model for the third-order polarizability γ), depends only on the transition energy of and transition dipole to the state $|e\rangle$. The second channel (denoted as the D' term) also depends on the change in state dipole moment $\Delta\mu$ resulting excitation from $|g\rangle$ to $|e\rangle$.

(ii) An interesting aspect regarding dipolar molecules is that the second-order polarizability β is proportional to $\Delta\mu$ (Ref. 22) the 2PA cross section (a third-order process) is proportional to $\Delta\mu^2$ (Ref. 23), and the D' part of the 3PA cross section (a fifth-order process) is proportional to $\Delta\mu^4$ [since according to Eq. (2), σ_3 is proportional to T^2].

(iii) There is no possibility for an energy-related resonance in T, i.e., a vanishing denominator. This aspect will be discussed in more detail below in the context of the quadrupolar molecules.

(iv) The two channels have different signs. Therefore, they will partly compensate each other.[19]

The 3PA cross section $\sigma_{3(2\text{-state})}$ obtained from Eqs. (2) and (3) reads

$$\sigma_{3(2\text{-state})} = \frac{36}{7}\frac{4\pi^3}{3n^3c^3\hbar}L^6\frac{1}{\Gamma}\left(\frac{E_{ge}}{3}\right)^3\left[\frac{9}{2}\frac{M_{ge}\Delta\mu_{ge}^2}{E_{ge}^2} - \frac{9}{4}\frac{M_{ge}^3}{E_{ge}^2}\right]^2. \quad (4)$$

2. Quadrupolar molecules

In centrosymmetric quadrupolar molecules, $\Delta\mu_{ge}$ is zero. From Eq. (3), this would leave only the N' term in an essential-state model for quadrupolar systems.[19] Quadrupolar chromophores, however, frequently possess strongly two-photon allowed excited states at relatively low energies.[21(d)] Therefore, here, we also consider (as a first approximation) one strongly two-photon allowed state $|e'\rangle$ in the derivation of the essential-state model. In principle, such a state could also contribute to 3PA in dipolar systems, but its influence in the investigated systems is only minor, as will become evident from the results presented below. The $|e'\rangle$ state then serves as an intermediate state in Eq. (1), as according to the 3PA selection rules, the lowest 3PA active state is again the 1PA active state $|e\rangle$; this means that compared to 2PA the roles of the final and intermediate states are reversed. The coupling between $|e\rangle$ and $|e'\rangle$ is described by the transition dipole $M_{ee'}$. For the resonance case ($\hbar\omega \to E_{ge}/3$), one then obtains from Eq. (1),

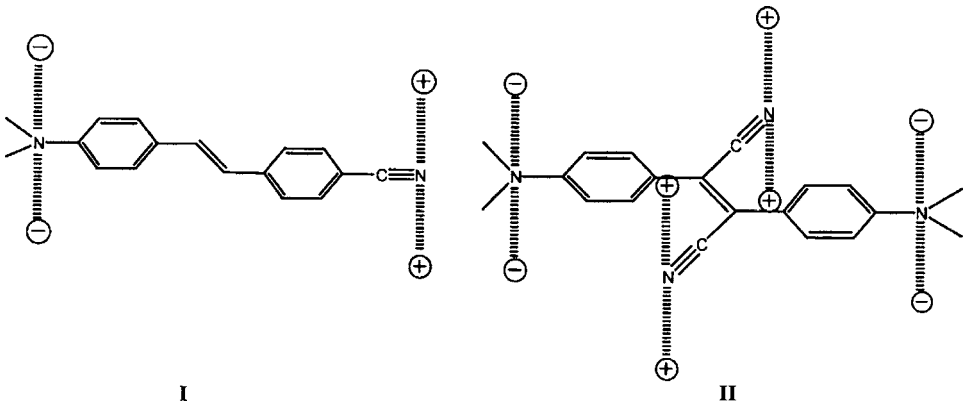
$$T_{g\to e} = 6\left(\frac{3}{2}\frac{M_{ge}M_{ee'}^2}{E_{ge}[E_{ge'} - (2/3)E_{ge}]} - \frac{9}{4}\frac{M_{ge}^3}{E_{ge}^2} \right). \quad (5)$$

Here also a factor of 6 is included to account for the permutation of the longitudinal components.

The conclusions that can be drawn from Eq. (5) are as follows.

(i) As in the dipolar molecules, there exist two "channels," one is purely one-photon in nature (N' term) and the other involves the 2PA state $|e'\rangle$ (T' term).

(ii) Again, there is no possibility for an energy-related resonance in T (i.e., a vanishing denominator), if we assume that $E_{ge} < E_{ge'}$. This is a reasonable assumption, as according to the work of Mazumdar



I II

FIG. 1. Chemical structures of the model systems for a dipolar chromophore (4-dimethylamino-4′-cyano-E-stilbene), I, and a quadrupolar chromophore (4,4′-bis(dimethyl)amino-α,β-dicyano-E-stilbene), II, together with an illustration of the system of point charges used to continuously vary the ground-state polarization.

et al.[21(b),21(c)] and our own experience,[21(f)] 2PA states below the 1PA state have vanishing 2PA cross sections and thus vanishing $M_{ee'}$. This has the important consequence that [as long as Eq. (5) is applicable] it prevents any preresonance enhancement effects for 3PA also in the case of quadrupolar molecules; this might be somewhat unexpected, as such effects have been predicted[21(f),24] and observed experimentally for degenerate[25] and nondegenerate 2PA (Ref. 26) in quadrupolar systems.

(iii) In analogy to the case of dipolar molecules, the two channels in Eq. (5) have different signs. Therefore, they will partly compensate each other.

In molecules with several 2PA states strongly coupled to $|e\rangle$, additional terms in the form of T' have to be added to Eq. (5). This prevents a straightforward analysis of the observed trends because an increasing number of microscopic parameters (transition dipole moments and energies) have to be considered; the general conslusions given above would, however, still hold.

Using Eq. (5), $\sigma_{3(3\text{-state})}$ for quadrupolar molecules can be expressed as

$$\sigma_{3(3\text{-state})} = \frac{36}{7}\frac{4\pi^3}{3n^3c^3\hbar}L^6\frac{1}{\Gamma}\left(\frac{E_{ge}}{3}\right)^3 \times\left[\frac{3}{2}\frac{M_{ge}M_{ee'}^2}{E_{ge}[E_{ge'}-(2/3)E_{ge}]}-\frac{9}{4}\frac{M_{ge}^3}{E_{ge}^2}\right]^2. \quad (6)$$

3. 3PA into higher-lying states

A possible way to achieve resonance enhancements would be to have a molecule that presents both, a one-photon state $|e\rangle$ at an energy close to 1/3 of the energy of the three-photon state and a strong two-photon state $|e'\rangle$ close to 2/3 of that energy. If $|e'\rangle$ then is strongly coupled to the three-photon state in question (here, denoted as $|e''\rangle$) through a large transition dipole $M_{e'e''}$, a resonance enhancement of the 3PA cross section by several orders of magnitude can be obtained.

In that case, one gets from (1) with $(\hbar\omega\rightarrow E_{ge''}/3)$,

$$T_{e''}=\frac{M_{ge}M_{ee'}M_{e'e''}}{[E_{ge}-(E_{ge''}/3)][E_{ge'}-(2E_{ge''}/3)]}, \quad (7)$$

which shows a resonance for

$$E_{ge}\rightarrow\tfrac{1}{3}E_{ge''} \text{ and } E_{ge'}\rightarrow\tfrac{2}{3}E_{ge''}. \quad (7a)$$

The occurrence of such an instance has, in fact, been predicted recently in the case of an anthracene-porphyrin-anthracene molecule.[18(c)]

III. COMPUTATIONAL APPROACH

We consider here prototypical dipolar and quadrupolar molecules, 4-dimethylamino-4′-cyano-E-stilbene (denoted as I) and 4,4′-bis(dimethyl)amino-α,β-dicyano-E-stilbene) (denoted as II). Their chemical structures are shown in Fig. 1. To modulate the degree of the ground-state polarization in the dipolar and quadrupolar molecules, we follow the strategy outlined in Ref. 27: a set of point charges is placed above and below the nitrogen atoms of the dimethylamino- and cyanosubstituents along the normal to the molecular plane, as shown in Fig. 1. Decreasing the distance between the point charges and the nitrogen atoms allows a systematical tuning of the degree of ground-state polarization. In the following, the difference between the lengths of the central double bond and the adjacent single bond (bond length alternation, BLA) will be used as a measure for the induced ground-state polarization (i.e., a large BLA is equivalent to a relatively small ground-state polarization, while approaching the cyaninelike limit at small BLAs corresponds to increasing the ground-state polarization).

In order to calculate the 3PA cross sections (σ_3), the molecular geometries are optimized with the semiempirical Austin model 1 (AM1) method[28] while constraining the molecules to a coplanar conformation. The electronic structures in the ground and excited states are calculated with the intermediate neglect of differential overlap[29] (INDO) Hamiltonian coupled to a multireference determinant single- and double-excitation configuration interaction (MRDCI) scheme.[30] This allows the inclusion of the correlation effects, which are important in the description of the nonlinear optical properties.[31] The Mataga-Nishimoto potential[32] is used to describe the Coulomb repulsion terms. The MRDCI technique adopted here has been extensively used in previous works[21(d),23,31,33] and is found to provide excitation energies

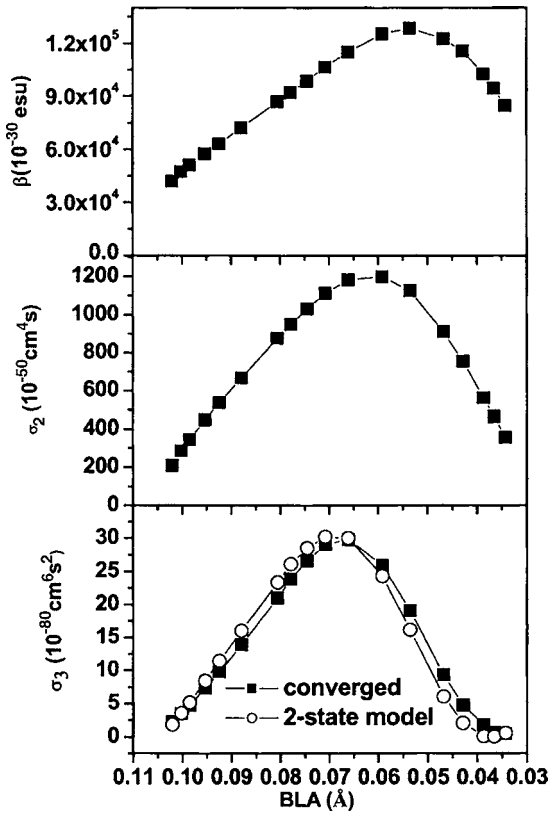


FIG. 2. Evolution of the second-order polarizability β (top), the 2PA cross section (σ_2) (middle), and the 3PA cross section (σ_3) obtained from the *T*-tensor approach and the two-state model (bottom) for molecule I, as a function of BLA.

and dipole matrix elements in good agreement with experiment. The details regarding the choice of the active space and reference determinants are given in Ref. 27 for molecule II. For I, we adopt an equivalent strategy. The same set of point charges are used in both AM1 and INDO calculations.

IV. RESULTS AND DISCUSSION

In order to gain a better insight into the evolution of σ_3 with BLA, we have compared the converged results derived from the *T*-tensor calculation including 200 excited states with those obtained from the essential-state models described by Eqs. (4) and (6). This should allow a discussion of the observed trends on the basis of a few microscopic parameters, such as transition energies and transition dipoles.

A. Dipolar system

The evolutions of σ_3 for 3PA into the lowest excited state of I with the BLA, as obtained from the *T*-tensor approach [Eq. (2)] and the two-state model, are shown at the bottom part of Fig. 2. The maximum field along the axis of the molecule varies between 4.11×10^6 V/cm for a point charge distance of 20 Å and 6.71×10^7 V/cm for a point charge distance of 5 Å. We find that with decreasing BLA (i.e., increasing ground-state polarization), σ_3 obtained from the *T*-tensor approach strongly increases, reaches a maximum, and then collapses. The largest σ_3 of about 3.0×10^{-79} cm^6 s^2 is reached at a BLA of 0.066 Å (central C–C bond lengths of 1.43 and 1.36 Å).

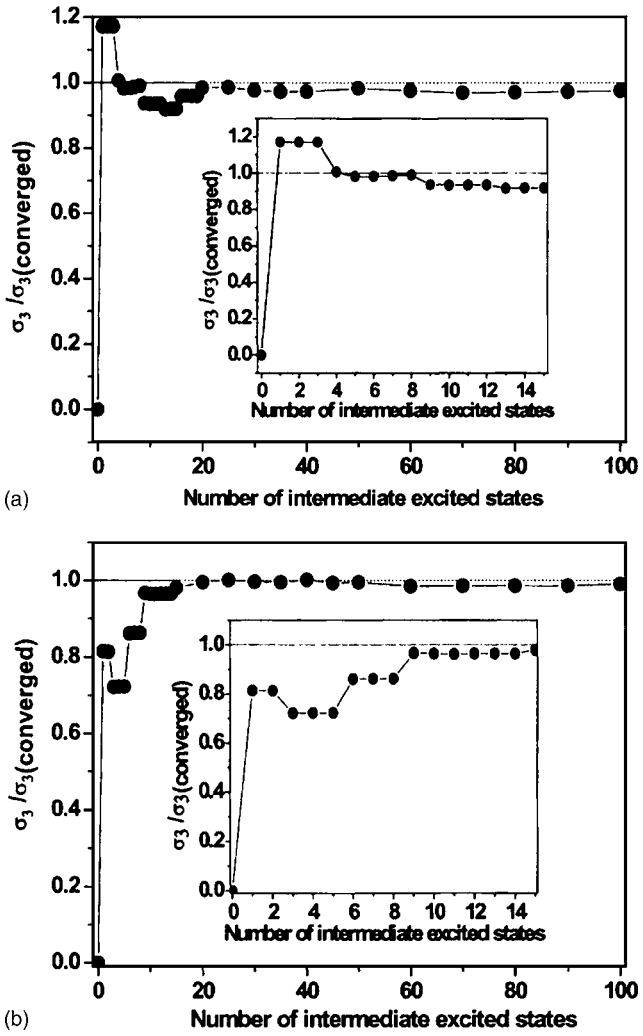


FIG. 3. Evolution of the *T*-tensor-based 3PA cross section into the first excited states of I with the number of intermediate states: (a) at a large BLA value (BLA=0.095 Å); (b) at a small BLA value (BLA=0.047 Å). $\sigma_{3(\text{converged})}$ is the value obtained when including 200 intermediate states. For the sake of clarity, a zoom into the full graph is shown in the inset.

The BLA dependence of σ_3 derived from the two-state model fully reproduces the trends obtained from the *T*-tensor approach (see Fig. 2). However, for the BLA value at which the cross section peaks, the σ_3 value is somewhat overestimated by the two-state model, while for smaller BLA, the opposite is the case.

In order to understand that slight difference and to ensure that the obtained agreement is not a result of cancellation effects between different channels, the evolution of σ_3 into the first excited state (S_1) as a function of the number of intermediate states in the *T*-tensor approach is shown in Fig. 3 for BLA's of 0.095 Å (small ground-state polarization) and 0.047 Å (large ground-state polarization). In both cases, σ_3 is converged when including about 15 intermediate states. The inclusion of just S_1 into the summation (i.e., one intermediate state in Fig. 3) already accounts for most of the converged σ_3. At small ground-state polarization, σ_3 is overestimated by ca. 17% when including only the first excited

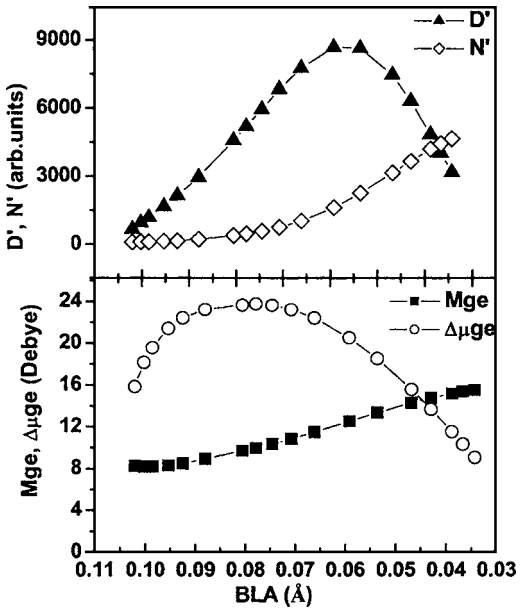


FIG. 4. Evolutions of the D' and N' terms from Eq. (4) (top) and of the transition dipole, M_{ge}, and change in state dipole moment, $\Delta\mu_{ge}$, (bottom) in I as a function of BLA.

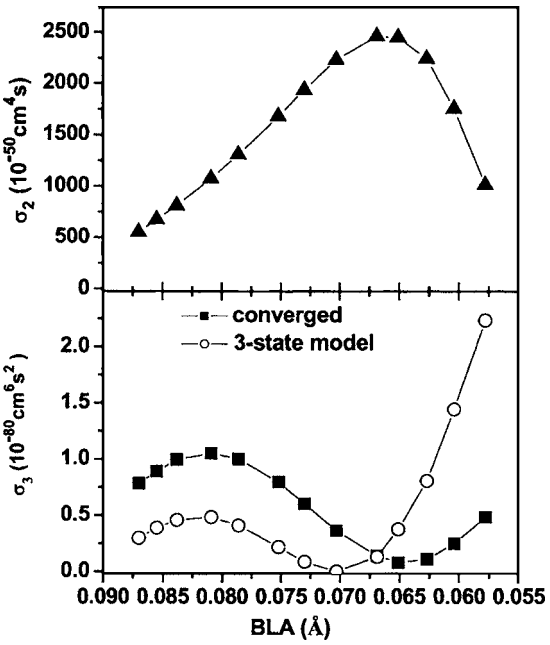


FIG. 5. Evolution of the 2PA (top) and 3PA (bottom) cross sections of molecule II as a function of BLA. For 3PA, the converged results obtained from the T-tensor approach are compared with those calculated using the three-state model [Eq. (5)].

state and gradually decreases to the converged value with the biggest step occurring when including the two-photon allowed excited state S_4 (which constitutes an additional channel like the one discussed in the context of essential-state models for quadrupolar molecules). At relatively large ground-state polarizations, the σ_3 value obtained by the two-state model underestimates the converged value by ca. 20%. Here, the deviation is caused by the two-photon allowed states S_6 and S_9.

Since the two-state model works well in the dipolar molecule I, the evolution of σ_3 can be discussed on the basis of the trends observed for the terms contributing to Eq. (4), that is the D' term: $(9/2)(M_{ge}\Delta\mu_{ge}^2/E_{ge}^2)$ and N' term: $(9/4)\times(M_{ge}^2/E_{ge}^2)$. Figure 4 shows that the D' term dominates the evolution and is responsible for the peak of σ_3. The contribution of the N' term is much smaller and has little effect on the observed trend. This behavior can be understood from the evolution of M_{ge} and $\Delta\mu_{ge}$ shown in the bottom part of Fig. 4. $\Delta\mu_{ge}$ is significantly larger than M_{ge} (at least for intermediate BLA's) and its BLA dependence is more pronounced. This implies that, while the strategy of minimizing $\Delta\mu_{ge}$ as suggested by Cronstrand *et al.* could be[19] useful for systems with small changes in dipole moment (i.e., when the N' term, or T' in the notation of Constrand *et al.*,[19] dominates), we found that for BLA leading to optimal 3PA, the D' term is dominant. Thus here the design strategy should be to maximize $\Delta\mu_{ge}$.

Interestingly, Eq. (3) also implies that when $M_{ge}=\sqrt{2}\Delta\mu_{ge}$, σ_3 vanishes. This is indeed the case at a BLA of ca. 0.035–0.040 Å (see Fig. 2). This feature could prove interesting, for example, for 3PA-sensing applications, as it implies that by designing molecules where those two contributions cancel and in which $\Delta\mu_{ge}$ or M_{ge} are (possibly only slightly) modified by the sensing process, huge relative changes in the 3PA response can be expected.

The dominance of the D' term also allows us to rationalize why the second-order polarizability β and the 2PA cross-section (σ_2) into the lowest excited state display qualitatively the same evolution with ground-state polarization as σ_3 (see top and central graphs of Fig. 2). In all three quantities, the trends are dominated by the evolution of $\Delta\mu_{ge}$ and M_{ge}, while M_{ge} enters quadratically into all corresponding essential-state models, β depends linearly on $\Delta\mu_{ge}$, σ_2 quadratically, and σ_3 to the fourth power. Given the pronounced peak of $\Delta\mu_{ge}$ and its rapid decrease at smaller BLA, together with the continuous increase of M_{ge}, this results in the maximum of β occurring at the smallest BLA (the biggest ground-state polarization), that of σ_2 at intermediate BLA, and that of σ_3 at the smallest ground-state polarization.

B. Quadrupolar system

The evolutions of σ_2 (Ref. 27) and σ_3 with ground-state polarization for the quadrupolar molecule II are shown in Fig. 5. For 3PA, the results are given for the converged T-tensor approach and the three-state model (including the ground state, the first excited state, and the second excited state). As for the dipolar system and σ_2 in both dipolar and quadrupolar molecules, σ_3 first increases with decreasing BLA and then drops sharply. The observed increase is, however, much less pronounced than for the case of dipolar molecules. This explains that while σ_3 in I and II without point charges are relatively similar (σ_3 of I and II without point charges is about 1.60×10^{-80} and 0.69×10^{-80} $\mathrm{cm}^6\,\mathrm{s}^2$, respectively), the maximum values in the dipolar system are more than an order of magnitude larger. Another difference is that, upon approaching the cyaninelike limit, one observes another increase in the 3PA cross section, which is not seen for 2PA (in the investigated range of BLA's). The maximum

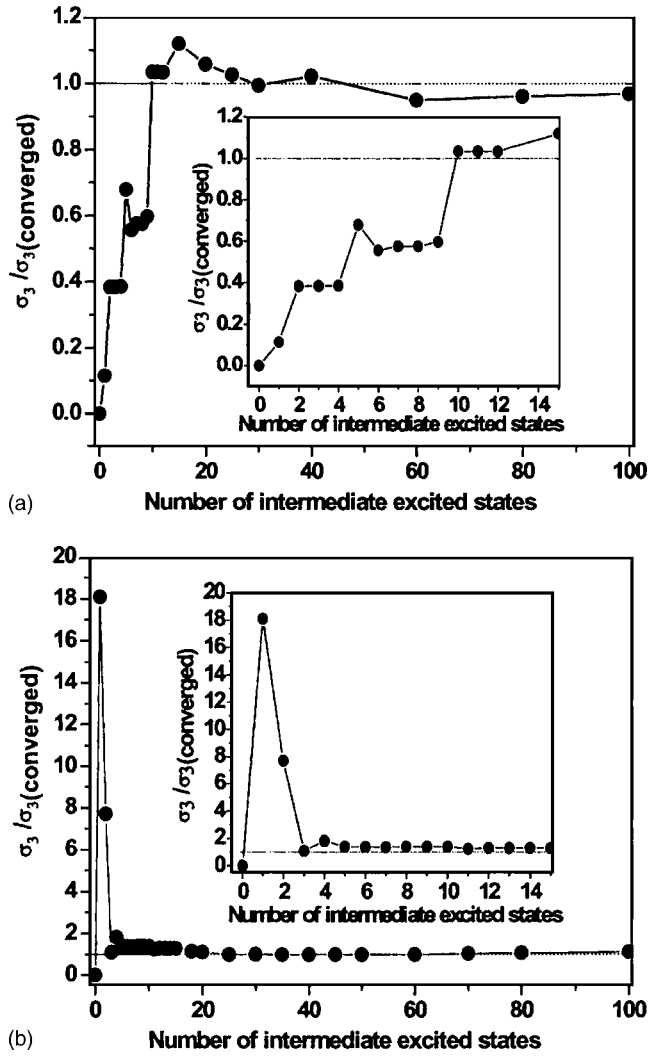


FIG. 6. Evolution of the 3PA T-tensor cross section into the most dominant excited states for quadrupolar molecule II, with the number of intermediate states at large BLA value (BLA=0.087 Å) (a) and at small BLA value (BLA=0.063 Å) (b). For the sake of clarity, a zoom into the full graph is shown in the inset.

of σ_3 occurs at much smaller ground-state polarizations than the 2PA maximum and the peaks in the evolutions of β, σ_2, and σ_3 for the dipolar system in Fig. 2.

To analyze this behavior, it would again be useful to apply an essential-state model. Unfortunately, as can be seen in Fig. 5, the three-state model reproduces only to a limited extent the trend seen in the converged calculations. The quantitative differences are significant. At large BLA values, σ_3 is severely underestimated by the three-state model. The reason can be seen in the convergence plot [see Fig. 6(a)] at large BLA (0.087 Å). When including only three states, σ_3 is underestimated by ca. 60%. Two additional 2PA active states (S_5 and S_{10}) need to be included as well to yield results close to the converged value. In contrast, for small BLA values, σ_3 is strongly overestimated by the three-state model. The reason can again be understood from the convergence plot in Fig. 6(b). Including only the 3PA state itself (i.e., applying a two-state model as discussed in Ref. 19) would result in an about 20-fold overestimation of the cross section. The inclusion of the two 2PA active states S_2 and S_3 eventually results in a significant decrease of σ_3 to a value close to the converged result.

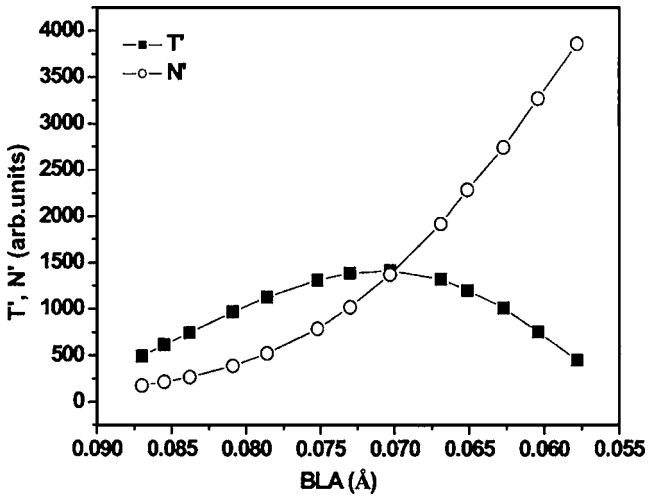


FIG. 7. Evolutions of the T' and N' terms from Eq. (6) in molecule II as a function of BLA.

The reason why the 2PA active states lead to a σ_3 increase at small ground-state polarizations and to a decrease at large ground-state polarizations can be understood from Fig. 7, where the T' and N' terms from Eq. (5) are shown. At large BLA values, the T' (two-photon) term is dominant and its inclusion is essential for the description of the 3PA response (i.e., one has to go beyond the two-state model, which, in fact, has been shown to fail for typical quadrupolar organic chromophores by response-theory calculations in Ref. 19). In that region, the N' term, which comes with an opposite sign, is of less importance. Upon increasing the ground-state polarization, M_{ge} increases steadily while E_{ge} decreases [for details, see Refs. 21(g) and 27]. Both evolutions contribute to the sharp increase in the N' term until it surpasses the contributions from T' (and eventually those of all other 2PA active states). This qualitatively explains the evolution shown in the bottom part of Fig. 5: The first maximum of σ_3 occurs when the difference between T' and N' is maximized at a BLA of ca. 0.082 Å (rather than at the maximum of the T' term itself); the much larger difference between N' and D' in the dipolar system (see Fig. 4) compared to the splitting between N' and T' (plus other T'-type channels) in the quadrupolar case can be held responsible for the smaller maximum 3PA cross section in the quadrupolar molecule. In this context it should, however, be kept in mind that according to Eq. (6), the essential-state model for quadrupolar molecules contains terms that are proportional to $M_{ee'}^4$. Thus, this situation might be modified, for example, for molecules with exceptionally large $M_{ee'}$, which are currently aimed at in the development of 2PA chromophores. The second increase at small BLA's is caused by a strong contribution from the N' term.

From the above results, the following conclusions can be drawn for tuning the 3PA cross section σ_3 of a typical quadrupolar chromophore such as II. At large BLA values, where the trends observed for σ_3 are dominated by contributions from channels including various low-lying 2PA allowed

states, strategies aimed at increasing the overall 2PA response of the molecule also boost σ_3. When approaching the cyaninelike limit, the one-photon-type contribution takes over and strong 2PA active states become detrimental to the 3PA response.

V. SYNOPSIS

In summary, we have developed structure-property relationships for typical dipolar and quadrupolar organic chromophores as a function of ground-state polarization. The ground-state polarization corresponds to an effective internal electric field and makes the bridge between structure and 3PA response. It modifies the structure, as characterized by the bond-length alternation, and the nonlinear absorption.

Our analysis is based on essential-state models. In the case of dipolar systems, the dominant channels are (i) a purely one-photon term, dominated by the transition dipole from the ground state to the 3PA active state, and (ii) a term dominated by the change in state dipole moment $\Delta\mu$ associated with that excitation. In the stilbene-based system we studied, the latter is dominant, which implies that the strategy typically applied to maximizing the second-order polarizability β or the 2PA cross section, that is, to try and increase $\Delta\mu$, is also applicable here.

In quadrupolar molecules, the situation is more complex and a larger number of channels need to be included to provide a reliable description of the observed trends. In general, we find a first 3PA maximum at a large BLA (small ground-state polarization), followed by a minimum at an intermediate BLA (ca. 0.065 Å) due to the competition between two-photon terms and purely one-photon related terms, and another increase at smaller BLAs. For the studied type of backbone, the maximum 3PA cross section in the quadrupolar system is significantly smaller than in the dipolar case.

ACKNOWLEDGMENTS

The work in Beijing is partly supported by the NSFC (Grant Nos. 20433070, 10425420, and 20420150034) and the Supercomputing Center of the Chinese Academy of Sciences. The work at Georgia Tech is partly supported by DARPA, by the National Science Foundation (CRIF 04-43564), and by the STC Program of the National Science Foundation under Award No. DMR-0120967. One of the authors (D.B.) is a senior research associate of the Belgian National Science Foundation (FNRS).

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