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Solvent effects on structure and optical properties of a D-π-A azobenzene dye*

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Time-dependent hybrid density functional theory in combination with Onsager reaction field model and supermolecular model has been applied to study solvent effects on the geometrical and electronic structures, as well as one/two-photon absorption properties, of 4-(N-(2-hydroxyethyl)-N-methyl)-amino-4'-nitroazobenzene. It is found that the short-range interaction has a large effect on the electronic structure of the solute molecule, namely, large red-shift of the maximum one-photon absorption is induced by hydrogen bonding. The solute molecule has a large two-photon absorption cross section, which is enhanced by the solvent effect. The computational results are in good agreement with measurements.

Keywords: solvent effects, response theory, hydrogen bonding, two-photon absorption
PACC: 3130L, 3380K, 3120A, 4265

1. Introduction

Molecules with large two-photon absorption (TPA) cross-section have attracted great interest theoretically and experimentally in recent years due to a variety of applications, such as two-photon-excited fluorescent microscopy, three-dimensional optical data storage, infrared detector, optical limiting, short wavelength tunable laser, and fabrication of photonic band gap crystals.[1−6] The strategy for synthesis of molecules with large TPA cross-sections has been studied both theoretically and experimentally, and a certain part of the structure-property relations have been explored. The available research results indicate that the most efficient TPA materials seem to be the ones with various electron donor (D) and electron acceptor (A) moieties attached symmetrically or asymmetrically to a conjugated linker (π centre). Moreover, conjugation length, D/A strength, and molecular symmetry are important factors responsible for the enhancement of TPA cross sections.[7−12] These factors have been extensively considered in the material design and synthesis. The push–pull π -conjugated charge transfer azobenzene organic molecules are known to be typical nonlinear optical materials and considered to be the best candidates for a wide range of photonic applications.[13−15]

It is known that the optical properties of organic dyes are normally measured in solution. The studies of solvent effects are related not only to the development of the existing theory, but also to the illustration of experimental results obtained in solution.[16] As is known, the interaction between solute and solvent molecules can be classified into two kinds. One is named short-range interaction, where hydrogen bonding is formed, and is shown to have larger influence on the optical properties of solute molecules.[17−19] The other is named long-range interaction, where the van der Waals force exists among molecules.[20−23] It is obvious that full description of solvent effect should take account of the two kinds of interactions if there exists hydrogen bonding.

An azobenzene dye 4-(N-(2-hydroxyethyl)-N-methyl)-amino-4'-nitroazobenzene (DR), a one-dimensional organic molecule with an electron-donor (D) and an electron-acceptor (A) attached to the π centre, has been synthesized, and shown to be a good nonlinear optical material.[14,24] The measurement was conducted in tetrahydrofuran (THF) solution, in which the hydrogen bond between molecules DR and THF was formed. In this paper, we will give a full description of the effect of solvent on optical properties

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of the molecule DR.

2. Method and computational detail

The transition probability of the one-photon absorption is given by oscillator strength

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

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 two-photon absorption (TPA) is calculated by using the Dalton Quantum Chemistry Program 2.0.[25] In terms of sum-over-state formula, the two-photon matrix element for the two-photon resonant absorption of identical energy is written as

$$S_{\alpha\beta} = \sum_j \left[\frac{\langle 0|\,\mu_\alpha\,|j\rangle\,\langle j|\,\mu_\beta\,|f\rangle}{\omega_j - \omega_f/2} + \frac{\langle 0|\,\mu_\beta\,|j\rangle\,\langle j|\,\mu_\alpha\,|f\rangle}{\omega_j - \omega_f/2}\right], \tag{2}$$

where $|0\rangle$ and $|f\rangle$ denote the ground and final states, respectively, $|j\rangle$ means all the intermediate states including the ground state, ω_j is the excitation energy of the excited states, $\alpha, \beta \in \{x, y, z\}$, and μ is the electronic dipole moment. Within the formalism of the response theory, the second rank tensors $S_{\alpha\beta}$ are obtained from the single residues of appropriate quadratic response functions. The TPA probability of molecules excited by a linearly polarized monochromatic beam can be calculated by means of

$$\begin{aligned}\delta_{\rm tp} &= 6(S_{xx}+S_{yy}+S_{zz})^2 \\ &\quad +8(S_{xy}^2+S_{xz}^2+S_{yz}^2-S_{xx}S_{yy} \\ &\quad -S_{xx}S_{zz}-S_{yy}S_{zz}).\end{aligned} \tag{3}$$

The TPA cross section, directly comparable with the experimental measurement, is defined as

$$\sigma_{\rm tp} = \frac{4\pi^2 a_0^5 \alpha}{15 c_0}\frac{\omega^2 g(\omega)}{\Gamma_f}\delta_{\rm tp}. \tag{4}$$

Here a_0 is the Bohr radius, c_0 the speed of light, α the fine structure constant, ω the photon energy of the incident light, and $g(\omega)$ denotes the spectral line profile, and is assumed to be a δ function. Γ_f is the lifetime broadening of the final state, which is assumed to be 0.1 eV.[16]

The self-consistent reaction field (SCRF) theory is used to discuss the influence of solvent effects on the molecular structure and optical properties. As a model of the SCRF theory, the Onsager reaction field model, in which the solute molecule is treated quantum mechanically as embedded in a spherical cavity inside a dielectric continuum, is applied so as to take into consideration the long-range interaction.[26] The short-range interaction is simulated using supermolecular (SM) approach, where the solute molecule with some of neighbouring solvent molecules is treated in a quantum mechanical way.

We optimize the geometries of molecules by use of the Gaussian package with the hybrid density functional theory (DFT/B3LYP).[27] The time-dependent density functional theory (DFT) is applied to calculate the excited energies and the transition dipole moment from the ground state to the excited state of the compounds. The TPA of the compounds is calculated by use of the response theory at DFT level implemented in DALTON2.0.[25] The basis set 6–31 G is used throughout all calculations.

3. Results and discussion

The molecular structure studied in the present paper is shown in Fig.1. Optimized results show that the azobenzene centres are in a plane and the acceptor functional groups lie on the same plane as the azobenzene centres, which favours the π electrons delocalization. The corresponding SM structure is constructed as shown in Fig.2.

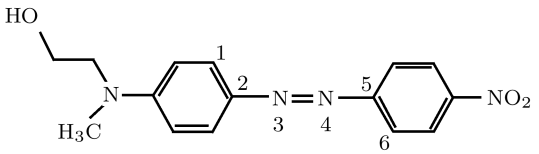


Fig.1. Structure of the DR molecule.

The results for some selective bond lengths of the compounds obtained from Onsager reaction field model (only long-range interaction is considered), supermolecular model (only short-range interaction is considered), and combined model (both interactions are considered) are displayed in Table 1. One can see

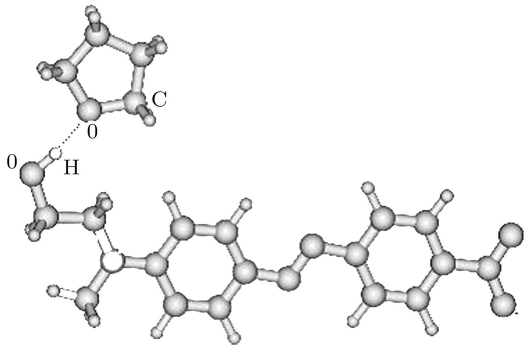


Fig.2. Structure of the DR molecule with hydrogen bonding in the solvent tetrahydrofuran (THF).

that the bond lengths of the compound have a little variation. However, the single bond lengths of C(2)–N(3) and N(4)–C(5) in THF are shorter than the counterparts in gas phase, and double bond lengths of C(1)–C(2), C(5)–C(6) and N(3)–N(4) in THF are longer than the counterparts in gas phase. Then the bond-length alternation (BLA) becomes weaker in THF.

Table 2 lists the excited energies and oscillator strengths of the molecule DR in gas phase and THF solvent. One can see that the second excited state has the largest oscillator strength, which is named a charge-transfer (CT) state. When the solvent effect is involved, the excited energy of the CT state has a red-shift. Moreover, the short-range interaction makes a large contribution to the solvatochromic shift of the CT state, where the excited energy is moved from 2.617 to 2.562 eV. However, the Onsager reaction field model shows little variation of the excited energy for the CT state caused by the long-range interaction. For the full description of solvent effect, the excited energy is 2.565 eV ($\lambda = 483.34$ nm), which is well consistent with the measurement of wavelength, $\lambda = 482$ nm.[24]

Table 1. The selective bond lengths (Å) of the compound in gas phase and solvent. The supermolecular(SM), Onsager reaction field, and combined models are employed.

solvent		C(2)–N(3)	N(4)–C(5)	C(1)–C(2)	C(5)–C(6)	N(3)–N(4)
gas($\varepsilon = 1$)		1.400	1.419	1.413	1.411	1.288
THF ($\varepsilon = 7.58$)	SM	1.399	1.419	1.413	1.411	1.289
	Onsager	1.395	1.416	1.415	1.412	1.292
	SM & Onsager	1.396	1.417	1.414	1.412	1.291

Table 2. Oscillator strength $\delta_{\rm op}$/arb. units, the excitation energy E/eV and corresponding wavelength $\lambda_{\rm op}$/nm of the four lowest excited states for the compound.

gas($\varepsilon = 1$)			THF($\varepsilon = 7.58$)								
			SM			Onsager			SM & Onsager		
E	λop	δop	E	λop	δop	E	λop	δop	E	λop	δop
2.159	574.35	0.000	2.156	575.16	0.000	2.146	577.82	0.000	2.150	576.66	0.000
2.617	473.77	0.817	2.562	483.92	0.813	2.616	473.87	0.861	2.565	483.34	0.833
										482*	
3.254	381.04	0.000	3.255	380.92	0.000	3.211	386.07	0.000	3.237	382.98	0.000
3.370	367.92	0.000	3.350	370.00	0.000	3.368	368.15	0.000	3.349	370.24	0.000

*From Ref.[24]

The charges in the molecule will be redistributed when it is excited from the ground state to CT state. For a better understanding of the charge transfer process, we calculate the charge variations for the donor and acceptor in the compound between the CT state and ground state (see Table 3). It is clearly seen that when the compound is excited to the CT state, the nitryl group gains charge of $\Delta Q_{\rm A} = Q'_{\rm A} - Q_{\rm A} = -0.424$ arb. units in the gas phase, as an acceptor, while the donor group donates charge of $\Delta Q_{\rm D} = Q'_{\rm D} - Q_{\rm D} = 0.295$ arb. units, where $Q_{\rm A}(Q'_{\rm A})$ and $Q_{\rm D}(Q'_{\rm D})$ are charges of respective acceptor and donor in the compound for the ground (CT) state. When the solvent effect is included, the charges obtained by the acceptor and given by the donor are respectively -0.357 arb. units and 0.217 arb. units, which are less than those in gas phase. It seems that the reaction field inside a cavity partly blocks charge transfer when the molecule is excited from the ground to CT state.

Table 3. The net charges of donor and acceptor in the ground state s_0 (Q_D and Q_A) and in the charge transfer state s_{CT} (Q'_D and Q'_A). ΔQ_D and ΔQ_A represent the charge variations between s_{CT} and s_0.

solvent	gas($\varepsilon = 1$)		THF($\varepsilon = 7.58$)					
			SM		Onsager		SM & Onsager	
	donor	accepter	donor	accepter	donor	accepter	donor	accepter
s_0	−0.160	−0.546	−0.180	−0.566	−0.156	−0.562	−0.128	−0.616
s_{CT}	0.135	−0.970	0.095	−0.974	0.106	−0.960	0.089	−0.974
ΔQ	0.295	−0.424	0.275	−0.408	0.262	−0.398	0.217	−0.357

We further calculate the TPA cross sections of the compound DR using response theory implemented in Dalton 2.0 package. For the lowest four excited states, the TPA cross sections σ_{tp} are shown in Table 4, where the second excited state has the maximum TPA cross section. One can see from Table 4 that this compound has a relative strong TPA characteristic. Furthermore, in the gas phase, the maximum TPA cross section occurs at 947.54 nm for the molecular material, $\sigma_{tp} = 248.21 \times 10^{-50}\,\mathrm{cm}^4 \cdot \mathrm{s} \cdot \mathrm{photon}^{-1}$. When the Onsager reaction field model is used, the maximum TPA cross section is enhanced to $265.61 \times 10^{-50}\mathrm{cm}^4 \cdot \mathrm{s} \cdot \mathrm{photon}^{-1}$. It is noted that the results with SM and combined models are not carried out here due to heavy computation. It is necessary to notice that the calculated value is much larger than the experimental result of $\sigma_{tp} = 102 \times 10^{-50}\mathrm{cm}^4 \cdot \mathrm{s} \cdot \mathrm{photon}^{-1}$ at 850 nm.[14] The discrepancy between theoretical and experimental results may be caused by the following factors. Firstly, the theoretical values are related to the two-photon resonant absorption and static condition. However, the experimental measurement may fail to tune the resonant condition. Secondly, the interaction between light and molecular medium has influence on the optical properties of the molecule, and accordingly, the dynamical determination of the TPA cross section should be carried out. Finally, the neglect of vibronic effects may also have contribution to the discrepancy.

Table 4. The TPA cross section $\sigma_{tp}/(10^{-50}\mathrm{cm}^4 \cdot \mathrm{s} \cdot \mathrm{photon}^{-1})$, the excitation energy E/eV and the corresponding two-photon wavelength λ_{tp}/nm for linear polarization light.

gas($\varepsilon = 1$)			THF($\varepsilon = 7.58$)		
			Onsager		
E	λ_{tp}	σ_{tp}	E	λ_{tp}	σ_{tp}
2.159	1148.70	0.06	2.146	1155.64	0.07
2.617	947.54	248.21	2.616	947.74	265.61
				(850*)	(102*)
3.254	762.08	0.01	3.211	772.14	0.15
3.370	735.84	0.36	3.368	736.30	0.22

*From Ref.[24]

4. Summary

We have combined the hybrid density functional theory (DFT/B3LYP) and the response theory to investigate the solvent effects on structures and one/two-photon absorption properties of a D-π-A azobenzene organic molecule. The calculated results show that solvent effects decrease bond length alternation, and cause the red-shift of one/two photon absorption. The theoretical simulation for one-photon absorption is well consistent with experimental measurement. The compound has large TPA cross section, $\sigma_{tp} \sim 10^{-48}\,\mathrm{cm}^4 \cdot \mathrm{s} \cdot \mathrm{photon}^{-1}$ in lower energy region, which shows that the compound can be used as an excellent candidate for the two-photon absorption material.

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