UNDERSTANDING THE TWO-PHOTON ABSORPTION SPECTRUM OF PE2 PLATINUM ACETYLIDE COMPLEX (POSTPRINT)

Thomas M. Cooper
AFRL/RXAP

AUGUST 2014
Interim Report

Distribution A. Approved for public release; distribution unlimited.
See additional restrictions described on inside pages

STINFO COPY

© 2014 American Chemical Society
Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the USAF 88th Air Base Wing (88 ABW) Public Affairs Office (PAO) and is available to the general public, including foreign nationals.

Copies may be obtained from the Defense Technical Information Center (DTIC) (http://www.dtic.mil).

AFRL-RX-WP-JA-2014-0188 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

//Signature//

THOMAS M. COOPER
Photonic Materials Branch
Functional Materials Division

//Signature//

CHRISTOPHER D. BREWER, Chief
Photonic Materials Branch
Functional Materials Division

//Signature//

TIMOTHY J. BUNNING, Chief
Functional Materials Division
Materials and Manufacturing Directorate

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government’s approval or disapproval of its ideas or findings.
**REPORT DOCUMENTATION PAGE**

<table>
<thead>
<tr>
<th>1. REPORT DATE (DD-MM-YYYY)</th>
<th>2. REPORT TYPE</th>
<th>3. DATES COVERED (From – To)</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 2014</td>
<td>Interim</td>
<td>06 May 2010 – 09 July 2014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4. TITLE AND SUBTITLE</th>
<th>5a. CONTRACT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNDERSTANDING THE TWO-PHOTON ABSORPTION SPECTRUM OF PE2 PLATINUM ACETYLIDE COMPLEX (POSTPRINT)</td>
<td>In-House</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5b. GRANT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>5c. PROGRAM ELEMENT NUMBER</td>
</tr>
<tr>
<td>62102F</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6. AUTHOR(S)</th>
<th>5d. PROJECT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>(see back)</td>
<td>4348</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5e. TASK NUMBER</th>
<th>5f. WORK UNIT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X09X</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</th>
<th>8. PERFORMING ORGANIZATION REPORT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>(see back)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</th>
<th>10. SPONSOR/MONITOR'S ACRONYM(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Force Research Laboratory</td>
<td>AFRL/RXAP</td>
</tr>
<tr>
<td>Materials and Manufacturing Directorate</td>
<td></td>
</tr>
<tr>
<td>Wright Patterson Air Force Base, OH 45433-7750</td>
<td></td>
</tr>
<tr>
<td>Air Force Materiel Command</td>
<td></td>
</tr>
<tr>
<td>United States Air Force</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFRL-RX-WP-JA-2014-0188</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>12. DISTRIBUTION / AVAILABILITY STATEMENT</th>
<th>13. SUPPLEMENTARY NOTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distribution A. Approved for public release; distribution unlimited. This report contains color.</td>
<td>PA Case Number: 88ABW-2014-2036; Clearance Date: 30 April 2014. Journal article published in the Journal of Physical Chemistry A 2014, 118, 5608–5613. © 2014 American Chemical Society. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display or disclose the work. The final publication is available at dx.doi.org/10.1021/jp503318u.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>14. ABSTRACT</th>
<th>15. SUBJECT TERMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herein, we report on the two-absorption crosssection spectrum of trans-Pt(PBu$_3$)$_2$ (C≡C–C$_4$H$_4$–C≡C–C$_4$H$_4$)$_2$ (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.</td>
<td>capacitors, carbon nanotubes, thin films</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>16. SECURITY CLASSIFICATION OF:</th>
<th>17. LIMITATION OF ABSTRACT</th>
<th>18. NUMBER OF PAGES</th>
<th>19a. NAME OF RESPONSIBLE PERSON (Monitor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. REPORT</td>
<td>b. ABSTRACT</td>
<td>c. THIS PAGE</td>
<td>SAR</td>
</tr>
<tr>
<td>Unclassified</td>
<td>Unclassified</td>
<td>Unclassified</td>
<td>10</td>
</tr>
<tr>
<td>19b. TELEPHONE NUMBER (include area code)</td>
<td>Thomas M. Cooper</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(937) 255-9620</td>
<td></td>
<td></td>
<td>(937) 255-9620</td>
</tr>
</tbody>
</table>
6. AUTHOR(S)

Thomas M. Cooper - Materials and Manufacturing Directorate, Air Force Research Laboratory, Functional Materials Division

Marcelo G. Vivas - Instituto de Ciência de Tecnologia, Universidade Federal de Alfenas, Cidade Universitário, BR

Leonardo De Boni and Cleber R. Mendonca - Grupo de Fotônica, Instituto de Física de São Carlos, Universidade de São Paulo, CP

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

AFRL/RXAP
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750

Instituto de Ciência de Tecnologia, Universidade Federal de Alfenas, Cidade Universitário, BR 267 Km 533, 37715-400 Poços de Caldas, MG Brazil

Grupo de Fotônica, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos, SP Brazil
Understanding the Two-Photon Absorption Spectrum of PE2 Platinum Acetylide Complex

Marcelo G. Vivas,*†‡ Leonardo De Boni, ‡ Thomas M. Cooper,§ and Cleber R. Mendonça*†

†Grupo de Fotônica, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos, SP Brazil
‡Instituto de Ciência de Tecnologia, Universidade Federal de Alfenas, Cidade Universitária—BR 267 Km 533, 37715-400 Poços de Caldas, MG Brazil
§Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States

ABSTRACT: Herein, we report on the two-absorption cross-section spectrum of trans-Pt(PBu3)2 (C≡C–C6H4–C≡C–C6H4≡Pt)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), ultrafast efficiency generation of singlet oxygen, intense two- (thousands of GM units) and three-photon absorption (∼10^-7 cm^6 s^2 photon^-2), ultrafast intersystem crossing (from femtosecond to picosecond) and long phosphorescence time (microsecond). 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. Among the possible applications of these materials, we can cite ones related with chemosensing, photodynamics therapy, and optical switching, to name a few.

One of the first PEs to have their nonlinear optical properties investigated was the trans-Pt(PBu3)2 (C≡C–C6H4≡C≡C–C6H4≡Pt)2, named PE2, by Staromlynska et al. 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 (S0) to the triplet state (T1) 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 S0 → T1 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. This relaxation of selection rule already had been reported by other authors using different techniques. Also according to Staromlynska et al., the S0 → T1 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 S0 to T1 followed by intersystem crossing to the T1 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, while the latter helps avoiding cumulative effects between consecutive pulses, coming...
from possible triplet–triplet absorption.\textsuperscript{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 $10^{15}$ 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.\textsuperscript{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 field intensity are monitored. For a 2PA process, the light field creates an intensity dependent absorption, $\alpha = \alpha_0 + \beta f_0$, in which $f_0$ is the laser beam intensity, $\alpha_0$ is the linear absorption coefficient, and $\beta$ 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

$$T(z) = \frac{1}{\sqrt{\pi \alpha_0(z, 0)}} \int_{-\infty}^{\infty} \ln[1 + q_0(z, 0)e^{-r^2}]dr$$

with

$$q_0 = \beta f_0 L (1 + (z^2/z_0^2))^{-1}$$

in which $L$ is the sample thickness, $z_0$ is the Rayleigh length, $z$ is the sample position, and $L_0$ is the laser intensity at the focus. The nonlinear coefficient $\beta$ is obtained by fitting the Z-scan data with eq 1. The 2PA cross section, $\sigma_{2PA}$, is determined from $\sigma_{2PA} = h\omega f/N$, in which $h\omega$ 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 Goppert–Mayer (GM) $(1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1})$.

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.\textsuperscript{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 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$ in dichloromethane. This band is related to the $S_0 \rightarrow S_1 (\pi\pi^*)$ transitions with strong metal-to-ligand charge transfer character.\textsuperscript{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.,\textsuperscript{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 $S_0 \rightarrow T_1$ 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 $S_0 \rightarrow S_n$ 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...
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 described as well as the irradiance employed during the experiments. The solid lines represent the fitting employing eq 1.

![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.](Image)

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 Staromysnka et al.\(^\text{14}\) 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 \((z_0 \approx 2.0 \text{ mm})\), and, therefore, eq 1 is not valid.\(^\text{20}\) 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.\(^\text{18}\)

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.\(^\text{21-23}\) 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 \((1300-1550 \text{ nm})\) extraordinary nonlinear optical effects.\(^\text{24}\)

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 \((635 \text{ GM at } 460 \text{ nm})\) 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 energy 2PA band. The solid lines represent the fit obtained using eq 1 at \(z = 0.0 \text{ cm (focal position)}\).

![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 \(z = 0.0 \text{ cm (focal position)}\).](Image)

Recently, Nguyen et al.\(^\text{9}\) 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.\(^\text{9}\) 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 \(C_{3v}(B_{1g})\) symmetry, which has two parallel aligned ethynylphenyl groups in the same plane of platinum core (solid line in Figure 2).\(^\text{9}\) 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 \(1^{1}A_g\)-like \(\rightarrow 3^{1}A_g\)-like transition that is related to the strong intramolecular interaction between the branches due to the presence of platinum atom.\(^\text{25,26}\) Contra- wise, the experimental 2PA spectrum presents a band around at 710 nm with 45 GM \((\hbar \nu = 355 \text{ nm})\), which does not appear in the theoretical spectrum with this magnitude \((45 \text{ GM})\) for any conformation. It is observed that this band has a spectral correspondence with the lowest-energy band of the linear
The Journal of Physical Chemistry A

Article

Distribution A. Approved for public release; distribution unlimited.

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

Recently has been shown that PEs in solution exhibit a mixing of centrosymmetric and noncentrosymmetric conformations. It is well-known that for centrosymmetric molecules, one-photon allowed transitions are two-photon forbidden. 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. 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 (\( \Delta \tilde{\mu} \)) that can be visualized as if the charge density is localized on only one ligand.

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:

\[
|\Delta \tilde{\mu}_{01}| = \left( \frac{5}{2(2\pi)^3} \times 10^4 \ln(10) \right) \frac{n}{L^2} e_{\text{max}}(\omega_{01}) \epsilon_{01}^{(2\text{PA}-\text{max})}(\omega_{01}) \right)^{1/2}
\]

where

\[
|\Delta \tilde{\mu}_{01}| = 3 \text{ D},
\]

in which \( h \) is Planck’s constant, \( c \) is the speed of light, and \( \Delta \tilde{\mu}_{01} \) is the difference between the permanent dipole moment vectors of the excited (\( \tilde{\mu}_{11} \)) and ground (\( \tilde{\mu}_{00} \)) 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. \( e_{\text{max}}(\omega_{01}) \) is the molar absorptivity in the frequency (\( \omega_{01} \)) of the peak of the lowest energy 1PA band, and \( N_h \) is Avogadro’s number.

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

Recently, Rebane et al. 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 (S0 \( \rightarrow \) T1) using the rate equation model. Considering the 160 fs duration of our pulse and including the S0 \( \rightarrow \) T1 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 important to mention that the 2PA cross section and irradiance values used in Figure 5 correspond to those employed here for 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 \( 1^{1}\text{Ag-like} \rightarrow 3^{1}\text{A_g-like} \) 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 conformations. Because of this effect, we observed that the PE2 undergoes a charge separation that corresponds to a permanent dipole moment change around \( \Delta \tilde{\mu} = 3 \text{ D,} \) 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 femtosecond-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.

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: mavivas82@yahoo.com.br.*
*E-mail:crmendon@ifsc.usp.br.*

**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**
Financial support from FAPESP (Fundação de Amparo à Pesquisa do estado de São Paulo, processo no. 2011/06489-6 and no. 2011/12599-0), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and the Air Force Office of Scientific Research (FA9550-12-1-0028) is acknowledged.

**REFERENCES**

