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Broadband three-photon absorption spectra of platinum acetylide complexes

Broadband three-photon absorption spectra of platinum acetylide complexes

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Abstract: We investigate the three-photon absorption spectra of four platinum acetylides complexes employing femtosecond pulses. We observed strong three-photon absorption cross-section in the near-infrared region (from 850 nm to 1200 nm). The three-photon absorption (3PA) spectra present resonance enhancement effect as two photons of the excitation wavelength approach the lower two-photon allowed states of the molecules as well as a 3PA allowed band around 1180 nm. The 3PA cross-section spectra were interpreted using the sum-over-essential-states approach, considering a three-energy-level diagram.

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1. Introduction

In the last few years, interest on multi-photon absorbing materials has significantly increased because of their promising technological applications such as frequency upconversion lasing [1], photonic devices [2], optical data storage [3], microfabrication [4,5], fluorescence imaging and photodynamic therapy [6]. These applications are related to the unique features of the multi-photon absorption, such as the spatial confinement of the excitation. Motivated by these applications, there has been a great effort to develop materials with remarkable multi-photon absorption cross-section [7]. Organometallic compounds have become interesting candidates for nonlinear optics because of the metal-to-ligand or ligand-to-metal charge transfer, which are commonly related to enhanced optical nonlinearities [8]. For example, it has been reported that the metalated arylalkynyl dendrimers 1,3,5-(3,5-[*trans*-((dppe)$_2$(NO$_2$C$_6$H$_4$-4-C≡C)RuC≡C)]$_2$C$_6$H$_3$-1-C≡CC$_6$H$_4$-4-C≡C)$_3$C$_6$H$_3$ presents a two-photon absorption (2PA) cross-section of approximately 4000 GM far from the resonance enhancement region [8]. Furthermore, organometallics usually present intersystem crossing to a triplet state, which can be assisted by 2PA [9]. In the class of organometallic compounds, platinum acetylide complexes have been attracting special attention as interesting candidates for applications [10,11]. These compounds present high conjugation length and a center with weak bound electrons, which may result in relatively high multi-photon cross-section [12,13]. Therefore, platinum acetylide compounds could be explored for applications associated to triplet states, such as triplet state absorption, intersystem crossing and phosphorescence.

In this paper, we report the three-photon absorption (3PA) spectra of four distinct platinum acetylides (PEs) complexes, named *trans*-Pt(PBu$_3$)$_2$ (C≡C-C$_6$H$_4$-C≡C-C$_6$H$_5$)$_2$ (**I**), *trans*-Pt(PBu$_3$)$_2$(C≡C-C$_6$H$_4$-C≡C-C$_6$H$_4$-C≡C-C$_6$H$_5$)$_2$ (**II**), *trans*-Pt(PBu$_3$)$_2$(C≡C-C$_6$H$_4$-C$_5$H$_{10}$-C$_6$H$_4$-N(C$_6$H$_4$)$_2$)$_2$ (**III**) and *trans*-Pt(PBu$_3$)$_2$(C≡C-C$_6$H$_4$-C$_5$H$_{10}$-C$_6$H$_4$-CNS-C$_6$H$_4$)$_2$ (**IV**) from the visible to the near-infrared. As shown in the Fig. 1, the compounds present high conjugation length, composed by alternate single and double (or triple) bonds, which should increase the nonlinear optical properties. The nonlinear spectra of all samples present high 3PA cross-sections along the near-infrared region (from 850 nm to 1200 nm), an interesting feature for technological applications. The 3PA cross-sections values reported here are comparable to the best ones presented in the literature for organic compounds, especially in

the near-infrared. To better understand the nonlinear optical response of the complexes and associate them with molecular parameters, we used the sum-over-essential-states approach to interpret the 3PA cross-section spectra.
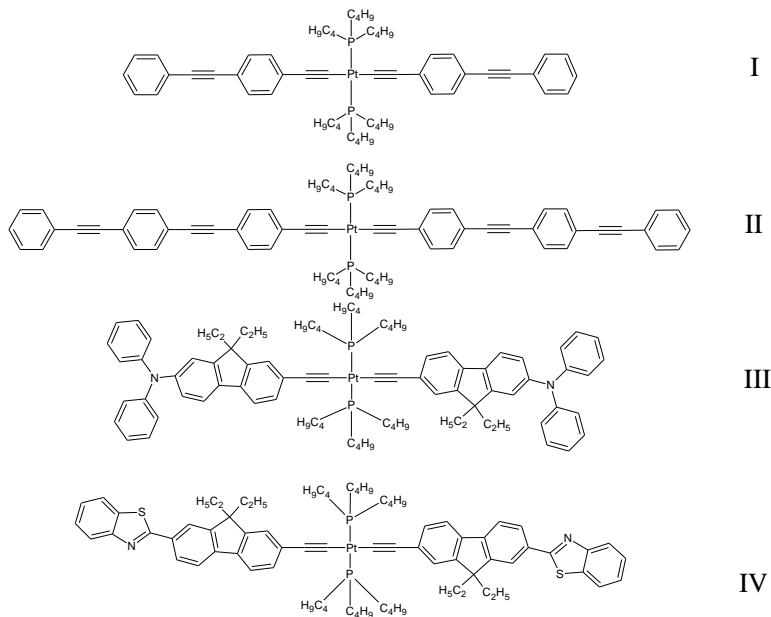

Fig. 1. Molecular structures of the platinum acetylide complexes; *trans*-Pt(PBu$_3$)$_2$ (C≡C-C$_6$H$_4$-C≡C-C$_6$H$_5$)$_2$ (**I**), *trans*-Pt(PBu$_3$)$_2$(C≡C-C$_6$H$_4$-C≡C-C$_6$H$_4$-C≡C-C$_6$H$_5$)$_2$ (**II**), *trans*-Pt(PBu$_3$)$_2$(C≡C-C$_6$H$_4$-C$_5$H$_{10}$-C$_6$H$_4$-N(C$_6$H$_4$)^2)$_2$ (**III**) and *trans*-Pt(PBu$_3$)$_2$(C≡C-C$_6$H$_4$-C$_5$H$_{10}$-C$_6$H$_4$-CNS-C$_6$H$_4$)$_2$ (**IV**).

2. Experimental and 3PA approach

A. Compounds

The compounds **I**, **II**, **III** and **IV,** shown in Fig. 1, were synthesized and purified according to the method described in [13,14].

B. Optical measurements

All compounds were dissolved in dichloromethane in a concentration of 5×10^{16} molecules/cm^3 (8.3×10^{-5} Mol/L) for the linear absorption measurements. The solutions were placed in a 2 mm fused-silica cell to measure the UV-Vis absorption spectrum using a Varian Spectrophotometer (Cary 17). A He-Cd *cw* laser, operating at 325 nm, was used to excite the samples fluorescence at room-temperature, which was collected perpendicularly to excitation through an optical fiber attached to a spectrometer.

The 3PA cross-section spectra were measured using the open-aperture Z-scan configuration. Z-scan measurements were performed with 120-fs pulses at 1 kHz repetition rate, delivered by a tunable optical parametric amplifier pumped at 775 nm by a Ti:Sapphire chirped pulse amplifier. For each wavelength, the pulse energy was kept at approximately 180 nJ. A Gaussian beam profile was obtained by spatial filtering the excitation beam before the Z-scan setup. For nonlinear measurements, the samples were prepared in a concentration of 10^{18} molecules/cm^3 (1.7×10^{-3} Mol/L) and placed in a 2 mm fused silica cell. For absorptive nonlinearities, the light field induces an intensity dependent absorption and $\alpha = \alpha_0 + \beta I + \gamma I^2 + ...$, where I is the laser beam intensity, α_0 is the linear absorption coefficient, β and γ are the 2PA and 3PA coefficients, respectively. Far from one- and two-photon

resonances, the power transmitted through the sample due to a 3PA process, for each wavelength, is integrated over time (assuming a pulse with a Gaussian temporal profile) to give the normalized energy transmittance,

$$T_{3PA}(z) = \frac{1}{\sqrt{\pi}\,\sqrt[3]{q_1}} \int_0^1 \frac{\ln\left(\sqrt{1+q_1 x^2} + \sqrt{q_1 x^2}\right)}{x\sqrt{-\ln(x)}} dx, \tag{1}$$

with

$$q_1 = 2\gamma L \left(\frac{I_0 w_0^2}{I_0 w_0^2 / w_z^2}\right)^2 \tag{2}$$

where L is the sample thickness, $w_z^2 = w_0^2\left(1+z^2/z_0^2\right)$ and w_0 are the beam waist at a z-position and at the focus, respectively; z_0 is the Rayleigh length, z is the sample position. The nonlinear coefficient γ is obtained by fitting the Z-scan data with Eq. (1). The three-photon absorption cross-section, σ_{3PA}, can be obtained through the expressions $\sigma_{3PA} = (h\nu)^2 \gamma / N$, where N is the number of molecules per cm^3, and $h\nu$ is the photon energy. Complete analysis of the Eqs. (1) and (2) can be found, for example, in [15].

C. Interpretation of the 3PA cross-section

The multiphoton absorption is a consequence of the nonlinear behavior in the light-matter interaction. The multiphoton absorption cross-section can be obtained by semi-classical time-dependent perturbation theory. In this approach, the three-photon absorption cross-section can be evaluated via third-order transition matrix elements, given by

$$S_{f\leftarrow g}^{(3PA)} = \sum_{m,n} \left[\frac{\omega_{fn}\omega_{nm}\omega_{mg}\left(\hat{e}\bullet\langle f|\vec{\mu}|n\rangle\right)\left(\hat{e}\bullet\langle n|\vec{\mu}|m\rangle\right)\left(\langle m|\vec{\mu}|g\rangle\bullet\hat{e}\right)}{\left(\omega_{mg}-\omega-i\Gamma\right)\left(\omega_{ng}-2\omega-i\Gamma\right)} \right], \tag{3}$$

where $\vec{\mu}$ is the dipole moment vector, Γ is the damping constant describing half width at half-maximum of the final state linewidth (assuming Lorentzian line-shape), $\omega_{f\leftarrow i}$ is the transition frequency and $\hat{e} = \vec{e}/e$ is the versor that describes the direction of polarization of light. The summation represents the sum-over-all real electronic states, i.e., the initial ($|g\rangle$), intermediates ($|m\rangle$ and $|n\rangle$) and final ($|f\rangle$) states. The 3PA cross-section, following the methodology described in the [16], can be written, in the cgs system of units, as:

$$\sigma_{f\leftarrow g}^{(3PA)} = 8\frac{(2\pi)^7}{(hc)^3} L^6 \omega^3 \left| \sum_{m,n} \left[\frac{\left(\hat{e}\bullet\vec{\mu}_{fn}\right)\left(\hat{e}\bullet\vec{\mu}_{nm}\right)\left(\vec{\mu}_{mg}\bullet\hat{e}\right)}{\left[(\omega_{fg}-\omega)-i\Gamma_{fg}(\omega)\right]\left[(\omega_{ng}-2\omega)-i\Gamma_{ng}(\omega)\right]} \right] \right|^2 g(3\omega) \tag{4}$$

where h is Planck's constant, c is the speed of light, ω is the excitation laser frequency, L is the Lorentz local field factor introduced to take into account the effect media [17] and $g(3\omega)$ represents the linewidth function.

Many molecules, including those studied here, do not present a center of inversion and, therefore, initial and final states have a static dipole moment. Thus, it is necessary to take into account the intermediate energy levels. In addition, non-centrosymmetric molecules do not follow the dipole-electric selection rule [18] and, therefore, one- (or three-) and two-photon transitions are allowed between any levels. In this case, taking into account the average over

all possible molecular orientations in an isotropic medium and considering that only one intermediate state, $|e\rangle$ (one and two-photon allowed), contributes significantly to the transition matrix elements, the 3PA cross-section can be written as (assuming linearly polarized light):

$$\sigma_{e'g}^{(3)}(\omega) \approx \frac{2}{7}\frac{(2\pi)^7}{(hc)^3}L^6\omega^3 \left\{ \frac{\left(|\vec{\mu}_{eg}||\Delta\vec{\mu}_{eg}|^2 - \frac{|\vec{\mu}_{eg}|^3}{2}\right)^2}{\omega^4} + \frac{\left[\left(|\vec{\mu}_{e'e}|^2|\vec{\mu}_{e'g}| + 2|\vec{\mu}_{e'e}||\vec{\mu}_{eg}||\Delta\vec{\mu}_{eg}|\right)^2\right]}{\omega^2\left[\left(\omega_{e'g}-2\omega\right)^2 + \Gamma_{e'g}^2(\omega)\right]} + \frac{2\left(\omega_{eg}-2\omega\right)|\vec{\mu}_{e'e}||\vec{\mu}_{eg}|}{\omega^3\left[\left(\omega_{eg}-2\omega\right)^2 + \Gamma_{eg}^2(\omega)\right]}\left(\frac{|\vec{\mu}_{e'e}||\vec{\mu}_{e'g}||\Delta\vec{\mu}_{eg}|^2 + 2|\Delta\vec{\mu}_{eg}|^3|\vec{\mu}_{eg}|}{-\frac{|\vec{\mu}_{e'e}||\vec{\mu}_{e'g}||\vec{\mu}_{eg}|^2}{2} - |\Delta\vec{\mu}_{eg}||\vec{\mu}_{eg}|^3}\right) \right\} g(3\omega). \tag{5}$$

where $\Delta\vec{\mu}_{eg}$ is the difference between permanent dipole moments in the excited ($\vec{\mu}_{ee}$) and ground ($\vec{\mu}_{gg}$) states. The following additional simplifications were used: $\omega_{e'g} - \omega \gg \Gamma_{e'g}$, $\omega_{eg} - \omega \gg \Gamma_{eg}$, $\omega_{e'g} - 2\omega = \omega$ and $\omega_{eg} - \omega = \omega$, since the final energy level is never in close resonance with excitation photons in a degenerate 3PA process [19]. As it can be seen from Eq. (5), 3PA cross-section is governed by three channels: the first corresponds to a 3PA transition in a two-levels system with a change of permanent dipole moment (purely one-photon nature), while the second channel corresponds to the transition in a three-levels system with the real intermediate state, $|e\rangle$. The last channel corresponds to an interference between the two contributions. Such term can contribute positively or negatively to the 3PA cross-section, depending on the spectral region and on combinations of dipole moment values. Assuming the linewidth function, $g(3\omega)$, as Lorentzian, the 3PA cross-section can be re-written as:

$$\sigma_{e'g}^{(3)}(\omega) \approx \frac{2}{7\pi}\frac{(2\pi)^7}{(hc)^3}L^6 \left\{ \frac{1}{\omega}\frac{\left(|\vec{\mu}_{eg}||\Delta\vec{\mu}_{eg}|^2 - \frac{|\vec{\mu}_{eg}|^3}{2}\right)^2\Gamma_{eg}(\omega)}{\left(\omega_{eg}-3\omega\right)^2 + \Gamma_{eg}^2(\omega)} + \frac{\omega}{\left(\omega_{eg}-2\omega\right)^2 + \Gamma_{eg}^2(\omega)}\left(\frac{\left(|\vec{\mu}_{e'e}|^2|\vec{\mu}_{e'g}| + 2|\vec{\mu}_{e'e}||\vec{\mu}_{eg}||\Delta\vec{\mu}_{eg}|\right)^2\Gamma_{e'g}(\omega)}{\left(\omega_{e'g}-3\omega\right)^2 + \Gamma_{e'g}^2(\omega)}\right) + \frac{2\left(\omega_{eg}-2\omega\right)|\vec{\mu}_{e'e}||\vec{\mu}_{eg}|\Gamma_{e'g}(\omega)}{\left[\left(\omega_{eg}-2\omega\right)^2 + \Gamma_{eg}^2(\omega)\right]\left[\left(\omega_{e'g}-3\omega\right)^2 + \Gamma_{e'g}^2(\omega)\right]}\left(\frac{|\vec{\mu}_{e'e}||\vec{\mu}_{e'g}||\Delta\vec{\mu}_{eg}|^2 + 2|\Delta\vec{\mu}_{eg}|^3|\vec{\mu}_{eg}|}{-\frac{|\vec{\mu}_{e'e}||\vec{\mu}_{e'g}||\vec{\mu}_{eg}|^2}{2} - |\Delta\vec{\mu}_{eg}||\vec{\mu}_{eg}|^3}\right) \right\} \tag{6}$$

It is important to observe that the second term of the Eq. (6) increases monotonically when two photons of the excitation wavelength approach the lower two-photon allowed state of the molecule, providing a resonance enhancement of the 3PA cross-section that can reach several orders of magnitude depending on the detuning, $\hbar\left(\omega_{eg}-2\omega\right)$.

3. Results and discussions

Figure 2 presents the normalized linear absorption (solid lines – left axes), one-photon excited fluorescence (empty squares) and 3PA (circles – right axes) spectra of the platinum acetylide

complexes studied. The absorption spectra of these complexes are related to $\pi\pi*$ transitions with metal-to-ligand charge transfer character. Previous studies have determined that the HOMO (Highest Occupied Molecular Orbital) of platinum acetylide complexes consists of a π orbital from acetylene and aromatic groups with contribution from $5d_{xy}$ orbital of the platinum, while the LUMO (Lowest Unoccupied Molecular Orbital) consists only of a $\pi*$ orbital, without platinum contribution [20]. The linear absorption spectra show that the samples are completely transparent in the visible, with absorption band entirely located in the near-UV ($\lambda < 430$ nm). The empty squares in Fig. 2 represent the fluorescence spectra excited at 325 nm. Such spectra present an emission-band shapes resulting from molecular vibronic progressions, including $C\equiv C$ and $C = C$ stretch vibrational modes [14], with maxima peaks at 412 nm for **I**, 420 nm for **II**, 432 nm for **III** and 444 nm for **IV.**

As is well-known for this family of molecules, the short intersystem crossing time (~330ps) [21] and long phosphorescence time (~40μs) [9] allow accumulation of molecules in the triplet state, which may influence the determination of the multi-photon absorption process. To avoid such excited state absorption effect on the 3PA determination, the optical nonlinearities were measured using femtosecond pulses at a 1 KHz repetition rate. The short pulse duration ensures negligible absorption from the population in the excited states [22,23], while the low repetition rate avoids cumulative effects between consecutive pulses.

Figure 2 displays the 3PA cross-section spectra of platinum acetylides from approximately 850 nm to 1200 nm (circles). As it can be seen, the 3PA cross-section increases as the excitation wavelength approaches the visible region, reaching values of approximately 3×10^{-78} cm^6 s^2 photon^{-2} for compounds **II**, **III** and **IV;** and 1.0×10^{-78} cm^6 s^2 photon^{-2} for compound **I**. Such behavior, observed for all compounds, is associated to the resonant enhancement of the nonlinearity that takes place when two photons of the excitation wavelength approach the lower two-photon allowed states of the molecules, which are located in visible. The 2PA spectra of this family of compounds cover the entire visible region [13], with peaks from 600 nm to 770 nm, depending on the compound. A similar enhancement behavior on the multi-photon absorption spectrum was also observed for polydiacetylenes [24] and MEH-PPV [25]. It is worth mentioning that the 2PA spectrum of the compounds studied here, at the near infrared (~850 nm), were determined to be approximately 40 GM. Considering this values, we can found that $\gamma I^3 \geq 5\beta I^2$ for the irradiance range used here, indicating that the dominant process is this region is, in fact, the 3PA. Additionally, the 3PA spectra for compounds **II**, **III** and **IV** present a band around 1180 nm that correspond to an one-photon allowed state located between 380 - 400 nm. Such transitions are allowed because the electric-dipole selection rules [18] are the same to both types of process (1PA and 3PA).
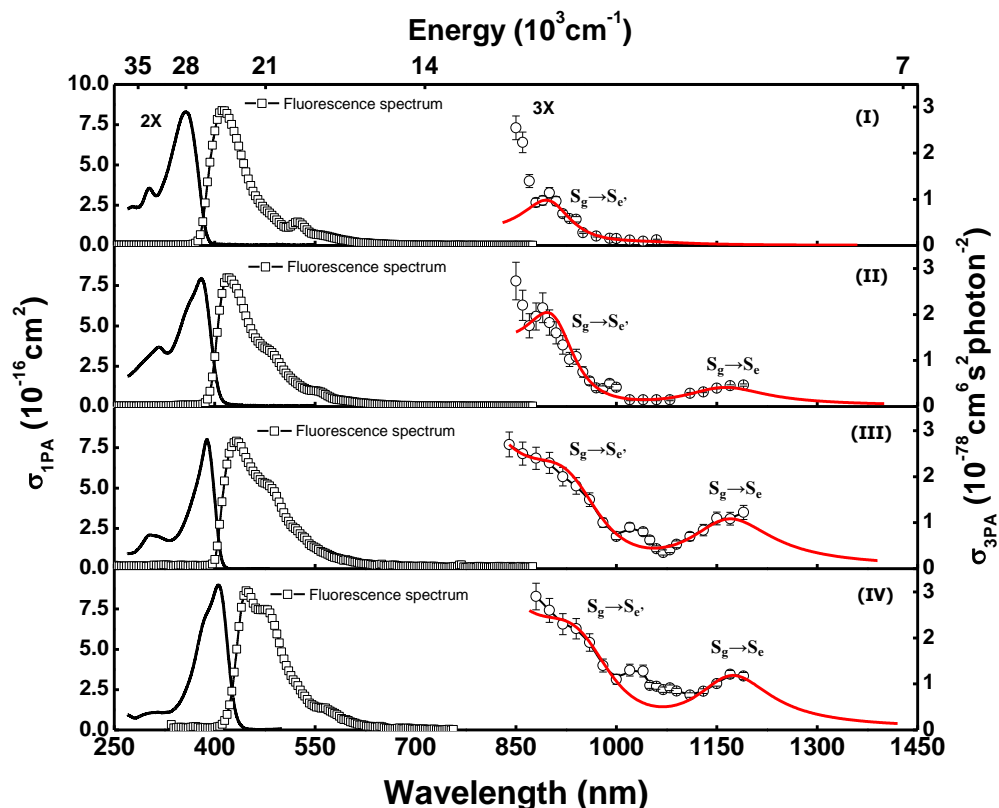
Fig. 2. One-photon cross-section (solid line – left axes), linear fluorescence (empty squares) and three-photon absorption (empty circles – right axes) spectra of platinum acetylide complexes. The solid line along the empty circles represents the theoretical fitting obtained with the sum-over-essential-states approach. It should be observed that for compound (**I**) the 1PA and 3PA cross-section spectra were multiplied by 2 and 3, respectively.

To confirm the actual three-photon absorption nature of the observed results (Fig. 2), we measured the dependence of the Z-scan normalized transmittance change (ΔT) as a function of the excitation irradiance. The slope derived from a linear fit (log-log scale) of ΔT as a function of excitation intensity indicates the mechanism of absorption. Therefore, a slope of 1.0 indicates a 2PA, while a slope of 2.0 reveals a 3PA. Slopes whose values are intermediate indicate a mixture of processes. As shown in Fig. 3 for 900 nm, a slope of approximately 2.0 was observed for all compounds, signifying a 3PA mechanisms [15]. In general, the dependence of the fluorescence on the excitation irradiance can also be used to check the order of the process. However, for the compounds studied here, the fluorescence signal in the wavelength range of interest (~850 nm to ~1200 nm) is too small to be used for this purpose. Another evidence of the three-photon nature of the observed nonlinear absorption is given in Fig. 4. In this figure we show the result we obtained for compound **III** at 900 nm (open squares).
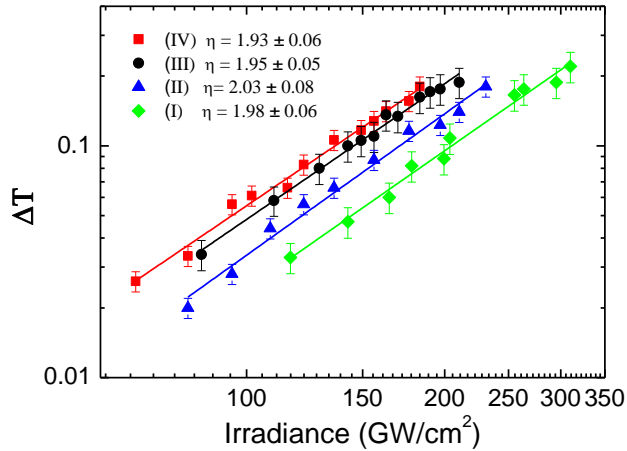
Fig. 3. Normalized transmittance change (ΔT) as a function of the excitation irradiance at 900 nm for the four acetylide platinum complexes. The inset shows the slope for each molecule.

The dotted line represents the best fitting obtained considering a 2PA process. As it can be seen, the fitting does not describe properly the experimental results. On the other hand, the fitting obtained when the 3PA is considered (solid line) agrees very well with the experimental data. It is important to mention that the value for w_0 we used (21 μm) was obtained by calibrating our Z-scan setup with fused silica (nonlinear refraction experiments). The same behavior was observed for the other compounds studied here.
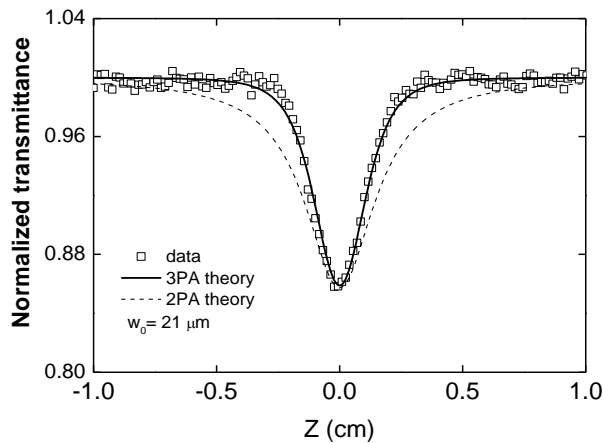

Fig. 4. Experimental **o**pen aperture Z-scan signature for compound **III** at 900 nm. The dotted and solid line represents the best fitting obtained considering a 2PA and 3PA process.

To illustrate the quality of the fitting to our data, in Fig. 5 we show some Z-scan curves and the corresponding 3PA fit for all studied compounds at 900 nm. Each curve corresponds to a distinct excitation intensity, which gives the dependence of ΔT with the intensity presented in Fig. 3.
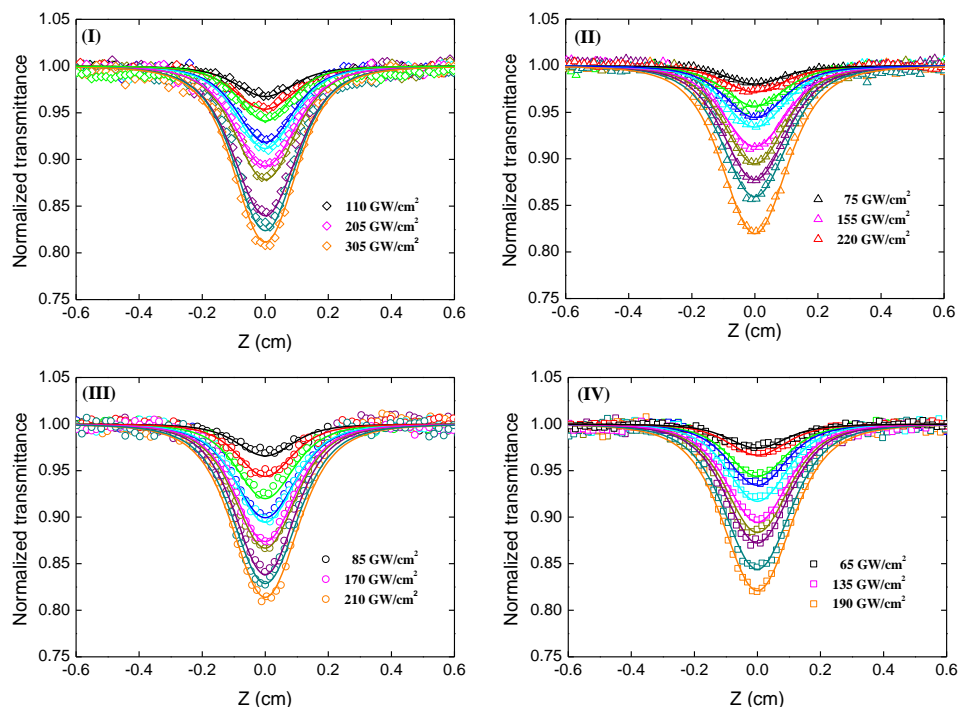
Fig. 5. Experimental **o**pen aperture Z-scan signature obtained for compound **I, II, III** and **IV** at 900 nm. Each curve in this figure corresponds to a distinct excitation intensity, which gives the dependence of ΔT with the intensity included in Fig. 3. The solid line represent the Z-scan data fitting obtained using Eq. (1).

To establish a relationship between the 3PA process observed and molecular properties of the compounds, the sum-over-essential-states approach, described in the section 2C, was used to analyze the results presented in Fig. 2. To interpret the 3PA spectra of the compounds, we considered the three-energy-level diagram shown in the Fig. 6, based on the excited states energies, obtained from the one- and three-photon absorption spectra presented in this study and on the 2PA spectra from [13].
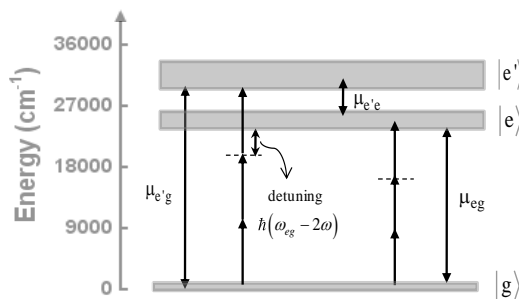

Fig. 6. Three-energy level diagram for platinum acetylide complexes. The contribution of the intermediate level, $|e\rangle$, is determined by the detuning between the excitation photon energy and the band gap of the material.

The solid line along the empty circles in Fig. 2 represents the fitting obtained using Eq. (6), with ν_{eg}, Γ_{eg} and μ_{eg} estimated from the linear absorption spectrum ($\pi\pi^*$ band located at 360 nm for **I**, 380 nm for **II**, 390 for **III** and 395 for **IV**) and $\nu_{e'g}$ and $\Gamma_{e'g}$ obtained from the 2PA spectra [12,13]. From the fitting we were able to determine $\Delta\mu_{eg,}$ $\mu_{e'e}$ and $\mu_{e'g}$ for all

compounds. Table 1 summarizes the spectroscopic parameters used/obtained in the sum-over-essential-states approach used to model the 3PA spectra.

Table 1. Spectroscopic Parameters Used/Obtained in the Sum-Essential-States Model

Parameters	I	II	III	IV
v_{eg} (cm^{-1})	27780 (360 ± 5 nm)	25850 (385 ± 5 nm)	25640 (390 ± 5 nm)	25300 (395 ± 5 nm)
$v_{e'g}$ (cm^{-1})	33900 (295 ± 5 nm)	32850 (305 ± 5 nm)	32335 (310 ± 5 nm)	31250 (320 ± 5 nm)
Γ_{eg} (cm^{-1})	2150 ± 200	2000 ± 200	1800 ± 200	1800 ± 200
$\Gamma_{e'g}$ (cm^{-1})	2000 ± 200	1800 ± 200	2500 ± 200	2500 ± 200
μ_{eg} (Debye)	11.0 ± 1	17.0 ± 2	18.0 ± 2	19.0 ± 2
$\mu_{e'e}$ (Debye)	11.5 ± 2	12.0 ± 2	14.0 ± 2	15.0 ± 2
$\mu_{e'g}$ (Debye)	6.0 ± 1	8.0 ± 1	7.0 ± 1	7.0 ± 1
$\Delta\mu_{eg}$ (Debye)	3.0 ± 1	4.0 ± 1	5.0 ± 1	5.5 ± 1

As seen in Fig. 2, all compounds present relatively high 3PA cross-section, in the order of 10^{-78} cm^6 s^2 photon^{-2}. Such values are comparable, although smaller, to the higher ones reported in the literature in near-infrared region [25,26]. The values observed for the optical nonlinearities are related to high transition dipole moments, μ_{eg} and $\mu_{e'e}$, that are probably associated to the high planarity of the ground-state equilibrium geometry for compounds **I** and **II**, as well as to the presence of strong electron-donor and acceptor groups for compounds **III** and **IV**, respectively, in accordance with [12,20].

The 3PA cross-sections of **II** is higher than the one obtained for **I** probably because of its higher transition dipole moment (μ_{eg}) and greater contributions from the intermediate level, $|e\rangle$, which are associated with the increase of the conjugation length. For compounds **II**, **III** and **IV**, the nonlinear absorption cross-sections are similar. Such similar values are probably related to the presence of the strong electron donors groups (ethynyl-diphenylaminolfluorene ligands in **III**) and the electron acceptors groups (ethynyl-benzothiazolyfluorene ligands in **IV**) that enhances the 3PA cross-section [13], balancing their smaller conjugation [20]. This trend can also be observed in the 1PA cross-section spectra and transition dipole moments obtained with the sum-over-essential-states model. Besides, the presence of acceptor and donor groups in **III** and **IV** reduces the energy gap [20], favoring the contribution of the 2PA allowed intermediate energy level, providing a resonance enhancement of the 3PA cross-section around 900 nm.

5. Conclusion

In this paper we reported the first broadband experimental investigation of the simultaneous three-photon absorption of platinum acetylide complexes, which are organometallic compounds with remarkable characteristics for technological applications. Large 3PA cross-sections were found, with values comparable to the best ones presented in the literature for organic compounds. We observed that these values are associated to the resonant enhancement of the nonlinearity that takes place when two photons of the excitation wavelength approach the lower two-photon allowed states of the molecules, which are located in visible. In addition, we observed the presence of a 3PA band around 1180 nm for the compounds **II**, **III** and **IV**, which correspond to one-photon allowed state located in the UV-blue region. These transitions are 3PA allowed since the electric-dipole selection rules [18] are the same for both types of process (1PA and 3PA). Employing the sum-over-essential-states approach, we were able to associate the 3PA cross-section exhibited by the

platinum acetylide complexes to basically two dominant contributions: one relate to a change in the permanent dipole moment and other one corresponding to a three-photon transition intermediate by a two-photon allowed state.