First principles studies on one-, two-, and three-photon absorption properties of a symmetric carbazole derivative both in gas phase and solution

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ABSTRACT

One-, two-, and three-photon absorption spectra of a novel symmetric carbazole derivative have been calculated by applying density functional response theory, both in gas phase and in a selection of solvents with increasing polarity. The effect from surrounding solvents is described by the polarizable continuum model. The effect of the choice of geometry, as well as the exchange–correlation functional has been carefully analyzed. It is found that the Coulomb attenuation method variant of Becke's three-parameter exchange and the Lee–Yang–Parr correlation functional (CAMB3LYP) can reproduce very well the experimental one-photon absorption lineshape. The dielectric solutions enhance both one- and multi-photon absorption properties. Possible explanations for the discrepancy between calculated and experimental three-photon absorption cross sections have been analyzed in details. The calculation suggests that the possible involvement of excite-state absorption in the experimental measurement cannot be ruled out.

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1. Introduction

Multi-photon absorption (MPA) in a variety of materials, with organics in particular, has received considerable attentions due to their wide applications in the fields of multi-photon fluorescence imaging, 3D optical data storage, optical limiting, photodynamic therapy and microfabrication [1]. In order to make a good understanding of the structure–property relationship of MPA materials, numerous organic materials have been investigated both experimentally and theoretically. Studies show that, in general, prolonging the π-bridge length, increasing the planarity and strengthening the donor and/or acceptor ability, will enhance the nonlinear optical effect [2–6].

A variety of conjugated organic units have been designed and synthesized as novel MPA materials, in particular, the chromophores with a structure of D(A)-π-D(A), and D(A)-π-D(A)-π-D(A), where D and A denote electron donating and accepting groups, such as triphenylamine [7,8] and fluorene [9–11]. Researches have found that carbazole chromophores and their derivatives have been attracting academic interests, since they are well known as a good electron-donating moiety due to its fully aromatic structure and they have attractive properties combining enhanced MPA and high fluorescence quantum yield. In 1980, Martin et al. [12] were

the first ones to find that carbazole had good two-photon excitation and fluorescence phenomenon. In 2007, Fitilisa et al. [13] have successfully designed and synthesized a series of novel symmetrical two-photon absorption (TPA) materials with carbazole core. Meanwhile, the attractive electron-rich properties of carbazole derivatives make them to be suitable substrates for chromophores with TPA-efficient blue emissions [14,15]. In a word, carbazole derivatives are used as promising materials for TPA optical applications because of their special photoelectrical properties, therefore have recently attracted extended attentions on the purpose of determining new MPA materials [15–20]. Liang Li and coworkers has reported that they have successfully designed and synthesized a strong three-photon absorption (3PA) material, a novel symmetrical carbazole derivative 3,6-bisphenanthrolinimidazole-N-*n*-octylcarbazole (D-π-D-π-D, abbreviated as POCP), which has terminals of 1,10-phenanthroline rings via carbon=nitrogen (C=N) double bond [21]. It is reported that the 3PA cross section of this carbazole derivative is enhanced because of the special linkage of the π chain with carbon=nitrogen (C=N) double bond and large π-conjugated terminal substituents, 1,10-phenanthroline. A theoretical study can be an effective way of gaining insight into the micro-essence of MPA. The solvent effect is also of important relevance in interpreting MPA processes, since strong solvent dependence has been observed in the TPA process from both experimental and theoretical studies, showing that the TPA cross section can be largely enhanced in solvents [22–28]. Moreover, it was also reported that for some systems the TPA cross section exhibited a nonmonotonic

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behavior against the static constant ε, increasing first with respect to the polarity of the solutions and reached to a maximum at $\varepsilon \leqslant 20.7$, and then decreasing [22,23,28]. A very sharp difference of TPA cross sections between different solvents has been observed by Wang et al. [23] for a conjugated polymer, whereas a relatively mild solvent-dependence has been seen for some other molecules [22,28] Therefore, in order to have a deep understanding of the solvent-dependence behavior for present case, it is worth to perform a systematic study on a set of solvents with increasing polarity.

In present paper, we employ a state-of-the-art computational method which applies first principles calculations to study the one-, two-, and three-photon absorption properties, of the symmetric carbazole derivative synthesized in Ref. 21, whose structure has been sketched in Fig. 1. A detailed comparison with the experiment will be made and the features appearing in experimental signals will be characterized in terms of molecular excitations. Different response behaviors between different processes will be highlighted. Here we will try to give: (1) a reliable assignment of the responsible excited states to the major experimental OPA peaks; (2) a systematic study on the solvent effect, covering a set of solvents with increasing polarity; (3) discussions on the different optical responses between different MPA processes; (4) a detailed comparison between computed and experimental OPA and 3PA properties.

The present paper will be organized as follows: The theoretical background will be summarized in Section 2. In Section 3 computational details will be briefly sketched. The results will be collected and discussed in detail in Sections 4 and 5 will give the main conclusions.

2. Theoretical background

2.1. One-photon absorption

The extinction coefficient of OPA is reported in the experiment, which can be written as [29,30]

$$
\begin{aligned}
\varepsilon_{OPA}(\omega) &= \frac{(2\pi)^2 \omega N_A}{3 \times 1000 \times \ln(10)\hbar c_0 (4\pi\varepsilon_0)} \\
&\quad \times \sum_f g(\omega, \omega_{gf}) \sum_{\alpha=x,y,z} |\mu_{gf}^\alpha|^2 \\
&= \frac{2\pi^2 e^2 \omega N_A}{1000 \times \ln(10) m_e c_0 (4\pi\varepsilon_0)} \times \sum_f g(\omega, \omega_{gf}) \frac{\delta_{gf}^{OPA}}{\omega_{gf}} \\
&\approx 1055.0 \times \omega \times \sum_f g(\omega, \omega_{gf}) \frac{\delta_{gf}^{OPA}}{\omega_{gf}}
\end{aligned} \tag{1}
$$

where N_A is Avogadro's number, c_0 the speed of light in vacuo and ε_0 the vacuum permittivity. ω is the circular frequency of the laser, and ω_{gf} is the transition energy from the initial state $|g\rangle$ to the final
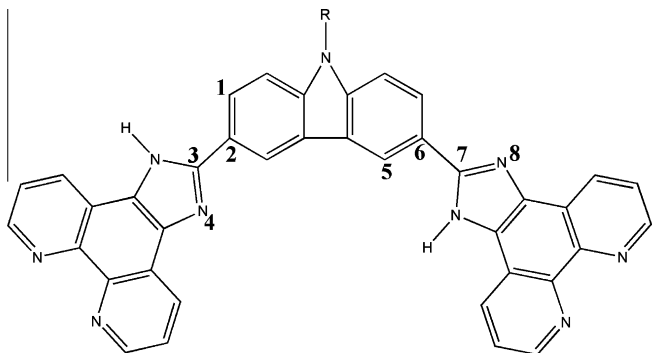

Fig. 1. Molecular structure.

state $|f\rangle$. The Cartesian ($\alpha = x, y, z$) component of the transition electric dipole moment can be explicitly evaluated as

$$
\mu_{gf}^\alpha = \langle g | \mu^\alpha | f \rangle \tag{2}
$$

with μ^α denoting the electric transition dipole operator. δ_{gf}^{OPA} is known as the oscillator strength, which is defined as

$$
\delta_{gf}^{OPA} = \frac{2m_e \omega_{gf}}{3\hbar e^2} \sum_\alpha |\mu_{gf}^\alpha|^2 \tag{3}
$$

$g(\omega, \omega_{gf})$ is the line broadening function, with here a Lorentzian function has been applied, which for a general n-photon absorption process is usually described as

$$
L(n\omega, \omega_{gf}) = \frac{1}{\pi} \frac{\Gamma_f}{(\omega_{gf} - n\omega)^2 + \Gamma_f^2} \tag{4}
$$

The last row of Eq. (1) yields the OPA observable in unit of L mol^{-1} cm^{-1} starting from circular frequencies given in atomic units.

2.2. Two-photon absorption

For two photons of equal frequency $\omega_1 = \omega_2 = \omega$, the TPA cross section σ_{TPA}, is given in a form directly comparable to experiment by the expression [29]

$$
\begin{aligned}
\sigma_{TPA} &= \frac{4\pi^3 a_0^5 \alpha}{15 c_0} \omega^2 \sum_f g(2\omega, \omega_{gf}) \times \delta_{gf}^{TPA}(\omega) \\
&= 8.35150 \times 10^{-4} \times \omega^2 \sum_f g(2\omega, \omega_{gf}) \times \delta_{gf}^{TPA}(\omega)
\end{aligned} \tag{5}
$$

Here α is the fine structure constant, a_0 Bohr radius, and the orientationally averaged two-photon probability $\delta_{gf}^{TPA}(\omega)$ is given by [31]

$$
\delta_{gf}^{TPA}(\omega) = \sum_{\alpha\beta} \left(F \times S_{gf}^{\alpha\alpha} S_{gf}^{\beta\beta,*} + G \times S_{gf}^{\alpha\beta} S_{gf}^{\alpha\beta,*} + H \times S_{gf}^{\alpha\beta} S_{gf}^{\beta\alpha,*} \right) \tag{6}
$$

where $S_{gf}^{\alpha\beta}$ is the two-photon transition matrix element, which is defined by the Sum-Over-State (SOS) expression as

$$
S_{gf}^{\alpha\beta}(\omega_0) = \frac{1}{\hbar} \sum_k \left[\frac{\langle g|\mu_\alpha|k\rangle \langle k|\mu_\beta|f\rangle}{\omega_k - \omega} + \frac{\langle g|\mu_\beta|k\rangle \langle k|\mu_\alpha|f\rangle}{\omega_k - \omega} \right] \tag{7}
$$

F, G and H assume values of 2, 2, 2 for linearly and -2, 3, 3 for circularly polarized beams, respectively.

Starting from a_0 and c_0 given in CGS units, and circular frequencies and two-photon transition probabilities given in atomic units, the resulting unit of σ_{TPA} in Eq. (5) is cm^4 s photon^{-1} mol^{-1} (10^{-50} cm^4 s photon^{-1} mol^{-1} = 1 Göppert–Mayer, 1 GM).

2.3. Three-photon absorption

Although 3PA is a fifth-order property, it can be obtained from the third-order transition matrix elements (here given for three photons of identical circular frequency $\omega_1 = \omega_2 = \omega_3 = \omega$)

$$
T_{gf}^{\alpha\beta\gamma} = \sum P_{\alpha,\beta,\gamma} \sum_{nm} \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\beta|n\rangle \langle n|\mu_\gamma|f\rangle}{(\omega_m - \omega)(\omega_n - 2\omega)} \tag{8}
$$

where $\sum P_{\alpha,\beta,\gamma}$ denotes the intrinsic permutation operator with respect to the Cartesian indices α, β, and γ. The 3PA cross section σ_{3PA} can be expressed as

$$
\begin{aligned}
\sigma_{3PA} &= \frac{4\pi^4 \alpha a_0^8 \omega^3}{3 c_0^2} \sum_f g(3\omega, \omega_{gf}) \times \delta_{gf}^{3PA}(\omega) \\
&= 6.4844 \times 10^{-8} \times \omega^3 \sum_f g(3\omega, \omega_{gf}) \times \delta_{gf}^{3PA}(\omega)
\end{aligned} \tag{9}
$$

where $\delta_{gf}^{3PA}(\omega)$ is the three-photon transition probability. The resulting SI unit for the cross section is cm^6 s^2 photon^{-2} mol^{-1}.