Vol 14 No 11, November 2005
1009-1963/2005/14(11)/2202-06

Chinese Physics

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Solvent effects on optical properties of a newly synthesized two-photon polymerization initiator: BPYPA*

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(Received 24 March 2005; revised manuscript received 11 May 2005)

Time-dependent hybrid density functional theory in combination with polarized continuum model is applied to study the solvent effects on the geometrical and electronic structures as well as one- and two-photon absorption processes, of a newly synthesized asymmetrical charge-transfer organic molecule bis-(4-bromo-phenyl)-[4-(2-pyridin-4-yl-vinyl)-phenyl]-amine (BPYPA). There exist two charge-transfer states for the compound in visible region. The two-photon absorption cross section calculated by a three-state model and solvatochromic shift of the charge-transfer states are found to be solvent-dependent, where a nonmonotonic behaviour with respect to the polarity of the solvents is observed. The numerical results show that the organic molecule exhibits a rather large two-photon absorption cross section as compared with the compound 4-trans-[p-(N, N-Di-n-butylamino)-p-stilbenyl vinyl] pyridine (DBASVP) reported previously, and is predicted to be a good two-photon polymerization initiator. The hydrogen-bond effect is analysed. The computational results are in good agreement with the measurements.

Keywords: few-state model, two-photon absorption, solvent effect
PACC: 3280K, 3120A, 4265

1. Introduction

The newly established two-photon technology has developed rapidly in recent years because it has many applications in a wide range of fields, such as laser scanning fluorescence microscopy,[1] optical limiting,[2] upconverted lasing,[3] three-dimensional optical data storage,[4] and microfabrication.[5] For the last two applications, two-photon polymerization plays a key role, which takes the advantage of a unique feature of the two-photon absorption (TPA), namely the quadratic dependence of the process on the intensity of laser pulse. Most importantly, the discovery of organic molecules with a very large TPA cross section has made these applications possible.[6,7] Great efforts have then been paid to establish a so-called structure-to-property relation of chromophores. The available research results indicate that the TPA activities of organic compounds are strongly related to a few factors such as the conjugated length, the π centre property, the symmetrical or asymmetrical arrangement of electron-donor(D) and electron-acceptor(A) attached to the π center and their strengths for pushing and pulling electrons, and the dimension of the molecule.[8−12] These factors have been extensively considered in the material design and synthesis.

Recently, a new two-photon polymerization initiator bis-(4-bromo-phenyl)-[4-(2- pyridin-4-yl-vinyl)-phenyl]-amine (abbreviates to BPYPA) has successfully been synthesized and shown to be a good two-photon polymerization initiator.[13] During the measurement, the initiator and oligomers are mixed in a thin film. Substantial medium effects on the electronic and geometrical structures of the initiator can thus be expected. Therefore, the studies of solvent effect are related not only to the development of the present theory, but also to the illustration of the experimental results conducted in solution.

In the present work, we carry out calculations

*Project supported by the National Natural Science Foundation of China (Grant No 10274044) and Shandong Natural Science Foundation (Grant No Y2004A08).

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for the newly synthesized two-photon polymerization initiator using the time-dependent density functional theory (DFT). The solvent effects on the electronic structure of the molecule, as well as one- and two-photon absorptions, are studied by means of polarized continuum model (PCM). The hydrogen-bond effect on the electronic structure of the molecule in ethanol solution is considered. The computational scheme further develops the model outlined in previous work and is applied to the present charge-transfer system.

2. Computation details

The transition probability of one-photon absorption (OPA) is given by oscillator strength

$$\delta_{\mathrm{opa}} = \frac{2\omega_f}{3} \sum_{\alpha} |\langle 0| \mu_\alpha |f\rangle|^2, \tag{1}$$

where μ_α is the electric dipole moment operator, ω_f denotes the excitation energy of the excited state $|f\rangle$, $|0\rangle$ denotes the ground state, and the summation is performed over the molecular x, y and z axes.

The TPA cross section that can be directly compared with experiment is defined as

$$\sigma_{\mathrm{tpa}} = \frac{4\pi^2 a_0^5 \alpha}{15 c_0} \frac{\omega^2 g(\omega)}{\Gamma_{\mathrm{f}}} \delta_{\mathrm{tpa}}, \tag{2}$$

where a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, and ω is the photon energy of the incident laser beam. $g(\omega)$ provides the spectral line profile, which is assumed to be a δ-function in the present work, and the level broadening Γ_{f} of the final state is assumed to have the commonly used value[6] Γ_{f}=0.1eV, with a corresponding lifetime of a few femtoseconds. δ_{tpa} is the microscopic TPA cross section defined by the TPA transition matrix element $S_{\alpha\beta}$ between the ground state $|0\rangle$ and the final state $|f\rangle$

$$S_{\alpha\beta} = \sum_i \left[\frac{\langle 0| \mu_\alpha |i\rangle \langle i| \mu_\beta |f\rangle}{\omega_i - \omega} + \frac{\langle 0| \mu_\beta |i\rangle \langle i| \mu_\alpha |f\rangle}{\omega_i - \omega} \right], \tag{3}$$

where α, $\beta \in (x, y, z)$, and ω is the photon energy of the incident laser beam, $2\omega = \omega_f$, ω_f is the energy difference between the initial and the final states. The microscopic TPA cross section of molecules excited by a linearly polarized monochromatic beam can be calculated by

$$\begin{aligned} \delta_{\mathrm{tpa}} =& 6 (S_{xx} + S_{yy} + S_{zz})^2 \\ &+ 8(S_{xy}^2 + S_{xz}^2 + S_{yz}^2 - S_{xx}S_{yy} \\ &- S_{xx}S_{zz} - S_{yy}S_{zz}). \end{aligned} \tag{4}$$

The calculation of TPA cross section requires in general the knowledge of all excited states. The most straightforward and reliable approach to computing TPA cross section is response theory, because the single residue of the quadratic response function is directly associated with the TPA transition matrix elements. On the other hand, for the conjugated charge-transfer molecules, a few-state model can often provide satisfactory results for the low-lying excited states.[6,8,14–17] For the one-dimensional chromophore,[13] only the component along the molecular conjugation backbone, the z axis needs to be included. If a three-state model is taken into consideration, Eq.(4) can be simplified as

$$\delta_{\mathrm{tpa}} = 6S_{zz}^2 = \delta_{\mathrm{tpa}}^1 + \delta_{\mathrm{tpa}}^2 + \delta_{\mathrm{tpa}}^{12},$$

and

$$\begin{aligned} \delta_{\mathrm{tpa}}^1 &= 24 \left(\frac{\mu_z^{01} \Delta\mu_z}{\Delta E_1} \right)^2, \\ \delta_{\mathrm{tpa}}^2 &= 24 \left(\frac{\mu_z^{02} \mu_z^{21}}{\Delta E_2} \right)^2, \\ \delta_{\mathrm{tpa}}^{12} &= 24 \frac{\mu_z^{01} \Delta\mu_z \mu_z^{02} \mu_z^{21}}{\Delta E_1 \Delta E_2}, \end{aligned} \tag{5}$$

where $\Delta E_i = \hbar\omega_i - \hbar\omega_f/2$ $(i = 1, 2)$, $\Delta\mu_z = \mu_z^{ff} - \mu_z^{00}$ denotes the dipole moment difference between the excited state $|f\rangle$ and the ground state, μ_z^{ij} means the transition dipole moment from the state $|i\rangle$ to $|j\rangle$.

The time-dependent DFT/B3LYP method implemented by GAUSSIAN package[18] is employed to obtain the transition dipole moment μ_z^{ij}, excitation energy $\hbar\omega_i$, and dipole moment of ground state. The dipole moments of excited states are calculated using a finite field approach. The solvent effects are solved by the PCM of Tomasi and Persico.[19] The equilibrium geometries of the molecule in gas phase and solutions are optimized at DFT/B3LYP level. The 6-31G basis set is used throughout all calculations.

3. Results and discussion

3.1. Molecular structures

The two-photon initiator BPYPA synthesized by Yan *et al*[13] is shown in Fig.1.

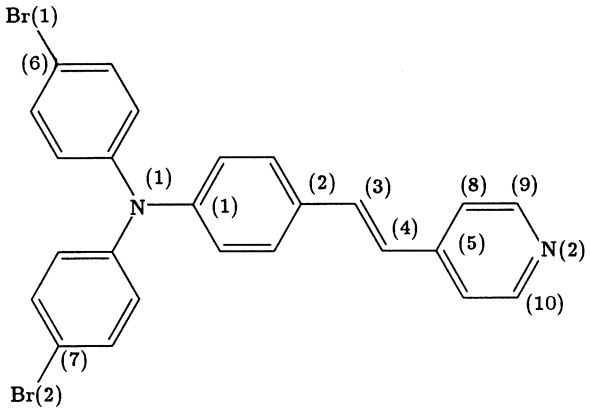


Fig.1. The geometrical structure of the molecule.

The optimized results show that the acceptor pyridine lies on the same plane as the π centre, which favours the π electrons delocalization, whereas the donor is found to be out of this plane in both gas phase and solutions. In general, the geometric parameters of the compound are slightly changed by solvents. However, there are some features for the bond length alteration with the polarity of the solution. The single bonds C(2)–C(3) and C(4)–C(5) are more stressed with the increase of the polarity, while the double bond C(3)–C(4) is more stretched. Furthermore, the solvent shows a relatively strong effect on the N(1)–C(1) bond and the C–Br bond. The bond length of N(1)–C(1) is shortened when the solvent polarity is reinforced, but the bond lengths of both C–Br bonds are lengthened.

Table 1. The bond length (nm) variation of BPYPA in different solvents (ε is the dielectric constant of the solvent). Here DMF is a short form of N, N-Dimethylformamide

	$\varepsilon = 1$	$\varepsilon = 4.9$	$\varepsilon = 20.7$	$\varepsilon = 24.55$	$\varepsilon = 36.7$
	Gas	Chloroform	Acetone	Ethanol	DMF
N(1)–C(1)	0.14250	0.14228	0.14225	0.14194	0.14190
C(2)–C(3)	0.14628	0.14611	0.14608	0.14605	0.14600
C(3)–C(4)	0.13534	0.13536	0.13539	0.13551	0.13549
C(4)–C(5)	0.14650	0.14633	0.14628	0.14627	0.14623
C(6)–Br(1)	0.19450	0.19475	0.19485	0.19590	0.19586
C(7)–Br(2)	0.19457	0.19478	0.19490	0.19603	0.19598

3.2. One-photon absorption

It is interesting to note that the compound exhibits two charge-transfer (CT) states in an optical region, which are observed by the two absorption peaks in the OPA spectrum. The excitation energies and oscillator strengths of the CT states in various solutions are listed in Table 2. It is noticed that the calculated excitation energies are in quite good agreement with the experimental results. The calculated solvatochromic shift of the molecule displays a nonmonotonic behaviour with respect to the polarity of the solvents, which is consistent with the measurement.

Table 2. The oscillator strength $\delta_{\rm opa}$ (arb. units) for the CT states with excitation energies E(eV), and the corresponding wavelength $\lambda_{\rm opa}$(nm) in different solvents.

solvent	ε	E	$\lambda_{\rm opa}$	$\delta_{\rm opa}$
Gas	1.0	3.113	398.29	0.871
		4.214	294.25	0.531
Chloroform	4.9	3.077	402.94 (380[a])	0.883
		4.200	295.24	0.438
Acetone	20.7	3.063	404.72(372[a])	0.884
		4.191	295.81	0.439
Ethanol	24.55	3.077	402.89(377[a])	0.925
		4.196	295.49	0.427
DMF	36.7	3.079	402.64(370[a])	0.927
		4.194	295.59	0.401

[a] From Ref.[13].

3.3. Two-photon absorption

For one-dimensional organic molecules with an asymmetrical D–π–A structure, it is known that the first excited state often has the maximal TPA cross section in low energy regime. Since there are two charge-transfer states in lowest excited states for BPYPA in both gas phase and various solutions, we need to include at least three states to calculate the TPA cross sections using Eq.(5). The variations of the transition dipole moments among the ground state and the CT states $\mu_z^{ij}(i = 0, 1,\ j = 1, 2,\ i \neq j)$ and the dipole moment difference $\Delta\mu_z$ between the ground state and the first CT state with respect to the polarity of solvents are shown in Table 3. It is seen that $\Delta\mu_z$ has a relatively large enhancement in solutions compared with that in gas, while other quantities are slightly influenced by solvents.

Table 3. The transition dipole moment μ_z^{ij} (a.u.), the dipole moment difference $\Delta\mu_z$ (a.u.) between the ground state and the first CT state in different solvents.

solvent	ε	μ_z^{01}	$\Delta\mu_z$	μ_z^{02}	μ_z^{21}
Gas	1.0	3.377	5.772	2.267	6.225
Chloroform	4.9	3.420	6.801	2.063	6.184
Acetone	20.7	3.423	7.132	2.065	6.186
Ethanol	24.55	3.499	7.096	2.034	6.207
DMF	36.7	3.501	7.096	1.969	6.239

The maximal TPA cross sections of the molecule in various solutions are listed in Table 4. It is noticed that the molecule has a larger TPA cross section ($\sim 10^{-47}\mathrm{cm}^4 \cdot \mathrm{s/photon}$) than the resembling compound DBASVP (with $\sim 10^{-48}\mathrm{cm}^4 \cdot \mathrm{s/photon}$),[14] which indicates that BPYPA seems to be a better two-photon polymerization initiator.

The TPA cross sections of the compound are enhanced with the increase of the polarity of solvents. However, the nonmonotonic behaviour for the enhancement of the TPA cross section with respect to the polarity of solvents is also observed, which is consistent with the finding in previous work.[14]

Table 4. The TPA cross section $\delta_{\mathrm{tpa}}(10^7$ a.u.) and $\sigma_{\mathrm{tpa}}(10^{-47}\mathrm{cm}^4 \cdot \mathrm{s/photon})$, the excitation energy E(eV) and the corresponding wavelength λ_{tpa}(nm) of the lowest excited states for BPYPA in different solvents.

solvent	ε	E	λ_{tpa}	δ^1_{tpa}	δ^2_{tpa}	$\delta^{12}_{\mathrm{tpa}}$	δ_{tpa}	σ_{tpa}
Gas	1.0	3.113	796.6	2.785	0.501	2.362	5.648	1.337
Chloroform	4.9	3.077	805.9	4.058	0.408	2.574	7.040	1.629
Acetone	20.7	3.063	809.4	4.524	0.410	2.723	7.657	1.756
Ethanol	24.55	3.077	805.8	4.622	0.401	2.722	7.745	1.792
DMF	36.7	3.079	805.3	4.622	0.380	2.652	7.654	1.773

Because of existing two CT states, there are two scattering processes, i.e. $S_{\mathrm{g}} \rightarrow S_1 \rightarrow S_1$ and $S_{\mathrm{g}} \rightarrow S_2 \rightarrow S_1$ (see Fig.2), for the two-photon excitation from ground state to the first excited state. The maximal TPA of the compound is mainly determined by these two individual scatting channels and the interference between them as shown in Eq.(5). For individual channel, one can see from Table 3 that the value of δ^1_{tpa} is quite larger than that of δ^2_{tpa}. The first scatting channel thus plays an important role in enhancing the TPA cross section. Beside this, the value of the interference term $\delta^{12}_{\mathrm{tpa}}$ between the two scattering channels is of the same order of magnitude as that of δ^1_{tpa}, which displays a very strong constructive effect and has a great contribution to the TPA cross section.

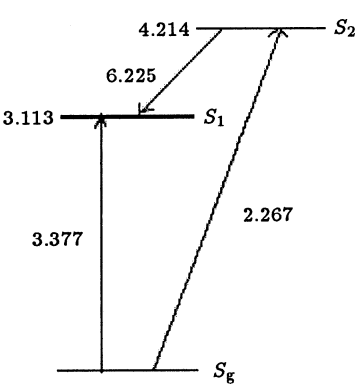


Fig.2. The two scattering channels for two-photon absorption. The excitation energies (boldface, eV) and transition dipole moments (a.u.) of BPYPA in gas phase. The final state is marked with a bold line.

The response theory at the level of random phase approximation (RPA) is also used to describe the two-photon absorption of the compound in gas phase.[13] The numerical result gives a rather weak two-photon absorption of the compound. It is caused not only by the ignorance of the solvent effect, but also by the neglect of the electron correlation.

3.4. The hydrogen-bond effect

In the above studies, only the long-range interaction between the solvent and solute is simulated by PCM model. However, it is known that the short-range interaction (hydrogen-bond) may exist in some polar solvents, and the hydrogen-bond can have obvious effects on the geometrical and electronic structures of the solute molecule.[20,21] We have designed a supermolecular (SM) structure of the BPYPA in ethanol solvent, including hydrogen-bond (see Fig.3). The general features of the geometrical structure of BPYPA have the similar trend to those given by the PCM. The optimized geometrical parameters are listed in Table 5. One can see that the hydrogen bond gives a relatively large effect on the structure of the pyridine, where the double bond C(10)–N(2) is shortened with the trend opposite to the PCM result, and the double bond C(8)–C(9) is further stressed compared with that given by the PCM. Moreover, the hydrogen bond gives little influence on the bond lengths of C(6)–Br(1) and C(7)–Br(2). The time-dependent density functional theory is applied to calculating the excitation energies of the CT states of BPYPA with SM model. The excitation energies, 3.008eV and 4.163eV, are pushed down by the hydrogen-bond effect, compared with them in gas phase, which shows the same trend as that given by the long-range interaction. The simulation including both long- and short-range interactions is quite a heavy calculation and will be considered further.

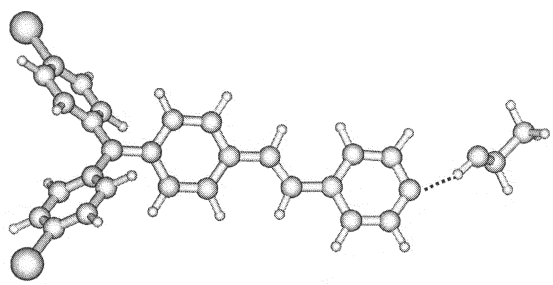


Fig.3. Structure of the BPYPA molecule hydrogen bonded with ethanol.

Table 5. Bond lengths (nm) of BPYPA with PCM and SM models in Ethanol solution

	N(1)–C(1)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5)–C(8)	C(8)–C(9)	C(9)–N(2)	C(10)–N(2)
Gas	0.14250	0.14628	0.13534	0.14650	0.14127	0.13932	0.13549	0.13522
SM	0.14234	0.14617	0.13539	0.14638	0.14135	0.13910	0.13567	0.13516
PCM	0.14194	0.14605	0.13551	0.14627	0.14142	0.13923	0.13579	0.13552

4. Conclusion

We have combined the time-dependent density functional theory with the polarized continuum model (DFT/PCM) to study the solvatochromic shift and two-photon absorption cross section of a newly synthesized asymmetrical charge-transfer organic molecule bis-(4-bromo-phenyl)-[4-(2-pyridin-4-yl-vinyl)-phenyl]-amine. The numerical results show that the BPYPA has two CT states in visible region. A three-state model is then formulated to calculate the TPA cross section. The compound has a large TPA cross section, $\sigma_{\rm tpa} \sim 10^{-47}{\rm cm}^4 \cdot {\rm s/photon}$, in visible region, which is larger than that of the compound DBASVP. The TPA cross section and solvatochromic shift of the CT states are found to be solvent-dependent, for which a nonmonotonic behaviour with respect to the polarity of the solvents has been observed. The numerical results based on DFT are more consistent with experimental measurements than those given by response theory at level of RPA, demonstrating the importance of the electron correlation for describing the one- and two-photon absorption of molecules.

References

[1] Denk W, Strickler J H and Web W W 1990 *Science* **248** 73

[2] Ehrlich J E, Wu X L, Lee L Y S, Hu Z Y, Rockel H, Marder S R and Perry J W 1997 *Opt. Lett.* **22** 1843

[3] Belfield K D, Ren X B, Van Stryland E W, Hagan D J, Dubikovsky V and Miesak E J 2000 *J. Am. Chem. Soc.*

122 1217

[4] Abbotto A, Beverina L, Bozio R, Bradamante S, Pagani G A and Signorini R 2001 *Synth. Met.* **121** 1755

[5] Cumpston B H, Ananthavel S P, Barlow S *et al* 1999 *Nature* (London) **398** 51

[6] Albota M, Beijonne D, Bredas J L *et al* 1998 *Science* **281** 1653

[7] Reinhardt B A, Brott L L, Clarson S J, Dillard A G, Bhatt J C, Kannan R, Yuan L, He G S and Prasad P N 1998 *Chem. Mater.* **10** 1863

[8] Wang C K, Macak P, Luo Y and Ågren H 2001 *J. Chem. Phys.* **114** 9813

[9] Cho B R, Son K H, Son S H, Lee S H, Song Y S, Lee Y K, Jeon S J, Choi J H, Lee H and Cho M 2001 *J. Am. Chem. Soc.* **123** 10039

[10] Macak P, Luo Y, Norman P and Ågren H 2000 *J. Chem. Phys.* **113** 7055

[11] Yoo J, Yang S K, Jeong M Y, Ahn H C, Jeon S J and Cho B R 2003 *Org. Lett.* **5** 645

[12] Su Y, Wang C K, Wang Y H and Tao L M 2004 *Acta Phys. Sin.* **53** 2112 (in Chinese)

[13] Yan Y X, Tao X T, Sun Y H, Xu G B, Wang C K, Yang J X, Ren Y, Zhao X, Yu X Q and Jiang M H 2004 *Mat. Sci. Eng.* B **113** 107

[14] Wang C K, Zhao K, Su Y, Yan R, Zhao X and Luo Y 2003 *J. Chem. Phys.* **119** 1208

[15] Cronstrand P, Luo Y and Ågren H 2002 *Chem. Phys. Lett.* **352** 262

[16] Cronstrand P, Luo Y and Ågren H 2002 *J. Chem. Phys.* **117** 11102

[17] Sun Y H, Zhao K, Wang C K, Luo Y, Yan Y X, Tao X T and Jiang M H 2005 *Chin. Phys.* **14** 115

[18] GAUSSIAN 98, reference in http://www.gaussian.com

[19] Tomasi J and Persico M 1994 *Chem. Rev.* **94** 2027

[20] Zhang F S and Lynden-Bell R M 2003 *J. Chem. Phys.* **119** 6119

[21] Wang C K, Wang Y H, Su Y and Luo Y 2003 *J. Chem. Phys.* **119** 4409