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Two-Photon absorption cross-section measurement by thermal lens and nonlinear transmission methods in organic materials at 532 nm and 1064 nm laser excitations

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Experimental results concerning two-photon absorption (TPA) cross-section measurement using nonlinear transmission (NLT) method and a new pump-probe mode-mismatched thermal lens (TL) scheme, in picosecond regime are reported. Both methods are used in a prospect of comparison. Values of the TPA coefficient and cross-section in three common solvents (Chloroform, Benzene and Nitrobenzene) and new synthesized perylenediimide derivatives (PDI) at 532nm and 1064nm wavelengths are given.

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1. Introduction

Materials that exhibit strong two-photon absorption (TPA) are currently of great interest because of their potential applications in optical limiting, frequency up-converted lasing, three-dimensional optical data storage multiphoton fluorescence microscopy, photonic crystal fabrication [1-10] and photodynamic therapy [11-13].

Usually, three kinds of methods are used to determine TPA cross section of a molecule: (1) transmission methods such as nonlinear transmission (NLT) and Z-scan techniques, (2) fluorescence methods such as two-photon induced fluorescence, (3) thermo-optical methods such as photo-acoustic and thermal-lens techniques.

Transmission methods [14-18] measure the light intensity transmitted by the sample as a function of the input intensity. To observe TPA with these methods, laser intensities of a few hundreds of 100MW/cm^2 at least, are necessary in many materials. At such high intensities, many kinds of non linear phenomena such as stimulated scattering (Raman and Rayleigh scattering), excited-state absorption, self-phase modulation, may compete strongly with TPA. In many cases it is very difficult to interpret the data correctly. Therefore, caution is warranted when using the transmission methods. Despite everything, nonlinear transmission (NLT) and open z-scan techniques methods are very much used in practice to study TPA [19-21].

The fluorescence method [22,23] is based to the measurement of the fluorescence induced by TPA only. This technique is more selective and thus more precise. Although this technique offers a better sensitivity than the methods by transmission, it is appropriate especially for the fluorescent molecules. For the non fluorescent or the slightly fluorescent molecules, this technique is inoperative.

The thermo-optical methods [24,26] belong to the class of highly sensitive absorbance techniques based on the measurement of the temperature rise following the conversion of absorbed optical radiation into heat through non-radiative relaxation processes. These methods are generally classified into two categories: *photo-acoustic spectroscopy* which refers to the generation of acoustic waves in the sample [27-31] and *thermal lens spectroscopy* which detects a change in the refractive index of the solvent [32-35]. These techniques are known in linear spectroscopy and are used to measure the small absorption in low-loss liquids and solids. Absorption as small as 10^{-6} cm^{-1} can be measured using thermo-optical techniques, but they are also appropriate in non linear spectroscopy, especially in the studies of some dyes in which non-radiative relaxation are predominant [31-33].

We can also recall that one of the most promising applications of TPA today is photodynamic therapy (PDT). From this viewpoint, the design for organic molecules that function as singlet oxygen sensitizers and that can generate singlet oxygen in a two- photon irradiation scheme is very active field of research. The two most important physical properties such sensitizers must posses are a large two-photon absorption (TPA) cross section and a large singlet oxygen quantum yield. In addition, it was shown that the high fluorescence quantum yield is counter productive singlet oxygen generation.

Consequently, for the TPA cross section measurement of such molecules, the fluorescence techniques are ineffective. In such cases, only the thermo-optical methods can be used.

In this paper we present the results of the TPA study of three classical solvents (chloroform, nitrobenzene and benzene), and in new PDI derivatives, using the non linear transmission (NLT) method and the mode-mismatched thermal lensing method. The goal of this study is to compare the results obtained by the two techniques.

Section 2 discusses the relevant parameters in TPA cross-section measurements using the two methods. The experimental setup is presented in Sections 3. In Section 4 we present our results in detail and discuss several key issues related to TPA cross-section measurements.

2. Theoretical models

2.1 Nonlinear transmission (NLT)

Let us start by briefly recalling, the expression of the nonlinear transmission of a sample. The change in intensity I experienced by a beam propagating along z through a medium exhibiting n-photon absorption process can be described by generalized Beer-Lambert law [15,16] :

$$\frac{dI}{dz} = -\alpha_{lin} I - \alpha^{<n>} I^n \quad ; \quad \text{n}>1 \tag{1}$$

The integration of this equation gives the non linear transmission of the sample which is written**:**

$$T_{n,photons} = \frac{T_{lin}}{\left[1+\alpha^{<n>} I_0^{(n-1)} L_{eff}^{<n>}\right]^{\frac{1}{(n-1)}}} \approx \frac{T_{lin}}{\left[1+\left(\frac{1}{n-1}\right)\alpha^{<n>} I_0^{(n-1)} L_{eff}^{<n>}\right]} \tag{2}$$

where I_0 is the input intensity, ℓ is the sample path length, $L_{eff}^{<n>} = \left[\frac{1-e^{-(n-1)\alpha_{lin}.\ell}}{\alpha_{lin}}\right]$ is its effective length, and $T_{lin} = \exp(-\alpha_{lin}.\ell)$ is the Lambert-Berr law in the linear absorption case. In the case of TPA, the non linear transmission is written:

$$T_{2,photons} \approx \frac{T_{lin}}{\left[1+\alpha^{<2>} I_0 \left(\frac{1-e^{-\alpha_{lin}.\ell}}{\alpha_{lin}}\right)\right]} \tag{3}$$

where $\alpha^{<2>}$ is the TPA coefficient which is related to the TPA cross-section σ_2 by the relation :

$$\alpha^{<2>} = 2N \frac{\sigma_2}{h.f} \tag{4}$$

where N represents the atomic /molecular number density and the factor 2 arises from the absorption of two photons. h is Planck's constant and f is the frequency of the excitation light.

If the linear absorption of the sample is weak at the wavelength of excitation ($\alpha_{lin} \approx 0)$, then the relation (3) becomes :

$$T_{2,photons} \approx \frac{1}{1+\alpha^{<2>} I_0 \ell} \tag{5}$$

This approximation assumes a uniform beam profile at the sample, which of course is not typically the case with the lasers which are medium with gain. For a pulse that is rectangular in time but Gaussian in space, it can be shown [16] that the transmission of the sample is:

$$T_{2,photons} = \frac{1}{\alpha^{<2>} I_0 \ell} \ln(1+\alpha^{<2>} I_0 \ell) \tag{6}$$

We analysed the data by performing fits of $T_{2,photon}$ defined by the relation above versus the input intensity I_0 assuming a pure two-photon process.

2.2 Thermal lens (TL)

The second method that we used to measure the TPA cross-section of absorption of the solvents studied is the thermal lens technique. Experiment was done in the pump-probe scheme and in the mode mismatched configuration. The TL signal in this special case has been calculated using Fresnel approximation [32,33]. For multi-photon absorption, considering Gaussian pump and probe beams and low thermal phase values, the TL signal can be expressed by:

$$S(z,t) = \frac{4n\Phi_0 m(z)\nu(z)}{\left[1+2nt/t_c(z)+2nm(z)\right]^2 + \upsilon^2\left[1+2nt/t_c(z)^2\right]\left[1-(z-z_b)^2/z_{0e}^2\right]} \tag{7}$$

where *n* is the number of absorbed photons,

$$\Phi_0 = \left[\left(\partial n_r / \partial T\right) 2\pi.\ell.N.\sigma_n.\hbar\omega_e /(\lambda_p \rho c_p)\right] \int_0^{\tau_e} \left|\varphi\left(t'\right)\right|^n dt', \tag{7a}$$

$$t_c(z) = w_e^2(z)/(4D) \tag{7b}$$

$$m(z) = w_p^2(z)/w_e^2(z), \tag{7c}$$

$$w_p = \left(\lambda_p z_p / \pi\right)^{1/2} \left[1 + \left(z - a_p\right)^2 / z_p^2\right]^{1/2}, \tag{7d}$$

$$w_e = \left(\lambda_e z_e / \pi\right)^{1/2} \left(1 + z^2 / z_e^2\right)^{1/2}, \tag{7e}$$

$$\nu(z) = (z - a_p)/z_p + \left[z_p/(d - z)\right]\left[1 + \left(z - a_p\right)^2 / z_p^2\right], \tag{7f}$$

In these relations, the indices *p* and *e* refer to the probe and excitation (or pump) beams respectively Hence, λ_p and λ_e are the wavelengths of the two beams, z_p and z_e are the confocal parameters. a_p is the probe beam waist position while the pump beam waist position is taken to be the origin of the optical system. Z *and* ℓ are the sample position and path length respectively. ω_e is the excitation field frequency. *N* is the atomic /molecular number density (measured in molecules per cm^3). φ is the incident photon flux at the beam waist. ρ, c_p, $\frac{\partial n_r}{\partial T}$ and D are the density, c_p is the heat capacity, $\partial n_r/\partial T$ is the thermal gradient of the refractive index, D heat diffusivity coefficient of the sample respectively and *d* is the detector position. Φ_0 represents the phase shift induced by TL effect. The law of variation of this parameter with the exciting beam intensity is such as:

$$\Phi_0 \propto I_0^n \tag{8}$$

Hence, the thermal lens signal is proportional to I_0^n where n is the photon number involved in absorption process. The relation (8) is valid only if the process of relaxation of the atom/molecule which absorbs is purely non-radiative (all absorbed energy is converted into heat). If not, we can observe in practice a variation with this relation [33]. As it is seen, the determination of the type of absorption which takes place in a material following an excitation with a given wavelength is a rather easy operation with TL technique. Indeed, the slope of the log-log plot of TL signal versus input energy represents the number of exciting photon *n*.

3. Experimental

The schematic representation of the experimental system is shown in figure 1. It is designed for z-scan experiments and adapts easily to the nonlinear transmission (NLT) and the dual-beam thermal lens (TL) experiments. The excitation (or pump) beam is provided by 30ps light pulses which are generated with an amplified mode-locked, frequency doubled, Quantel Nd:YAG laser, operating at a repetition rate of 1Hz.

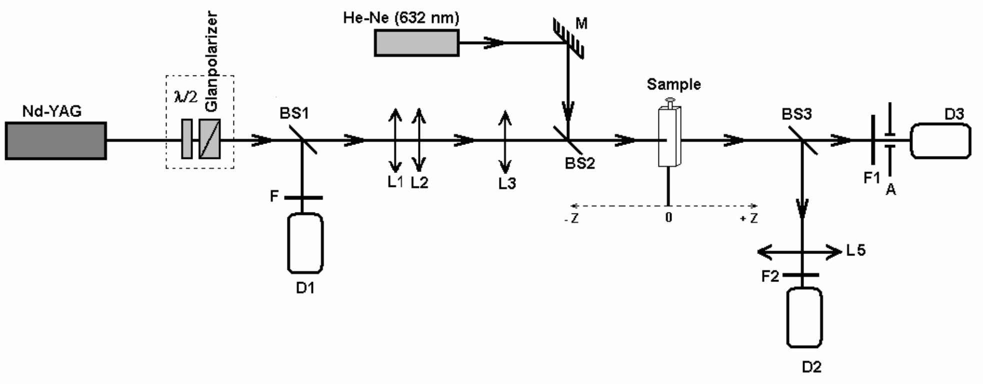

Fig. 1. Experimental scheme consisting of a Nd-YAG laser (pump beam), a He-Ne laser (probe beam), Half wave plate, a Glan-polarizer, beam splitters BS1, BS2 and BS3, lenses L1, L2, L3, L4 and L5; filters F1 and F2, a sample, aperture A, photodiodes D1, D2 and D3.

The probe beam is generated by a cw He-Ne laser (632 nm, 1mW), which is directed toward the sample collinearly with the pump beam and without focusing using beam splitter BS2. The sample is contained in a glass cell $\left(\ell = 5mm \text{ or } \ell = 2mm\right)$ and located on a translation stage that allows its displacement through the z-axis. Let us note that in these experiments, the sample keeps a fixed position, while incident energy on the sample is variable.

The unit consisted the half-wave plate and the polarizer, is used to modulate the energy of the pump beam and the photodiode D1 allows to follow the fluctuations of this energy of one shooting to the other. The lenses L1 and L2 constitute an afocal system which allows to obtain the beam waist wished after the focusing lens L3.

For the NLT experiment, the energy of the pulse before and after the sample was monitored by two calibrated photodiodes. The laser beam transmitted by the sample, after passing through several optical neutral density filters, was focused onto the second photodiode D2, which measures the energy of the transmitted pulse. The special interference filter F2 cancels the probe light allowing transmittance of only the pump light. The transmitted pump light is focused onto detector D2 using the 10-cm focal length lens L5. The pump beam waist in the focus was estimated to be 8.7 µm (FWHM). The focal point was located in the centre of cell and approximately 1mm away from its side window.

In the pump-probe TL experiment, behind the sample, the beam-splitter BS3 redirects the beams toward photodiodes D2 and D3. Before impinging detector D3 (which gives, the mode-mismatched TL signal), the pump light is filtered by the special interference filter F1, which allows only the transmittance of probe light to the aperture A and then to detector D3. The photodiode D2 allows if necessary, to detect open z-scan signal which is also a measurement the absorption of the sample to the wavelength of the pump-beam.

We studied the multiphoton absorption properties of two kinds of materials: a) three common solvents which are chloroform, Benzene and Nitrobenzene and b) new synthesized PDI derivatives.

The solvents studied, are often used to study new organic molecules designed and synthesized for their non linear optical properties. In this respect, their multiphoton absorption properties are interesting to know. To study the mutliphoton properties of these solvents, we chose the wavelength of 532nm as exciting wavelength. Indeed, their UV-IVS spectra indicate the presence two photon of absorption (TPA) in each of these materials at 532nm wavelength [33]

As for the perylene diimide derivatives, they are widely used in the fields of paints and lacquers; but they are also key chromophores for high-technological applications such as photovoltaic cell, optical switches lasers and light emitting diodes [36, 37].

Figure2 presents the chemical structures and the UV-VIS spectra PDIs derivatives studied in this contribution. These compounds were functionalized by different substituents [Br_2, $(OPhtBu)_2$ and $(OPhtBu)_4$] to improve their solubility in various organic solvents and their electronic properties. Some of the PDIs derivatives functionalized were also covalently linked to C_{60} to improve their photovoltaic properties [38-41]. Considering the absorption spectra presented above, we used 1064nm as excitation wavelength of these PDIs derivatives.

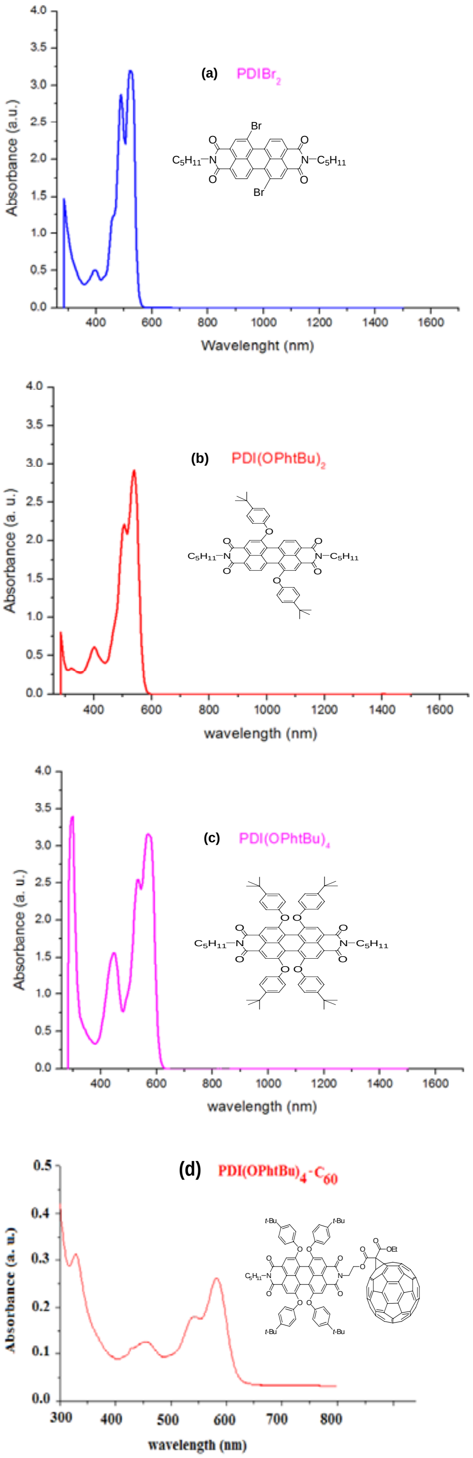

Fig. 2. UV-visible absorption spectra and molecular structures of PDIs derivatives studied:(a): PDI-Br_2, (b): PDI$(OPhtBu)_2$, (c): PDI$(OPhtBu)_4$ and (d): PDI$(OPhtBu)_4$-C_{60}

The molecular structure of the PDIs and their linear absorption spectra in toluene (1-mm-path) are shown in Figure 2. These spectra indicate that the one photon absorption of the four compounds studied is situated in the spectral region of 350 - 600nm and beyond, there is no linear absorption. However, we found that under the excitation of a 1064nm IR laser beam, a two-photon absorption could readily be observed.

For the multiphoton absorption measurements, we used two methods with a comparative aim: non linear transmission (NTL) and Thermal lens (TL) methods.

4. Results and discussions

4.1 Measurements in solvents at 532 nm wavelength

We measured the TPA cross-sections of three well known traditional solvents which are chloroform, Benzene and Nitrobenzene by using two experimental methods (NLT and TL) with a comparative aim.

The curves of figure 3 represent the NLT of the three solvents as a function of the incident laser intensity. They reveal that the exciting intensity from which the nonlinear losses appear depends on material. This intensity is about 1.2 GW/cm^2 for Chloroform, 0.4 GW/cm^2 for Benzene and 0.1 GW/cm^2 for Nitrobenzene.

On the other hand, these curves do not give any indication on the possible presence of other non linear effects.

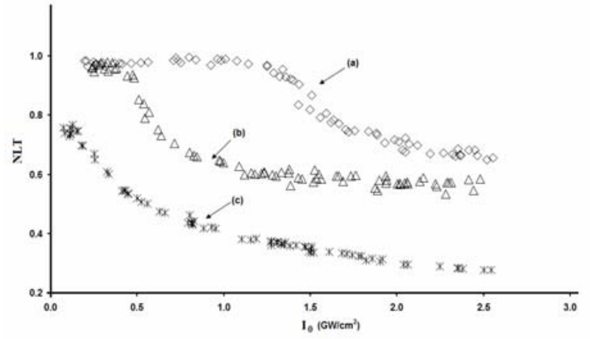

Fig. 3. Non Linear Transmission of the samples as a function of the incident intensity I_0 and λ_e = 532 nm (a): Chloroform, (b): Benzene , (c): Nitrobenzene.

To determine the non linear absorption coefficients of materials, we made the assumption of a prevalence of TPA. This assumption is based on the UV-VIS spectra of studied solvents which are presented elsewhere [33]. These spectra show indeed that, these materials exhibit TPA when they are excited with a wavelength of 532 nm.

Thus, by fitting the experimental data with the relation (6), we deduced the TPA coefficients $\alpha^{<2>}$ of the 3 materials. Consequently, we determined using the relation (4), the corresponding TPA cross-section σ_2. These results are presented in table 2 and we observe that the values of σ_2 (and of $\alpha^{<2>}$) are all the more low as the intensity threshold of appearance of nonlinear absorption is high:

$$\sigma_2\left(Chloroform\right) < \sigma_2\left(Benzene\right) < \sigma_2\left(Nitrobenzene\right)$$

The curve of figure 4 in log-log scale represents the TL signal as a function of the pump beam energy in Chloroform.

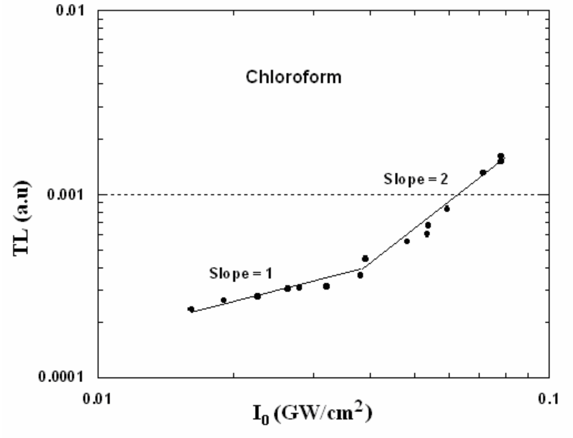

Fig. 4. Thermal Lens signal in chloroform (1mm path) versus pump beam intensity. λ_e = 532 nm.

Since it was underlined previously (§ 2.2), the TL signal depends on the phase shift Φ_0 induced by the pump beam, which in addition is proportional to I_0^n, where n the number of photons involved in the process of absorption. The curve of the TL signal as a function of the energy (or the intensity) of pump beam in log-log scale shows a linear trend. The slope of the second straight line gives directly n.

Thus, on the curves of figure 4, the line of slope 1 is characteristic of one photon absorption while the line of slope 2 relates to two photons absorption. Measurements in two other solvents (i.e. Benzene and Nitrobenzene) reveal the same kind of curves with two slopes n=1 and n=2 as expected.

Tables 1 and 2 show the physical characteristics of the solvents studied and the results of measurements from the two techniques used. In particular, in the table 2, we present the two photon absorption cross-section deducted from our measurements.

Table 1. Physical parameters characteristic of solvents. n_0: refractive index, K: thermal conductivity (W/°C.m), : thermal gradient of refractive index ,C_p: heat capacity (J/°C.g), ρ: density (g/m^3), Mm: molecular weight (g/mol), N: molecular density (10^{-20}molecules/cm^3) D: heat diffusivity coefficient (10^4cm^2/s) ,Φ_0: phase shift induced by photothermal effect.

Materials	n_o	K	$\frac{dn_r}{dT}$	c_p	ρ	Mm	N	D	Φ_0
Chloroform	1.443	0.145	6.0	0.96	1.489	119.4	75	10.2	0.34
Benzene	1.506	0.159	6.4	1.727	0.880	78.12	67.75	10.5	0.5
Nitrobenzene	1.556	0.163	5.1	1.430	1.204	123.11	58.87	9.47	0.14

From the relation (7a) where we put n=2, from the values of Φ_0, and the physical parameters characteristic of the solvents which are also indicated in table 1, we deduced the values of the two photons absorption cross sections σ_2 of the three samples. These values are indicated in table 2. Their comparison shows that: $\sigma_2(Chloroform) < \sigma_2(Benzene) < \sigma_2(Nitrobenzene)$. What is in agreement with the tendency observed for NLT technique. $I_{0,th}$ represents the threshold intensity.

Table 2. Comparison of the TPA parameters, $\alpha^{<2>}$ (10^{-8}cm.W^{-1}) and σ_2 (10^{-50}cm^4.s.molecule^{-1}) obtained by NLT and TL methods at λ_e = 532 nm.

Materials	NLT				TL				$\frac{I_{0,th}^{<NLT>}}{I_{0,th}^{<TL>}}$		$\frac{\sigma_2^{<NLT>}}{\sigma_2^{<TL>}}$
	$I_{0,th}$	$\alpha^{<2>}$	σ_2		$I_{0,th}$	$\alpha^{<2>}$	σ_2				
Chloroform	1.4	0.10	2.5		0.04	0.034	0.84		35		3
Benzene	0.4	0.25	6.88		0.02	0.078	2.5		20		2.75
Nitrobenzene	0.1	0.87	27.6		0.016	0.13	4.12		6.25		6.7

On the other hand, the comparison of the values obtained by the two techniques shows that

$$\sigma_2(NTL) > \sigma_2(TL).$$

4.2 Measurements in PDI derivatives

Towards the spectres of linear absorption shown figure2, we used 1064nm as wavelength of the beam pumps to study the multiphoton absorption properties of the PDIs derivatives. Chloroform was used as solvent because this solvent has no multiphoton absorption at 1064nm.

As in the previous section (4.a), we used NLT and TL and as techniques of measurement. The non linear transmission curves observed for four PDI derivatives studied, present the same tendency as those of the figure3: the transmission in each of the samples decreases when the incident intensity laser I_0 increases. The values of the coefficients $\alpha^{<2>}$ and σ_2 deducted from these measurements are indicated in the table3.

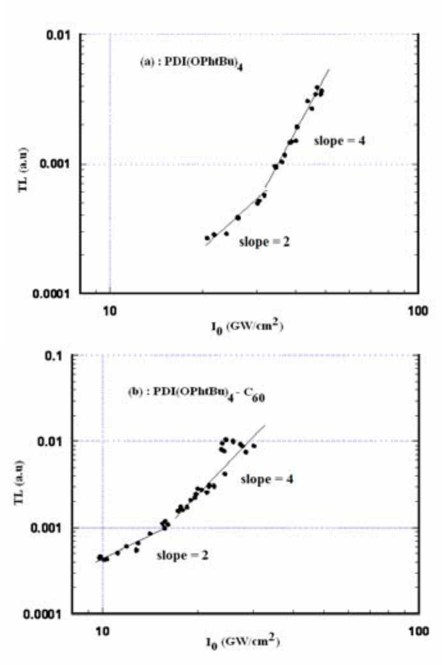

Fig. 4. Thermal Lens signal versus pump beam energy at λ_e = 1064 nm for PDI-(OPhtBu)$_4$ and PDI-(OPhtBu)$_4$-C$_{60}$

In figures 4a and 4b, we present the results of measure of thermal lens in the samples of PDI-(OPhtBu)$_4$ and PDI-(OPhtBu)$_4$-C$_{60}$ as a function of the incident pump-beam laser intensity. These curves are representative results obtained in 4 samples; what means that in each of the sample, we obtain a straight line of slope 2 and another straight line of slope 4.

The straight line of slope 2 is characteristic of the two-photon absorption (TPA) process whereas the right of slope 4 is characteristic of another multiphpton process [33].

The experimental values obtained by both methods of measurement are given in the table3.

We can note that as in the case of the study of solvents at 532nm, the values of the two photon absorption cross-section σ_2 obtained by the NTL method, are more higher than those obtained by the TL technique. However, we can note that for the same method of measurement, the values of σ_2 of the various of PDI derivatives are the same order of magnitude. What means in other words that the various substituents used in the fonctionnalisation of the perylene diimide do not play major role in the two absorption process of these compounds.

Table 3. Comparison of the TPA parameters $\alpha^{<2>}$ (10^{-10}cm.W^{-1}) and σ_2 (10^{-50}cm^4.s.molecule^{-1}) obtained by NLT and TL methods for PDI derivatives at λ_e = 1064 nm, Mm: molecular weight (g/mol), Φ_0 : phase shift induced by photothermal effect. I_0 : pump beam intensity(GW/cm^2) at the beam waist.

				NLT		**TL**	
Materials	**Mm**	I_0	Φ_0	$\alpha^{<2>}$	σ_2	$\alpha^{<2>}$	σ_2
PDI-Br$_2$	688	14.64	0.17	7.9	5.66	0.12	0.086
PDI-(OPhtBu)$_2$	826	14.15	0.19	6.7	5.76	0.17	0.146
PDI-(OPhtBu)$_4$	1122	14.27	0.19	7	8.18	0.17	0.199
PDI-(OPhtBu)$_4$-C$_{60}$	1928	8.28	0.07	3.6	7.23	0.18	0.361

5. Conclusions

Chloroform, Benzene and Nitrobenzene excited with the wavelength of 532 nm by picosecond pulses show two photon absorption phenomenon. The nonlinear transmission method (NTL) and the thermal lens (TL) technique in pump-probe modes miss-match were used to measure the two-photon absorption cross-section of these solvents.

Using the same experimental techniques, but with a pump-beam at the wavelength of 1064nm, we revealed , in perylene-diimide (PDI) derivatives newly synthesized, two types of mutliphoton process: a two photon absorption and a four-photon absorption process.

Our results show that the intensity of the pump beam from which nonlinear absorption appears depends not only on the measurement technique used, but also of material studied. This threshold intensity is indeed higher in the NLT technique than in the technique TL . We also noticed that whatever the material, the TPA cross-sections obtained by NLT method are higher than those obtained by the TL method.

Finally, we can note that, the TL technique is particularly advantageous, because it is not only more sensitive, but it also allows to identify without any ambiguity the type of absorption induced in material.

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