Two-Photon Absorption in Linear Bis-dioxaborine Compounds—The Impact of Correlation-Induced Oscillator-Strength Redistribution

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Quantum-chemical calculations of the two-photon absorption (TPA) cross-sections are used to determine the characteristics of the electronic excited states responsible for the observed peaks in the TPA spectra of two bis-dioxaborine-substituted biphenyl derivatives. We find two distinct TPA-active states with very different TPA cross-sections; the difference is explained on the basis of electron correlation. These effects, on the one hand, lead to TPA cross-sections of up to 500 \( \times 10^{-50} \text{cm}^2 \text{s photon}^{-1} \) for the state favored by correlation; on the other hand, they limit the overall cross-sections achievable in this class of materials.

1. Introduction

Two-photon absorption (TPA) in organic molecules has recently been utilized in numerous applications including optical limiting,[1] 3D microfabrication,[2] and 3D fluorescence microscopy.[3] Recently, numerous studies have shown that donor and/or acceptor substitution of \( \pi \)-conjugated systems can lead to a tremendous increase in the TPA cross-section, \( \delta \), for dipolar,[4,5,6] quadrupolar,[5,7,8,9] as well as octupolar[10,11] substitution patterns. Large \( \delta \) values have also been found for substituted dendrimers[12] and porphyrins.[13]

Although the enhancement of the TPA response through substitution with electron-withdrawing and -donating groups is well-established experimentally and is reproduced by numerous calculations, the electronic origin of the enhancement is not yet fully understood. In centrosymmetric molecules, the increase can be related to a stronger dipole coupling between the one- and two-photon allowed states[5] and this coupling has been predicted to depend on subtle aspects of electron correlation.[14] However, the latter prediction still lacks experimental verification; at this point, it is not clear to what extent the correlation-induced oscillator-strength redistribution predicted in ref.[14] can really be exploited to enhance the TPA response of \( \pi \)-conjugated chromophores.

We have recently reported that bis(2,2-difluoro-1,3,2(2H)-dioxaborin-4-yl (DOB) derivatives of biphenyl, fluorene, and carbazole show high two-photon cross-sections, that some of these materials have a combination of properties which makes them suitable for the two-photon-induced deposition of silver metal,[15] and that sum-over-states (SOS) methods[16] can be used to estimate their peak TPA cross-sections. Here we analyze in more detail the SOS results for two of these chromophores (see insets of Figure 1 and Figure 2) and show how these molecules prove useful for understanding correlation-induced oscillator-strength redistribution effects in two-photon absorption processes.

We focus on the electronic contributions to the TPA response, which, as discussed in ref.[17], are expected to dominate over contributions arising from Herzberg–Teller coupling in the present class of molecules. However, for the electronically weakly TPA-allowed \( S_1 \) state, the experimental findings suggest that channels through vibrationally excited states play a role; this aspect will be discussed below in the context of the results presented in ref.[18].

To facilitate the interpretation of the calculated spectra, approximations are applied to the full SOS expression.[18] For the case of a two-photon resonance to a specific two-photon allowed state \( |e'\rangle \) (i.e., when \( 2\hbar \omega \to E_{e'} \)), the SOS expression for \( \delta \) can be simplified, provided that a single excited state \( |e'\rangle \) dominates the linear absorption (\( T \) term) and is then given by

\[
\delta = \frac{\langle e' | H | e \rangle^2}{\langle e' | \delta \delta | e \rangle}
\]

where \( H \) is the Hamiltonian and \( \delta \) is the dipole moment. The expression reduces to

\[
\delta = \frac{\langle e' | H | e \rangle^2}{\langle e' | \delta \delta | e \rangle}
\]

for the case of a two-photon resonance to a specific two-photon allowed state \( |e'\rangle \) (i.e., when \( 2\hbar \omega \to E_{e'} \)).

Supporting information for this article is available on the WWW under http://www.chemphyschem.org or from the authors.
Equation (1):\[7\]

\[ \delta_{3\text{-state}} \propto \left( \frac{E_{ge}}{2} \right)^2 \frac{M_{ge}^2}{(E_{ge} - E_{ge}/2)^2/I} \]  

Here, \( E_{ge} \) and \( E_{ge}' \) are the transition energies to the one-photon and two-photon allowed states, and \( M_{ge} \) and \( M_{ee} \) refer to the transition dipoles between the ground state and the one-photon state and between the one-photon and two-photon states, respectively.\[20\]

In molecules that lack a center of inversion, one-photon allowed states can also contribute to the TPA response. The approximate expression for the TPA cross-section is then given by the so-called D term, which is dominated by \( M_{ge} \) and the change-in-state dipole moment between the ground state and the one-photon excited state.\[6\]

2. Results and Discussion

2.1. General Features of the TPA Spectra

The calculated TPA spectra for chromophores I and II are compared with the experimental data in Figures 1 and 2, respectively. (Emission, linear and nonlinear absorption spectra for chromophore I can also be found in ref. [15]). In both chromophores, a two-peak structure is observed with a weak maximum around 1.75 eV for I and 1.65 eV for II and a much stronger feature centered at 2.10 eV in I and 2.04 eV in II. The calculations reproduce the experimental observations very well; the main difference is a slight overestimation of the excited-state energies (note that the horizontal scales for the calculated spectra in Figure 1 and Figure 2 are offset by 0.2 eV relative to the experimental spectra, to ease the comparison). The calculated excited-state energies and transition dipole moments for the S1, S2, and S3 states in chromophores I and II are summarized in Table 1. Based on the quantum-mechanical modeling (see below), we assign the strong feature to an excitation into the S3 state, while the weak feature is assigned to TPA into the S2 state.

2.2. Electronic Nature of the Two-Photon Active Excited States

The large difference in TPA cross-section for excitation into the S2 and S3 states appears surprising at first sight, as Table 2 indicates that the configuration interaction (CI) descriptions of

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**Figure 1. Calculated (top) and measured (bottom) two-photon absorption cross-sections of chromophore I as a function of the energy of the incident photon. The vertical bars in the upper graph correspond to half of the energies of the excited states; the states plotted above \( S_3 \) have only very small associated TPA cross-sections. The large circles in the low-energy region correspond to half of the energies of the excited states; the states plotted above \( S_3 \) have only very small associated TPA cross-sections.**

**Figure 2. Calculated (top) and measured (bottom) two-photon absorption cross-sections of II as a function of the energy of the incident photon. The vertical bars in the upper graph correspond to half of the energies of the excited states; the states plotted above \( S_3 \) have only very small associated TPA cross-sections. The large circles in the low-energy region correspond to half of the energies of the excited states; the states plotted above \( S_3 \) have only very small associated TPA cross-sections.**

**Table 1. INDO/MRDCI calculated excitation energies and transition dipoles for the relevant states in the investigated molecules.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>State</th>
<th>( E_{ge} ) [eV]</th>
<th>( M_{ge} ) [Debye]</th>
<th>State</th>
<th>( E_{ge}' ) [eV]</th>
<th>( \frac{E_{ge}}{2} - E_{ge}/2 ) [eV]</th>
<th>( M_{ee} ) [Debye]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( S_1 )</td>
<td>3.57</td>
<td>11.0</td>
<td>( S_2 )</td>
<td>3.80</td>
<td>1.1</td>
<td>3.5</td>
</tr>
<tr>
<td>II</td>
<td>( S_1 )</td>
<td>3.43</td>
<td>11.1</td>
<td>( S_2 )</td>
<td>4.64</td>
<td>1.9</td>
<td>11.8</td>
</tr>
</tbody>
</table>

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both states are dominated by the same determinants (characterized by one-electron excitations from HOMO to LUMO +1, from HOMO−1 to LUMO, and from HOMO−4 to LUMO +1). Understanding the reasons for the large cross-section differences between S2 and S3 should allow us to gain a more fundamental understanding of the nature of strongly TPA-active states and, therefore, help in developing new strategies for further enhancing nonlinear absorption properties. In the following we focus on chromophore I, with the same behavior obtained for II.

As a first step to analyze the difference between the S2 and S3 states, the microscopic parameters (transition dipoles and excitation energies) entering the three-state description of their TPA response need to be compared (Eq. (1) here represents the primary TPA channel for these states). The details in Table 1 show that the main origin of the difference in δ values associated with the S2 and S3 states is in the transition dipole moments Mμe. There is a factor of 3.4 increase in the Mμe transition dipoles on going from the S2 to the S3 state, which leads to nearly a factor of 12 increase in the corresponding δ value for I. This increase of Mμe is reminiscent of the observation made for the lowest TPA active state when going from stilbene to its donor/acceptor/donor substituted derivatives,11 with the main difference here being that the two states in question belong to the same molecule. An additional factor of 3 in δ comes from the detuning factor [(Eμ/2)/(Eμ−Eμ/2)]2, since the transition energy of the S1 state is closer to half the transition energy of the S3 state than to half that of the S2 state.

To better understand the differences in Mμe between the S2 and S3 states, we plot in Figure 3 the atomic transition densities (ρμe(r)) for the relevant excitations in I. We recall that transition densities are defined as the products (or more rigorously speaking, integrals over all-but-one electron coordinates of the products) of the initial and final state wavefunctions. Consequently, transition dipoles are integrations over space of the transition densities multiplied by the position vector given in Equation (2):

$$M_{\mu e} = \langle \Psi_f | \mu | \Psi_i \rangle = -e \int \rho_{\mu e}(r) rdr$$ (2)

Here, e is the elementary charge and μ the dipole-moment operator. Examination of transition densities allows the determination of the parts of the molecule that contribute most strongly to the transition dipoles. The obtained transition dipole moment is independent of the choice of the origin of the coordinates and it is customary to take it as the molecular center of mass. It is then clear from Equation (2) that transition densities at the extremities of the molecule contribute more strongly to the transition dipoles and that contributions from adjacent atomic transition densities with opposite phases (signs) partly compensate.

Figure 3 illustrates that the atomic transition densities between S2 and S3 responsible for Mμe spread over the whole molecule; in contrast, the transition densities describing the Mμe transition dipole between the S1 and S3 or S1 and S2 states are localized on the DOBrings. It has been shown in ref. [14] that

![Figure 3. INDO/MRDCI calculated transition densities associated with each atom of I in the ZDO approximation, for the transitions (from top to bottom) between S1 and S2, S1 and S3, and S2 and S3. The diameters of the circles are proportional to the magnitudes of the transition densities and the shading represents their phase.](image)

| Table 2. Most significant contributions to the CI description of the excited states in I and II. (H−L) corresponds to an excited Slater determinant with an electron promoted from the HOMO to the LUMO. |
|-----------------|-----------------|-----------------|-----------------|
| I−S1 | 0.78 (H−L−1) + 0.48 (H−1−L+1) |
| S1 | 0.62 (H−L+1) + 0.59 (H−1−L−1) + 0.34 (H−4−L+1) |
| S2 | 0.64 (H−L+1) − 0.41 (H−1−L) + 0.59 (H−4−L+1) |
| II−S1 | 0.83 (H−L−1) + 0.37 (H−2−L+1) |
| S1 | 0.67 (H−L+1) + 0.50 (H−2−L) + 0.30 (H−4−L+1) |
| S2 | 0.57 (H−L+1) + 0.52 (H−2−L) + 0.34 (H−4−L+1) |

site signs on the two rings). As a result, when multiplied by the position vector, they all add up and result in a large value of $M_m$.

To understand the origin of the strongly different transition dipoles for the $S_1 \rightarrow S_2$ and $S_1 \rightarrow S_3$ transitions, we note that in an (uncorrelated) independent-particle picture, the transition dipoles between these determinants would directly enter the perturbative SOS description. As several of them are very large (and strongly differ from the values measured and calculated for the molecules investigated here, on the order of $500 \times 10^{-30}$ cm$^2$ photon$^{-1}$), they all add up and result in a large value of $M_m$.

Using the values from Table 2 and Table 3, the transition dipoles between $S_1$ (represented here by $0.08 \, |H\rightarrow L| + 0.48 \, |H\rightarrow L+1|$) and the determinants dominating $S_2$ and $S_3$ are calculated to be: $S_2 |H\rightarrow L+1| = -10.5 \, D$, $S_3 |H\rightarrow L+1| = 1.3 \, D$, and $S_1 |H\rightarrow L+1| = -9.9 \, D$. From the CI description of $S_2$ and $S_3$, it follows that the contributions from the individual transition dipole terms for excitation from $S_1$ to $S_2$ nearly cancel ($-2.4 \, D$), since the $|H\rightarrow L+1|$ and $|H\rightarrow L+1|$ determinants enter with different signs. They, however, interact in a constructive manner for the excitation from $S_1$ to $S_3$ ($-11.6 \, D$). This results in the large differences in the associated TPA cross-sections shown in Figure 1 and Figure 2.

Such a correlation-induced oscillator strength redistribution has been predicted theoretically in ref. [14] for quadrupolar donor/acceptor/donor-substituted stilbenes at very large degrees of ground-state polarization. To our knowledge, the present work provides the first experimental observation of this oscillator strength redistribution in the context of nonlinear absorption and highlights that electron correlation affects the TPA response of organic chromophores not only quantitatively but also qualitatively.

In ref. [14] it was also predicted that the higher-lying excited state for which the individual transition dipoles add constructively could have a very large TPA cross-section, if $E_{ee}$ were lower than $E_{ee}$ (as is the case here), with the actual value strongly depending on the detuning energy ($E_{ee} - E_{ee}$). The $\delta$ values measured and calculated for the molecules investigated here, on the order of $500 \times 10^{-30}$ cm$^2$ photon$^{-1}$, are thus somewhat disappointing. To understand this feature it is useful to take a closer look at the $S_1$ state. In donor/acceptor/donor-substituted stilbenes (the molecules discussed in ref. [7, 14]), the description of this state is always largely dominated by a single determinant (namely the one in which an electron is promoted from the HOMO to the LUMO) independent of the donor and acceptor strengths. In the present case, however, the description of $S_1$ involves a significant mixing between the $|H\rightarrow L|$ and $|H\rightarrow L+1|$ determinants. It turns out that this mixing in $S_1$ is detrimental to the TPA cross-section. For instance, the transition dipole from the $|H\rightarrow L|$ excited determinant to the $S_1$ state (represented by the three determinants given in Table 2) is very large ($-21.6 \, D$), but is offset by that from $|H\rightarrow L+1|$ to $S_1$ ($-10.9 \, D$). Thus, in the molecules studied here, while configurational mixing in the description of the $S_1$ state is beneficial for the TPA response, this positive feature is partly compensated by unfavorable correlation effects affecting $S_1$.

We have focused on the five determinants appearing in Table 2, which dominate the descriptions of the $S_1$, $S_2$, and $S_3$ states.\cite{21} We note that in an (uncorrelated) independent-particle picture, the transition dipoles between these determinants would directly enter the perturbative SOS description. As several of them are very large (and strongly differ from the values listed in Table 1), a totally different TPA response would be expected when configuration mixing is neglected.

\begin{table}
\centering
\begin{tabular}{|l|c|}
\hline
Configuration & $M_m$ [D] \\
\hline
(SCF) $|\mu| |H\rightarrow L|$ & 5.64 \\
(SCF) $|\mu| |H\rightarrow L+1|$ & 10.54 \\
$|H\rightarrow L| |H\rightarrow L+1|$ & -23.41 \\
$|H\rightarrow L| |H\rightarrow L|$ & 16.13 \\
$|H\rightarrow L+1| |H\rightarrow L+1|$ & 0.00 \\
$|H\rightarrow L+1| |H\rightarrow L|$ & 16.13 \\
$|H\rightarrow L+1| |H\rightarrow L+1|$ & -23.41 \\
$|H\rightarrow L+1| |H\rightarrow L|$ & -20.60 \\
\hline
\end{tabular}
\caption{Transition dipole moments between individual determinants in L. (SCF) refers to the self-consistent field-determinant. In the excited determinants, $H$ denotes excitations from the HOMO and $L$ excitations to the LUMO. Here, we give the transition dipoles along the long molecular axis, $\alpha$, as this eases the addition and subtraction of transition dipole moments described in the text (the influence of off-axis components is negligible).}
\end{table}

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\end{flushright}
shows that: i) the onset of linear and nonlinear absorption occurs at the same energy and ii) in chromophore II the vibronic progression of linear absorption into the S₅ state is also found in the TPA spectrum. Both aspects suggest that TPA into the S₅ state might play a role. (Note that in Figure 4, the spectra are shown as a function of state energy rather than of photon energy, which accounts for the factor of two difference in the energy scales in Figure 1/Figure 2 and Figure 4.)

To explain this, we suggest the following scenario: TPA is very well-described by purely electronic calculations for excitations into moderately (S₂) and strongly (S₅) two-photon allowed states that are coupled to the ground state through T-type terms. For TPA into states for which the purely electronic channels are small (as it is the case for the S₁ state here), or more generally, into states gaining the electronic contribution to the TPA cross-section from dipolar (D-type) terms, T-type channels [Eq. (1)], involving vibrationally rather than electronically excited intermediate states can become significant. This has been described in detail by Painelli and co-workers for donor-π-acceptor molecules.¹⁸ They also predicted that the maximum in the TPA spectrum obtained when this type of coupling is operative should be shifted to higher vibronic sublevels compared to the one-photon spectrum,¹⁸ a feature that is present in our experimental data (Figure 4). Thus, the weak feature between 1.5 eV and 1.8 eV appears to be a superposition of TPA into the S₅ state through electronic channels and TPA into S₅ mediated by channels involving intermediate vibrational states.

At this point it should be mentioned that also in non-centrosymmetric, L-shaped DOB-containing molecules we find a blue-shift for TPA into states that gain the electronic part of their cross-section through D-type terms.²²

Summary and Conclusions

We have studied the two-photon absorption properties of two acceptor-π-acceptor systems with dioxaborine acceptor units using highly correlated quantum-mechanical simulations, and found excellent agreement with nanosecond and femtosecond spectroscopic data. In the accessible spectral region, there are two significant TPA features. The calculations show that the large difference in the nonlinear absorption response of the two states involved is a consequence of correlation-induced oscillator strength redistribution; this emphasizes that electron correlation is the key to understanding the factors governing the TPA response in π-conjugated organic chromophores. Configuration mixing also affects the lowest one-photon excited state and, in this way, reduces the overall TPA response that can be achieved. Moreover, we find strong indications that TPA into the one-photon allowed state (S₁) is mediated by channels involving vibrational sublevels of the ground state, thereby supporting the theoretical predictions in ref. [18]

Methodology

Details regarding the synthesis of the compounds and their spectroscopic investigations are contained in the Supporting Information. The specific values of the fluorescence quantum yields determined for I and II are 68 and 72%, respectively. Quantum-Chemical Modeling: To calculate the TPA cross-sections, we start from molecular geometries optimized with the semiempirical AM1 Hamiltonian.²³ No constraints on the geometry were imposed, which for chromophore I results in a twist angle of 40° between the phenylene rings and 23° between the core and the DOB units. We note that, depending on the molecular conformation, the biphenyl derivative can be centrosymmetric or not. This influences the selection rules for the TPA process. While in centrosymmetric cases a state is either one- or two-photon allowed, this mutual exclusivity does not apply in non-centrosymmetric molecules. Therefore, we have tested several molecular conformations to obtain unambiguous results. The observed differences are, however, only minor and unless otherwise stated, the results for the biphenyl derivative are given for the chiral conformation with C₅ symmetry; those for the fluorine derivative are calculated for the equivalent conformation, which has C₁ symmetry due to the broken symmetry of the central fluorene unit. Excited-state energies and state and transition dipoles are obtained by coupling the intermediate neglect of differential overlap (INDO)²⁴ Hamiltonian to a multireference determinant single and double-excitation configuration interaction (MRDCI)²⁵ scheme. We use the Mataga–Nishimoto potential²⁶ to express the Coulomb repulsion term (note that comparative calculations performed with the Ohno–Klopman potential²⁷ yield a less satisfactory quantitative agreement between experimental and theoretical data, see also ref. [11] although the general effects discussed below are reproduced). Bearing in
mind that the accessible CI-active space is far from being complete and that the actual choice of the CI-space somewhat influences the quantitative aspects of the calculated data, we have extensive-
ly tested the size of the CI active space to ensure the reliability of the obtained results. (The details of the chosen CI space are described in the Supporting Information).

Describing the TPA Response: The TPA cross-sections are evaluated using the perturbative sum-over-states (SOS) approach\cite{10} including the electronic coupling among the 300 lowest-lying excited states to ensure full convergence of $\delta$. (We note that this approach is equivalent to using the TPA tensor,\cite{11} as has been shown by Luo et al.\cite{12}) and that the actual choice of the CI-space somewhat influences the obtained results. (The details of the chosen CI space are described in the Supporting Information).

The damping factors ($G$) entering the SOS expression for the various excited states [see Eq. (1)] are assumed to be equal and set to 0.1 eV, in accordance with previous studies. However, the observed TPA peaks are broader, as they include the intrinsic linewidth as well as the vibronic structure and inhomogeneous broadening. We have thus convoluted the calculated TPA response with a normalized Gaussian function, whose width has been chosen so that the calculated spectra match the full width at half maximum of the measured spectra (typical broadenings are 0.165 and 0.175 eV for the biphenyl and fluorene derivatives, respectively). An equivalent effect can be achieved by increasing the (somewhat arbitrarily chosen) damping factor. As the increased width is most likely due to inhomogeneous broadening, the convolution with the normalized Gaussian function is, however, in better accordance with the actual experimental procedure.

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References:


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