Understanding the Two-Photon Absorption Spectrum of PE2 Platinum Acetylide Complex

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ABSTRACT: Herein, we report on the two-absorption cross-section spectrum of trans-$Pt(PBu_3)_2$ ($C\equiv C-C_6H_4-C\equiv C-C_6H_5)_2$ (**PE2**) platinum acetylide complex employing the femtosecond wavelength-tunable Z-scan technique. The **PE2** complex can be visualized as two branches containing two phenylacetylene units, each one linked by a platinum center, completely transparent in the visible region. Because of this structure, large delocalization of π-electrons allied to the strong intramolecular interaction between the branches is expected. The 2PA absorption spectrum was measured using the femtosecond wavelength-tunable Z-scan technique with low repetition rate (1 kHz), in order to obtain the 2PA spectrum without excited-state contributions. Our results reveal that **PE2** in dichloromethane solution presents two 2PA allowed bands located at 570 and 710 nm, with cross section of about 320 and 45 GM, respectively. The first one is related to the strong intramolecular interaction between the molecule's branches due to the presence of platinum atom, while the second one is associated with the breaking of symmetry of the chromophore in solution due, most probably to a large twisting angle of the ligand's phenyl rings relative to the Pt core.
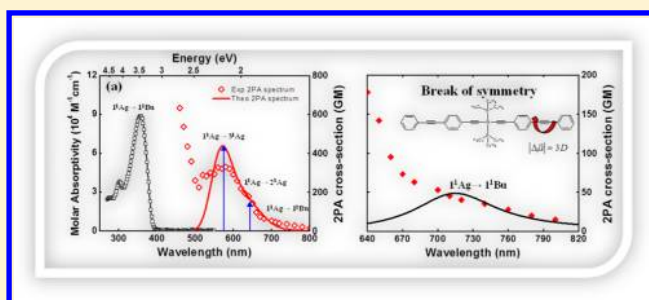
1. INTRODUCTION

The platinum acetylide complexes (PEs) are materials with remarkable optical properties as such as high singlet and triplet absorption (from 10^4 to 10^5 M^{-1} cm^{-1}),[1-4] efficient generation of singlet oxygen,[5] intense two- (thousands of GM units)[3,6] and three-photon absorption ($\sim 10^{-78}$ $cm^6 \cdot s^2 \cdot photon^{-2}$),[7] ultrafast intersystem crossing (from femtosecond to picosecond) and long phosphorescence time (microsecond).[8] These characteristics are directly associated with the acetylide group that allows high electron mobility and the metallic center (platinum) with weak bound electrons, which provides a metal-to-ligand or ligand-to-metal charge transfer, ideal to nonlinear optical applications.[9,10] Among the possible applications of these materials, we can cite ones related with chemosensing,[11] photodynamics therapy,[8,12] and optical switching,[13] to name a few.

One of the first PEs to have their nonlinear optical properties investigated was the trans-$Pt(PBu_3)_2$ ($C\equiv C-C_6H_4-C\equiv C-C_6H_5)_2$, named **PE2**, by Staromlynska et al.[14] In that report, they studied the origin of strong nonlinear absorption of **PE2** using 27 ps and 2 ns pulses at 455 and 595 nm, respectively. According to their results, there is a direct transition from the singlet ground state (S_0) to the triplet state (T_1) at 520 nm, indicating that the triplet-state absorption dominates the nonlinear optical effect for pulse lengths from picoseconds to hundreds of nanoseconds. Although the $S_0 \rightarrow T_1$ transition is

spin forbidden, it has been observed in molecules containing heavy atoms, which enhanced the spin−orbit coupling contributing to the mixing between the single and triplet states.[15] This relaxation of selection rule already had been reported by other authors using different techniques.[16,17] Also according to Staromlynska et al.,[14] the $S_0 \rightarrow T_1$ transition has molar absorptivity extremely low (1.3 M^{-1} cm^{-1}). Besides, they reported that at 595 nm there is two-photon absorption from S_0 to S_1 followed by intersystem crossing to the T_1 state. Once again, the nonlinear effect has a contribution of the triplet state. In addition, they modeled transmittance versus peak intensity curves for picosecond laser pulses and found 2PA cross section around 235 GM at 595 nm for the **PE2** in dichloromethane solution (0.08 M).

In this report, we obtain the 2PA spectrum of **PE2** platinum acetylide complex (whose molecular structure is displayed in Figure 1), using 160 fs laser pulses operating at a repetition rate of 1 kHz. The combination of short pulse duration and low repetition rate allows obtaining pure 2PA, because the first assures that negligible absorption from the population generated in the excited states occurs,[18] while the latter helps avoiding cumulative effects between consecutive pulses, coming
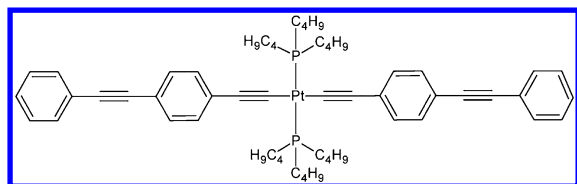
Figure 1. Molecular structure of platinum acetylide complexes *trans*-Pt(PBu$_3$)$_2$ (C≡C—C$_6$H$_4$—C≡C—C$_6$H$_5$)$_2$.

from possible triplet–triplet absorption.[19] We have observed two 2PA bands for **PE2** in dichloromethane that are located in the visible and near-infrared region of the spectrum. Such bands were shown to be related to a strong intramolecular interaction and to a breaking of symmetry of the chromophore in solution, respectively.

2. EXPERIMENTAL SECTION

All compounds were dissolved in dichloromethane in a concentration of about 10^{16} and 10^{18} molecules/cm^3 for the linear and nonlinear absorption measurements, respectively. The solutions were placed in a 2 mm fused silica cell to measure the UV–vis absorption spectrum using a Shimadzu UV-1800 spectrophotometer. The 2PA spectrum was measured using the Z-scan technique in the open-aperture configuration.[20]

In the open-aperture Z-scan technique, 2PA cross section is determined by translating the sample through the focal plane of a focused Gaussian beam, while transmittance changes in the far field intensity are monitored. For a 2PA process, the light field creates an intensity dependent absorption, $\alpha = \alpha_0 + \beta I$, in which I is the laser beam intensity, α_0 is the linear absorption coefficient, and β is the 2PA coefficient. Far from one-photon resonances, the power transmitted through the sample due to a 2PA process, for each wavelength, is integrated over time (assuming a pulse with a Gaussian temporal profile) to give the normalized energy transmittance

$$T(z) = \frac{1}{\sqrt{\pi}\, q_o(z, 0)} \int_{-\infty}^{\infty} \ln[1 + q_o(z, 0)e^{-\tau^2}]\mathrm{d}\tau \quad (1)$$

with

$$q_0 = \beta I_0 L(1 + (z^2/z_0^2))^{-1} \quad (2)$$

in which L is the sample thickness, z_0 is the Rayleigh length, z is the sample position, and I_0 is the laser intensity at the focus. The nonlinear coefficient β is obtained by fitting the Z-scan data with eq 1. The 2PA cross section, σ_{2PA}, is determined from $\sigma_{2PA} = \hbar\omega\beta/N$, in which $\hbar\omega$ is the excitation photon energy and N is the number of molecules per cm^3. Usually, the 2PA cross section is expressed in units of Göppert–Mayer (GM) (1 GM = 1 × 10^{-50} cm^4 s·photon^{-1}).

3. RESULTS AND DISCUSSION

Figure 2 presents the experimental molar absorptivity (squares), experimental 2PA spectra (diamonds), and theoretical 2PA spectra (solid line), in which the last one was obtained by Nguyen et al.[9] for the **PE2** platinum acetylide complex. The **PE2** absorption spectrum presents the lowest energy band centered at 357 nm with maximum molar absorptivity of 8.95×10^4 M^{-1} cm^{-1} in dichloromethane. This band is related to the S$_0$ → S$_1$ ($\pi\pi^*$) transitions with strong metal-to-ligand charge transfer character.[17]

The linear spectrum (molar absorptivity) reveals that the absorption is entirely located in the near-UV region, shorter than 400 nm, which indicates it is completely transparent in the visible range, ideal to applications in photonics. In addition, as previously described by Staromlynska et al.,[14] **PE2** presents a very small absorption peak at 520 nm with molar absorptivity extremely low (1.3 M^{-1} cm^{-1}) assigned to the direct S$_0$ → T$_1$ transition. In Figure 2a, the diamonds illustrate the 2PA spectrum obtained for the **PE2** in dichloromethane solution using 160 fs laser pulses and low repetition rate (1 kHz). As can be noted in Figure 2, the experimental 2PA spectrum for the **PE2** exhibits two bands located at 570 and 710 nm with cross section of approximately 320 and 45 GM, respectively, as well as the resonant enhancement effect observed for wavelengths shorter than 500 nm. Figure 2b shows the zoom of the lowest energy 2PA band of **PE2** in solution. As can be seen, a monotonous decrease of the 2PA cross section, related to the S$_0$ → S$_n$ transitions (between 640 and 690 nm), is interrupted by a practically flat 2PA cross-section region, when the excitation photons approach the lowest energy one-photon
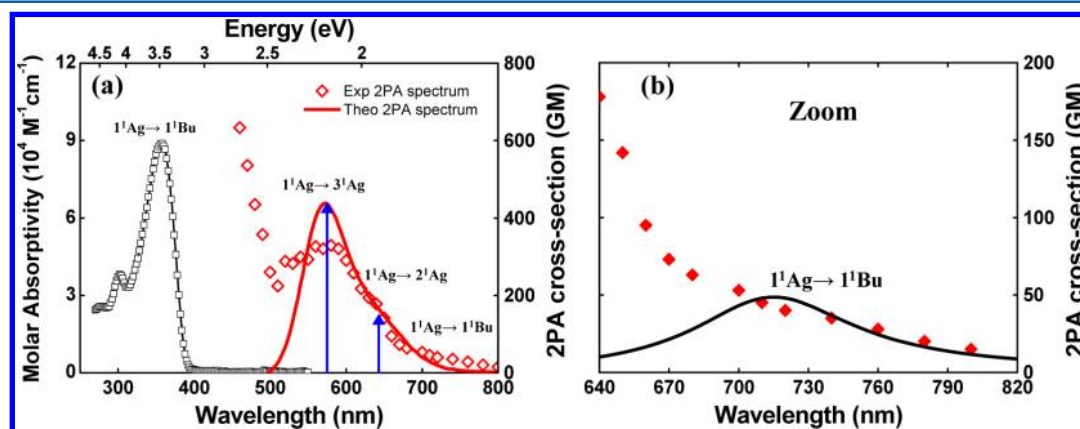

Figure 2. (a) Ground-state molar absorptivity (squares, left axes), experimental 2PA spectra (diamonds, right axes), and theoretical 2PA spectra (solid line) of **PE2**, in which the latter was reported in ref 9. The standard deviation in the experimental 2PA cross section was determined to be 20%. (b) Zoom of the lowest energy 2PA band indicating the break of molecular symmetry of **PE2** in solution. The solid lines represent the fit using the two-level energy model within the sum-over-essential states approach with $|\vec{\mu}_{01}| = 10$ D and $|\Delta\vec{\mu}_{01}| = 3$ D. The scattered triangles show the 2PA probability obtained from DFT framework for each specific transition reported in ref 9.

allowed transition ($S_0 \rightarrow S_1$), indicating that this state also is 2PA allowed.

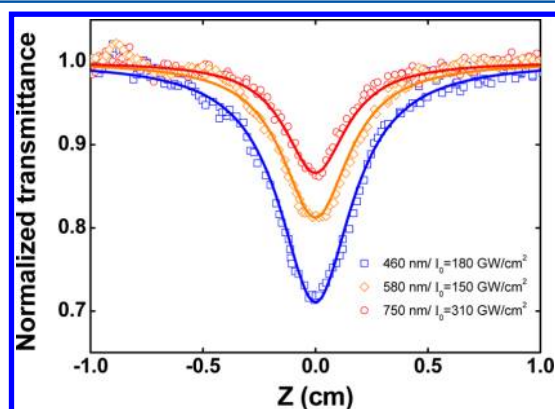In Figure 3, we show a few of our Z-scan curves corresponding to the three spectral regions previously

Figure 3. Open-aperture Z-scan curves for the three different regions described along the nonlinear spectrum as well as the irradiance employed during the experiments. The solid lines represent the fitting employing eq 1

described as well as the irradiance employed during the experiments. The decrease observed in the normalized transmittance as a function of the z position indicates a 2PA process, since excitation took place in nonresonant conditions.

It is worth mentioning that at 595 nm we found a 2PA cross-section value around 290 GM for the **PE2**, which is approximately 1.23 times higher than one obtained by Staromlynska et al.[14] by means of picosecond laser pulses. This value is within our experimental error estimated at 20%. Moreover, the authors from ref 14 used a 10 mm cuvette for the nonlinear absorption measurements, which is much higher than the Rayleigh length of the laser beam ($z_0 \sim 2.0$ mm), and, therefore, eq 1 is not valid.[20] In addition the authors used a concentration 10 times higher than the ones used in our Z-scan measurements, which may interfere considerably in suitable determination of the 2PA cross section due to the presence of aggregates. Another point that can be considered to explain the difference in the 2PA cross section is the population on the excited singlet and triplet states. In this case, for longer pulse widths (picosecond and nanosecond), excited-state absorptions are not anymore negligible. Consequently, for longer pulses, the total absorption cross section has contribution from a 2PA transition and 1PA excited-state transitions that, in the present case, could decrease the effective absorption cross section due to a lower excited-state absorption cross section at the excitation wavelength.[18]

It is important to mention here that in the past few years, in nonlinear optical measurements, the resonant enhancement has been widely explored because it is possible to obtain nonlinear optical effects extremely high only tuning the excitation wavelength close to the first one-photon allowed excited state.[21−23] Alternatively, it is also possible to tune the optical bandgap of material through the molecular engineer to obtain in determined spectral range as the telecommunications region (1300−1550 nm) extraordinary nonlinear optical effects.[24] Based on these points, we can observe that **PE2** presents a monotonic increase in the 2PA cross section in the enhancement effect region given an increase of about 14 times of

magnitude (635 GM at 460 nm) if compared with the lowest energy 2PA band peak at 710 nm.

In order to verify if the maximum peak intensity used in Z-scan experiments could cause photodegradation or interfere in determination of the 2PA cross section, we display the normalized transmittance as a function of the irradiance at 570 nm in Figure 4, corresponding to the peak of the higher
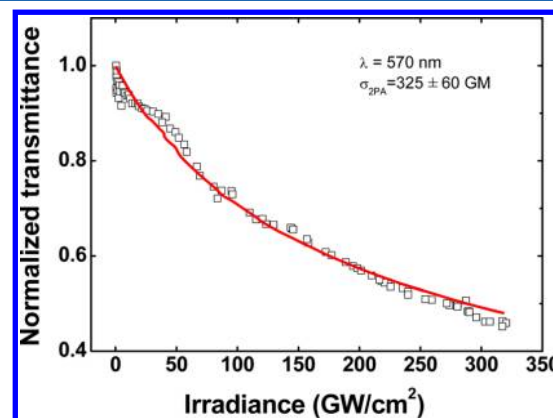

Figure 4. Normalized transmittance as a function of irradiance at 570 nm for **PE2** in dichloromethane solution (optical length of cuvette used 2 mm). The solid lines represent the fit obtained using eq 1 at $z = 0.0$ cm (focal position).

energy 2PA band. The solid line represents the fit obtained using eq 1 at $z = 0.0$ cm (focal position). As can be seen, in the irradiance range used, the **PE2** molecule does not present any spurious effect that could contribute to an inappropriate determination of the 2PA cross section. The value obtained through of this experiment corresponds exactly to one found by means of Z-scan technique at 570 nm. Alternatively, to verify if any photodecomposition was taking place during the Z-scan, we measured the linear absorption spectra after the experiment, and we did not observe any degradation for the intensity range used.

Recently, Nguyen et al.[9] theoretically investigated the one- and two-photon absorption spectra of platinum acetylide chromophores using time-dependent density functional theory (TDDFT). In that paper, they studied the influence of different conformations on the ground-state geometry of the chromophores on the linear and 2PA spectra.

Because of the facile rotations of the trimethylphosphinyl and phenylene groups, PEs may exhibit several conformations with different symmetries. Nguyen et al.[9] calculated the 2PA cross-section spectrum for nine distinct conformers. Among these conformations, the one that generates the 2PA spectrum that most closely matches our experimental spectrum is the C_{2h}(B,t) symmetry, which has two parallel aligned ethynylphenyl groups in the same plane of platinum core (solid line in Figure 2).[9] As can be seen, the theoretical spectrum reproduces well the higher energy 2PA-allowed band for both spectral position and 2PA cross-section magnitude. This band has been assigned preferentially to the 1^1A_g-like $\rightarrow 3^1A_g$-like transition that is related to the strong intramolecular interaction between the branches due to the presence of platinum atom.[25,26] Contrariwise, the experimental 2PA spectrum presents a band around at 710 nm with 45 GM ($h\nu = 355$ nm), which does not appear in the theoretical spectrum with this magnitude (45 GM) for any conformation. It is observed that this band has a spectral correspondence with the lowest-energy band of the linear

absorption spectrum (~357.5 nm). This same behavior was verified for the **PE2** in THF solution,[19] however, for few wavelengths.

Recently has been shown that PEs in solution exhibit a mixing of centrosymmetric and noncentrosymmetric conformations.[3] It is well-known that for centrosymmetric molecules, one-photon allowed transitions are two-photon forbidden.[27] However, as PEs exhibit this mixing of conformations, it is expected that the selection rules are relaxed since it is not possible to define precisely the excited-state parity.[9,10,28] Consequently, transitions are allowed by one and two-photon absorption. As a result, the nature of the lowest-energy 2PA band for the PEs is associated with the breaking of symmetry of these chromospheres in solution. Such behavior generates a permanent dipole moment change ($\Delta\vec{\mu}$) that can be visualized as if the charge density is localized on only one ligand.[3]

In the context of the sum-over essential states approach, the value of the permanent dipole moment change is proportional to the 2PA cross section at the peak in the same transition and can be written as[28,29]

$$|\Delta\vec{\mu}_{01}|$$

$$= \left(\frac{5}{2(2\pi)^3} \frac{N_A hc}{3 \times 10^3 \ln(10)} \frac{n}{L^2} \frac{\omega_{01}}{\varepsilon_{max}(\omega_{01})} \sigma_{01}^{(2PA-max)}(\omega_{01}) \right)^{1/2}$$

(3)

in which h is Planck's constant, c is the speed of light, and $\Delta\vec{\mu}_{01}$ is the difference between the permanent dipole moment vectors of the excited ($\vec{\mu}_{11}$) and ground ($\vec{\mu}_{00}$) states. $L = 3n^2/(2n^2 + 1)$ is the Onsager local field factor introduced to take into account the medium effect with $n = 1.424$ for dichloromethane at 20 °C. $\varepsilon_{max}(\omega_{01})$ is the molar absorptivity in the frequency (ω_{01}) of the peak of the lowest energy 1PA band, and N_A is Avogadro's number.

Substituting the 2PA cross-section value obtained through the femtosecond Z-scan technique (~45 GM at 710 nm), we found $|\Delta\vec{\mu}_{01}| = 3.0$ D. We used this result to simulate the lowest-energy 2PA band highlighted in Figure 2b (solid line) within the sum-over-essential states approach[26,30] with $|\vec{\mu}_{01}| = 10$ D obtained from the linear absorption spectrum.[30]

Recently, Rebane et al.[31] reported this same break of symmetry in PEs with molecular geometry similar to **PE2**. They explained this effect due to a large twisting angle of the ligand's phenyl rings relative to the Pt core, which generates a permanent dipole moment difference between the excited- and ground-state non-null, as reported here to **PE2**. This means that $\Delta\mu$ observed in the experiment is, most probably, related to the nonlinear optical effect generated by many different PEs conformations present simultaneously in solution. Because of this, from the quantum chemical calculations point of view, it still remains a challenge to describe correctly the molecular symmetry breaking of PEs in solution and, consequently, the correct lowest-energy 2PA-allowed band magnitude observed experimentally.

In order to corroborate that the 2PA spectra do not have significant contributions coming from the triplet-state absorption, we estimate the fraction of the population excited by 2PA that is transferred to the triplet state through intersystem crossing (~300 ps intersystem-crossing time) and direct transition ($S_0 \rightarrow T_1$) using the rate equation model.[30] Considering the 160 fs duration of our pulse and including

the $S_0 \rightarrow T_1$ transition in the methodology reported in ref 30, the population transferred to the triplet state at 595 nm, after the 160 fs and 27 ps pulse interaction, is shown in Figure 5. It is
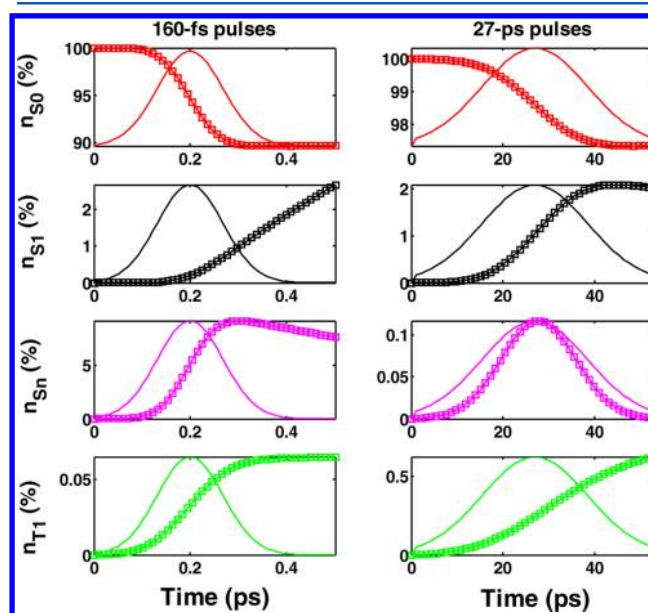

Figure 5. Calculation of the population dynamics induced by 2PA described by the rate equations at 595 nm (see ref 30). The left side shows the population dynamics after femtosecond-pulses irradiation while the right side shows the picosecond-pulses irradiation. The solid lines show the normalized laser pulse, while the squares describe the distribution of populations excited by 2PA.

important to mention that the 2PA cross section and irradiance values used in Figure 5 correspond to those employed here to femtosecond pulses (290 GM, 260 GW/cm²) and reported in ref 14 to picosecond pulses (235 GM, 10 GW/cm²). As can be noted, the population transferred to the triplet state after femtosecond-pulses irradiation calculated is less than 1% of the population excited to singlet states while to picosecond pulses the percentage is of approximately 30%. Therefore, the influence of the triplet-state population in the total nonlinear absorption excited via femtosecond pulses is negligible within our experimental error.

4. FINAL REMARKS

In the present paper, we studied and interpreted the 2PA cross-section spectrum of **PE2** platinum acetylide complex in dichloromethane solution, an interesting material for photonic applications. We showed that the 2PA spectrum displays two bands located at 570 and 710 nm as well as the resonant enhancement effect. The former band is related mainly to the 1^1A_g-like $\rightarrow 3^1A_g$-like transition as shown through the TDDFT framework described in ref 9. We compared our results with ones reported in this same reference and observed a good agreement between them for both spectral position as 2PA cross-section magnitude. On the other hand, the lowest energy 2PA band located at 710 nm was attributed to molecular symmetry breaking of **PE2** in solution that exhibits a mixing of centrosymmetric and noncentrosymmetric conforms. Because of this effect, we observed that the **PE2** undergoes a charge separation that corresponds to a permanent dipole moment change around $\Delta\vec{\mu} = 3$ D, which is related with the breaking of symmetry of the **PE2** in solution. Finally, we have shown

through the use of a rate equations model that after femtosecnd-laser irradiation the conversion to the triplet state through intersystem crossing (induced by 2PA) and direct transition ($S_0 \rightarrow T_1$, induced by one-photon absorption) is negligible; i.e., both effects do not have significant contribution to the 2PA spectrum of **PE2** on femtosecond excitation and low repetition rate.

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Author Contributions
M.G.V. conceived the idea of this study and performed together with L.D.B. the linear and nonlinear optical measurements. T.M.C. and C.R.M. supervised this study. All authors contributed to the writing of this manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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