ARTICLE

Theoretical Studies on One-photon and Two-photon Absorption Properties of Pyrene-core Derivatives

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The analytic response theory at density functional theory level is applied to investigate one-photon and two-photon absorption properties of a series of recently synthesized pyrene-core derivatives. The theoretical results show that there are a few charge-transfer states for each compound in the lower energy region. The one-photon absorption properties of the five investigated compounds are highly consistent with those given by experimental measurements. The two-photon absorption intensities of the compounds are greatly enhanced with the increments of the molecular sizes, in which the two-photon absorption cross section of the four-branched compound is about 5.6 times of that of the mono-branched molecule. Furthermore, it is shown that the two-photon absorption properties are sensitive to the geometrical arrangements.

Key words: Two-photon absorption, Response theory, Pyrene-core derivative

I. INTRODUCTION

Along with the invention of the intense coherent laser, two-photon absorption (TPA) process between the initial and final states by simultaneously absorbing a pair of photons has been experimentally demonstrated. In comparison with the conventional one-photon absorption (OPA) process, the TPA process has two prominent features, one is a high penetrating capability into materials as a result of the longer excitation wavelength, and the other is a high spatial confinement because of quadratic dependence of excitation probabilities on the incident light intensity [1]. Thus, materials exhibiting a large TPA cross section are expected to have lots of applications, such as three-dimensional optical storage memory [2, 3], two-photon microscopy [4, 5], upconverted lasing [6], optical power limiting [7], and photodynamic therapy [8]. Numerous experimental syntheses and theoretical calculations have been carried out to develop organic materials with large TPA cross sections [9–14]. Much effort has been made to establish the so-called structure-property relationship for chromophore. The available results have demonstrated that the TPA cross sections increase with the donor-acceptor strength, conjugation length, molecular dimensionality, and planarity of the π-center [9].

The pyrene moiety is considered to be the most attractive π-center for two-photon materials because it not only is planar but also has been extensively studied in various areas of chemical biology as a fluorophore by introducing appropriate structural modification. Moreover, many applications of its derivatives, such as, microenvironment sensors [15], liquid crystals [16], organic light-emitting diodes [17], have been presented. Kim et al. has utilized it as the π-center to firstly synthesize a series of pyrene-core derivatives with 4-(N,N-dimethylamino) phenylethynyl group as the substituent [18]. Their TPA properties were experimentally investigated.

In order to understand the optical properties of these new compounds, we provide a theoretical characterization for their OPA and TPA by means of the response theory at density functional theory (DFT) level. The comparison with the experimental results is also made.

II. METHOD AND COMPUTATIONAL DETAIL

The transition probability of the OPA is given by an oscillator strength

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

(1)

where $\mu_\alpha$ is the electric dipole moment operator, $\omega_f$ 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.

In terms of sum-over-state formula, the TPA transition matrix element for the two-photon resonant absorption of identical energy is written as

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

(2)
here $|j\rangle$ means all the intermediate states including the ground state $|0\rangle$, $\omega_j$ is the excitation energy of the excited states $|j\rangle$, $\mu$ is the electric dipole moment operator, $\alpha, \beta = \{x, y, z\}$. Within the formalism of the response theory, the second rank tensors $S_{\alpha\beta}$ can be obtained from the single residues of appropriate quadratic response functions. The TPA probability of a molecule excited by a linearly polarized monochromatic beam can be calculated by

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

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

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

Among them $a_0$ is the Bohr radius, $c_0$ is the speed of light, $\alpha$ is the fine structure constant, $\omega$ is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile, here it is assumed to be a $\delta$ function. $\Gamma_f$ is the lifetime broadening of the final state, which is assumed to be 0.1 eV [19].

We optimize the geometries of molecules using Gaussian package [20] with the hybrid density functional theory (DFT/B3LYP). The TPA cross sections are calculated using the response theory at DFT level implemented in DALTON [21]. The basis set 6-31G* is used throughout all calculations. When the compounds are excited from the ground to excited states, the charge-transfer process is visualized by MOLEKEL program [22].

III. RESULTS AND DISCUSSION

Schematic molecular structures are shown in Fig.1. Figure 2 gives the optimized structures of the five compounds (noted as B1, B2, B3, B4, B5), in which the pyrene moiety acts as the $\pi$-conjugated center and the 4-(N,N-dimethylamino) phenylethynyl group is used as the substituent. The optimization results show that the pyrene moiety has a perfectly planar characteristic and almost each phenylethynyl group has a highly coplanar structure with the pyrene moiety. Moreover, one phenylethynyl group in B4 and four in B5 have a little tilting angle, where the dihedral angle between the phenyl group and the pyrene moiety is about 4°.

A. One-photon absorption

The oscillator strengths, excitation energies, and wavelengths of the lowest six excited states for the five compounds in gas phase are listed in Table I. From Table I, one can see that, for each compound, the dominating OPA state is contributed by the lowest excited state. The corresponding wavelengths for the compounds B1–B5 locate at 391, 435, 436, 463, and 496 nm, respectively, showing a red-shift in the order of B1 < B2 < B3 < B4 < B5. The numerical results are in good agreement with the measurement of both the values and the trend. The observation is understandable that the enlarged $\pi$-electron delocalization as increment of the conjugated length is favorable for decreasing the HOMO-LUMO energy gap. Furthermore, one can see that the dominating oscillator strengths for the compounds are in the order of B1 < B3 < B4 < B5 < B2, while the measured molar extinction coefficients are in the order of B1 < B3 < B4 < B2 < B5. The values of the molar extinction coefficients given by the measurement [18] are

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TABLE I Oscillator strength $\delta_{\text{op}}$ (in a.u.) and wavelength $\lambda_{\text{op}}$ (in nm) of the six lowest excited states for the five compounds in gas phase.

<table>
<thead>
<tr>
<th>Molecule state</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{op}}$</td>
<td>391</td>
<td>396</td>
<td>340</td>
<td>323</td>
<td>286</td>
</tr>
<tr>
<td>$\delta_{\text{op}}$</td>
<td>0.9</td>
<td>1.59</td>
<td>0.1</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>$\lambda_{\text{op}}$</td>
<td>435</td>
<td>431</td>
<td>381</td>
<td>352</td>
<td>323</td>
</tr>
<tr>
<td>$\delta_{\text{op}}$</td>
<td>1.6</td>
<td>6.69</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>$\lambda_{\text{op}}$</td>
<td>436</td>
<td>430</td>
<td>386</td>
<td>347</td>
<td>312</td>
</tr>
<tr>
<td>$\delta_{\text{op}}$</td>
<td>1.0</td>
<td>4.06</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>$\lambda_{\text{op}}$</td>
<td>463</td>
<td>478</td>
<td>406</td>
<td>393</td>
<td>340</td>
</tr>
<tr>
<td>$\delta_{\text{op}}$</td>
<td>1.2</td>
<td>6.06</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\lambda_{\text{op}}$</td>
<td>496</td>
<td>508</td>
<td>420</td>
<td>414</td>
<td>374</td>
</tr>
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<td>1.3</td>
<td>6.94</td>
<td>0.5</td>
<td>0.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Experimental results taken from Ref.[18].

TABLE II Two-photon absorption cross section $\sigma_{\text{tp}}$ (in $10^{-50}$ cm$^4$s/photon) and the two-photon wavelength $\lambda_{\text{tp}}$ (in nm) of the six lowest excited states for the five compounds in gas phase.

<table>
<thead>
<tr>
<th>Molecule state</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{tp}}$</td>
<td>782</td>
<td>680</td>
<td>646</td>
<td>588</td>
<td>572</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>180.4</td>
<td>190.3</td>
<td>607.4</td>
<td>646</td>
<td>4.7</td>
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<tr>
<td>$\lambda_{\text{tp}}$</td>
<td>870</td>
<td>762</td>
<td>704</td>
<td>656</td>
<td>646</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>0.1</td>
<td>2887.5</td>
<td>0.1</td>
<td>0.6</td>
<td>355.6</td>
</tr>
<tr>
<td>$\lambda_{\text{tp}}$</td>
<td>872</td>
<td>772</td>
<td>694</td>
<td>670</td>
<td>624</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>62.7</td>
<td>966.6</td>
<td>137.3</td>
<td>563.9</td>
<td>531.6</td>
</tr>
<tr>
<td>$\lambda_{\text{tp}}$</td>
<td>926</td>
<td>812</td>
<td>786</td>
<td>726</td>
<td>680</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>17.1</td>
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<td>2581.6</td>
<td>125.2</td>
<td>237.9</td>
</tr>
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<td>992</td>
<td>840</td>
<td>828</td>
<td>804</td>
<td>748</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>0.0</td>
<td>1.8</td>
<td>1349.7</td>
<td>3407.9</td>
<td>0.1</td>
</tr>
<tr>
<td>$\lambda_{\text{tp}}$</td>
<td>830</td>
<td>830</td>
<td>662</td>
<td>726</td>
<td>662</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>50</td>
<td>367.5</td>
<td>293.2</td>
<td>3407.9</td>
<td>387.6</td>
</tr>
<tr>
<td>$\lambda_{\text{tp}}$</td>
<td>760</td>
<td>760</td>
<td>760</td>
<td>760</td>
<td>694</td>
</tr>
<tr>
<td>$\sigma_{\text{tp}}$</td>
<td>490</td>
<td>230</td>
<td>293.2</td>
<td>3407.9</td>
<td>387.6</td>
</tr>
</tbody>
</table>

* Experimental results taken from Ref.[18].

quite larger than those of the oscillator strengths. It is understandable that the oscillator strength is a dimensionless quantity, while the molar extinction coefficient has a dimension of mol$^{-1}$cm$^{-1}$. The direct comparison of the two quantities is impossible now, because a direct relationship of the two quantities is not derived. The order of the transition strength for the compounds given by the numerical calculation is consistent with that by the measurement except for the compounds B2 and B5. The discrepancy may result from the solvent effect.

It is interesting to note that the maximum OPA intensity of the compound B2 is larger than that of B3, however, the compound B3 owns more charge-transfer states than B2 has. These features are attributable to the longer effective conjugated length for B2 and stronger coupling interactions between the branch chains for B3. Therefore, the conjugated length is helpful for enhancing the OPA ability, and the branch-branch interaction is helpful for increasing the number of the charge-transfer states.

### B. Two-photon absorption

Table II presents the calculated TPA cross sections of the lowest six excited states for the five compounds in gas phase. It is observed that the dominating TPA states are different from the OPA states, which results from the fact that OPA and TPA processes follow different selection rules. From Table II, we can see that among all compounds, B1 has the weakest TPA intensity, and its maximum TPA cross section is $607\times10^{-50}$ cm$^4$s/photon located at 646 nm. Referring to B2 and B3, their maximum TPA cross sections are all owned by the second excited state. However, their TPA abilities are quite different. It is seen that the maximum TPA cross section for compound B2 is $2888\times10^{-50}$ cm$^4$s/photon, which is about three times of that for B3, demonstrating the obvious role of geometrical arrangement for enhancing the TPA ability. The maximum TPA cross section for the three-branched molecule B4 is $2582\times10^{-50}$ cm$^4$s/photon, located at 786 nm, which is smaller than that of B2, but larger than those of B1 and B3. For the four-branched compound B5, it has the strongest TPA ability among the investigated compounds, with the maximum TPA cross section of $3408\times10^{-50}$ cm$^4$s/photon. From the calculated results shown above, one may conclude that the multi-branched effect enhances the TPA intensity of compounds, at the same time, the geometrical arrangement, namely, the symmetrical feature of structures has a great influence on the TPA intensity of compounds.
FIG. 3 The two-photon absorption spectra for the five compounds.

Furthermore, the symmetrical structures (B2 and B5) gain an advantage over those asymmetrical structures (B1, B3, and B4) for increasing the TPA abilities.

By carrying out a Lorenz expansion of the TPA cross sections, we obtain the TPA spectra from 720 nm to 920 nm for the five compounds (see Fig.3). One can see that these compounds display relatively broad TPA spectral profiles because of several active TPA states in the lower energy region. The TPA spectra profile was similar to that given by the measurement [18]. When the incident light wavelengths are chosen as 830, 760, 760, 780, and 820 nm for compounds B1, B2, B3, B4, and B5, respectively, the calculated TPA cross sections are respectively $92 \times 10^{-50}$, $2914 \times 10^{-50}$, $1032 \times 10^{-50}$, $2828 \times 10^{-50}$, and $3937 \times 10^{-50}$ cm$^4$/s/photon. One can see that the theoretical calculations are generally consistent with the measured results in tendency. However, the calculated values are larger than the measured ones. The possible mechanisms for the discrepancy are as follows. The theoretical simulations just give the intrinsic TPA cross sections contributed by electronic motion in gas phase. The vibration contribution is not considered here. Furthermore, the experimental measurements are implemented in solvent, thus, the interactions between solvents and solute molecules may have influences on the optical properties of the compounds [23]. Moreover, the interaction between laser and molecules results in that the TPA cross sections are dependent on the laser parameters [24].

C. Charge transfer process

It is known that the charge transfer (CT) state plays a key role in determining optical properties of compounds. When the compound is excited from the ground to the CT states, the charges in the molecule will be redistributed. In order to examine the CT process clearly, the charge density differences between the CT (the lowest excited state) and the ground states for the compounds in gas phase are visualized in Fig.4, by means of the MOLEKEL program. From Fig.4, one can see that for all compounds, the branch chains act as the electron donors, while the pyrene-core parts served as the electron acceptors. Upon the excitation, the charges mainly flow from the branch chains to the central pyrene moieties of the compounds.

IV. CONCLUSION

We have numerically analyzed the OPA and TPA properties of five newly synthesized compounds based on the response theory at the DFT level. The calculated results show that, in the UV-visible region, the maximal OPA intensities for these compounds appear in the first excited states. With the increments of molecular sizes, the excited energies show red-shift, and the OPA intensities are nonmonotonically increased. The molecule B5 has the largest TPA cross section $3408 \times 10^{-50}$ cm$^4$/s/photon, which is about 5.6 times of that of mono-branched molecule B1. It demonstrates that the molecular size is in favor of enhancing the TPA ability. Meanwhile, the symmetrical structures are superior to the unsymmetrical cases (B1, B3, B4) for improving their TPA properties, which provides a referable strategy for the design and synthesis of the efficient TPA materials. Other hybrid exchange-correlation functionals and larger basis sets are also used for the calculations.

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[21] DALTON, in http://www.kjemi.uio.no/software/dalton/

[22] MOLEKEL, in http://www.cscs.ch/molekel/
