

Few-states models for three-photon absorption

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Few-states models are derived for the calculation of three-photon absorption matrix elements. Together with earlier derived few-states models for two-photon absorption, the models are evaluated against results from response theory calculations that provide the full sum-over-states values. It is demonstrated that not even for systems with charge-transfer character, where few-states models for two-photon absorption are in excellent agreement with response theory, do the models provide a quantitatively correct description for three-photon absorption. The convergence behavior, merits, and shortcomings of the models are elucidated in some detail. The role of various characteristics of the electronic structure, such as symmetry, charge transfer, and conjugation—important for the formation of a large three-photon cross section—is analyzed. As for two-photon absorption cross sections, it is essential to consider generalized few-states models also for three-photon absorption, that is, to account for dipolar directions and laser beam polarization. Despite their poor quantitative performance, it is argued that few-states models at times can be useful for interpretation purposes when applied to three-photon absorption. © 2004 American Institute of Physics.

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I. INTRODUCTION

Owing to the discovery of organic systems with significant two-photon absorption (TPA) cross sections, the field of multiphoton absorption has experienced a growing interest. TPA, in particular, has generated a large number of experimental as well as theoretical studies in order to increase the general understanding and supply guidelines to control the nonlinear optical processes.^{1–10} Far less examined are the corresponding higher-order properties, such as three-photon absorption (3PA), although these might possess even greater technological applicability in comparison with TPA. Three-photon absorption shares the conceptual features with TPA, but with the more distinct characteristics that the dependence on the intensity is cubic and that the spatial confinement is even higher. To a large extent, the range of potential applications therefore overlap those proposed for TPA, i.e., up-converting lasing, optical limiting, nondestructive imaging, and data storage.¹¹ However, the essential ability of reaching an excited state with photon energies equal one-third of the excitation energy means that a typical band gap of 2 eV can be overcome with radiation in the IR region. This opens several possibilities within bioapplications as the penetration depth, in, for instance, human tissue, increases substantially. In general, the 3PA cross sections are low, but, on the other hand, one can expect to benefit from the versatility of modern synthetic chemistry to produce chromophores with high 3PA cross sections. In this context, theoretical modeling will play an important role in order to guide the synthetic work.

From a theoretical perspective, the evaluation of a fifth-order property such as $\chi^{(5)}$, which determines the 3PA cross section σ^{3PA} , is indeed a computational challenge. However, decisive simplifications can be achieved by realizing that, in analogy to TPA, the key quantity is not $\chi^{(5)}$ as such, but the third-order transition tensor elements. The simplifying scheme employed for TPA, i.e., the evaluation of the second-order transition matrix elements S_{zz} as the residue of the quadratic response function, is for 3PA replaced by the calculation of the third-order transition matrix elements T_{zzz} as the residue of the cubic response function. Response theory thus offers a considerable down shift of the computational effort by enabling first-, third-, and fifth-order properties to be computed with reference to the first-, second-, and third-order response functions. Thus with response theory, the cross sections for a given order of the multiphoton process can be obtained from the same order of the polarizability.

The explicit formulas for the transition matrix and tensor elements are normally given as sum-over-states (SOS) expressions. An option is therefore to enforce a truncation of the SOS expression and only include a few dominating states and excitation channels. This may be motivated by the increasing energy term in the denominator or the assumption that only a few excitation paths actually will contribute in a full summation. The convergence rates with respect to the inclusion of states in the summation are known to be slow, except for charge-transfer (CT) systems which fortunately—but not surprisingly—coincides with a class of systems proposed for TPA and 3PA applications. These so-called few-states models where only a limited set of excited states and

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accompanying transition moments are addressed to represent the full excitation scheme clearly is inferior to response theory as a methodology, but the decomposition into simple properties such as excitation energies and transition dipole moments can enable valuable interpretation and promote an enhanced intuitive understanding through so-called structure-to-property relations. For TPA this has resulted in many design strategies for optimizing TPA cross sections. Another advantage is that the quantities needed, excitation energies and transition moments, are attainable within several computational schemes, and, hence, when a system has shown to be well described by a few-states model the accuracy can be further advanced in a higher-order computational model. The calculations are then far more effective than implementing the full SOS or response theory. In conjunction with this the objection naturally arises how well a restricted set of states represent the full excitation scheme even from a pure qualitative standpoint. In practice, there is an additional issue in quantum chemical calculations, namely, how to estimate the effects of truncations in the one-electron space by finite basis sets and also in the N -electron space in order to obtain converged results within the number of states included. The purpose of this paper is to present few-states models for TPA and, in particular, 3PA, and to outline their validity for several systems ranging from lithium hydride, which can be treated at the full-configuration interaction (FCI) level of theory, to a series of large π -conjugated systems.

II. THEORY

A. Multiphoton absorption

The starting point for all multiphoton absorption processes is the rate of time averaged energy absorbed by matter when subjected to radiation,¹²

$$\left\langle \frac{d}{dt} \left(\frac{\text{absorbed energy}}{\text{volume}} \right) \right\rangle_{\text{time}} = \langle \mathbf{j} \cdot \mathbf{E} \rangle. \quad (1)$$

All magnetic contributions as well as electric quadrupole and higher-order multipole interactions are neglected, so the current \mathbf{j} induced in the medium is given as

$$\mathbf{j} = \frac{\partial \mathbf{P}}{\partial t}, \quad (2)$$

where \mathbf{P} is the induced polarization inside the medium, which can be expanded as

$$\mathbf{P} = \mathbf{P}^1 + \mathbf{P}^2 + \mathbf{P}^3 + \mathbf{P}^4 + \mathbf{P}^5 + \dots \quad (3)$$

Since only odd orders of \mathbf{P} survives the averaging procedure, we find that the two- and the three-photon absorption are proportional to the third- and fifth-order polarization, respectively,

$$P_i^3(\omega) e^{-i\omega t} = \chi_{ijkl}^{(3)} E_j^\omega e^{-i\omega t} E_k^{\omega*} e^{i\omega t} E_l^\omega e^{-i\omega t}, \quad (4)$$

$$P_i^5(\omega) e^{-i\omega t} = \chi_{ijklmn}^{(5)} E_j^\omega e^{-i\omega t} E_k^{\omega*} e^{i\omega t} E_l^\omega e^{-i\omega t} E_m^{\omega*} e^{i\omega t} E_n^\omega e^{-i\omega t}. \quad (5)$$

The energy absorbed in a two-photon process is thus proportional to the square of the electric-field intensity and the imaginary part of third-order susceptibility, in accordance with the expression

$$\left\langle \frac{d}{dt} \left(\frac{\text{absorbed energy}}{\text{volume}} \right) \right\rangle_{\text{time}}^{(3)} = 6\omega \text{Im}[\chi_{ijkl}^{(3)}(-\omega; \omega, -\omega, \omega)] E_i^{\omega*} E_j^\omega E_k^{\omega*} E_l^\omega, \quad (6)$$

and the energy absorbed in a three-photon process is proportional to the cube of the electric-field intensity and the imaginary part of the fifth-order susceptibility, in accordance with the expression

$$\left\langle \frac{d}{dt} \left(\frac{\text{absorbed energy}}{\text{volume}} \right) \right\rangle_{\text{time}}^{(5)} = 20\omega \text{Im}[\chi_{ijklmn}^{(5)}(-\omega; \omega, -\omega, \omega, -\omega, \omega)] \times E_i^{\omega*} E_j^\omega E_k^{\omega*} E_l^\omega E_m^{\omega*} E_n^\omega. \quad (7)$$

By introducing the intensity as $I = nc/(2\pi\hbar\omega)E^2$ (in cgs units),¹³ we can identify the two- and three-photon cross sections as

$$\sigma^{\text{TPA}} = \frac{24\pi^2\hbar\omega^2}{n^2c^2} \text{Im}[\chi_{ijkl}^{(3)}(-\omega; \omega, -\omega, \omega)], \quad (8)$$

$$\sigma^{\text{3PA}} = \frac{160\pi^3\hbar^2\omega^3}{n^3c^3} \text{Im}[\chi_{ijklmn}^{(5)}(-\omega; \omega, -\omega, \omega, \omega, -\omega)]. \quad (9)$$

The conventional definitions of two- and three-photon absorption coefficients—denoted by β and γ , respectively—are found in, for instance, Ref. 14 and are introduced by the variation of the intensity along the line of propagation

$$\frac{dI}{dz} = -\alpha I - \beta I^2 - \gamma I^3. \quad (10)$$

In order to comply with these definitions, the relations between the multiphoton cross sections' and the multiphoton absorptions' coefficients are defined according to

$$\sigma^{\text{TPA}} = \frac{\hbar\omega\beta}{N}, \quad (11)$$

$$\sigma^{\text{3PA}} = \frac{\hbar^2\omega^2\gamma}{N}. \quad (12)$$

The expressions above provide the relation between the macroscopical observables and the microscopical origin of the TPA and 3PA processes via susceptibilities. However, the formulas for the susceptibilities are computationally demanding to evaluate, and the complex susceptibility $\chi^{(5)}$ is, as of today, not implemented in standard response theoretical approaches applicable to polyatomic molecules. Nevertheless, by examining the SOS expressions for $\chi^{(3)}$ and $\chi^{(5)}$ at their respective resonant conditions, i.e., $\omega = \omega_f/2$ and $\omega = \omega_f/3$, one can decompose the TPA and 3PA cross sections into two- and three-photon transition probabilities δ_{TP} and δ_{3P} ,

$$\delta_{\text{TP}} = \langle |\lambda_A \mu_B S_{AB}|^2 \rangle_{\text{av}}, \quad (13)$$

$$\delta_{3\text{P}} = \langle |\lambda_A \mu_B \nu_C T_{ABC}|^2 \rangle_{\text{av}}, \quad (14)$$

where the averages are to be performed over all orientational directions. The expressions for the absorption cross sections have thus been recast in terms of summations of squared multiphoton transition matrix elements S_{AB} and T_{ABC} which can be obtained at a lower order of response theory.

B. Two-photon absorption

The two-photon matrix element S_{ab} can be identified from the SOS formula

$$S_{ab} = \sum_i \left[\frac{\langle 0 | \mu_a | i \rangle \langle i | \mu_b | f \rangle}{\omega_i - \omega_f/2} + \frac{\langle 0 | \mu_b | i \rangle \langle i | \mu_a | f \rangle}{\omega_i - \omega_f/2} \right], \quad (15)$$

where the summation includes the ground state and $a, b \in \{x, y, z\}$. The total two-photon absorption probability δ_{TP} for a molecule in gas phase or in solution can subsequently be obtained by applying oriental averaging according to McClain¹⁵ as

$$\delta_{\text{TP}} = F \delta_F + G \delta_G + H \delta_H, \quad (16)$$

where F , G , and H are defined as

$$F = -|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 + 4|\mathbf{e}_1 \cdot \mathbf{e}_2|^2 - 1, \quad (17)$$

$$G = -|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 - |\mathbf{e}_1 \cdot \mathbf{e}_2|^2 + 4, \quad (18)$$

$$H = 4|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 - |\mathbf{e}_1 \cdot \mathbf{e}_2|^2 - 1, \quad (19)$$

and where \mathbf{e}_1 and \mathbf{e}_2 are the polarization vectors of the fundamental laser beams, and

$$\delta_F = \sum_{a,b} S_{aa} S_{bb}^*, \quad \delta_G = \sum_{a,b} S_{ab} S_{ab}^*,$$

$$\delta_H = \sum_{a,b} S_{ab} S_{ba}^*, \quad (20)$$

which for linearly polarized light implies that $F = G = H = 2$. The relation between the macroscopic cross section and the transition probability is given by

$$\sigma^{\text{TPA}} = \frac{4\pi^2 a_0^5 \alpha}{c_0} \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{\text{TP}}. \quad (21)$$

Provided that cgs units are used for a_0 and c_0 and atomic units for δ_{TP} , ω , and Γ_f , the final cross sections will be given in units of $\text{cm}^4 \text{s photon}^{-1}$.

C. Three-photon absorption

The three-photon transition tensor element T_{abc} for three photons of identical frequency is defined as

$$T_{abc} = \sum \mathcal{P}_{a,b,c} \sum_{n,m} \frac{\langle 0 | \mu_a | m \rangle \langle m | \mu_b | n \rangle \langle n | \mu_c | f \rangle}{(\omega_m - 2\omega_f/3)(\omega_n - \omega_f/3)}, \quad (22)$$

where $\sum \mathcal{P}_{a,b,c}$ performs the summation over the six permutations with respect to the indices a , b , and c . Orientational averaging similar to the case of TPA is performed¹⁶ to arrive at a three-photon absorption probability $\delta_{3\text{P}}$ for linearly (L) and circularly (C) polarized light that is written as

$$\delta_{3\text{P}}^{\text{L}} = \frac{1}{35}(2\delta_G + 3\delta_F), \quad (23)$$

$$\delta_{3\text{P}}^{\text{C}} = \frac{1}{35}(5\delta_G - 3\delta_F), \quad (24)$$

where

$$\delta_F = \sum_{i,j,k} T_{ijj} T_{kkj}, \quad (25)$$

$$\delta_G = \sum_{i,j,k} T_{ijk} T_{ijk}. \quad (26)$$

In complete analog with TPA, we relate the orientationally averaged three-photon absorption probabilities $\delta_{3\text{P}}$ to the three-photon cross section $\sigma^{3\text{PA}}$ as

$$\sigma^{3\text{PA}} = \frac{4\pi^3 a_0^8 \alpha}{3c_0^2} \frac{\omega^3 g(\omega)}{\Gamma_f} \delta_{3\text{P}}. \quad (27)$$

With the same convention concerning the units as for TPA the final cross sections will be obtained in units of $\text{cm}^6 \text{s}^2 \text{photon}^{-1}$.

D. Few-states models

Few-states models are obtained by truncating the summations in Eqs. (15) and (22) to include a finite number of excited states. By confinement to two states, the long-in-plane component S_{zz} of the TP transition matrix can be written as

$$S_{zz} = \frac{4\mu_z^{0f}(\mu_z^{ff} - \mu_z^{00})}{\omega_f} = \frac{4\mu_z^{0f} \Delta\mu_z}{\omega_f}, \quad (28)$$

where μ_z^{0f} denotes the z component of the transition dipole moment between the ground state $|0\rangle$ and the final excited state $|f\rangle$, and μ_z^{00} and μ_z^{ff} are the permanent dipole moments of the ground and final states, respectively. It is clear that the two-states model is not applicable to molecules with an inversion center. For such molecules, an intermediate state $|1\rangle$ is required and the corresponding three-states model is written as

$$S_{zz} = \frac{2\mu_z^{01} \mu_z^{1f}}{\omega_1 - \omega_f/2}. \quad (29)$$

The corresponding two-photon absorption probability with a linearly polarized light source is

$$\delta_{\text{TP}}^{\text{L}} = 6(S_{zz})^2. \quad (30)$$

An extension to multidimensional systems and an arbitrary number of states was originally proposed in Refs. 17 and 18,

$$\delta_{TP}^L = 8 \sum_{ij} \frac{3(\boldsymbol{\mu}^{0i} \cdot \boldsymbol{\mu}^{if})(\boldsymbol{\mu}^{0j} \cdot \boldsymbol{\mu}^{jf}) + (\boldsymbol{\mu}^{0i} \times \boldsymbol{\mu}^{if}) \cdot (\boldsymbol{\mu}^{0j} \times \boldsymbol{\mu}^{jf}) - 2(\boldsymbol{\mu}^{0i} \times \boldsymbol{\mu}^{0j}) \cdot (\boldsymbol{\mu}^{if} \times \boldsymbol{\mu}^{jf})}{\Delta E_i \Delta E_j}. \quad (31)$$

Here the emphasis lies on the vector nature of the transition dipole moments and the obvious implications of the above formula are that additional competing excitation channels unavoidably will introduce destructive interference and reduce the nonlinear response.

For 3PA, the corresponding transition element T_{zzz} based on a two-states model can be written as

$$\begin{aligned} T_{zzz} &= 27 \left[\frac{2\mu_z^{0f}(\mu_z^{00} - \mu_z^{ff})^2 - (\mu_z^{0f})^3}{2\omega_f^2} \right] \\ &= 27 \left[\frac{\mu_z^{0f}[2(\Delta\mu_z)^2 - (\mu_z^{0f})^2]}{2\omega_f^2} \right] \end{aligned} \quad (32)$$

and, for a one-dimensional system, the total three-photon absorption probability δ_{3P}^L for linearly polarized light will become

$$\delta_{3P}^L = \frac{(T_{zzz})^2}{7}. \quad (33)$$

No analog to Eq. (31) has presently been derived for 3PA. For two- and three-dimensional systems, where several tensor elements may contribute to the total 3PA probability, the expression for δ_{3P}^L cannot be casted in a simple form. Unlike TPA, a two-states model is sufficient to capture the key features of the excitation scheme for molecules without (non-symmetric) as well as with (symmetric) a center of inversion. Equation (32) reveals some key features of three-photon absorption.

(i) For symmetric molecules, only the transition dipole moment between the ground state and the final state μ^{0f} will contribute to the final cross section.

(ii) For nonsymmetric, polar, molecules, on the other hand, the transition dipole moment between the ground and final states μ^{0f} and the corresponding dipole moment fluctuation $\Delta\mu$ will always counteract.

In order to quantify this counteraction, it is useful to introduce the following decomposition:

$$T_{zzz} = T_{zzz}^1 + T_{zzz}^2, \quad (34)$$

$$T_{zzz}^1 = -27 \frac{(\mu_z^{0f})^3}{2\omega_f^2}, \quad (35)$$

$$T_{zzz}^2 = 27 \frac{\mu_z^{0f}(\mu_z^{00} - \mu_z^{ff})^2}{\omega_f^2}, \quad (36)$$

and the ratio

$$R = \frac{T_{zzz}^1}{T_{zzz}^2} = \frac{(\mu^{0f})^2}{2(\mu^{00} - \mu^{ff})^2}. \quad (37)$$

A strategy for maximizing T_{zzz} which is suggested by Eq. (32) is to enhance the transition dipole moment between the ground and the final states while minimizing the dipole mo-

ment fluctuation. This strategy is different from that suggested by Eq. (28) for two-photon absorption which is to maximize both the transition moment and the dipole moment fluctuation, and it contrasts the differences in the design of multiphoton active materials.

E. Response functions

During the last 15 years, response theory has rapidly developed along two lines: (i) increasing the number of properties and (ii) enlarging the variety of wave functions. Presently the computable properties include a wide selection of electric and magnetic (time-dependent) properties of first, second, and third order and can be based on a manifold of wave functions ranging from low-scaling Hartree–Fock to highly correlated coupled cluster (CC) methods. An advantage is that the majority of available properties can be retrieved within the same computational scheme irrespective of the actual parametrization of the wave function. This enables, for instance, the use of hierarchies of CC wave functions in order to monitor correlation effects for a certain property, but also the possibility to perform rigorous comparisons of the direct response results with SOS evaluations obtained at the same level of theory. The desired quantities in order to accomplish the latter analysis for multiphoton absorption are the excitation energies ω_n , the transition dipole moments between the relevant states μ^{ij} , the second-order transition matrix elements S_{zz} , and the third-order transition matrix elements T_{zzz} . These are in multiconfigurational self-consistent field response theory all evaluated through the following matrices:¹⁹

$$S_{jk}^{[2]} = \langle 0 | [O_j^\dagger, O_k] | 0 \rangle, \quad (38)$$

$$S_{jkl}^{[3]} = -\frac{1}{2} \langle 0 | [O_j^\dagger, [O_l, O_k]] | 0 \rangle, \quad (39)$$

$$E_{jk}^{[2]} = \langle 0 | [O_j^\dagger, [O_k, H_0]] | 0 \rangle, \quad (40)$$

$$E_{jkl}^{[3]} = \frac{1}{2} \langle 0 | [O_j^\dagger, [O_k, [O_l, H_0]]] | 0 \rangle, \quad (41)$$

where the operators O_j are the nonredundant orbital and state transfer operators. The overlap matrices $S^{[2]}$ and $S^{[3]}$ are not to be confused with the two-photon transition matrix elements S_{ab} , which are calculated by the matrix equation

$$\begin{aligned} S_{ab} &= N_j^A(\omega_f/2) B_{jk}^{[2]} N_k^F(\omega_f) + N_j^B(-\omega_f/2) A_{(jk)}^{[2]} N_k^F(\omega_f) \\ &\quad + N_j^A(\omega_f/2) (E_{j(kl)}^{[3]} + \frac{1}{2} \omega_f S_{jlk}^{[3]} - \omega_f S_{jkl}^{[3]}) \\ &\quad \times N_j^B(-\omega_f/2) N_k^F(\omega_f). \end{aligned} \quad (42)$$

The corresponding matrix equation for the three-photon transition matrix elements T_{abc} is written as²⁰

$$\begin{aligned}
T_{abc} = & N_j^A(\omega_f/3)T_{jklm}^{[4]}(-\omega_f/3, -\omega_f/3, \omega_f)N_k^B(-\omega_f/3)N_l^C(-\omega_f/3)N_m^F(\omega_f) - N_j^A(\omega_f/3)[T_{jkl}^{[3]}(-\omega_f/3, 2\omega_f/3) \\
& \times N_k^B(-\omega_f/3)N_l^{CF}(-\omega_f/3, \omega_f) + T_{jkl}^{[3]}(-\omega_f/3, 2\omega_f/3)N_k^C(-\omega_f/3)N_l^{BF}(-\omega_f/3, \omega_f) + T_{jkl}^{[3]}(\omega_f, -2\omega_f/3) \\
& \times N_k^F(\omega_f)N_l^{BC}(-\omega_f/3, -\omega_f/3)] - N_j^A(\omega_f/3)[B_{j(kl)}^{[3]}N_k^C(-\omega_f/3)N_l^F(\omega_f) + C_{j(kl)}^{[3]}N_k^B(-\omega_f/3)N_l^F(\omega_f)] \\
& + N_j^A(\omega_f/3)[B_{jk}^{[2]}N_k^{CF}(-\omega_f/3, \omega_f) + C_{jk}^{[2]}N_k^{BF}(-\omega_f/3, \omega_f)] + A_{(jk)}^{[2]}[N_j^B(-\omega_f/3)N_k^{CF}(-\omega_f/3, \omega_f) \\
& + N_j^C(-\omega_f/3)N_k^{BF}(-\omega_f/3, \omega_f) + N_j^F(\omega_f)N_k^{BC}(-\omega_f/3, -\omega_f/3)] - A_{(jkl)}^{[3]}N_j^B(-\omega_f/3)N_k^C(-\omega_f/3)N_l^F(\omega_f), \quad (43)
\end{aligned}$$

where

$$N_j^X(\omega_a) = (E^{[2]} - \omega_a S^{[2]})_{jk}^{-1} X_k^{[1]}, \quad X \in \{A, B, C\}, \quad (44)$$

$$(E^{[2]} - \omega_f S^{[2]})_{jk} N_k^F(\omega_f) = 0, \quad (45)$$

and

$$\begin{aligned}
[E^{[2]} - (\omega_1 + \omega_2)S^{[2]}]N_j^{BC}(\omega_1, \omega_2) \\
= T_{klm}^{[3]}(\omega_1, \omega_2)N_l^B(\omega_1)N_m^C(\omega_2) \\
- C_{kl}^{[2]}N_l^B(\omega_1) - B_{kl}^{[2]}N_l^C(\omega_2), \quad (46)
\end{aligned}$$

$$\begin{aligned}
[E^{[2]} - (\omega_f - \omega_1)S^{[2]}]N_j^{XF}(\omega_1, \omega_f) \\
= T_{klm}^{[3]}(-\omega_1, \omega_f)N_l^X(-\omega_1)N_l^F(\omega_f) - X_{kl}^{[2]}N_l^F(\omega_f), \\
X \in \{B, C\}. \quad (47)
\end{aligned}$$

The terms $T_{jkl}^{[3]}$ and $T_{jklm}^{[4]}$, which are *separate* from the three-photon transition matrix elements, are short-hand notation for

$$T_{jkl}^{[3]}(\omega_1, \omega_2) = (E_{j(kl)}^{[3]} - \omega_1 S_{jkl}^{[3]} - \omega_2 S_{jkl}^{[3]}), \quad (48)$$

$$\begin{aligned}
T_{jklm}^{[4]}(\omega_1, \omega_2, \omega_3) = (E_{j(klm)}^{[4]} - \omega_1 S_{jk(lm)}^{[4]} - \omega_2 S_{jl(km)}^{[4]} \\
- \omega_3 S_{jm(kl)}^{[4]}), \quad (49)
\end{aligned}$$

and, we refer to Ref. 20 for a thorough description of the terminology. Admittedly, the matrix equations are not very illuminating, but there is an interesting remark to be made which establishes a connection to the more familiar SOS expressions. Let us compare Eqs. (15) and (42). In a situation where the orbital and state transfer parameters couple the reference state and the eigenstates of the unperturbed Hamiltonian, i.e., $H_0 O_n |0\rangle = E_n |n\rangle$, it is clear from Eqs. (38) to (41) that the second-order Hessian and overlap matrices will be diagonal and the third-order matrices will vanish. The third term in the matrix equation for the TP transition moment [Eq. (42)] will therefore vanish and the remaining two terms will equal the SOS expression in Eq. (15). This case is of special interest to us since the SOS and response approaches converge to the same final value for the absorption cross sections, whereas, at other levels of theory, the two approaches will be different even when including the complete spectrum of excited states. For this reason, we include a FCI calculation on lithium hydride. The same arguments hold also in the case of three-photon absorption.

For a comparative SOS approach, we also need excitation energies, transition dipole moments, and permanent dipole moments. In response theory the transition dipole mo-

ment between the ground state $|0\rangle$ and an excited state $|f\rangle$ is given by the residue of the linear response function as

$$\langle 0|A|f\rangle\langle f|B|0\rangle = A_f^{[1]}B_f^{[1]}. \quad (50)$$

The transition dipole moments between excited states ($e \neq f$) as well as the excited state dipole moments ($e = f$) are evaluated as double residues of the quadratic response function as

$$\begin{aligned}
\langle e|A|f\rangle - \delta_{ef}\langle 0|A|0\rangle \\
= (A_{kl}^{[2]} + A_{lk}^{[2]})N_k^E(-\omega_e)N_l^F(\omega_f) + N_j^a(\omega_f - \omega_e) \\
\times [E_{jkl}^{[3]} + E_{jlk}^{[3]} + \omega_e S_{jkl}^{[3]} - \omega_f S_{jlk}^{[3]}]N_l^E(-\omega_e)N_k^F(\omega_f). \quad (51)
\end{aligned}$$

We emphasize that the calculation of excited state properties is performed with an optimization only of the ground state $|0\rangle$. The information of the excited states enters through the eigenvectors solved for in Eq. (45). It is also noteworthy that the dipole moment fluctuation $\Delta\mu$, which enters in the few-states models for multiphoton absorption, is evaluated directly from the double residue of the second-order response functions. The agreement between the two described approaches—(i) directly through response and (ii) indirectly through restricted SOS or few-state models—crucially depends on the matrices $S^{[3]}$ and $E^{[3]}$. For exact states, or at the full-configuration interaction level, these will be zero, whereas in other cases, such as for instance Hartree–Fock, the coupling contained in $E^{[3]}$ seemingly determines the rate of agreement between the two approaches.

III. COMPUTATIONAL DETAILS

The chosen systems range from lithium hydride (LiH) to *para*-nitroaniline (pNA), some nearly one-dimensional conjugated *trans*-stilbene systems with various substituents, and a series of organic chromophores (see Fig. 1). The chromophores have previously been characterized as promising TPA molecules and are either based on *N,N*-diphenyl-7[2-(4-pyridinyl)ethynyl]-0,9-*n*-decylfluorene-2-amine (AF) or dithienothiophene (DTT) but modified with various electron accepting (A) or donating (D) substituents. Computational limitations require a slight modification by shortening the alkyl chains, otherwise they agree with the systems described by Kannan *et al.*²¹ and Kim *et al.*²² The system denoted DTT-AA bears close resemblance with a system proposed by Ventelon *et al.*²³

Calculations on LiH were based on a geometry optimized at FCI with Sadlej's polarization basis set.²⁴ All other

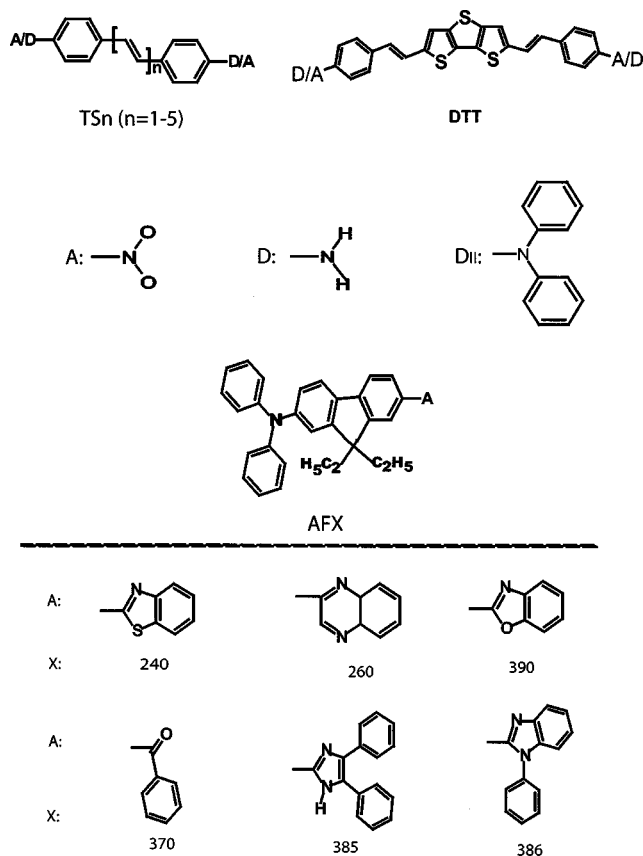


FIG. 1. Molecular structures.

investigated systems were optimized at the density functional theory (DFT) level with the B3LYP exchange-correlation functional and using the GAUSSIAN 98 (Ref. 25) program. The DFT structure optimizations were performed using the 6-31++G basis set²⁶ for pNA and the 6-31G basis set²⁶ for the other molecules. The molecular properties—TPA and 3PA matrix elements, the electric dipole transition moments, excitation energies, and permanent dipole moments—were calculated with the response methodology as implemented in the DALTON (Ref. 27) program and employing the Hartree-Fock approximation with the 6-31G basis set.²⁶ An exception is LiH for which the STO-3G basis set²⁸ was used.

The choice of basis sets in the property calculations is made with the intent of evaluating the proposed computational methods rather than to provide basis set limiting values. It is also a result of the limited computational capacity for large molecules. In the evaluation of three-photon cross

sections the lifetime broadening has been assumed to be 0.1 eV, which is in accordance with what have been employed in similar studies for TPA.

IV. RESULTS AND DISCUSSION

A. LiH

We include calculations on LiH with the STO-3G basis set since we will be able to include *all* excited states in the SOS summations both at the self-consistent field (SCF), or equivalently Hartree-Fock, and the FCI levels. Table I presents the results for two- and three-photon transition matrix elements between the ground state $X^1\Sigma^+$ and the two lowest singlet excited states of Σ^+ symmetry. The results confirm that, at the FCI level, the SOS and response methodologies agree on the final property values, whereas, at the SCF level, this is no longer so due to the contributions from the third-order Hessian matrix. The discrepancy is more pronounced for the higher-order property T_{zzz} in this case.

At the FCI level, we note a rapid convergence for all properties with respect to the number of states included in the SOS summations. Already with inclusion of five of the total 29 excited states, the properties are converged to within 1%. At the SCF level, on the other hand, the number of states are limited to four in the current basis set, and it is therefore not meaningful to discuss the convergence of few-states models. The SCF values predicted by SOS (all states included) and response agree to within a few percent for S_{zz} and for T_{zzz} of the first excited state. For the second excited state, however, the results predicted with the two methods differ by a factor of 2. This shows that the quality of truncated SOS models depends not only on the property at hand but is also state specific.

B. pNA

For more extensive systems and larger basis sets the number of states soon becomes overwhelming and one therefore has to enforce truncations in the summations. *Para*-nitroaniline constitutes an interesting example of a CT system of moderate size. The highest occupied molecular orbital in the ground state X^1A_1 is located on the NH_2 group. The linear absorption spectrum is strongly dominated by an intense transition to the 2^1A_1 state, which is characterized by a one-electron excitation to the lowest unoccupied molecular orbital located on the NO_2 group. Due to the fact that this transition is so dominant, it is reasonable to assume that a

TABLE I. Two-photon S_{zz} and three-photon matrix elements T_{zzz} for LiH at the SCF and FCI levels with the STO-3G basis set. All quantities are given in a.u.

Property	State	SCF		FCI	
		SOS ^a	Response	SOS ^a	Response
S_{zz}	$1^1\Sigma^+$	42.417	42.406	76.490	76.490
	$2^1\Sigma^+$	10.680	10.344	-8.2558	-8.2558
T_{zzz}	$1^1\Sigma^+$	5939.8	5857.6	13 355.1	13 355.1
	$2^1\Sigma^+$	-663.65	-1134.7	-39.695	-39.695

^aThe SOS calculations include all states in the given representation.

TABLE II. A comparison of truncated sum-over-states values with response results for two-photon S_{zz} and three-photon T_{zzz} matrix elements. Results are obtained for the 2^1A_1 charge-transfer state of pNA at the SCF/6-31G level. All quantities are given in a.u.

States	S_{zz}	T_{zzz}
1	-62.867	-1767.6
2	-62.836	-1763.8
3	-62.774	-1746.3
4	-61.970	-1596.7
5	-80.226	-3210.7
6	-75.316	-2214.0
7	-71.047	-3032.2
8	-70.996	-3017.9
9	-71.030	-3012.1
10	-71.165	-3021.9
11	-70.458	-2942.4
12	-70.416	-2954.8
13	-70.946	-3106.7
14	-70.548	-3236.4
15	-70.528	-3236.6
Response	-70.142	-5442.7

two-states model including the ground and the CT state should describe the response properties well. For the same reason, one also neglects the electronic response in the short in-plane and out-of-plane directions. The CT state is also two- and three-photon allowed, and the two-states model is commonly adopted also here.

In Table II and Fig. 2, we show the two- and three-photon transition matrix elements (S_{zz} and T_{zzz}) for the $X^1A_1 \rightarrow 2^1A_1$ transition as determined at the SCF level. We compare the analytic response values with the SOS method truncated at inclusion of between 1 and 15 singlet excited states of A_1 symmetry. The most striking observation to be made in Table II is the difference in convergence rate for S_{zz} and T_{zzz} . Whereas S_{zz} can be considered to be converged at eight states with an agreement of 2% with respect to the response value, we cannot reach convergence at all for T_{zzz} . When including 15 states the SOS value of T_{zzz} still underestimates the response value by 50%. The number of excita-

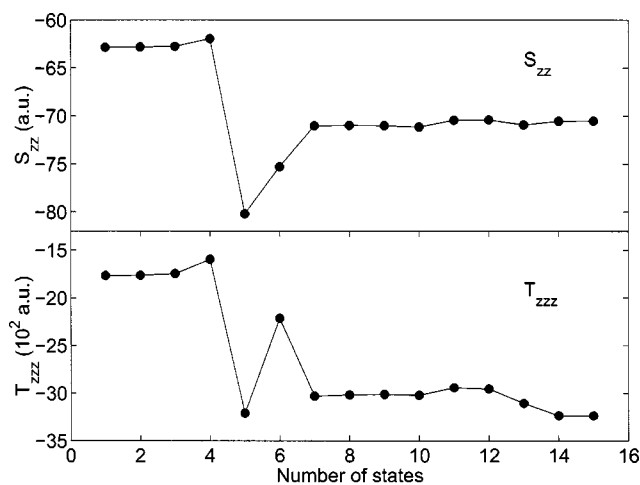


FIG. 2. The convergence of S_{zz} and T_{zzz} for pNA with respect to the inclusion of excited states.

tion channels are an order of magnitude larger for T_{zzz} than for S_{zz} , and cancellations may thus have a greater influence on the final value. Similar features have also been described for the second-order hyperpolarizability γ by Norman *et al.*²⁰ We also note that the often advocated two-states model for pNA is accurate neither for two- nor for three-photon absorption.

C. *trans*-stilbene

The combination of being a nearly one-dimensional π -conjugated system and hosting several possible locations suitable for substituents makes *trans*-stilbene (TS) an attractive and frequently employed model system in nonlinear optics. We here consider the effects of adding a strongly electron accepting NO_2 group (A) and a donating NH_2 group (D) at terminal locations and the effects of increasing the conjugation length.

The TS backbone belongs to the C_{2h} point group, and thus possesses a center of inversion. This aspect of symmetry is important in multiphoton absorption processes, since two- and three-photon spectra for molecules with high symmetry may be spectroscopically separated. This fact must then also be taken into account when constructing few-states models, as we pointed out in connection with Eq. (28). The donor-acceptor substitutions may, or may not, alter the molecular symmetry, and we will separate “symmetric” substitutions that maintain the symmetry from “asymmetric” substitutions that break the symmetry.

Since symmetric substitutions are defined to maintain the molecular symmetry of *trans*-stilbene, the dipole fluctuation $\Delta\mu$ will be zero in such cases. As a direct consequence, the three-photon absorption matrix element T_{zzz} will, within a two-states model, be determined solely by μ^{of} . We see that, although the number of included states is small—only three states for symmetric (in the C_{2h} point group) and two states for asymmetric (in the C_s point group) molecules—the few-states model (FSM) predictions for S_{zz} agree well with the results from response calculations, see Table III and Fig. 3. All major transition channels thus appear to be addressed in the two-photon case. In contrast to this observation, the FSM predictions for T_{zzz} are in poor quantitative agreement with the response results. The FSM results for TS and TS-DD overestimate the response values, whereas for TS-AA the response values are somewhat underestimated.

The attachment of both an acceptor and a donor will localize the otherwise conjugated highest occupied and lowest unoccupied molecular orbitals at the donor and acceptor groups, respectively. In addition, it will alter the symmetry and introduce a competition between terms involving only the transition dipole moment $(\mu^{of})^3$ and terms involving transition moments in a combination with permanent dipole moments $\mu^{of}\Delta\mu^2$ in Eq. (32). This is the reason for the substantial discrepancy between FSM and response results which exceeds a factor of 8 for T_{zzz} in TS-AD, and it is clearly seen as a drop in the FSM values for three-photon absorption in going from TS-DD and TS-AA to TS-AD. We note that the response results show that, in comparison with TS, TS-DD, and TS-AA, the asymmetric TS-AD system is the most effective three-photon compound. The implication

TABLE III. A comparison of truncated sum-over-states values with response results for two-photon S_{zz} (a.u.) and three-photon T_{zzz} ($\times 10^4$ a.u.) matrix elements. Results are obtained for acceptor (A) and donor (D) substituted *trans*-stilbene (TS) with increasing conjugation length (TS-AD_{*n*}) at the SCF/6-31G level. The excitation energies ΔE are given in eV.

Molecule	State	ΔE	Osc. str.	S_{zz}		T_{zzz}	
				SOS ^a	Response	SOS ^b	Response
TS	1^1B_u	4.59	0.941	1.14	0.94
	2^1A_g	5.82	...	20.6	20.3
TS-DD	1^1B_u	4.35	1.211	1.92	1.54
	2^1A_g	5.87	...	99.4	112.6
TS-AA	1^1B_u	4.22	1.304	2.09	2.29
	2^1A_g	5.50	...	172.3	180.1
TS-AD	$2^1A'$	4.05	1.336	228.6	221.2	0.52	4.40
TS-AD ₂	$2^1A'$	3.78	1.938	329.1	301.2	2.74	7.45
TS-AD ₃	$2^1A'$	3.54	2.526	428.8	382.1	6.70	11.49
TS-AD ₄	$2^1A'$	3.36	3.117	518.3	456.3	13.06	16.43
TS-AD ₅	$2^1A'$	3.11	3.684	730.0	633.6	21.26	27.23

^aCalculations of S_{zz} for molecules with an inversion center employ a three-states model, whereas a two-states model is used otherwise (identical to that used in the calculations of T_{zzz}).

^bCalculations of T_{zzz} employ a two-states model.

of this fact is that the design strategy mentioned in connection with Eq. (34), which favors molecules in the C_{2h} point group, is cast in doubt.

When increasing the conjugation length the T^1 term grows more rapidly, as seen in Fig. 4, and dominate the total value of T_{zzz} for molecules with at least four double bonds. Figure 3 shows that the three-photon transition matrix elements for the donor-acceptor substituted stilbenes are systematically underestimated with a constant amount by the few-states models, which means that the relative error will be strongly reduced with conjugation length. The quality of the few-states models is clearly lower when the contributing terms, T^1_{zzz} and T^2_{zzz} , are of similar magnitude.

A perhaps less obvious feature of Table III is that while the agreements for T_{zzz} improves with conjugation length, the deviations for S_{zz} increase and reach a final value of

15%. This is possibly caused by the mixed nature of the expression for the few-states model for asymmetric systems, i.e., $\mu^{0f}\Delta\mu$.

The strength of the attached acceptors and donors will also influence the 3PA probability. Table IV shows a clear correlation between δ_{3P}^L and the strength of the acceptor and donor groups.

D. Chromophores

Two important classes of systems, independently proposed for TPA applications, are based on the π -conjugated, organic, backbones DTT and AF, see Fig. 1. The conjugation bridges for all compounds contain ring structures. All DTT compounds have an identical backbone, but differs with respect to the terminal substituent acceptor-acceptor, donor-donor, or acceptor-donor combinations. We have utilized two different donors, namely, NH_2 (denoted by *D*) and

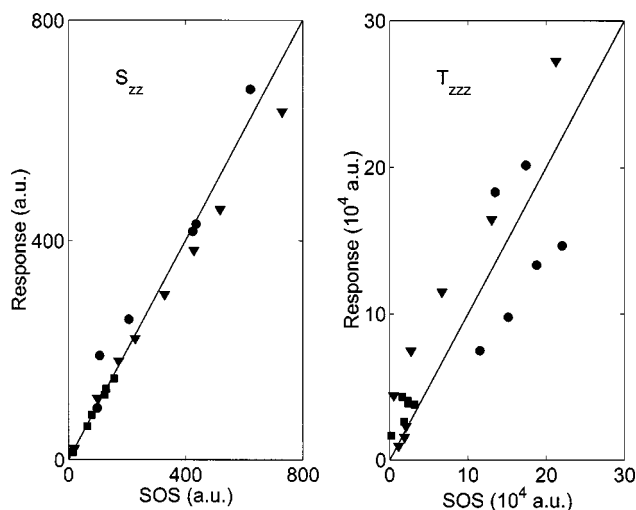


FIG. 3. The correlation between results obtained with few-states models and the response method for two-photon S_{zz} and three-photon T_{zzz} matrix elements. The systems included are derivatives of stilbene (triangle), AF (square), and DTT (ring).

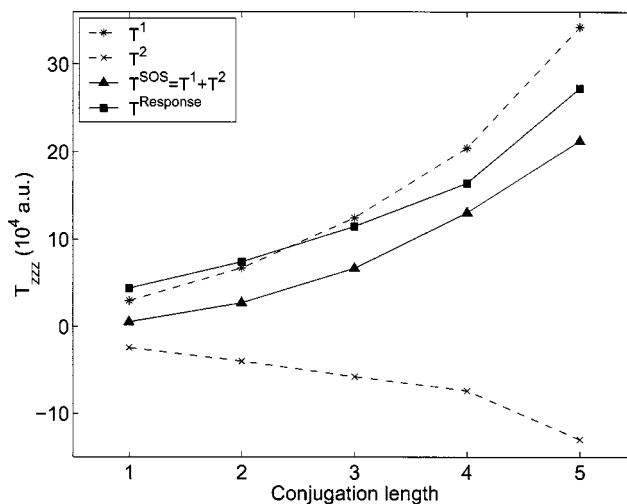


FIG. 4. The components of T_{zzz} in a two-states model for *trans*-stilbene with increasing conjugation length.

TABLE IV. Three-photon absorption probability $\delta_{3p}^f (\times 10^6 \text{ a.u.})$ for the $2^1A'$ state of *trans*-stilbene with various acceptor (CN and NH_2) and donor (CH_3 , OCH_3 , and NH_3) substituents. Results are obtained at the SCF/6-31G level using response theory.

	CN	NO_2
CH_3	48.9	119
OCH_3	62.8	160
NH_2	106	289

$\text{N}[\text{O}_6\text{H}_6]_2$ (denoted by D_{II}) but a common acceptor, namely, NO_2 (denoted by A). The DTT-backbone belongs to the C_{2v} point group, and the terminal donor–acceptor substitutions will therefore result in two different classes of molecules: symmetric (in the C_{2v} point group) with DD or AA substituents or asymmetric (in the C_s point group) with AD substituents. In contrast to *trans*-stilbene, DTT has a permanent dipole moment. The dipole moment of DTT, however, is perpendicular to the axis of conjugation, and much of the discussion on the symmetry aspects will therefore be the same as for the TS systems. All AF compounds are all asymmetric, and therefore less readily characterized in terms of symmetry.

As depicted in Table V and Fig. 3, the agreement between the few-states models and response methods for S_{zz} is striking for all compounds. The deviation for TPA is occasionally 10%, but mostly below 5% if DTT-DD is disregarded. This is in sharp contrast to the performance of FSMs for T_{zzz} which—in spite of these molecules being true CT systems and the clear agreements for S_{zz} —shows substantial discrepancies when compared against response results. The mean value of deviation is close to 40%, and the errors can occasionally exceed 200%. Perhaps even more crucial is the

fact that few-states models fail to predict the same ordering of the compounds as the response values with respect to the strength of T_{zzz} . As we noted for the TS systems, there is a drop in the FSM values for three-photon absorption when going from the symmetric DTT-DD and DTT-AA systems to DTT-AD. Again this has its explanation in the competition between permanent and transition dipole moments along the axis of conjugation, and, again, this observation has no counterpart in the response calculations.

In view of Fig. 3, one is inclined to consider the errors in the few-states models as stochastic. A more careful analysis, however, reveals that the disagreements of response and the few-state models for DTT do follow a pattern. We note that the FSM results for symmetric molecules overestimate the response values by a factor of approximately 1.5, whereas, for the asymmetric molecules, an underestimation by the same factor is observed. We emphasize that the situation is not improved by inclusion of the four lowest singlet excited states in the summations. All AF compounds are more or less asymmetric, and the three-photon matrix elements are underestimated by the few-states models just as for the DTT systems.

Notwithstanding the deviation for each particular compound, both methods do agree about the general features of the two types of systems. The DTT systems have undoubtedly larger multiphoton capabilities, both for TPA and 3PA, than the AF systems. Most likely one can expect that documented good TPA systems also will function as good 3PA materials. The final conclusion is that, unlike TPA, few-states models cannot routinely be employed in order to calculate 3PA for extensive systems, though they may still provide valuable tools for interpretation of observed features.

TABLE V. A comparison of truncated sum-over-states values with response results for two-photon S_{zz} (a.u.) and three-photon $T_{zzz} (\times 10^4 \text{ a.u.})$ matrix elements, and three-photon cross sections σ^{3PA} in $10^{-82} \text{ cm}^6 \text{ s}^2 \text{ photon}^{-1}$. Results are obtained for a series of chromophores at the SCF/6-31G level. The excitation energies ΔE are given in eV.

Molecule	State	ΔE	Osc. str.	S_{zz}		T_{zzz}		σ^{3PA}	
				SOS ^a	Response	SOS ^b	Response	SOS ^b	Response
AF-240	$2^1A'$	4.08	1.328	129.2	129.4	2.31	4.05	0.53	1.87
AF-260	$2^1A'$	4.11	1.222	156.4	148.2	1.61	4.30	0.26	2.19
AF-370	$2^1A'$	4.30	0.365	79.5	81.9	0.22	1.65	0.01	0.41
AF-385	$2^1A'$	4.13	1.477	15.7	14.0	3.20	3.78	1.05	1.54
AF-386	$2^1A'$	4.27	1.159	65.0	60.9	1.84	2.61	0.39	1.15
AF-390	$2^1A'$	4.16	1.430	123.2	118.2	2.36	3.86	0.59	1.64
DTT	1^1B_1	3.17	1.886	11.54	7.48	6.20	2.63
	2^1A_1	4.34	...	99.0	94.0
DTT-DD	1^1B_1	3.10	2.153	15.15	9.78	9.99	4.20
	2^1A_1	4.19	...	107.3	190.2
DTT- $D_{II}D_{II}$	1^1B_1	3.04	2.545	22.06	14.68	20.0	9.04
	2^1A_1	4.07	...	206.5	256.5
DTT-AA	1^1B_1	3.01	2.275	18.79	13.35	14.1	7.25
	2^1A_1	4.04	...	622.0	674.4
DTT-AD	$2^1A'$	2.97	2.219	436.4	430.0	13.51	18.31	6.99	12.9
DTT- AD_{II}	$2^1A'$	2.97	2.390	424.9	416.7	17.44	20.15	11.6	15.8

^aCalculations of S_{zz} for DTT molecules with C_{2v} symmetry and AF-370 employ a three-states model, whereas a two-states model is used otherwise (identical to that used in the calculations of T_{zzz}).

^bCalculations of T_{zzz} employ a two-states model for all molecules except AF-370 where a three-states model was used (identical to that used in the calculations of S_{zz}).

V. CONCLUSION

The rising attention directed to applications based on three-photon absorption is followed by a demand to theoretically describe the fundamental photophysical process. As for two-photon absorption, there is a clear advantage in a two-fold approach where the nontruncated values from direct response calculations are supported by interpretable and simple formulas deduced from few-states models. A reasonable mutual numerical agreement is an obvious prerequisite for such an analysis. We have calculated two-photon absorption (TPA) and three-photon absorption (3PA) matrix elements for a range of systems using two different approaches, namely, truncated sum-over-states (SOS), or few-states models, and response theory. Formulas for few-states models in three-photon absorption are presented here. The mutual agreement found for LiH, where a complete summation can be performed, is not transferred to larger systems. Already for pNA, where 15 states were included in the summations, the deviation for the third-order transition matrix element T_{zzz} was approximately a factor of 1.5, whereas for the second-order transition matrix element S_{zz} the deviation was less than 0.5%. This feature was repeatedly demonstrated for various modifications of *trans*-stilbene as well as larger systems denoted by AF and DTT. Apparently, the terms in the two-states model are hard to balance, since, in comparison with results from response theory, one notes a regular underestimation for asymmetric systems and an overestimation for symmetric systems. On the other hand, the performance of the few-states models for S_{zz} indicates that all major transition channels are addressed. Both few-states models and response theory point out donor-acceptor substituted systems with long conjugation lengths as the strongest three-photon absorbing molecules. We summarize by emphasizing that not even a quantitative accuracy of few-states models for two-photon absorption guarantees the same models to perform well for the higher-order property of three-photon absorption.

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- ¹M. Albota, D. Beljonne, J. L. Brédas *et al.*, *Science* **281**, 1653 (1998).
- ²B. A. Reinhardt, L. L. Brott, S. J. Clarson *et al.*, *Chem. Mater.* **10**, 1863 (1998).
- ³G. S. He, P. P. Markowicz, T. Lin, and P. N. Prasad, *Nature (London)* **415**, 767 (2002).
- ⁴P. Norman, Y. Luo, and H. Ågren, *Chem. Phys. Lett.* **286**, 8 (1998).
- ⁵C.-K. Wang, O. Macak, Y. Luo, and H. Ågren, *J. Chem. Phys.* **114**, 9813 (2001).
- ⁶P. Norman, Y. Luo, and H. Ågren, *J. Chem. Phys.* **111**, 7758 (1999).
- ⁷P. Cronstrand, Y. Luo, and H. Ågren, *J. Chem. Phys.* **117**, 11102 (2002).
- ⁸P. Macak, Y. Luo, P. Norman, and H. Ågren, *J. Chem. Phys.* **113**, 7055 (2002).
- ⁹P. Macak, Y. Luo, and H. Ågren, *Chem. Phys. Lett.* **330**, 447 (2000).
- ¹⁰Y. Luo, P. Norman, P. Macak, and H. Ågren, *J. Phys. Chem. A* **104**, 4718 (2000).
- ¹¹B. A. Reinhardt, *Photonics Sci. News* **4**, 21 (1999).
- ¹²H. Mahr, in *Quantum Electronics*, edited by H. Rabin and C. L. Tang (Academic, New York, 1975), Vol. IA:225.
- ¹³R. W. Boyd, *Nonlinear Optics* (Academic, London, 2003).
- ¹⁴R. L. Sutherland, *Handbook of Nonlinear Optics* (Dekker, New York, 1996).
- ¹⁵W. M. McClain, *J. Chem. Phys.* **55**, 2789 (1971).
- ¹⁶W. M. McClain, *J. Chem. Phys.* **57**, 2264 (1972).
- ¹⁷P. Cronstrand, Y. Luo, and H. Ågren, *Chem. Phys. Lett.* **352**, 262 (2002).
- ¹⁸P. Cronstrand, Y. Luo, and H. Ågren, *J. Chem. Phys.* **117**, 11102 (2002).
- ¹⁹J. Olsen and P. Jørgensen, *J. Chem. Phys.* **82**, 3235 (1985).
- ²⁰P. Norman, D. Jonsson, O. Vahtras, and H. Ågren, *Chem. Phys.* **203**, 23 (1996).
- ²¹R. Kannan, G. S. He, L. Yuan *et al.*, *Chem. Mater.* **13**, 1896 (2001).
- ²²O.-K. Kim, K.-S. Lee, H. Y. Woo, K.-S. Kim, G. S. He, J. Swiatkiewicz, and P. N. Prasad, *Chem. Mater.* **12**, 284 (2000).
- ²³L. Ventelon, L. Moreaux, J. Mertz, and M. Blanchard-Desce, *Chem. Commun. (London)* **1999**, 2055 (1999).
- ²⁴A. J. Sadlej, *Collect. Czech. Chem. Commun.* **53**, 1995 (1988).
- ²⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Gaussian Inc., Pittsburgh PA, 1998. See <http://www.gaussian.com>
- ²⁶W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
- ²⁷T. Helgaker, H. J. Aa. Jensen, P. Jørgensen *et al.*, DALTON, an *ab initio* electronic structure program, Release 1.2. See <http://www.kjemi.uio.no/software/dalton/dalton.html>, 2001.
- ²⁸W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).