Visualizations of transition dipoles, charge transfer, and electron-hole coherence on electronic state transitions between excited states for two-photon absorption

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The one-photon absorption (OPA) properties of donor- π -bridge-acceptor- π -bridge-donor $(D-\pi-A-\pi-D)$ -type 2,1,3-benzothiadiazoles (BTD) were studied with two dimensional (2D) site and three dimensional (3D) cube representations. The 2D site representation reveals the electron-hole coherence on electronic state transitions from the ground state. The 3D representation shows the orientation of transition dipole moment with transition density, and the charge redistribution on the excited states with charge difference density. In this paper, we further developed the 2D site and 3D cube representations to investigate the two-photon absorption (TPA) properties of $D - \pi - A - \pi - D$ -type BTD on electronic transitions between excited states. With the new developed 2D site and 3D cube representations, the orientation of transition dipole moment, the charge redistribution, and the electron-hole coherence for TPA of $D-\pi$ - $A-\pi$ -D-type BTD on electronic state transitions between excited states were visualized, which promote deeper understanding to the optical and electronic properties for OPA and TPA. © 2008 American Institute of Physics. [DOI: 10.1063/1.2829407]

I. INTRODUCTION

Molecular two-photon absorption¹ (TPA) has gained interest over recent years owing to its applications in various fields, including spectroscopy, optical data storage,² optical power limitation,³ microfabrication,⁴ and three-dimensional imaging.⁵ Various design strategies have been employed to synthesize organic molecules with large two-photon absorption cross sections, such as donor-bridge-acceptor $(D-\pi-A)$ and donor-bridge-donor $(D-\pi-D)$ derivatives, donoracceptor-donor (D-A-D), acceptor-donor-acceptor (A-D-A)and $D - \pi - A - \pi - D$, and star structure.⁶⁻¹⁶

TPA is a nonlinear absorption process wherein two photons are absorbed simultaneously. Characteristic features are adherence to even-parity selection rules and quadratic intensity dependence, while one-photon absorption processes typically conform to odd-parity selection rules and linear intensity dependence. The two-photon absorption coefficient α_2 is proportional to the imaginary part of the third-order susceptibility tensor.¹⁷ At the molecular level, the macroscopic χ_3 can be replaced by the third-order molecular nonlinearity. Thus, the molecular two-photon absorption cross section can be characterized by the imaginary part of the molecular third-order nonlinear polarizability, defined at an absorption frequency of ω as $\alpha_2(\omega) \propto \text{Im } \gamma(-\omega)$.^{18,19} It can also be determined by computing the TPA transition matrix elements between the initial and finial states based on the

sum-over-state formalisms.²⁰⁻²⁴ With the recent advances in the theory and application of DFT to time dependent properties and quadratic response functions, such applications have absorption.^{25–29} proposition in two-photon

Visualization tools and techniques have become very useful tools to understand the excited state properties.³⁰ We have developed visual methods [two dimensional (2D) site and three dimensional (3D) cube representations]³¹⁻³³ for one-photon absorption (OPA). The 2D site representation reveals visually the electron-hole coherence during electronic transitions from the ground state. The 3D cube representations show visually the orientation of transition dipole moment by transition density, and the charge redistribution on the excited states by charge difference density.

The purpose of this study is to further develop the 2D site and 3D cube representations for TPA on electronic transitions between excited states. With which the orientation of transition dipole moment, the charge redistribution, and the electron-hole coherence for TPA of molecules (with nonlinear properties) on electronic transitions between excited states were visualized. It should be noted that our 2D and 3D representations are specifically designed to be used with sum-over-state formalisms where all states are constructed. In this paper, the $D-\pi$ - $A-\pi$ -D-type 2,1,3-benzothiadiazoles (BTD) (see Fig. 1) was investigated to examine our new developed methods, as an example, since $D-\pi$ -A- π -D-type BTD have shown the excellent nonlinear optical excited state properties.¹⁴

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FIG. 1. (Color online) (a) The chemical structure of $D-\pi -A-\pi -D$ -type 2,1,3-benzothiadiazoles. (b) It is classified for A-J units for Figs. 6 and 9.

II. METHODS

A. Two-photon absorption

The OPA properties of charge transfer and electron-hole coherence on the electronic transition from the ground state were detailed described in Ref. 31–33. In this paper, we focus on the TPA properties on the electronic transitions among excited states with the visualized 2D site and 3D cube representations.

The TPA cross section, directly comparable with experimental measurement, is defined as $^{20-22}$

$$\sigma_{\rm tp} = \frac{4\pi^2 a_0^3 \alpha}{15c_0} \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{\rm tp},\tag{1}$$

where α_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, ω is the photon energy of the incident light, and $g(\omega)$ denotes the spectral line profile, here it is assumed to be a δ function. Γ_f is lifetime broadening of the final state.⁹ The TPA probability [δ_{tp} in Eq. (1)] of molecules excited by a linearly polarized monochromatic beam can be calculated by

$$\delta_{tp} = 6(S_{xx} + S_{yy} + S_{zz})^2 + 8(S_{xy}^2 + S_{xz}^2 + S_{yz}^2 - S_{xx}S_{yy} - S_{xx}S_{zz} - S_{yy}S_{zz}), \qquad (2)$$

where $S_{\alpha\beta}$ a is two-photon matrix element for the two-photon resonant absorption of identical energy. $S_{\alpha\beta}$ can be calculated with sum-over-state formulas,

$$S_{\alpha\beta} = \sum_{j} \left[\frac{\langle f | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | g \rangle}{\omega_{j} - \omega_{f} / 2 - i\Gamma_{f}} + \frac{\langle f | \mu_{\beta} | j \rangle \langle j | \mu_{\alpha} | g \rangle}{\omega_{j} - \omega_{f} / 2 - i\Gamma_{f}} \right], \tag{3}$$

where $|g\rangle$ and $|f\rangle$ denote the ground state and final states, respectively, $|j\rangle$ means all the states, ω_j is the excited energy of excited states, and μ is electronic dipole moment. If we take into account only the products of two-photon transition matrix elements with the same intermediates state (j=j') and neglect the products having different intermediate states $(j \neq j')$, δ_{tp} is expected as^{22,24}



FIG. 2. (Color online) The schematic representation of the electronic configurations from Ref. 23.

$$\delta_{tp} = 8 \sum_{\substack{j \neq g \\ j \neq f}} \frac{|\langle f | \boldsymbol{\mu} | j \rangle|^2 |\langle j | \boldsymbol{\mu} | g \rangle|^2}{(\omega_j - \omega_f / 2)^2 + \Gamma_f^2} (1 + 2 \cos^2 \theta_j) + 8 \frac{|\Delta \boldsymbol{\mu}_{fg}|^2 |\langle f | \boldsymbol{\mu} | g \rangle|^2}{(\omega_f / 2)^2 + \Gamma_f^2} (1 + 2 \cos^2 \phi),$$
(4)

where θ_j is the angle between the vector $\langle f | \boldsymbol{\mu} | j \rangle$ and $\langle j | \boldsymbol{\mu} | g \rangle$, $\Delta \boldsymbol{\mu}_{fg} = \langle f | \boldsymbol{\mu} | f \rangle - \langle g | \boldsymbol{\mu} | g \rangle$ is the difference between the permanent dipole moments of the excited and ground states, and the ϕ is the angle between the two vectors $\Delta \boldsymbol{\mu}_{fg}$ and $\langle f | \boldsymbol{\mu} | g \rangle$. In the derivation of Eq. (4), the two-photon resonance condition, $\omega_j = \omega_f / 2$, is used. The first and the second terms are called the three state term and the dipole (two states) terms, respectively. For the central symmetrical molecules, the dipole terms is vanishingly small, because of $\Delta \boldsymbol{\mu}_{fg} = \langle f | \boldsymbol{\mu} | f \rangle$ $\approx \langle g | \boldsymbol{\mu} | g \rangle \approx 0.^{23} \Delta \boldsymbol{\mu}$ can be obtained by a finite field method on the excitation energy. The transition energy dependence on the static electric field F can be expressed as³⁴

$$E_{\rm exc}(F) = E_{\rm exc}(0) - \Delta \mu F - \frac{1}{2} \Delta \alpha F^2, \qquad (5)$$

where $E_{\text{exc}}(0)$ is the excitation energy at zero field, and $\Delta \alpha$ is the change in polarizability.

B. 3D cube representation for TPA

The singlet B_u (OPA allowed) and A_g (TPA allowed) excited states (see Fig. 2) can be written as, respectively,

$$|\psi_{j}(B_{u})\rangle = \sum_{\substack{\mu \in unocc\\ o \in occ}} C_{j\mu o}(a_{u} \leftarrow b_{g})a_{\mu}^{+}(a_{u})a_{o}(b_{g})|\psi_{g}(A_{g})\rangle$$
(6)

and

$$\begin{aligned} |\psi_k(A_g)\rangle_{\pm} &= \sum_{\substack{m \in unocc\\n \in occ}} \left[C_{kmn}(b_g \leftarrow b_g) a_m^+(b_g) a_n(b_g) \right. \\ &\pm C_{kmn}(a_u \leftarrow a_u) a_m^+(a_u) a_n(a_u) \right] |\psi_g(A_g)\rangle. \end{aligned}$$

In Eq. (7), $|\psi_k(A_g)\rangle_-$ and $|\psi_k(A_g)\rangle_+$ stand for the second and the higher A_g (two-photon allowed) excited states, respectively.²³ So, the electronic state dipolar transitions from $|\psi_i(B_u)\rangle$ to $|\psi_k(A_g)\rangle$ can be written as

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$${}_{\pm} \langle \psi_k(A_g) | \boldsymbol{\mu} | \psi_j(B_u) \rangle = \sum_{m,\mu \in unocc} C_{kmn}(b_g \leftarrow b_g)$$

$$\times C_{j\mu o}(a_u \leftarrow b_g) \boldsymbol{\mu}_{m \leftarrow u}(b_g \leftarrow a_u)$$

$${}_{\pm} \sum_{n,o \in occ} C_{kmn}(a_u \leftarrow a_u)$$

$$\times C_{j\mu o}(a_u \leftarrow b_g) \boldsymbol{\mu}_{n \leftarrow o}(a_u \leftarrow b_g).$$

$$(8)$$

The relation between transition dipole moment and transition density is³⁵

$$\mu_{k,j} = e \int \mathbf{r} \rho_{k,j}(\mathbf{r}) d^3 \mathbf{r}, \qquad (9)$$

and the transition density contains information about the spatial location of the excitation. Thus, the transition density on electronic transition between excited states for TPA can be written as

$$\rho_{\pm} = \sum_{m,\mu \in unocc} C_{kmn}(b_g \leftarrow b_g) C_{j\mu o}(a_u \leftarrow b_g) \varphi_m \varphi_u$$
$$\pm \sum_{n,o \in occ} C_{kmn}(a_u \leftarrow a_u) C_{j\mu o}(a_u \leftarrow b_g) \varphi_n \varphi_o, \quad (10)$$

where the $\varphi_m(\varphi_u)$ and $\varphi_n(\varphi_o)$ stand for the unoccupied and occupied molecular orbitals (cubes). The charge difference density on the electronic transition from the *j* excited state to the *k* excited states for TPA can be written as

$$\Delta \rho_{\pm,k,j} = \Delta \rho_{\pm,m,u} \pm \Delta \rho_{\pm,n,o},\tag{11}$$

where $\Delta \rho_{\pm,m,u}$ and $\Delta \rho_{\pm,n,o}$ are

$$\Delta \rho_{\pm,m,u} = \sum_{\substack{m,m',\mu \in unocc}} C_{j\mu o}(a_u \leftarrow b_g) C_{kmn}(b_g \leftarrow b_g)$$
$$\times C_{km'n}(b_g \leftarrow b_g) \varphi_m \varphi_{m'}$$
$$- \sum_{\substack{m,\mu,u', \in unocc}} C_{j\mu o}(a_u \leftarrow b_g)$$
$$\times C_{j\mu'o}(a_u \leftarrow b_g) C_{kmn}(b_g \leftarrow b_g) \varphi_u \varphi_{u'}$$
(12)

and

$$\Delta \rho_{n,o} = \sum_{n,n' \, o \in occ} C_{kmn}(a_u \leftarrow a_u) C_{kmn'}(a_u \leftarrow a_u)$$
$$\times C_{j\mu o}(a_u \leftarrow b_g) \varphi_n \varphi_{n'}$$
$$- \sum_{n,o,o' \in occ} C_{kmn}(a_u \leftarrow a_u) C_{j\mu o}(a_u \leftarrow b_g)$$
$$\times C_{i\mu o'}(a_u \leftarrow b_g) \varphi_o \varphi_{o'}. \tag{13}$$

C. 2D site representation

The electron-hole coherence on the electronic transition from the j excited state to the k excited states for TPA can be analyzed by the transition density matrix in a site representation. We characterize the nature of the various excited states by calculating the electron-hole two-particle wave functions at the INDO/SCI level. This leads to a twodimensional grid running over all the carbon sites along each axis. Each data point (x, y) gives the probability $|\psi(x, y)|^2$ of finding one charged particle on site x and the second one on site y. The probability amplitudes $|\psi_j(B_u, q, r)\rangle$ (OPA allowed) and $|\psi_k(A_g, q, r)\rangle_{\pm}$ ($|\psi_k(A_g, q, r)\rangle_{-}$ and $|\psi_k(A_g, q, r)\rangle_{+}$ stand for the second and the higher A_g two-photon allowed excited states, respectively) have one charged particle in atomic orbital q (which can be a 2s, 2px, 2py, or 2pz orbital) on site x and the second in atomic orbital r on site y given by

$$|\psi_j(B_u,q,r)\rangle = \sum_l C_l^{\text{CI}}(a_u \leftarrow b_g) C_q^{\text{LCAO}}(a_u,h^+) C_r^{\text{LCAO}}(b_g,e^-)$$
(14)

and

$$\begin{aligned} |\psi_k(A_g,q,r)\rangle_{\pm} \\ &= \sum_l C_l^{\text{CI}}(b_g \leftarrow b_g) C_q^{\text{LCAO}}(b_g,h^+) C_r^{\text{LCAO}}(b_g,e^-) \\ &\pm \sum_l C_l^{\text{CI}}(a_u \leftarrow a_u) C_q^{\text{LCAO}}(a_u,h^+) C_r^{\text{LCAO}}(a_u,e^-), \end{aligned}$$
(15)

where $C_q^{\text{LCAO}}(h^+)$ and $C_r^{\text{LCAO}}(e^-)$ are the corresponding linear combination of atomic orbitals coefficients in the occupied and unoccupied molecular orbitals involved in the *l*th configuration. The C_l^{CI} are the associated configurationinteraction (CI) expansion coefficient. The orthonormalization of the basis set imposed by the ZDO approximation ensures that

$$P_{k \leftarrow j}(A_g \leftarrow B_u) = \big|_{\pm} \langle \psi_k(A_g, x, y) \big| \psi_j(B_u, x, y) \rangle \big|^2$$
$$= \sum_{q \in x} \sum_{r \in y} \big|_{\pm} \langle \psi_k(A_g, q, r) \big| \psi_j(B_u, q, r) \rangle \big|^2.$$
(16)

D. Quantum chemical calculations

All the quantum chemical calculations were performed with GAUSSIAN 03 suite.³⁶ The ground state geometry was optimized with PM3 method.³⁷ The excited state properties were done with ZINDO method.³⁸ The ZINDO calculation consists of a Hartree-Fock calculation on a parameterized STO basis and a subsequent diagonalization of the singleconfiguration-interaction (single-CI) Hamiltonian. All integrals are parameterized except for the exchange integrals in

TABLE I. Transition energies (eV, nm) and their oscillator strengths (f) and CI coefficients for the orbital transitions for OPA.

	eV	nm	f	CI coefficients
S_1	2.7187	456.05	0.3841	$0.564\ 89\ (H-2\rightarrow L);\ -0.351\ 31\ (H\rightarrow L)$
S_2	3.4926	355.00	0.0014	
S_3	3.5926	345.11	0.0026	$-0.408\ 90\ (H-3\rightarrow L);\ 0.410\ 97(H\rightarrow L)$
S_4	3.9525	313.69	0.0114	$-0.55876 (H-10 \rightarrow L)$
S_5	3.9629	312.86	0.5048	
S_6	4.0536	305.86	0.1268	$0.558\ 13\ (H-7 \to L)$
S_7	4.1295	300.24	1.3399	
S_8	4.1726	297.14	0.0718	
S_9	4.1774	296.80	0.0331	
S_{10}	4.1952	295.54	0.0416	

TABLE II. The transition dipole moments (a.u.) for three strong absorption peaks for OPA, and the permanent static dipole moment on the ground state.



the two-electron interaction among orbitals belonging to different centers. This parameterization implicitly takes into account a part of the electron correction, which is not included in *ab initio* single-CI calculation.

The parameters for simulating the OPA and TPA spectra are the transition energies, the transition moments between the ground state and excited states, and the transition moments between the different excited states (with keyword ZINDO=All TransitionDensities), which were listed in Tables I–III. For simulating the OPA spectrum, the lowest 20 excited states were taken into account. This choice is enough since the energy of 20th excited state is up to ~250 nm. For simulating the TPA spectrum, the lowest seven excited states were taken accounted, since the transition dipole moments (excitation from the ground state) for higher excited states are small.

III. RESULTS AND DISCUSSION

A. One-photon absorption

Before discussing the TPA properties, we firstly discuss the OPA properties obtained from the calculation. From the simulated OPA spectrum (the damping constant is set to 3000 cm^{-1}), there are three strong electronic states below 4.133 eV (300 nm) in [see Fig. 3(a)]. The orbital transitions for the first ten excited states were listed in Table I, which were also used in the calculations for TPA. The observed absorption peak is ~426 nm, while the calculated S_1 is at 456 nm. The shifts of 30 nm between experimental and theoretical result from the ignorance of solvent effect. The calculated transition dipole moments were listed in Table II. The orientations of three transition dipole moments were shown in Fig. 4, which is consistent with the calculated results in Table II. Furthermore, the transition dipole moment for the neutral species (see Fig. 4) is constitute with a series of small transition dipoles-one permonomeric unit.^{32,35} The charge difference density allows us to follow the change of TABLE III. The transition dipole moments (a.u.) between excited states for three strong absorption peaks of TPA.

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	x	У	Z
S _{1,0}	-2.4010	-0.0037	0.0490
S _{2,1}	0.0335	-0.2701	-0.0409
S _{3,1}	2.9218	0.0087	-0.0755
S _{4,1}	1.6201	-0.0034	-0.0390
S _{5,1}	-0.0991	-0.1443	0.0617
S _{6,1}	-1.3807	-0.0032	0.0355
S _{7,1}	-0.0274	0.7309	-0.1072
S _{3,2}	-2.0617	-0.0417	0.0599
S _{4,2}	2.4633	0.0796	-0.0734
S _{5,2}	0.0587	-1.1118	-1.1118
S _{6,2}	0.2768	0.0027	-0.0074
S _{7,2}	-0.0399	-0.6317	0.0920
S _{4,3}	0.3342	0.9204	-0.1754
S _{5,3}	-6.1115	0.0532	0.1428
S _{6,3}	-0.0199	0.5270	-0.0694
S _{7,3}	-3.8198	0.0056	0.0912
S _{5,4}	3.1672	0.0445	-0.0875
S _{6,4}	-0.0039	-0.3414	0.1478
S _{7,4}	1.7550	0.0339	-0.0405
S _{6,5}	0.2696	-0.0286	0.0094
S _{7,5}	0.1328	-0.6243	0.1196
S _{7,6}	0.5249	-0.0022	-0.0234

the static charge distribution upon excitation. From Fig. 5, all of these three excited states with strong absorption are the charge transfer excited states, and all the electrons transfer from the donor or bridge to the acceptor, but with different charge transfer capabilities. For example, for the first excited states, the electrons on the BTD (the acceptor) transferred only from the nearest bridges, while the electrons on the BTD transferred from all the four bridge units (except that from the donor units) for S_5 , which means that the electron oscillation of S_5 is stronger than that of S_1 . From Fig. 5, S_7 is of the strongest charge transfer capability (or the largest size of electron oscillation) among these three excited states, and the donor units also provide electrons. The charge transfer properties of these three excited states were also studied with 2D site representation (see Fig. 6), with which the electronhole coherence on the excitation can also be clearly observed. The exciton sizes (largest off-diagonal extent of the nonzero matrix area)³⁹ for these excited states are also consistent with the results of charge difference densities.

B. Two-photon absorption

The simulated TPA spectrum is shown in Fig. 3(b), where the damping constant is set to 0.1 eV, which is the commonly used value,⁹ and corresponds to lifetimes of a few femtoseconds. In the simulation, the transition dipole moments between excited states were listed in Table III. From



FIG. 3. (Color online) The (a) one-photon absorption and (b) two-photon absorption spectra.

the TPA spectrum, the absorption strengths of lowest two singlet excited states are very weak. For the first singlet excited state of TPA, the only contribution is from the dipolar term in Eq. (4). The $\Delta \mu_{10}$ is very small, since the electronic static permanent dipole moments at the ground and the excited states are very small, respectively, because $D-\pi -A-\pi -D$ -type BTD is the central symmetrical molecule.²³ So, the absorption of the first excited state is very weak. The second singlet excited state of TPA is mainly



FIG. 4. (Color online) The transition densities for OPA on the electronic state transition from the ground state. The green and red colors stand for hole and electron, respectively. The isovalue is 4×10^{-4} in a.u.



FIG. 5. (Color online) The charge difference densities for OPA on the electronic state transition from the ground state. The green and red colors stand for hole and electron, respectively. The isovalue is 4×10^{-4} in a.u.

contributed from the three state term in Eq. (4). The transition dipole moment $\langle 1 | \boldsymbol{\mu} | 0 \rangle$ is large (see data in Table II), while the transition dipole moment $\langle 2|\boldsymbol{\mu}|1\rangle$ is vanishingly data in Table (see III). So, small $\delta_{\rm tn}(S_2)$ $= [|\langle 2|\boldsymbol{\mu}|1\rangle|^2 |\langle 1|\boldsymbol{\mu}|0\rangle|^2 / (\omega_1 - \omega_2/2)^2 + \Gamma^2](1 + 2\cos^2\theta_1)$ is very small. The reason why $\langle 2|\boldsymbol{\mu}|1\rangle$ is small can be interpreted with Eq. (10). In Eq. (10), the transition dipole moment for S_2 is $\rho_{-}(S_2)$, and the first term is almost equal to the second term in $\rho_{-}(S_2)$, according to the alternancy symmetry (hole-particle symmetry).⁴⁰⁻⁴⁴ In case of neutral alternant π -conjugated hydrocarbon systems, this symmetry strictly holds in the framework of π -electron theory such as simple Hückel or Pariser-Parr-Pople-CIS methods, which gives rise to the simple rules, $\rho_{-}(S_2)=0$, due to a selection rule called pseudoparity selection rule.⁴² For the ZINDO calculation, the calculated orientation of transition density for $S_{2,-1}$ is from F to E unit of BTD (see Fig. 7), which is consistent with the result in Table III. Since the orientation of transition density is perpendicular to the molecular axis from F to E unit of BTD, the electrons should transfer from F to E unit, which can be seen from the charge difference density in Fig. 8. The contour plot of transition density matrix of S_2 (see Fig. 9) supports the above conclusion, since the electron-hole coheres between E and F units of BTD. For $S_{2\leftarrow 1\leftarrow 0}$ in TPA, the first step $(S_{1,-0})$ is that some electrons transfer from E to F unit, while for the second step $(S_{2\leftarrow 1})$, the transferred electrons on F unit move back to E unit. So, the second step contraflows the orientation of electron transfer in the first step for TPA.

From Fig. 3(b), the third excited state is the strong absorption in TPA, and there are two channels for this excited state, $\delta_{tp}(S_3 \leftarrow S_2 \leftarrow S_0)$ and $\delta_{tp}(S_3 \leftarrow S_1 \leftarrow S_0)$. μ_{2-0} is small, though μ_{3-2} is large (see data in the Table III), so $\delta_{tp}(S_3 \leftarrow S_2 \leftarrow S_0)$ should be small. Since μ_{1-0} and μ_{3-1} are large (see data in Tables II and III), the strong absorption of S_3 for TPA is mostly contributed from $\delta_{tp}(S_3 \leftarrow S_1 \leftarrow S_0)$. For OPA, the transition density, charge difference density, and electronhole coherence for the electronic state transition from the ground state to the first excited state have been visualized in



FIG. 6. (Color online) Contour plots of transition density matrix for OPA. The color bar is shown at the right of last figure, and the absolute values of matrix elements are scaled to a maximum value of 1.0.

Figs. 4–6. For TPA, it is of great significant to visualize them, since they can promote deeper understanding to the optical and electronic properties for TPA. The transition density of $\rho_{3\leftarrow 1}$ can be seen from Fig. 7. By comparing the $\rho_{3\leftarrow 1}$ and $\rho_{1\leftarrow 0}$, one can see that they are of the opposite orientation, and $\mu_{3\leftarrow 1}$ should be larger than $\mu_{1\leftarrow 0}$, since the electrons and holes for $\rho_{3\leftarrow 1}$ are localized at both ends of the molecule, while the electrons and holes for $\rho_{1\leftarrow 0}$ are localized at center of the molecule. $\mu_{3\leftarrow 1} > \mu_{1\leftarrow 0}$ can be sup-



FIG. 7. (Color online) The transition densities for TPA on the electronic state transition between excited states. The green and red colors stand for hole and electron, respectively. The isovalue is 4×10^{-4} in a.u.

ported by the calculated results in Tables II and III. The orientation and strength of $\mu_{3\leftarrow 1}$ derived from $\rho_{3\leftarrow 1}$ are consistent with the calculated results in Table III. Because $\mu_{3\leftarrow 1} > \mu_{1\leftarrow 0}$, the charge transfer capability for $S_{3\leftarrow 1}$ is larger than that of $S_{1\leftarrow 0}$, which can be supported by the charge difference densities listed in Fig. 8. For $S_{1\leftarrow 0}$, the electrons transferred from the nearest bridges to BTD, while for $S_{3\leftarrow 1}$ is larger than that of $S_{1\leftarrow 0}$. Furthermore, from Fig. 8, the electrons bridge and BTD. From Fig. 9, the exciton size of $S_{3\leftarrow 1}$ is larger than that of $S_{1\leftarrow 0}$. Furthermore, from Fig. 8, the electrons on BTD for $S_{3\leftarrow 1}$ are all transferred from the outer bridge, since there are no electron-hole pairs on the BTD, while for $S_{1\leftarrow 0}$ there is much localized excitation on BTD,



FIG. 8. (Color online) The charge difference densities for TPA on the electronic state transition between excited states. The green and red colors stand for hole and electron, respectively. The isovalue is 4×10^{-4} in a.u.



FIG. 9. (Color online) Contour plots of transition density matrix for TPA, which are $S_{1,0}$ and $S_{3,1}$. The color bar is shown at the right of last figure, and absolute values of matrix elements are scaled to a maximum value of 1.0.

IV. CONCLUSION

Based on our previous development on the visualization methods of 2D site and 3D cube representations for OPA on the electronic transition from the ground state, the visualization methods of 2D site and 3D cube representations for TPA on the electronic transitions between excited states have been successfully further developed, which promote deeper understanding to the optical and electronic properties for TPA.

V. PROSPECTIVE

The 2D and 3D representations in this paper are specifically designed to be used with sum-over-state formalisms where all states are constructed. Equation (3) is often called transition polarizability,^{48,49} or (first order) transition hyperpolarizability,^{48,49} which is directly connected with the TPA probability. The visualizations of the transition polarizability or (first order) transition hyperpolarizability with 2D and 3D representations are on the way. The advantage of response theory^{25–29} is that intermedi-

The advantage of response theory^{23–29} is that intermediate states are never explicitly constructed, so one does not have to worry about convergence issues with respect to number of intermediate states. We are also trying to implement our 2D and 3D representations in conjunction with quadratic response function techniques in the DALTON program.⁵⁰

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