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Two-Photon Absorption Cross Sections of *trans*-Stilbene, and 7,8-Disubstituted Stilbenes in Different Molecular Conformations: A Model Exact Study

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The correlated Pariser−Parr−Pople model Hamiltonian for interacting π-electrons is employed for calculating the two-photon absorption (TPA) cross section in *trans*-stilbene and its derivatives using a correction vector (CV) approach. The resulting TPA cross sections are model exact, since the CV approach is equivalent to a full configuration interaction calculation, and all excited states are included in the sum-over-states for the computation of the two-photon transition matrix element. Our study reproduces the experimental TPA cross section of *trans*-stilbene satisfactorily. The TPA cross section of 7,8-disubstituted stilbene is computed for the identical nature of both substituents. We find that the TPA cross section depends only weakly on the strength of the electron-donating or -withdrawing character of the substituents. Both electron-donating and electron-withdrawing characters influence the TPA cross section identically. We find that steric changes in the molecule due to pedallike rotation reduces the TPA cross section both with and without substituents. However, twist about the central double bond of the substituted stilbene molecule leads to a large TPA enhancement for twist angle of about 60°. Thus, stereochemistry changes, besides electronic effects, are important in enhancing the TPA cross sections.

1. Introduction

The study of two-photon absorption (TPA) cross section of conjugated organic materials has received considerable attention in view of the potential that these materials have in diverse applications such as up-converted lasing,[1] optical power limiting,[2] photodynamic therapy,[3] and three-dimensional (3D) microfabrication.[4] The research in this area is focused on identification of molecular design strategies for the development of materials with large TPA cross sections. In this context various classes of two-photon chromophores have been investigated theoretically as well as experimentally. These include donor−acceptor quadrupolar molecules incorporating a variety of conjugated bridges,[5−9] bifluorene[10] and polyfluorene[11] systems, octupolar molecules,[12] multibranched structures,[13] and dendrimer systems.[14] The dendrimer systems synthesized by Chung et al.[14] is a new class of TPA materials based on dithienothiophene (DTT) as a π center. The TPA cross sections of the DTT-based materials were found to be 1 order of magnitude larger than those based on fluorene, which indicates that the π-center is playing an important role in the TPA activity of these materials. Besides, the TPA cross section was found to increase superlinearly with number of DDT units, indicating rather large π-coherence lengths in these conjugated systems. The results of these studies indicate that the most efficient TPA materials are the ones with various electron-donor (D) and electron-acceptor (A) groups attached symmetrically or asymmetrically to a conjugated linker π-center and that the TPA cross sections increase with increasing conjugation length and D/A strength. Reinhardt et al., who studied various dipolar conjugated donor−acceptor molecules[15] with fluorene as a π-center, also emphasized the importance of planarity.

Generally, it is difficult to compare experimentally observed absolute TPA cross sections obtained by different groups. This is either due to different experimental conditions employed by different groups or due to measurement being carried out at only a single, but different, wavelength by different groups.[14,15] On the other hand, theoretical calculations should be able to provide us with a fair comparison of intrinsic TPA cross sections among different isolated molecules. There are a variety of approaches to model the TPA cross sections computationally.[5,16−21] These approaches range from using comparatively simple models such as the extended Hückel model to the use of ab initio methods. However, even with the ab initio methods only limited configuration interaction (CI) is employed for treating electron correlations, although it is well-known that electron correlations play an important role in describing the linear as well as nonlinear optical properties of conjugated molecules. As it was pointed out by McWilliams et al.[16] the TPA spectra of the interacting π-electron in conjugated polymers are qualitatively different from any single-particle description, including the Hartree−Fock limit, and hence, it is essential to go well beyond Hartree−Fock theories and include electron correlation effects, for instance, via an extensive CI scheme. Besides, like with all other nonlinear optic (NLO) coefficients, the computation of TPA appears to require explicitly a large number of excited states and transition dipole matrix elements among these states.

Often, even when extensive CI is employed in the computation of the ground and excited states, only a small subset of the excited states (typically a few tens) are used in the computation of TPA. Even so, such an approach is prohibitive for smaller systems and currently impossible for larger systems. Thus, for reasons of practicality, many of the quantum chemical calculations resort to an incomplete or restricted CI calculation. Usually, in the CI step of the calculations, only singly and doubly excited configurations with respect to a few reference configurations in the molecular orbital space are employed. In the step involving computation of the NLO coefficients, the number of

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states included is often far smaller than the number of configurations employed in the CI step. However, for comparing TPA cross sections across different molecules of different sizes, it is necessary to perform a complete CI calculation, where possible, to obtain the "exact" TPA cross sections, as it is known that limited CI calculations are not size consistent. By now, it is widely accepted that a complete CI calculation within the π-framework based on the Pariser−Parr−Pople (PPP) model Hamiltonian with transferable parameters can accurately reproduce many of the properties of low-lying states of conjugated organic molecules studied experimentally. It has also been demonstrated that exact calculations on oligomers of different sizes can be used to successfully extrapolate properties of a system to the polymer limit.[17]

Stilbene, with its large π-conjugated framework, has the structural characteristic that usually indicates large TPA cross sections. In fact, the TPA in stilbene was first observed in 1979 by Anderson[18] in a two-photon excitation to the state at an energy of 38873 cm^{-1} above the ground state. It has also been observed that stilbene exhibits a nearly planar conformation in the gas phase. However, when the substituents are present on the chain, conformation can be substantially nonplanar. The extent of deviation from planarity of the molecule depends on the relative positions of substituents as well as the ability of the substituents to participate in the hydrogen-bonding interactions with the other atoms or groups of the system.[19] The molecular geometry also significantly affects the structure of the system in the solid state. For instance, it has been shown from X-ray studies by Martsen et al.[20] that the presence of two methoxy side groups on the rings along the PPV chain leads to a regular three-dimensional packing of the chains, whereas the presence of methyl side groups at the same position leads to a disordered structure. According to them, the disordered structure in poly(dimethyl *p*-phenylenevinylene) is mostly due to steric interactions between the methyl side groups and the hydrogen atoms attached to the vinylene double bonds; such interactions are not present in poly(dimethoxy *p*-phenylenevinylene). As the molecule becomes nonplanar, the electron coupling between the donor and acceptor substituents in a molecule reduces due to the decrease in the overlap between the π orbitals of the conjugated bridge. This in turn could affect the TPA cross sections due to changes in charge distribution between of the ground and two-photon excited states. It has indeed been reported in the literature that the torsional distortion from the planarity of 4-quinopyran donor−acceptor has led to increase in the TPA through increased charged localization and thereby tuning in the "triple" resonance conditions.[21] However, theoretical studies on difuranonaphthyl molecule indicates that TPA cross section, δ, is relatively insensitive to torsions of the terminal acceptor groups up to angles of about 50° and then the cross section decreases rapidly with increasing torsion angle.[22] Furthermore, the position of the substituents can by themselves affect the TPA cross sections of the molecule due to altered conjugation length of the π-framework in the molecule as well as due to changes in the distance of charge separation.

The above discussion of TPA in stilbene and related systems brings to the fore most of the important issues relevant to TPA in "two-photon" molecules. A thorough study of TPA in stilbene and its derivatives will thus provide insights into the factors important for designing molecules with large TPA cross sections. In this paper, we have carried out a detailed study of the TPA cross sections of stilbene and its derivative by employing the PPP Hamiltonian for the π-system. The novelty of this study is that within the given PPP model, the TPA cross sections are obtained exactly, by employing a correction vector technique for computing the TPA cross sections. The correction vector technique allows taking into account all the eigenstates of the CI-matrix exactly in the computation of the NLO coefficients without having to explicitly obtain all the excited states. Since the PPP Hamiltonian is represented by a CI-matrix using the full many-body space of the model Hamiltonian during the computation of the TPA coefficients, these coefficients thus obtained are model exact. We have carried out calculation of the TPA cross sections for stilbene with D or A substitutions at various positions and for a large number of geometries to mimic steric effects. In the next section we discuss the model Hamiltonian and the methodology. We then proceed to describe the geometries of the molecule considered by us. We present our results on the role of donor (acceptor) substitutions around the vinylic double bond. Last, we discuss the effect of steric factors on the TPA cross sections. We end the paper with a summary of the salient results.

2. Methodology

The PPP model Hamiltonian[23] is a π-electron Hamiltonian which takes into account explicit long-range electron−electron interactions among the electrons in π-orbitals. The noninteracting part of the PPP Hamiltonian is identical to the Hückel model. While considering electron−electron interactions, a zero differential overlap (ZDO) approximation is resorted to. This approximation retains only interaction terms in the electron repulsion part that is diagonal in the real space representation. If within the ZDO approximation, the range of the electron repulsions is truncated to only on-site terms, we get the familiar Hubbard model.[17,24] The long-range electron repulsions are further parametrized so that the repulsion integrals smoothly interpolate between the on-site repulsion U and e^2/r, in the limit $r \rightarrow \infty$. There are two interpolation schemes in vogue, namely, the Mataga−Nishimoto[25] interpolation and the Ohno interpolation.[26] The latter has been widely used with PPP parameters for sp^2 carbon as well as for nitrogen (with either the lone pair or the sp^2 orbital) atoms involved in π-conjugation. The parameters are quite universal and transferable from molecule to molecule.

The PPP Hamiltonian in the second-quantized form is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{int}}$$
$$\hat{H}_0 = \sum_i \epsilon_i \hat{n}_i + \sum_{\langle ij \rangle,\sigma} t_{ij}(\hat{a}^{\dagger}_{i\sigma}\hat{a}_{j\sigma} + \hat{a}^{\dagger}_{j\sigma}\hat{a}_{i\sigma})$$
$$\hat{H}_{\mathrm{int}} = \sum_i \frac{U_i}{2}\hat{n}_i(\hat{n}_i - 1) + \sum_{i>j} V_{ij}(\hat{n}_i - z_i)(\hat{n}_j - z_j) \qquad (1)$$

where $\hat{a}^{\dagger}_{i\sigma}(\hat{a}_{i\sigma})$ creates (annihilates) an electron with spin σ in the orbital involved in conjugation at site i, ϵ_i is the orbital energy of the orbital involved in conjugation at site i, t_{ij} is the transfer integral or the Hückel resonance integral between the bonded sites i and j, and U_i is the on-site correlation energy of the orbital at site i. The inter-orbital or inter-site electron repulsion parameter V_{ij} in the Ohno parametrization[26] is given by

$$V_{ij} = 14.397\left[\left(\frac{28.794}{U_i + U_j}\right)^2 + r_{i,j}{}^2\right]^{-(1/2)} \qquad (2)$$

where the distances r_{ij} are in Å, the energies U_i, V_{ij} are in eV and z_i is the local chemical potential of the orbital given by the number of electrons contributed by the orbital i to the conjugation backbone.

The PPP Hamiltonian considers only one active orbital per site, namely the π orbital on the site. This approximation is valid when the σ and π excitations are well separated energetically, which appears to be the case in systems with long conjugated backbone. Restricting to only one orbital per site has the advantage that the full CI space though large is manageable even for fairly large molecules. The Hamiltonian matrix in this space is also rather sparse and hence routinely allows accessing several low-lying states for full CI space of a few million configurations. For a given molecule, an ab initio calculation within a restricted CI space gives quite reliable excitation spectrum. However, while comparing conjugated systems of different sizes, the restricted ab initio CI calculations have the disadvantage of not preserving size consistency. Even while comparing electronic properties of molecules of the same size, but with different push−pull substituents, it is necessary to have model exact solutions for making dependable comparisons. In this regard, using a properly parametrized PPP model within full CI scheme is known to lead to reliable description of the polymer limit as well as comparisons between similar sized molecules with widely different substitutions.[27]

The PPP Hamiltonian, being spin independent, conserves both total spin and the z-component of total spin. While Slater determinants conserve the latter, a single Slater determinant is usually not an eigenstate of the total spin. Exploiting total spin symmetry has the advantage of reducing the size of the complete basis one needs to deal at a given time as well as providing complete spin-labeling of the state. However, constructing total spin eigenstates is nontrivial. We have employed the valence bond technique for constructing the total spin eigenstates. This method exploits Rumer−Pauling rules,[28] which are easily generalized to higher total spin states and configurations with doubly occupied orbitals. The resulting basis is complete although nonorthogonal. This results in a nonsymmetric matrix representation of the Hamiltonian operator. Several low-lying eigenstates of the matrix can be obtained using Rettrup's modification[29] of the Davidson algorithm.[30]

The most widely used theoretical method involved in calculating the TPA is the sum-over-states method (SOS).[31] In the SOS method, energies of several (about 30 or more) low-lying excited states and transition dipole moments among these states are computed for the Hamiltonian of the system. Using these quantities, explicit perturbation summations for each coefficient are performed at desired frequencies. In this method, the number of excited states retained is arbitrary. The assumption is that the sums are well behaved and convergence would be achieved with as few as 10−30 low-lying excited states even though the dimension of the configuration space is much larger (in millions or more). However, such summations lead to uncontrolled errors in the optic coefficients.[32] Morley et al.[33] have achieved convergence within the first 50 states of polyenes. On the other hand, Docherty and co-workers[34] have shown that convergence could not be achieved in the case of 4,4′-*N*,*N*-dimethylaminonitrostilbene.

The problem of convergence which is inherent in the SOS method can be completely avoided by employing the correction vector (CV) technique developed by Ramasesha and Soos[35] for the computation of general dynamic NLO coefficients. In this method, we can obtain the NLO coefficients without resorting to the usual procedure of explicitly solving for a large number of excited states of the CI Hamiltonian, followed by a computation of the transition dipoles among these states. The first-order CV, $\phi_i^{(1)}(\omega)$, is defined by the inhomogeneous linear algebraic equation

$$(\mathbf{H} - E_\mathrm{G} + \hbar\omega + i\Gamma)|\phi^{(1)}{}_i(\omega)\rangle = \tilde{\mu}_i|G\rangle \tag{3}$$

where $\mathbf{H}$ is the CI Hamiltonian matrix in the chosen many-body basis, E_G is the ground-state energy, ω is the frequency, $\tilde{\mu}_i = \hat{\mu}_i - \langle G|\hat{\mu}_i|G\rangle$, is the ith component of the dipole displacement operator ($i = x, y, z$) and h/Γ is the average lifetime of the excited states. It can be shown that $\phi_i^{(1)}(\omega)$, if expressed in the basis of the eigenstates $\{|R\rangle\}$ of the CI Hamiltonian $\mathbf{H}$ is given by

$$\phi_i^{(1)}(\omega) = \sum_R \frac{\langle R|\tilde{\mu}_i|G\rangle}{E_\mathrm{R} - E_\mathrm{G} + \hbar + i\Gamma}|R\rangle \tag{4}$$

Thus, by computing $\alpha_{ij}(\omega)$ as

$$\alpha_{ij}(\omega) = {}^1/_2[\langle\phi^{(1)}{}_i(\omega)|\mu_j|G\rangle + \langle\phi^{(1)}{}_i(-\omega)|\mu_j|G\rangle] \tag{5}$$

we would obtain a full SOS or equivalently, model exact $\alpha_{ij}(\omega)$ of the system. Since $\phi_i^{(1)}(\omega)$ can be solved in any basis, such as the constant M_S (Slater determinant) basis or a VB basis, we bypass the rather impossible task of computing all the eigenstates and the associated transition dipole matrix elements of the full CI Hamiltonian of large systems, otherwise necessary to get the exact $\alpha_{ij}(\omega)$. Thus, the correction vector technique affords a simple and direct way of taking into account all the excited states of a given many-body Hamiltonian in computing the dynamic linear and nonlinear response coefficients of a system. The higher order dynamic NLO coefficients require higher order CVs. A higher order CV can be defined hierarchically by replacing the ground state on the rhs in eq 4 by a CV of order one less than the unknown CV. The linear algebraic equations (eq 3) are cast in matrix form using a VB basis and are solved efficiently by using a small matrix algorithm.[36]

The standard expression for the (ij)th component of the transition matrix element for TPA to the state $|2A\rangle$ is given by[37]

$$s_{ij}(\omega) = \sum_R \left[\frac{\langle G|\tilde{\mu}_i|R\rangle\langle R|\tilde{\mu}_j|2A\rangle}{E_\mathrm{R} - E_\mathrm{G} - \omega} + \frac{\langle G|\tilde{\mu}_j|R\rangle\langle R|\tilde{\mu}_i|2A\rangle}{E_\mathrm{R} - E_\mathrm{G} - \omega}\right] \tag{6}$$

The above expression can be rewritten using the first-order CV as

$$s_{ij} = \langle\phi_i{}^{(1)}(-\omega)|\hat{\mu}_j|2A\rangle + \langle\phi_j{}^{(1)}(-\omega)|\hat{\mu}_i|2A\rangle \tag{7}$$

Orientational average of the TPA cross section $\delta_\mathrm{TP}(\omega)$ which corresponds to the observed cross section in solutions, is given by[18]

$$\delta_\mathrm{TP} = \frac{1}{30}\sum_{ij}(2s_{ii}s_{jj}^* + 4s_{ij}s_{ij}^*) \tag{8}$$

The TPA cross section can also be shown to be proportional to the imaginary part of the tumbling averaged third-order nonlinear polarizability $\bar{\gamma}$, defined at the absorption frequency of ω, i.e.

$$\delta_\mathrm{TP} \propto \mathrm{Im}\ \bar{\gamma}(-\omega{:}\omega, -\omega,\omega) \tag{9}$$

To compare the calculated TPA cross sections δ_{TP} obtained in atomic units, with experimental results, it is necessary to have a cross section with the units cm^4 s/photon (the so-called

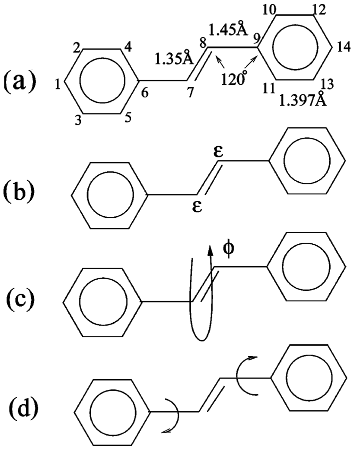

Figure 1. (a) Idealized ground-state geometry of *trans*-stilbene. (b) Stilbene with two push or two pull groups on the vinyl double bond. Magnitude ϵ correspond to strength of the substituent group and sign to the push or pull nature of the substituent. (c) Bond around which the twist is introduced. (d) Bonds around which rotations are introduced for pedallike motion.

Goppert−Mayer units). Hence, the TPA cross section directly comparable with experiment is defined as

$$\sigma_{G\rightarrow 2A} = \frac{4\pi^3 a_0{}^5 \alpha\omega^2 g(\omega)\delta_{\mathrm{TP}}}{c\Gamma} \tag{10}$$

where a_0 is the Bohr radius, c is the speed of light, α is the fine structure constant, and $\hbar\omega$ is the photon energy. The factor $(g(\omega)/\Gamma)$ relates the theoretical results to the shape of the exciting laser line defined by the function $g(\omega)$ and $\hbar/\Gamma$ is the lifetime broadening of the final state in atomic units. To make sensible comparison with previous results Γ is set equal to 0.1 eV and $g(\omega)$ is assumed to be a constant, set equal to 1. It is important to note that such a broadening corresponds to a lifetime of a few femtoseconds, which is shorter than the typical lifetime of an optically excited state.

3. Computational Details

The theoretical as well as experimental studies of *trans*-stilbene are consistent with a planar geometry in the ground state. Hence, in our studies we have taken the geometry of stilbene to be planar. Furthermore, we have assumed all bond-angles to be 120°, the ring bond-lengths to be 1.397 Å, and 1.45 and 1.35 Å for the vinylic single and double bonds, respectively (Figure 1). For the PPP model, we use the usual molecular parameters;[38] $t = 2.40$ eV for the ring transfer integrals, and 2.232 and 2.568 eV for the vinylic single and double bonds, respectively. The on-site correlations U for the carbon atom is taken to be 11.26 eV, and Ohno interpolation is employed for the intersite interactions. These values are transferable among conjugated hydrocarbons, both molecular and polymeric. Inversion and e−h symmetry lead to a $^1\mathrm{A}_g^+$ ground state,with two-photon excitations to $m^1\mathrm{A}_g^+$ states and one-photon excitations to $n^1\mathrm{B}_u^-$ states. The calculations on unsubstituted stilbene corresponds to the molecular geometry in Figure 1a. Calculations on 7,8-substituted stilbene are carried out for planar geometry by introducing site energies, ϵ at positions 7 and 8 (Figure 1b). The substitutions at the 7,8 sites could lead to a twist around the central double bond as shown in Figure 1c. Steric effects could also lead to rotations about the (6,7) and (8,9) single bonds leading to pedallike motion as shown in Figure 1d.

TABLE 1: Comparison of the Experimental and Theoretical Two-Photon $\lambda_{\max}$ and Corresponding TPA Cross Sections

	two-photon $\lambda_{\max}$ (nm)	σ (10^{-50} cm^4 s photon^{-1})
approx calcn[5]	466	27.3
experiment	514	12
exact PPP results	619	9.54 (11.6 at 514 nm)

4. Results and Discussion

Comparing TPA cross sections between experiment and theory as well as between different theories has many difficulties. To begin with, there is some uncertainty associated with the transformation of the experimental as well as theoretical quantities to Goppert−Mayer units. Besides, the model used for describing the TPA cross sections could change the TPA cross sections drastically. For instance, although a three state model is the minimal model which is used for describing the two-photon absorption of the dominating TPA state for a symmetrical molecule, as pointed earlier[39] the three state model underestimates the TPA cross section roughly by 10%. In the same context, it was pointed out by Poulsen[22] that when using a traditional sum-over-states method, one must be cautious when considering TPA cross sections obtained by summing over only a very few intermediate states. Therefore, to calibrate our studies, we have first calculated the TPA cross section of stilbene and compared them with the TPA cross section obtained by different method as well as with experiments (Table 1). We note that our calculated δ values are in far better agreement with the experimental value than those obtained from earlier theoretical calculation. However, we also note that the experimental $\lambda_{\max}$ is lower than the PPP $\lambda_{\max}$. When we calculated the TPA cross section for $\lambda = 514$ nm, there was considerable improvement in agreement between the experimental and theoretical values.

The lower TPA cross section from the exact solution of the PPP model, when compared with earlier theoretical results, is due to the fact that electron correlations are not properly taken into account in the earlier study. In the valence bond language, electron correlations reduce the weight of the “ionic” valence bond structures in low-lying states and thereby lead to smaller transition dipole matrix elements. This in turn reduces both linear and nonlinear optical response coefficients of the correlated system. It is also possible that the solvent molecules influence the TPA cross section both by reducing the excitation gaps of the low-lying states and by stabilizing the “ionic” structures and thereby increasing the contribution of these structures in the low-lying excitations.

We have also explored the effect of donor and acceptor (electron push and pull) substituents around vinylic linkage in stilbene (Figure 1). The donor or acceptor character of a given carbon atom is simulated by introducing an orbital energy for the π orbital at that site. Thus, a negative orbital or site energy, ϵ, at that site would imply favoring occupancy of the orbital and thus creating higher electron density at that site, which is equivalent to a donor group being attached to the site. An acceptor group attached to a site is simulated by a positive site energy at the site. In our study, we have introduced two donor or two acceptor groups at the vinylic site. The reason behind introducing both groups of the same type is to retain the A and B symmetry of the states. For this reason, we have also assumed that the donor strengths are identical at both the vinylic carbon atoms. We also find that the behavior of TPA is identical irrespective of having either both donor susbstituents or both acceptor substituents at the vinylic sites. Therefore, we report our studies for only the acceptor substituents at both vinylic

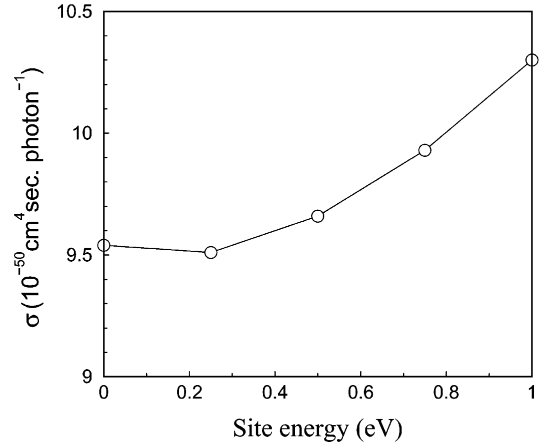

Figure 2. TPA cross section as a function of the strength of electron-donating group.

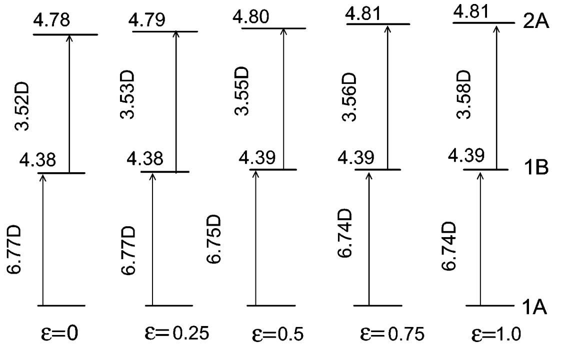

Figure 3. Energy levels (eV) and transition dipole moments (in Debye) for the three lowest singlet states for different strengths of the push−pull groups attached at vinylic position in stilbene.

sites. We find that as the strength of the donor group is increased (increasing site-energy, ϵ), the TPA cross section increases slightly, as shown in Figure 2.

In Figure 3, we have plotted the energy levels and transition dipole moments (in Debye) for the three lowest singlet states for various donor strengths represented by the magnitude of site energy, ϵ. We observe that as the site energy increases the 1A−1B transition dipole moment and the 1B−2A transition dipole moment as well as the energy gaps increase gradually. This appears to be reflected in the gradual change in the TPA cross sections. The monotonic increase in TPA cross sections implies that the TPA property of stilbene cannot be significantly altered by push or pull susbstituents.

It was conjectured by Albota[5] that symmetric charge-transfer, from the ends of a conjugated systems to the middle, or vice versa, upon excitations leads to enhanced value of δ_{tp}. We have calculated the charge density to find out the extent of charge-transfer taking place in the system upon pull group substitution for different strengths. The charge density at each site for two values of site energies, ϵ are shown below (Figure 4) in the 1^1A (ground state), the 1^1B, and the 2^1A states.

In the ground state, the charges at various sites scale linearly with ϵ. The sign of the charges at various sites can be easily rationalized in terms of resonance structures. In the 2A state, the sign of the charges on the sites are the same as in the ground state but the magnitude is slightly larger. Similar but slightly larger charge densities are seen in the 1B state. The charge density figures clearly are consistent with the conjecture of Albota[5] since the TPA cross sections also show only a slight variation with ϵ. We also note that 1^1B and 2^1A energies are also fairly insensitive to the pull strength of the substituents. This is also consistent with the earlier work of Moore et al.,[40] where enhancement in TPA cross section is associated with the lowering of one-photon gap.

We have also computed the TPA cross sections by placing the susbstituents at positions 1 and 14. Just as with the 7,8-substituted stilbene, we find very small changes in charge density distributions with strength of the electron pull groups. Electron correlations have a tendency to distribute the electron charge densities uniformly over all the sites as this would minimize electron repulsions. Thus, the correlated models show small site charge densities in the presence of substitutions and also small TPA enhancements.

5. Role of Steric Effects on the TPA Cross Sections

It is known in the literature[21,41] that the TPA cross section as well as the second harmonic generation (SHG) coefficients increase if the molecule is twisted around the bond to which the chromophores are attached. We have carried out the TPA cross section calculations for stilbene and 7,8-disubstituted stilbene for different types of rotational motions of the molecule (Figure 1, parts c and d). When substituents are placed symmetrically on the vinylic double bond, the steric effects will force a twist of the molecule around this double bond. Another type of molecular twist that can be envisaged in the case of stilbene is associated with the pedallike motion in which the rotations in opposite directions occur around the two single bonds between the phenyl carbon and the vinylic carbon atoms.[42]

It is expected that introducing a twist either by rotation about the vinylic double bond or through the pedallike motion would reduce the π-conjugation and effectively reduce the TPA cross section as in the case of fluorene.[15] This is indeed seen in unsubstituted stilbene for both pedallike motion (Figure 5, top left) and for rotation around the central double bond (Figure 5, top right). Indeed the minimum in the TPA cross section is seen when the conjugation over the whole molecule is broken by a 90° twist. It is also observed that at 90° rotation there is a sudden decrease in the transition dipole moment between 1A−1B and 1B−2A states. The drop in TPA cross section for pedallike motion is sharper than for the twist about the central double bond.

In 7,8-disubstituted stilbene, with both substituents alike (both donors or both acceptors) the effect of steric distortions is markedly different. While the pedallike motion continues to show a similar trend as with unsubstituted stilbene (Figure 5 top left), the twist around the central double bond shows a sharp increase in the TPA cross section at 60° twist angle before vanishing at a twist angle of 90° (Figure 5 bottom right).

To understand this peculiar behavior, we have computed the lowest one-photon and two-photon excitation gaps in all the four cases, namely, twist and pedal motion without and with substituent groups. These are also shown in Figure 5. We note that in the unsubstituted cases for the angles for which we have computed the energy gaps, the one- and the two-photon gaps are different. But in the substituted cases, we find a different behavior. In the case of pedallike motion with substitution, the one- and two-photon gaps are distinct at all angles except 90° while in the case of twist with substitution the one- and two-photon gaps are very nearly the same for twist angles between 30 and 90°. If only energetics were to control the TPA cross section and we could associate large TPA cross section with degeneracy of the lowest one- and two-photon states, then we should have observed large TPA cross sections at 90° in pedallike motion and between 30 and 90° for twist (both cases with substitutions). However, we note a large TPA cross section only in twist distortion at 60°. To understand this behavior, we

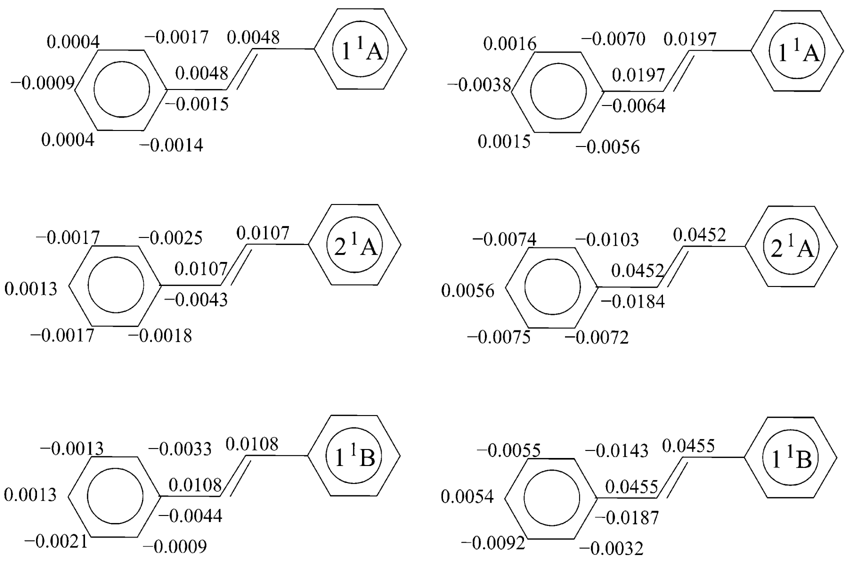

Figure 4. Site charge densities for site energy $\epsilon = 0.25$ eV (left panel) and for $\epsilon = 1.0$ eV (right panel) for the 1^1A, the 1^1B, and the 2^1A states.

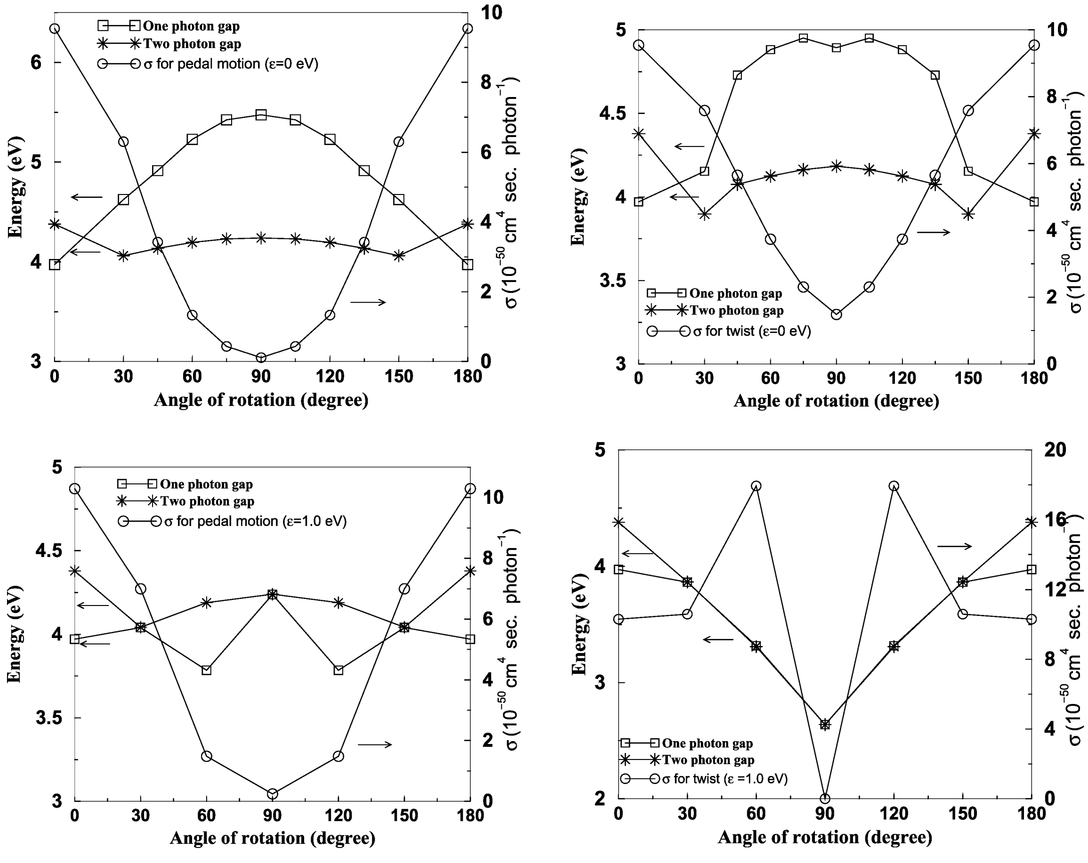

Figure 5. Two-photon absorption cross section and one- and two-photon energy gaps for pedallike motion without substitution (top left), pedallike motion with substitution (bottom left), twist without substitution (top right), and twist with substitution (bottom right).

also computed the transition dipole moments for the 1^1A → 1^1B and 2^1A → 1^1B transitions. This is presented in Table 2. We note that, at 90°, at least one of the transition dipoles is very small or vanishing. This could explain why the degeneracy of the states do not contribute to large TPA cross section. At 60°, however, in the twist distortion, both the transition dipoles are significant. This, together with degenerate one- and two-photon states, could be giving rise to a very large TPA cross section.

The behavior seen in TPA was also seen in calculations of the SHG coefficients in push−pull polyenes and in tetraalkyl-substituted-4-quinopyran.[43] In theoretical studies of substituted polyenes, it was seen that for some excited states the dipole moment showed very similar behavior.[44] The rise in TPA cross sections, just as with the SHG coefficients can be attributed to both a degeneracy of the one- and two-photon states and a nonvanishing transition dipole of the one-photon state between the ground state and the two-photon state simultaneously, in the system. What is interesting from the standpoint of design of TPA molecules is that bulkier substituents groups which lead to large twist angles are more effective in increasing the cross sections than just strong donor (acceptor) substituents with smaller steric effects. This behavior is in marked contrast to the planarity emphasized in the case of fluorene.[15]

TABLE 2: Magnitude of the Transition Dipole Vector for the $1^1A \rightarrow 1^1B$ and $2^1A \rightarrow 1^1B$ Transitions for Different Configurations of Substituted and Unsubstituted Stilbenes with and without Substitutions

angle (deg)	pedal ($\epsilon = 0.0$) $G \rightarrow B$	pedal ($\epsilon = 0.0$) $T \rightarrow B$	pedal ($\epsilon = 1.0$) $G \rightarrow B$	pedal ($\epsilon = 1.0$) $T \rightarrow B$	twist ($\epsilon = 0.0$) $G \rightarrow B$	twist ($\epsilon = 0.0$) $T \rightarrow B$	twist ($\epsilon = 1.0$) $G \rightarrow B$	twist ($\epsilon = 1.0$) $T \rightarrow B$
	transition dipole moments (D)							
0	6.77	3.52	6.74	3.58	6.77	3.52	6.77	3.52
30	6.16	0.68	0.20	0.66	6.81	0.72	0.45	1.08
60	3.68	0.37	0.07	0.21	5.90	1.93	5.77	1.59
90	1.04	0.09	0.000	0.00	0.00	11.10	0.00	11.27

[a] G refers to the ground state (1^1A), T to the two-photon state (2^1A), and B to the one-photon state (1^1B).

6. Conclusion

We have demonstrated that exact PPP calculations using model Hamiltonian can adequately model the TPA cross section of *trans*-stilbene. We have varied the site energies in the PPP model to simulate donor or acceptor substitution and have computed the TPA cross section in the 7- and 8-disubstituted stilbene with both substituent groups being identical. The results do not depend on the type of substituents (donor or acceptor). The dependence of the TPA cross sections on the strength of donor groups is weak and monotonic. Introducing either a twist around the central double bond or a pedallike rotation on unsubstituted stilbene results in a gradual decrease in the TPA cross section. This emphasizes planarity as with fluorenes. Similar effect is observed when the susbstituents are placed and the rotation carried out is from the pedallike motion. However, twisting a substituted stilbene system around the central double bond shows a nonmonotonic dependence of the TPA cross section on the twist angle. At a twist angle of about 60° the TPA cross section increases sharply (by ≈70%). This increase is associated with near degeneracy of the one- and two-photon states together with nonvanishing transition dipole between the one-photon state and the ground and two-photon states. This study shows that bulky electron-donating or electron-withdrawing substituents which can twist the stilbene molecule around the central double bond could lead to molecules with very large TPA cross sections.

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