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Two-Photon Absorption Cross Section Determination for Fluorene Derivatives: Analysis of the Methodology and Elucidation of the Origin of the Absorption Processes

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A comprehensive analysis of the well-known open aperture Z-scan method, using a modified equation for the change in transmittance, is presented and accounts for discrepancies in two-photon absorption (2PA) cross sections between picosecond and femtosecond excitation. This new approach takes into account excited-state absorption and stimulated emission of the molecules studied. The two-photon absorption cross-section spectra of a series of six fluorene-based derivatives, determined using picosecond pulses, over a broad spectral range (500–900 nm), and this approach using a modified fitting procedure in the open aperture Z-scan is reported. We demonstrate that the fluorene derivatives exhibit two-photon absorption cross-section values between 700 and 5000 GM, when excited into the two-photon allowed electronic state. Excitation anisotropy spectra, measured to investigate the nature of the observed linear and nonlinear absorption bands, are presented and provide insight into the 2PA process.

I. Introduction

The determination of the two-photon absorption (2PA) spectra of organic molecules is a subject of great interest for a number of applications, such as two-photon fluorescence imaging,[1,2] three-dimensional (3D) optical data storage,[3,4] two-photon photodynamic cancer therapy,[5,6] two-photon optical power limiting,[7,8] and so forth. One of the frequently used methodologies for 2PA measurements is the open aperture Z-scan method developed by Sheik-Bahae and co-workers.[9] This simple and powerful technique permits the determination of the nonlinear absorption coefficient of optical materials. It consists of the measurement of the transmittance, $T(z)$, through a sample that is scanned in the z direction across the focal plane of a focused Gaussian beam.[9] In order to obtain the nonlinear coefficients and corresponding 2PA cross sections, the theoretical fitting of the experimental Z-scan curves is required. In the case of pure 2PA processes, the function $T(z)$ for open aperture can be obtained analytically, and a relatively simple fitting procedure allows the determination of the 2PA cross section. However, when excited-state absorption (ESA) from the 2PA-generated excited state becomes significant, a more complex $T(z)$ function to fit the experimental Z-scan curves has to be implemented for the complete analysis.[10–12] The fitting procedure for the complex analysis was first described by Van Stryland and co-workers, after performing Z-scan measurements in semiconductors.[13] Their method was based on the assumption that the population of the ground state from which 2PA originates is nearly constant. In general, however, depopulation of the ground state can be sufficiently large and should be taken into account. Simultaneously, other developments of the $T(z)$ function for open

aperture Z-scan have been reported for the rapid and broadband characterization of degenerate and nondegenerate 2PA.[14–17] Nevertheless, those measurements, for organic materials, are based on the classical fitting procedure assuming exclusive 2PA.

Fluorene-based organic molecules have attracted attention because of their potential for numerous nonlinear optical applications (see, e.g., refs 18–20). In this work, the single wavelength open aperture Z-scan method[9] was used for determination of the degenerate 2PA spectra of several fluorene derivatives. The analysis of possible nonlinear absorption mechanisms was performed and taken into account. The 2PA spectra of the fluorene derivatives were investigated previously[21–24] by open aperture Z-scan,[9] two-photon induced fluorescence,[25] and femtosecond white-light continuum pump–probe methods.[14] All of these measurements were based on the classical pure 2PA fitting procedure,[9] in which possible reabsorption and stimulated emission processes were neglected. Moreover, little is known about the nature of 2PA bands of such fluorenyl structures. Accurate and reliable measurements of the 2PA bands of fluorenyl structures that permit the elucidation of their nature and that consider the possibility of other nonlinear processes participating during the excitation temporal regime are essential for the design of new and better 2PA materials.

In this paper, we show 2PA measurements obtained via open aperture Z-scan considering other nonlinear processes. The degenerate 2PA spectra of six different fluorene derivatives with diverse molecular motif are shown. A primary goal of this paper is the analysis of the fitting methodology for two-photon Z-scan measurements and determination of the correct 2PA spectra of several key fluorene derivatives with promising nonlinear optical properties. It was shown that ESA should be taken into account, even for femtosecond measurements. Our work also suggests that stimulated emission processes need to be considered when excitation wavelengths, λ_{exc}, overlap with

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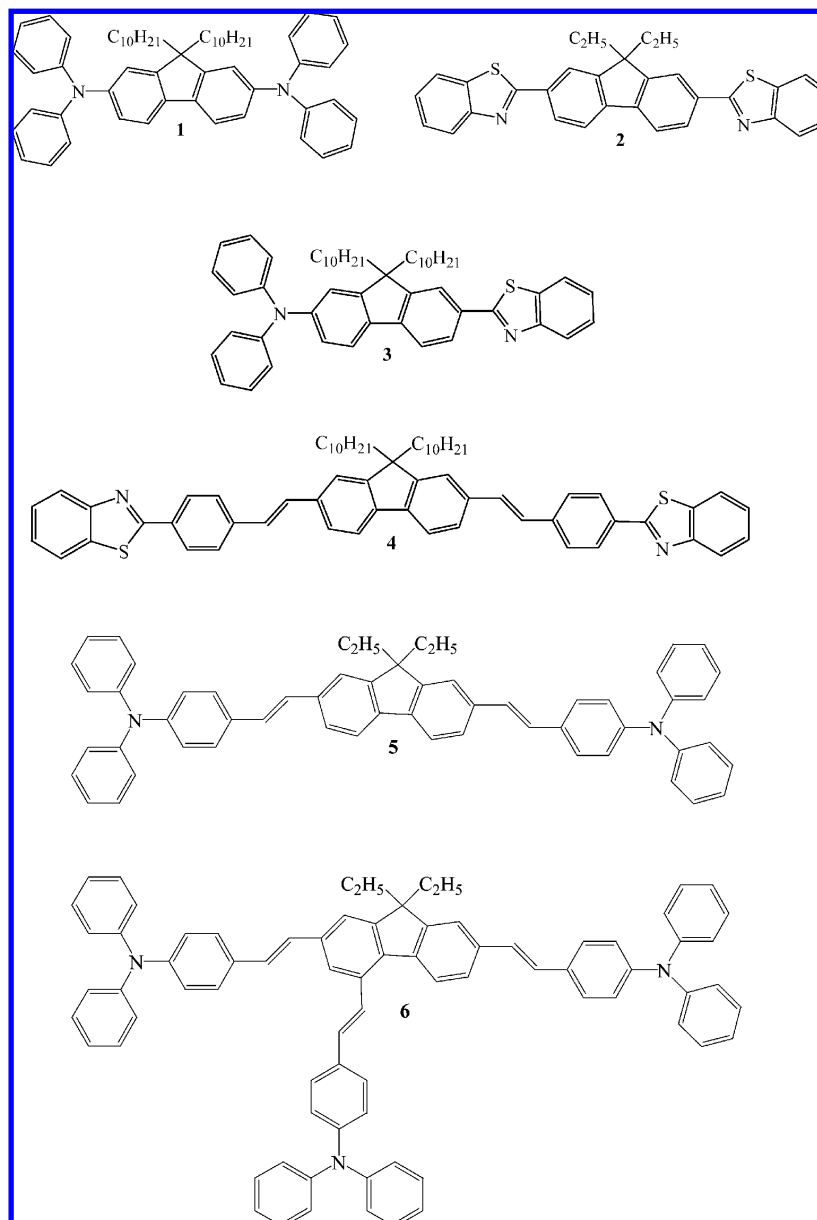‡ CREOL.
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Figure 1. Molecular structure of compounds **1**−**6**.

fluorescence emission of the molecule and/or sufficiently large pulse energies are utilized in the experiments (nanosecond or picosecond excitation). All of these processes can dramatically alter the values of 2PA cross sections, δ_{2PA}, obtained by the Z-scan method.

II. Experimental Description and Theoretical Analysis

A. Materials and Methods. Fluorene derivatives 9,9-didecyl-2,7-bis-(*N*,*N*-diphenylamino)fluorene (**1**), 9,9-diethyl-2,7-bis-(*N*,*N*-benzothiazoyl)fluorene (**2**), (7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)-diphenylamine (**3**), 2,7-bis-[4-(9,9-didecyl-fluoren-2-yl)-vinyl]phenylbenzothiazole (**4**), 4,4′-[[9,9-bis(ethyl)-9H-fluorene-2,7-diyl]di-2,1-ethenediyl]bis(*N*,*N*-diphenyl)benzeneamine (**5**), and 4,4′,4″-[[9,9-bis(ethyl)-9H-fluorene-2,4,7-triyl]tri-2,1-ethenediyl]tris(N,N-diphenyl)benzeneamine (**6**) were synthesized previously as described in references 20, 21, 26, and 27. Their chemical structures are presented in Figure 1. Spectroscopic grade solvents, hexane and tetrahydrofuran (THF), were used. The linear absorption spectra of **1**−**6** were measured with an Agilent 8453 UV−visible spectrophotometer in 10 mm path length quartz cuvettes at concentrations $C \le 2 \times 10^{-5}$ M. The optical densities of more concentrated solutions prepared for 2PA measurements ($5 \times 10^{-4} \le C \le 4 \times 10^{-2}$ M) were measured in 1 mm, 0.1 mm, and 0.01 mm quartz cuvettes. The fluorescence and excitation anisotropy spectra were determined with a PTI Quantamaster spectrofluorimeter in dilute solutions ($C \le 10^{-6}$ M) using 10 mm fluorometric quartz cuvettes. The 2PA cross sections, δ_{2PA}, were determined employing the well-known open aperture Z-scan method[9] (see Figure 2) with a picosecond Nd:YAG laser (PL 2143 B Ekspla) coupled to an optical parametric generator (OPG 401/SH). The excitation laser beam with pulse duration ≈ 35 ps (fwhm), pulse energies 0.05 μJ $\le E_P \le 8$ μJ, and repetition rate 10 Hz was tuned over the spectral range 500−900 nm. The values of δ_{2PA} were determined by the modified fitting procedure (see section IIB). For Z-scan measurements, compounds **1**−**6** solutions were placed in a 1 mm quartz cuvette at concentrations $10^{-3} \le C \le 4 \times 10^{-2}$ M.

B. Modified Z-Scan Fitting Procedure. In the case of degenerate pure 2PA, the values of the time integrated energy

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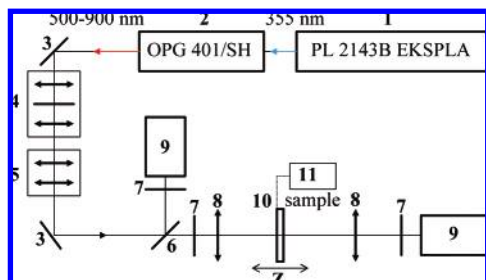*J. Phys. Chem. B, Vol. 111, No. 44, 2007* **12725**

Figure 2. Experimental setup of open aperture Z-scan. Picosecond laser (1); optical parametric generator (2); 100% reflection mirrors (3); space filter (4); telescope (5); beam splitter (6); filters (7); focusing lens, 25 cm (8); silicon detectors (9); 1 mm cuvette (10); and step motor (11).

Figure 3. Simplified three-level electronic molecular model for the modified fitting: S_0, S_1, and S_2 are the ground, first, and second excited singlet electronic states, respectively; σ_{10}, σ_{12}, and δ_{2PA} are the one- and two-photon absorption cross sections of the corresponding transitions, respectively; τ_1 and τ_2 are the lifetimes of the first and second excited states, respectively; I is the irradiance of excitation.

transmittance in Z-scan measurements (see Figure 2) can be analytically expressed for spatially and temporally Gaussian beam profiles as:[9]

$$T(z) = \frac{1}{\sqrt{\pi}\beta I_0(z)L} \int_{-\infty}^{+\infty} \ln[1 + \beta I_0(z)L \exp(-t^2)]\, dt \quad (1)$$

where β is the 2PA coefficient, L is the length of the sample, and z and t are the longitudinal space coordinate and time, respectively. $I_0(z) = 2E_P/\pi^{3/2}\omega(z)^2\tau$, where E_P is the pulse energy, $\omega(z)$ is the transverse size of the beam (HW1/e²M), and τ is the laser pulse duration (HW1/eM). The value of β and 2PA cross section are correlated through, $\delta_{2PA} = \beta \cdot h\upsilon/N$ ($h\upsilon$ is the photon energy, and N is the molecular concentration in the sample)[28] and β can be determined by fitting eq 1 to the experimental data. It should be noted that eq 1 is based on the following assumptions: (i) thin sample approximation, that is, $L < z_0 = \pi \cdot \omega(z = 0)^2/\lambda$ (λ is the laser wavelength); (ii) nearly all molecules in the excited volume of the sample remain in their ground electronic state under excitation, that is, the population of the first excited state, $N_1 \ll N_0 \approx N$, where N_0 is the ground state population per unit volume; and (iii) no reabsorption and stimulated emission processes occur upon excitation.

The comprehensive analysis of these assumptions is needed to make correction for the determination of the coherent δ_{2PA}. Pure 2PA processes, under the assumptions described above, should be characterized by a nearly linear dependence of $1/T(0) - 1$ on the pulse energy E_P. Therefore, accurate determination of this dependence for a wide range of E_P serves as a proof of pure 2PA process. Unfortunately, the range of suitable values of E_P for Z-scan measurements is restricted by the sensitivity of the equipment on one hand and by the necessary conditions i and ii on the other hand. Therefore, results for δ_{2PA} determination can have relatively low accuracy. Moreover, most organic molecules possess a significant ESA contribution that can be considerably important in the determination of nonlinear absorption coefficients. In this case, assumption iii cannot be fulfilled, and the correct determination of δ_{2PA} by Z-scan measurements and the fitting procedure with eq 1 is not accurate, even for femtosecond excitation where the population of the excited states is sufficiently small ($N_1 \ll N_0$).

In this work, a modified fitting procedure was developed and implemented for the Z-scan method, on the basis of a three level molecular model (Figure 3). This approach takes into account possible reabsorption and stimulated emission processes. Also, it is assumed that excitation pulse remains of Gaussian shape in space and time within the sample because of sufficiently small Z-scan signals, when maximum changes in transmittance did
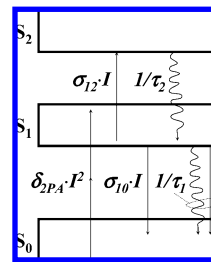
not exceed $10-20\%$. Triplet electronic states have been excluded because of the small intersystem crossing rate constants for the fluorene derivatives, studied herein.[29] The distribution of the molecules between electronic levels under pulsed excitation can be described by the following differential equations:

$$dN_0(z,r,t)/dt =$$
$$-N_0(z,r,t)\delta_{2PA}I(z,r,t)^2/2 + N_1(z,r,t)[\sigma_{10}I(z,r,t) + 1/\tau_1]$$

$$dN_1(z,r,t)/dt = N_0(z,r,t)\delta_{2PA}I(z,r,t)^2/2 -$$
$$N_1(z,r,t)[(\sigma_{10} + \sigma_{12})I(z,r,t) + 1/\tau_1] + N_2(z,r,t)1/\tau_2$$

$$dN_2(z,r,t)/dt = N_1(z,r,t)\sigma_{12}I(z,r,t) - N_2(z,r,t)1/\tau_2 \quad (2)$$

where $N_i(z,r,t)$ ($i = 0, 1, 2$) are the population per unit volume of electronic levels S_0, S_1, and S_2, respectively. σ_{10}, σ_{12}, τ_1, and τ_2 are the one-photon absorption cross sections and lifetimes of the corresponding levels, as shown in Figure 3. $I(z,r,t)$ is the irradiance of a spatially and temporally Gaussian beam profile with units $cm^{-2}\ sec^{-1}$. The set of eqs 2 was solved by the Runge−Kutta method.[30] The sample transmittance on z was numerically determined by the expression:

$$T(z)_{Mod} = \frac{4}{\sqrt{\pi}\omega(z)^2\tau} \int_r \int_t \exp[-2r^2/\omega(z)^2 - t^2/\tau^2] \times$$
$$[1 - k(z,r,t)L]r\, dr\, dt \quad (3)$$

where the nonlinear absorption coefficient $k(z,r,t)$ was calculated from eqs 2 as:

$$k(z,r,t) = N_0(z,r,t)\delta_{2PA}I(z,r,t) + N_1(z,r,t)(\sigma_{12} - \sigma_{10}) \quad (4)$$

τ_1 and σ_{10} can be determined from the linear absorption and fluorescence spectra. The unknown parameters δ_{2PA}, σ_{12}, and τ_2 can be varied to obtain the best fit of eq 3 to two or three experimental Z-scan curves simultaneously. Under these conditions, the absolute values of δ_{2PA} can unambiguously be determined from the experimental data with an accuracy of $20-25\%$. The same procedure was performed at different excitation wavelengths, λ_{exc}, and 2PA spectra of the fluorenes derivatives were obtained over a broad spectral range.

III. Results and Discussion

A. Linear Spectral Properties of Fluorene Derivatives. Figure 4 shows the normalized absorption and fluorescence emission spectra of compounds **1−6** in hexane and their excitation anisotropy spectrum in *p*THF (see Table 1). In concentrated solutions, which are typically used for Z-scan
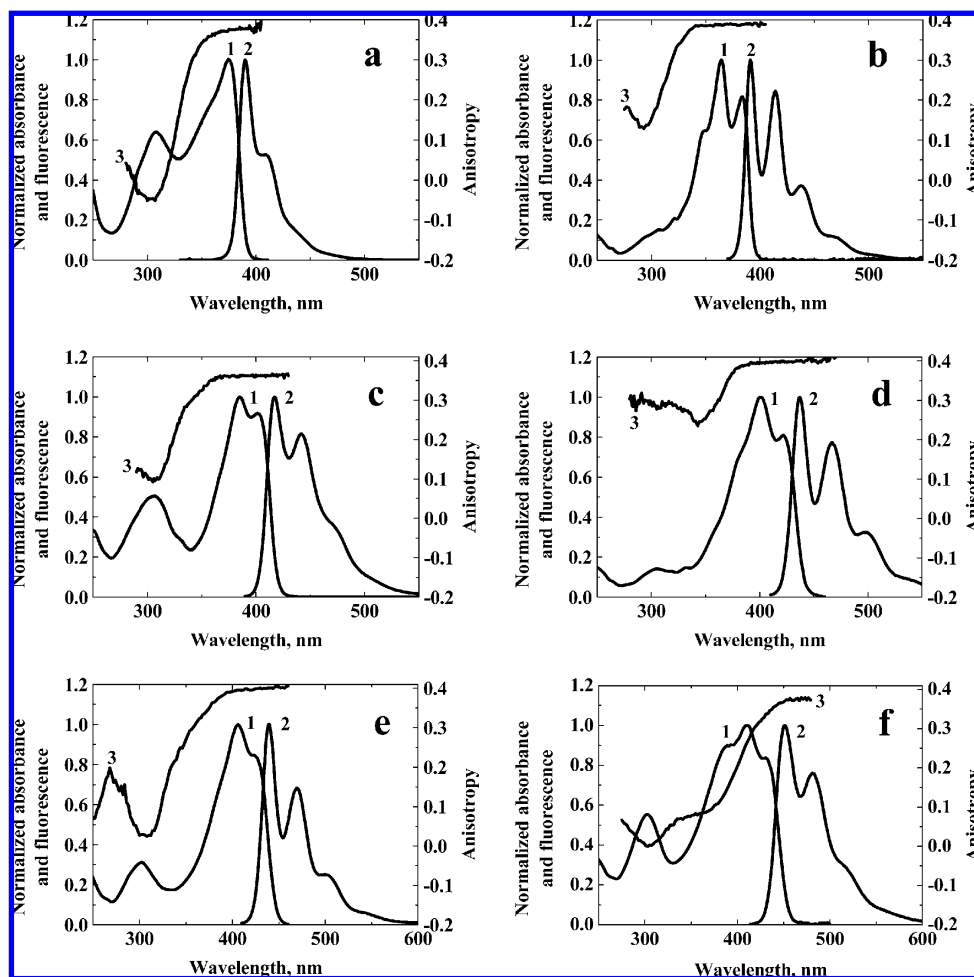
Figure 4. Normalized absorption (1), fluorescence (2) and excitation anisotropy (3) spectra in hexane (1, 2) and pTHF (3): (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

TABLE 1: One-Photon Absorption Cross Sections at the Maximum of the Main Absorption Band, σ_{01}^{max}, and Lifetimes of the First Excited State, τ_1, for 1−6 in Hexane

N/N	1	2	3	4	5	6
$\sigma_{01}^{max} \times 10^{16}$, cm^2	1.7 ± 0.1	2.8 ± 0.15	2.0 ± 0.1	2.2 ± 0.2	3.8 ± 0.2	3.8 ± 0.2
τ_1,[a] ns	0.95 ± 0.05	0.78 ± 0.05	1.25 ± 0.05	1.5 ± 0.2[b]	0.97 ± 0.05	1.11 ± 0.05

[a] References 31 and 33. [b] Estimated from the steady-state spectral data.[31,34]

measurements, the formation of molecular aggregates, such as dimers, can affect the corrected determination of δ_{2PA}. Therefore, the influence of molecular concentration, C, on the absorption spectrum of fluorenes (Figure 4, curves 1) was investigated. The values of maximum one-photon cross sections σ_{01}^{max} and the shape of the absorption spectrum remained intact in all six fluorene derivatives for concentrations up to 3×10^{-2} M. Hence, a negligible amount of aggregated molecules formed in high concentration fluorene solutions utilized in our Z-scan measurements.

The fluorescence spectra of **1−6** are characterized by well-defined vibronic structures and relatively small Stoke's shifts in hexane (Figure 4, curves 2). No specific charge transfer was observed for the emitting excited states of these fluorenes.[31] Therefore, one can estimate the values of $\sigma_{10}(\lambda_{exc})$ by the known σ_{01}^{max} from the absorption and the fluorescence spectra.[32] This data along with the corresponding lifetimes (Table 1) were utilized in the modified Z-scan fitting procedure (modified change in transmittance equations).

The excitation anisotropy spectra of **1−6** (Figure 4, curves 3) provide information regarding the nature of the linear

absorption bands. Constant values of anisotropies in the range of excitation wavelength, $\lambda_{exc} \geq 360$ nm (fluorenes **1** and **3**), $\lambda_{exc} \geq 340$ nm (**2**), and $\lambda_{exc} \geq 390$ nm (**4**, **5**), correspond to the main absorption bands primarily associated with one-photon electronic transition $S_0 \rightarrow S_1$. The change in the anisotropy of branched fluorene **6** (Figure 4f, curve 3) at $\lambda_{exc} \geq 360$ nm indicates the complex nature of the main absorption band of this compound. This band includes at least two one-photon allowed electronic transitions associated with different conjugated chromophore systems.[35] The minimum anisotropy values of **1−6** in the short wavelength region at $\lambda_{exc} \approx 305$ nm (compounds **1**, **3**, **5**, and **6**), $\approx$295 nm (**2**), and $\approx$340 nm (**4**) indicate the spectral position of higher energy electronic transitions $S_0 \rightarrow S_n$ that can play an important role in 2PA processes.

B. Z-scan Measurements and 2PA Spectra. The modified Z-scan fitting described above (see section IIB) allows us to obtain the time- and space-dependent molecular distribution between electronic states, $N_i(z,r,t)$ ($i = 0, 1, 2$), under different types of excitation (see Figure 5a,b, curves 2,3). From Figure 5a,b, it can be seen that, for picosecond excitation with $E_P \geq 1$
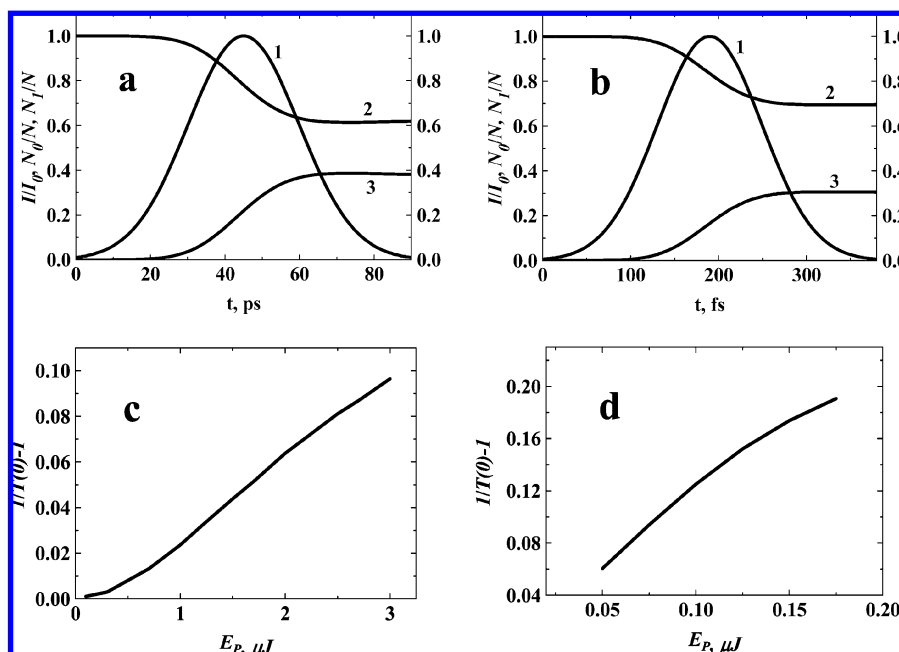
Figure 5. Calculated dependences: (a) shows the time-dependent excitation irradiance $I(0,0,t)/I_0(0)$ (1), distribution of the molecular population $N_0(0,0,t)/N$ (2), and $N_1(0,0,t)/N$ (3) at $\sigma_{10} = \sigma_{12} = 0$; $\tau_1 = 1$ ns and $\delta_{2PA} = 300$ GM under picosecond excitation ($\tau = 21$ ps (35 ps fwhm); $E_P = 1$ μJ; $\omega(0) = 10$ μm; $I_0(0) = 8 \times 10^{28}$ cm$^{-2}\cdot$s^{-1}); (b) shows $I(0,0,t)/I_0(0)$ (1), $N_0(0,0,t)/N$ (2), and $N_1(0,0,t)/N$ (3) at $\sigma_{10} = \sigma_{12} = 0$; $\tau_1 = 1$ ns and $\delta_{2PA} = 300$ GM under femtosecond excitation ($\tau = 84$ fs (140 fs fwhm); $E_P = 0.1$ μJ; $\omega(0) = 10$ μm; $I_0(0) = 10^{30}$ cm$^{-2}\cdot$s^{-1}); (c) shows the dependences $1/T(0) - 1 = f(E_P)$ at $\sigma_{10} = 0$; $\sigma_{12} = 10^{-17}$ cm^2; $\tau_1 = 1$ ns; $\tau_2 = 1$ ps; $\delta_{2PA} = 300$ GM, and $C = 10^{-3}$ M under picosecond excitation ($\tau = 21$ ps; $\omega(0) = 10$ μm; $\lambda_{exc} = 700$ nm); and (d) shows $1/T(0) - 1 = f(E_P)$ at $\sigma_{10} = 0$; $\sigma_{12} = 10^{-17}$ cm^2; $\tau_1 = 1$ ns; $\tau_2 = 1$ ps; $\delta_{2PA} = 300$ GM, and $C = 10^{-3}$ M under femtosecond excitation ($\tau = 84$ fs, $\omega(0) = 10$ μm; $\lambda_{exc} = 700$ nm).
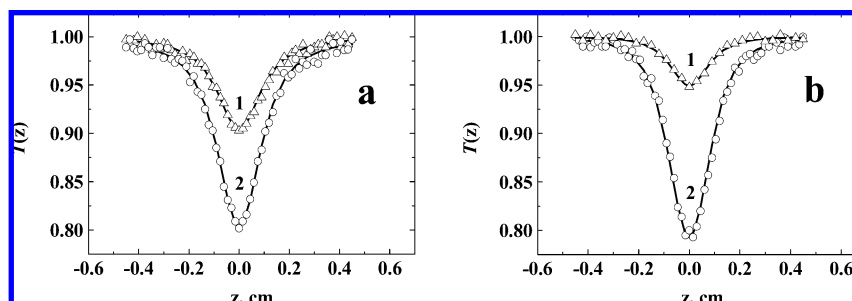

Figure 6. Open aperture Z-scan traces for fluorene compounds **1** (a) and **2** (b) in hexane at $\lambda_{exc} = 500$ nm and corresponding concentrations 1.8 $\times 10^{-2}$ M and 4.4 $\times 10^{-3}$ M. The solid lines are the best theoretical fitting of both open aperture Z-scan curves with different energies: (a) $E_P = 1$ μJ (1) and 2 μJ (2); (b) 2 μJ (1) and 5 μJ (2).

μJ (a) and femtosecond excitation with $E_P \geq 0.1$ μJ (b), the thin sample approximation is not satisfied at the center of the excitation pulse, $z = 0$ and $r \approx 0$ for pure 2PA processes ($\sigma_{10} = \sigma_{12} = 0$). Typical molecular parameters used were $\tau_1 = 1$ ns and $\delta_{2PA} = 300$ GM. This means that the energy range corresponding to the fulfillment of conditions i and ii is sufficiently restricted, and experimental proof of the linearity for the dependence $1/T(0) - 1 = f(E_P)$ is not accurate (where $f(E_P) \approx \beta L/\pi\omega(0)^2 \tau E_P$). On the other hand, the dependences $1/T(0) - 1 = f(E_P)$ calculated for 2PA considering additional ESA processes ($\sigma_{12} \neq 0$) are close to a linear function over a broad range of E_P (Figure 5c,d). In this case, it is difficult to extract information about possible participation of ESA from the nonlinear absorption processes from the shape of the experimental curves $1/T(0) - 1 = f(E_P)$ because of low experimental accuracy. From this analysis, it is apparent that the modified Z-scan fitting procedure provides a more accurate determination of δ_{2PA}, regardless of the type of excitation.

Experimental Z-scan curves, obtained under picosecond excitation, for fluorenes **1** and **2**, are shown in Figure 6. Similar

Z-scan data were obtained for **1−6** over the spectral range 500 nm ≤ λ_{exc} ≤ 900 nm and at different E_P. The values of δ_{2PA} obtained by the modified fitting procedure with simultaneous fit of two experimental Z-scan curves by eq 3 are presented in Figure 7 curves 2. It should be noted that the best fitting for pure 2PA, using eq 1, yield values that are up to 30 times larger than those obtained using eq 3 (see Table 2 for comparison). The 2PA spectra of compounds **5** and **6**, determined using $T(z)_{Mod}$ (Figure 7c−f, curves 2), are in good agreement with the corresponding spectra obtained using the femtosecond two-photon fluorescence method.[24]

As shown in Figure 7, compounds **1** and **2**, the more centrosymmetric fluorene derivatives of our series, exhibit smaller δ_{2PA} in the main linear absorption band than the other four. These results were expected since two-photon transitions within that band are forbidden for centrosymmetric molecules. In contrast, longer symmetrical fluorenes such as **4** and **5** exhibited stronger 2PA within the stronger linear absorption bands. Perhaps, vibronic coupling in **4** and **5**, resulting in
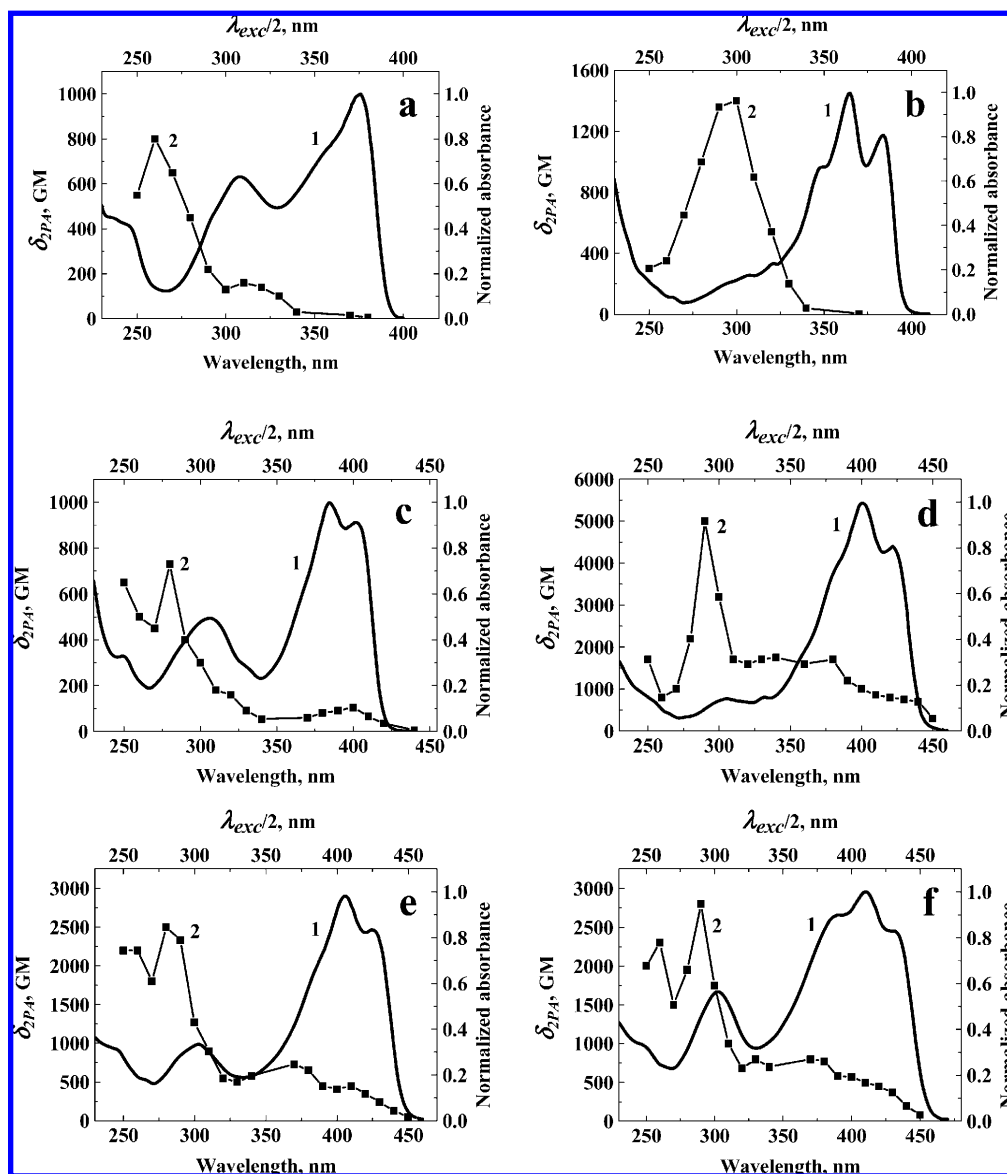
Figure 7. Linear absorption (1) and 2PA (2) spectra of compounds **1−6** in hexane: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

TABLE 2: 2PA Cross Sections of Fluorenes 1−6 Obtained with Modified and Classical 2PA Fitting

compound	λ_{exc}, nm	δ_{2PA}, GM		
		modified 2PA fitting[a]	classical 2PA fitting[a]	ref data[b]
1	600	130	2400	∼ 200[e]
	740	15	110	-
2	600	1400	4900	-
	680	40	440	<50[d]
3	600	300	2800	-
	740	60	2200	60−80[e]
4	600	3200	5300	6000[d]
	800	1000	3900	1700[c]
5	600	1270	5250	1300[c]
	800	410	3600	500[c]
6	600	1750	8000	2200[c]
	800	570	6000	700[c]

[a] Data corresponding to picosecond excitation. [b] Data corresponding to femtosecond excitation. [c] Reference 21. [d] Reference 27. [e] Reference 36.

symmetry breaking of the well-defined parity of the molecular wavefunctions, induces a stronger 2PA at that transition.[37]

Fluorene derivatives with acceptor-end substituents, **2** and **4**, exhibited higher 2PA cross sections into two-photon allowed electronic states (Figure 7b,d) than their corresponding donor-end substituted molecules **1** and **5** (Figure 7a,e). These difference are determined by the nature of higher excited singlet electronic states that can enhance the excited-state transition dipoles for acceptor-end substituted fluorenes.[36]

The maximum of the 2PA spectrum of **2** (Figure 7b, curve 2) corresponding to a two-photon allowed electronic state is revealed in the one-photon excitation anisotropy spectrum (Figure 4b, curve 3). However, it is not observed in the linear absorption spectrum (curves 1). The short wavelength peaks in the linear absorption spectra of **1**, **3**, **5**, and **6** at a wavelength approximately 310 nm (Figure 7a,c,e,f curves 1) correspond to the diphenylamino-end substituents[35] and do not coincide with the 2PA maxima (curves 2). Therefore, it can be assumed that the electronic states of diphenylamino-end groups do not strongly participate in pure 2PA.

The nature of the pure 2PA mechanism and the experimental values of δ_{2PA} for **1−6** can be analyzed by the simplified three-level model, well-described in refs 38 and 39. According to this model, δ_{2PA}, within the two-photon allowed electronic state

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(S_f) is determined by the square of the transition dipoles μ_{01} and μ_{1f} between the corresponding electronic states $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_f$. The values of μ_{01}, μ_{1f}, and corresponding 2PA cross sections for compounds **1**−**6** were estimated from the quantum-chemical calculations performed in ref 36, where optimized geometries were obtained by a semiempirical AM1 method[40] for molecules in vacuum and electronic properties, including excited-state energies and transition dipoles calculated with INDO Hamiltonian in combination with the MRD CI technique.[41] A good agreement between experimental and calculated values has been found. Therefore, the simplified three-level model seems to be appropriate for 2PA in fluorene-based compounds. Additionally, fluorene derivatives **1**−**6** possess relatively large 2PA cross sections ($\delta_{2PA} \sim 700$−5000 GM) and are good candidates for a number of practical applications, including two-photon fluorescence imaging and 3D optical data storage.

IV. Conclusions

The experimental methodology and fitting procedure of the open aperture Z-scan method were analyzed for the case when ESA and stimulated emission processes occur in the medium. Weak ESA processes can dramatically change the values of 2PA cross sections determined from the pure 2PA fit and should be taken into account, even for femtosecond excitation. This analysis and corresponding fitting procedure affords the accurate determination of δ_{2PA}, independent of the type of excitation. This becomes extremely important considering the more wide-spread availability of broadly tunable picosecond relative to femtosecond systems.

The 2PA spectra of fluorene derivatives **1**−**6** with different electronic nature were determined over the broad spectral range (500−900 nm) by a picosecond open aperture Z-scan method with modified fitting that takes into account reabsorption and stimulated emission. The spectra are in good agreement with their corresponding ones obtained with the femtosecond up-converted fluorescence method. The electronic states of di-phenylamino end groups of compounds **1**, **3**, **5**, and **6** do not directly participate in 2PA processes. Fluorenes **1**−**6** exhibited high 2PA cross sections ~700−5000 GM upon excitation in two-photon allowed electronic states and have a great potential for various nonlinear optical applications.

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