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Published in:
ChemPhotoChem

Link to article, DOI:
[10.1002/cptc.201900121](https://doi.org/10.1002/cptc.201900121)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Avila Ferrer, F. J., Angeli, C., Cerezo, J., Coriani, S., Ferretti, A., & Santoro, F. (2019). The intriguing case of the one-photon and two-photon absorption of a prototypical symmetric squaraine: comparison of TDDFT and wave-function methods. *ChemPhotoChem*, 3(9), 778-793. <https://doi.org/10.1002/cptc.201900121>

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Title: The intriguing case of the one-photon and two-photon absorption of a prototypical symmetric squaraine: comparison of TDDFT and wavefunction methods

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemPhotoChem* 10.1002/cptc.201900121

Link to VoR: <http://dx.doi.org/10.1002/cptc.201900121>

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A Journal of

The intriguing case of the one-photon and two-photon absorption of a prototypical symmetric squaraine: comparison of TDDFT and wave-function methods

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June 11, 2019

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Abstract

We face the challenging description of the excited states responsible for one photon (OPA) and two photon (TPA) absorption in squaraine dyes, adopting both time-dependent density functional theory and a large variety of post Hartree Fock methods, including coupled cluster and adiabatic diagrammatic construction methods (ADC, to the second and third order), symmetry adapted cluster configuration interaction (CI), CASSCF including second-order perturbative corrections (PT2) with standard CASPT2 recipe and according to n-electron valence PT2 (NEVPT2) approach, and an additional multireference CI with PT2 corrections (CI-MRPT2). We selected a small prototypical symmetric squaraine dye for which these accurate computations are feasible and experimental data are available. We show that while all methods reasonably reproduce the OPA spectrum, an acceptable description and assignment of the states responsible for TPA is only possible through ADC(3) and multireference calculations, due to the strong involvement of double-excitations. The nature of ground state and OPA and TPA states is investigated with a rigorous reading of the CASSCF wavefunctions in terms of localized molecular orbitals on the donor and acceptor fragments, showing that these states arise from a balance of many

different contributions including biradical configurations, local excitations and charge-transfer states where both side aromatic rings and the carbonyls of the squarylium moiety act as donors.

1 Introduction

Squaraine dyes are obtained from the condensation of squaric acid with aromatic or heterocyclic components [1, 2], and are usually considered as donor-acceptor-donor (D-A-D) systems where the oxocyclobutenolate acts as the acceptor core. In the last decades, they have attracted large interest for different applications as solar cell dyes [3–7], fluorescent probes [8, 9], photosensitizers for photodynamic therapy [10–12], and nonlinear optical chromophores [13–20].

Figure 1 reports the structure of the simple squaraine dye that will be studied in this contribution, since now on referred to as SQ0. Inspection of the chemical structure suggests that both bi-radical and zwitterionic (charge-transfer, CT) resonance formulas are possible. Considering the general class of squaraine dyes, the relative importance of these different characters in the ground and electronic excited states will clearly depend on the nature of the aromatic side rings, their symmetry/asymmetry and on the environment. It is expected that these factors will also rule the optical linear and non-linear properties of the system. For instance, squaraines are characterized by a strong red or near infrared absorption which has been alternatively attributed to the biradicaloid or to the CT character [21–26].

Despite their large practical interest, the literature on computational studies of the excited electronic states of squaraine dyes is not very rich. Going in more details, even if one of their main interest is toward non-linear properties, most of the existing computational characterizations were focused on linear absorption [21–31]. As a matter of fact, from the pure computational point of view, the first strong absorption band has been simulated with reasonable accuracy both with symmetry-adapted cluster-configuration interaction (SAC-CI)[21, 22] and with the second-order algebraic diagrammatic construction of the polarization propagator (ADC(2)), [27, 28] with the latter providing 0-0 excitation energies extremely close to the experiment for SQ0. However, even time-dependent Density functional Theory (TD-DFT) performs reasonably well, with only a moderate overestimation of the excitation energy [27–29, 32]. On the contrary, very few papers have dealt with non linear properties like second order polarizability [23] or two-photon absorption [18, 33].

Based on these considerations, in this contribution we face the problem of obtaining a satisfactory and balanced description of the excited states relevant for OPA and TPA of squaraines. To this end, we selected the SQ0 system of Figure 1. On one side, it is the smallest member of the series of squaraines for which both OPA and TPA experimental spectra are available, together with fluorescence anisotropy

measurements [34]. On the other side, it is symmetric and small enough to allow the application of highly accurate post-Hartree-Fock methods. Its OPA in toluene is characterized by a strong narrow band peaked at ~ 635 nm (~ 1.95 eV) and by a very weak signal at ~ 375 nm (~ 3.3 eV). The emission spectrum is pretty much mirror-symmetric with respect to the strong OPA band. As far as TPA is concerned, two strong peaks can be noticed at ~ 840 nm and at 690 nm (more intense). Since we here focus on the molecular excited states, when discussing OPA and TPA in the following, we will always implicitly refer to the vertical energy of the final states with respect to the ground state, and not to the photon energy. In this case, the experiment shows the existence of two TPA-active states at ~ 2.95 eV and ~ 3.60 eV, respectively. A further weak and broad band is observed in the region of the strong OPA absorption (~ 2.10 eV). Moreover, dips of the excitation anisotropy suggest a (weak) OPA absorption with polarization different from the fluorescence from states lying in the same region of the TPA-active ones.

Apart from the already mentioned CT transitions, SQ0 is expected to exhibit also local $\pi\pi^*$ excitations, on either the donor or the acceptor, with a possible biradical character, and $n\pi^*$ transitions involving the oxygen lone pairs. All of them need to be described in a balanced way for a confident assignment of the above mentioned spectroscopic signatures. Besides this challenge, additional difficulties came to light during our work. In fact, we found that the methods discussed above, TD-DFT, ADC(2) and SAC-CI are not able to give a fair description of the excitation energies of the states responsible for the strong TPA of SQ0. We therefore present an investigation of the electronic states of SQ0 with a large variety of ab initio electronic methods ranging from TD-DFT to affordable methods within the coupled cluster family (namely Coupled Cluster Singles and approximate doubles, CC2 and Equation of Motion Coupled Cluster Singles and Doubles, EOM-CCSD), algebraic diagrammatic construction (ADC(2) and ADC(3)) and multireference methods. In the latter family, we adopted CASSCF, corrected by different variants of multireference perturbation theory (MRPT) to introduce the electron dynamic correlation, namely CASPT2 [35, 36] and Multistate (MS) CASPT2[37] and the N-electron valence perturbation theory (NEVPT2) [38–40]. Additionally, we used an iterative variational-perturbative scheme (CI-MRPT2) [41]. In this way, we singled out relevant double-excitation contributions to the states responsible for two-photon absorption. Finally, in order to get further insight into the characteristics of the OPA and TPA states, we resorted to an alternative and rigorous representation of the CASSCF wavefunctions in terms of symmetry-adapted localized orbitals on the donor and acceptor moieties. This representation allows to write down the relevant wavefunctions in terms of a few electronic configurations with a chemically clear meaning, like zwitterionic states representing D $\rightarrow$ A CT or A $\rightarrow$ D back-donations and local excitations

on the carbonyl and/or phenyl moieties, providing a picture closer to the chemist's view of the squaraine electronic structure in terms of resonance formulas.

Figure 1: Structure of SQ0 dye.

2 Computational Details

Experimental OPA and TPA data are available for SQ0 with n-butyl substituents at the Nitrogen atoms, Bu-SQ0 [34]. However, for computational convenience, most of our calculations were performed on Me-SQ0 (hereafter generally named as SQ0) where n-butyl groups are replaced by methyls, since it is smaller and, more importantly, it belongs to a higher-symmetry point group, D_{2h} . The latter fact facilitates the computations and makes the assignment and interpretation of the spectra clearer. Test calculations discussed in the Supplementary Information (SI) indicate that this substitution has a negligible effect on the excitation energies of the states of interest.

We adopted Müliken convention and placed therefore the molecule on yz plane where z is the long molecular axis.

As mentioned, to characterize the electronic states of the molecule we explored several electronic structure methods: TD-DFT, LR-CC2, EOM-CCSD, ADC(2), ADC(3), CASSCF, (MS)CASPT2, (MS)NEVPT2 and CI-MRPT2. Moreover, we used SAC-CI, since results with this method have already been reported in literature for similar squaraine species [21–23]. Extensive preliminary calculations were carried out with DFT and TD-DFT employing two different functionals, the standard hybrid B3LYP and the long-range corrected CAM-B3LYP, both in gas-phase and in toluene described by linear-response (LR) polarizable continuum model (PCM) [42], and exploiting different basis sets ranging from the compact 6-31G(d), up to larger sets like 6-311+G(d,p) and 6-311++G(2d,2p). As shown in the next section, these calculations indicate that the effect of the extension of the basis on the OPA and TPA transition energies is quite limited. Even if the dependence of the computed energy differences on the basis set is expected to be quite different in DFT and in wave function methods (in particular it is more marked in the last case), for

the more expensive wavefunction-based calculations, we mainly used the 6-31G(d) basis set, although some benchmark calculations with larger bases, including either polarization or diffuse functions were also performed, and are reported in Table S9 in the SI).

CASSCF calculations of Me-SQ0 are challenged by the impossibility to include a full π active space (AS), which would require 22 electrons and 20 orbitals $(22e, 20o) = (6e, 6o)_{SQ} + 2 \times (6e, 6o)_{Ph} + 2 \times (2e, 1o)_N$, where the subscripts *SQ*, *Ph* and *N* represent the central squaraic ring, the phenyl rings and the Nitrogens, respectively. Starting from the full π active space, we reduced it to an affordable $(14e, 14o) = (6e, 6o)_{SQ} + 2 \times (4e, 4o)_{Ph}$, where two nitrogen's non-bonding orbitals are not fully included, each phenyl is described with a $(4e, 4o)$ AS and the SQ central ring with a $(6e, 6o)$. The resulting CASSCF AS molecular orbitals (MOs) are plotted in Figure 2, labelled by symmetry and distinguished by a numeric index. While the N non-bonding orbitals are actually partially taken into account since they mix with Ph orbitals (see for example MOs 5-7 b_{3u} , and $4b_{2g}$), at first glance it may seem surprising that they do not fully participate to the AS, since they are supposed to act as electron donors. However, in the SI, we report test calculations on a smaller SQ0 analogue, obtained replacing the Ph-N(Me)₂ donor groups with smaller CH₃-C(NH₂)=CH-ones, for which a full π^* space plus the two oxygen p_y non-bonding orbitals $(18e, 14o)$ can be treated. Such calculations confirm that N non-bonding orbitals are not significantly involved in the lowest excited states of the system. This conclusion is in line with what already observed in the literature, at least for the $S_0 \rightarrow S_1$ transition[21, 43]. On the other hand, it is clear that it is necessary to include all the π orbitals and electrons of the squaraic central ring both to describe the aromaticity of this fragment and due to the importance of these orbitals in the description of the electronic states of interest. For $1B_{1g}$ and $1B_{3u}$ states, which have a $n\pi^*$ nature, the active space was increased to $(18e, 16o)$ including the $13b_{3g}$ and the $19b_{1u}$ non-bonding Oxygen orbitals.

The CASSCF description is perturbatively corrected with different schemes in order to describe the electron dynamical correlation. We used both standard State-Specific (SS) CASPT2[35, 36] and its multi-state (MS) variant[37] and the n-electron valence state perturbation theory (NEVPT) in its SS [38–40] and Quasi-Degenerate[44] (QD) variants, in all cases to the second order to the energy. CASPT2 and NEVPT2 are multireference perturbation theories, both based on CASSCF zero-order wavefunctions but with a different zero order Hamiltonian $\mathcal{H}_0$ (monelectronic in nature in CASPT2, bielectronic in NEVPT2). More details on these two approaches can be found in literature.

For CASPT2 calculations we applied a modified zeroth-order Hamiltonian, standard IPEA = 0.25, that is an empirical correction that takes its name from an analogy with MP2, in which, thanks to Koopmans' theorem, the energies of the occupied orbitals correspond to the ionization potentials (IP), while the

virtual orbital energies correspond to electron affinities (EA). Imaginary shift was set to 0.1 a.u. to avoid inclusion of intruder states. At the MS-CASPT2 and QD-NEVPT2 level the energy differences are computed using the eigenvalues of the second order corrected effective Hamiltonian. For SS-CASPT2 the transition dipole moments are computed using the perturbatively modified CASSCF wavefunctions.

CI-MRPT2 calculations were performed with the 6-31G(d) basis set. We started from a standard Hartree-Fock set of Molecular Orbitals (MOs) (85 occupied and 195 virtual MOs) obtained by a GAMESS SCF calculation[45] and we froze the occupation of the first 24 MOs corresponding to the 1s orbitals of the non-hydrogen atoms. A reduced active set of MOs is then considered, made by the highest-energy 40 doubly occupied and lowest-energy 150 empty MOs. The initial configurational space included all the possible single excitations from the HOMO–15 to the LUMO+20 and a few double excitations. This initial variational space was then enlarged (usually 3 times), adding the configurations with the largest second order perturbative correction to the energy of the CI states, increasing each time its dimension by a multiple k of the previous space. The final diagrammatic MRPT2 calculation also includes the perturbative contribution of the configurations involving the MOs outside the active 40-150 space. Further details on the method and its implementation in the BALOO code can be found in Ref. [41]. The main difference between CI-MRPT2 and CASSCF/PT2 is that, in the former, a larger AS can be considered, since one begins from a smaller configurational space whose enlargement is guided by PT. This strategy should, in principle, allow to incorporate in the variational space the contribution of the most relevant MOs for the eigenstates considered at an affordable computational cost. On the other hand, some formal properties (like the strict additivity of the energy for non interacting systems), which are satisfied by the CASSCF/PT2 approaches, cannot be guaranteed in CI-MRPT2.

Vibronic spectra, including the effect of all molecular vibrations, have been computed in the harmonic approximation with a pre-screening time-independent method [46–49]. We quadratically expanded both initial and final states around their own equilibrium geometries. CASPT2 optimizations were performed with numerical gradients. Since we cannot obtain CASPT2 Hessians, for both CASPT2 and TD-DFT we adopted the Adiabatic Shift (AS) model, which assumes that the Hessian of the final state S_f is equal to the ground state one (S_0) [50]. For CASPT2, we actually used the computational strategy we proposed in Ref. [51]. Therefore, we approximated the S_0 normal modes with those obtained at CAM-B3LYP level, but computed the displacement vector $\mathbf{K}[\text{PT2}]$, ruling the intensity of the vibronic progressions, considering the initial and final state CASPT2 geometries according to the following expression: $\mathbf{K}[\text{PT2}] = \mathbf{K}_{f0} - \mathbf{K}_{00}$, with $\mathbf{K}_{f0} = \mathbf{K}[S_f(\text{CASPT2}) - S_0(\text{CAM-B3LYP})]$ and $\mathbf{K}_{00} = \mathbf{K}[S_0(\text{CASPT2}) - S_0(\text{CAMB3LYP})]$.

All DFT and TD-DFT calculations were performed with Gaussian 16 b.01 [52], CASSCF and CASPT2 calculations with MOLCAS [53], ADC(2), ADC(3) and EOM-CCSD [54–56] with Qchem [57], CC2 with Psi4 [58]

and CI-MRPT2 with BALOO[41]. NEVPT2 results are obtained with computational codes developed at the University of Ferrara [38–40, 44]. Vibronic spectra were obtained with the freely available code *ℱclasses* code [59] developed at ICCOM-CNR.

Figure 2: Active space orbitals used in the CAS calculations for SQ0 with D_{2h} symmetry, isovalue= ± 0.04 au.

Figure 3: Hartree-Fock MOs used in CC2, EOM-CCSD, ADC, SAC-CI and CI-MRPT2 calculations with D_{2h} symmetry, isovalue= ± 0.04 au.

3 Results

Squaraines optical properties are thought to arise from two different main characteristics: (i) the D-A-D (donor-acceptor-donor) structure which might induce CT transitions between the central and lateral moieties, and (ii) its possible biradicaloid[60] electronic structure[31]. The biradicaloid character of Me-SQ0 has been estimated to be only moderate (16%) in Ref. [25], based on B3LYP calculations. Our calculations of the HOMO-LUMO and the singlet-triplet gap with different methods, reported in the SI, support this conclusion. Further discussion on this aspect is postponed to Section 3.5, where we analyze CASSCF functions in terms of localized orbitals.

3.1 TD-DFT Calculations

We start our discussion from the TD-DFT results obtained with CAM-B3LYP and B3LYP, since, due to their limited computational cost, they allowed us to test in detail the effect of the extension of the basis set, from 6-31G(d) up to 6-311++G(2d,2p), and of the toluene solvent, described within LR-PCM approach. The ground state equilibrium geometry has been re-optimized for each combination of functional and

basis set, both in gas phase and in solution and the Cartesian coordinates are reported in the SI. Table 1 lists all excitation energies for each irreducible representation (irrep) of the D_{2h} point group, up to at least 4 eV. The first strong OPA state (the transition moment is given in Table S3 in the SI) is $1B_{1u}$ which, according to CAM-B3LYP/6-31G(d), is at 2.46 eV in gas phase and 2.26 eV in toluene, while it lies at 2.36 eV in gas-phase and at 2.19 eV in toluene with B3LYP/6-31G(d). Both predictions compare acceptably with the experimental OPA maximum in toluene at 1.95 eV [34], especially if vibronic effects are taken into account (see Section 4), even if some overestimation of the excitation energy is noticed, in agreement with what already reported in Refs. [26–28]. This state is well described as a HOMO→LUMO transition ($6b_{3u} \rightarrow 5b_{2g}$). Table 1 shows that extension of the basis set has a very small effect on its energy. It is noteworthy that a dark B_{1g} state, corresponding to a $n\pi^*$ excitation from the $13b_{3g}$ MO, strongly involving the lone-pairs of the oxygens, to the LUMO orbital is predicted to lie close to the OPA state. However, it is the second excited state in toluene, already with the small 6-31G(d) according to CAM-B3LYP, and with the large 6-311+G(d,p) basis set according to B3LYP. On the balance, extension of the basis set and inclusion of solvent effect leads to a net destabilization of this state with respect to $1B_{1u}$ by ~ 0.5 eV (CAM-B3LYP data).

The experimental TPA shows two peaks at ~ 420 nm (~ 2.95 eV) with a intensity of $\sim 2 \times 10^3$ GM and at ~ 345 nm (~ 3.6 eV) with a intensity of $\sim 2 \times 10^4$, together with a weaker, but yet significant ($\sim 10^2$ GM), broad band peaked at ~ 590 nm (~ 2.10 eV). Due to the low energy, the latter peak may only arise from either $1B_{1u}$ or $1B_{1g}$. However, the first is forbidden by symmetry and the second is predicted to be extremely weak according to non-resonant quadratic response theory calculations with Dalton code [61, 62] (see Table 2). Further discussion on this point is given in Section 4. It is expected that strong TPA signals should involve *gerade* states, so that possible candidates are the $2A_g$, $3A_g$, $1B_{3g}$, and $1B_{2g}$ states. $1B_{2g}$ is predicted to be well above 4 eV with both B3LYP and CAM-B3LYP, independently of the basis set and the inclusion of the solvent effect, while $1B_{3g}$ is above 4 eV for CAM-B3LYP and 3.85 eV for B3LYP. Moreover, at CAM-B3LYP level of theory, their intensity is predicted to be very weak (Table 2), and therefore incompatible with the experimental data. Also $2A_g$ and $3A_g$ are predicted to be well above 4 eV for CAM-B3LYP, whereas the former can be as low as 3.37 eV for B3LYP (in toluene with the 6-311+G(d,p)) but, in any case, $3A_g$ is never lower than 4.42 eV. A computation of the TPA intensity at CAM-B3LYP/6-31G(d) level of theory in gas phase predicts a peak of 2.1×10^3 for $2A_g$, and 8.6×10^6 for $3A_g$ but the latter is not reliable due to the quasi-resonance of the exciting photon with the real transition $1A_g \rightarrow 1B_{1u}$, which challenges the use of non-resonant quadratic response theory [18]. The fact that both states are strongly TPA active is in line with the large excited states transition dipoles (see Table S3 in SI).

with the intermediate quasi-resonant $1B_{1u}$.

Further analysis of the results indicates that $3A_g$ is more sensitive than $2A_g$ to the extension of the basis set, but the redshift is in any case moderate (~ 0.1 eV). Despite the low polarity of the solvent, LR-PCM predicts significant shifts for $2A_g$ (0.17 eV), as a consequence of the high polarizability of the electron density of SQ0. Finally, independently of the basis set and the solvent effect, the pair of states $1B_{2u}$ and $1B_{3g}$ is predicted to be always almost degenerate. However, it is at ~ 4.4 eV for CAM-B3LYP and at ~ 3.85 eV for B3LYP.

On the balance, both B3LYP and CAM-B3LYP provide a good description of the OPA strong state, while none of them can give a reasonable prediction of the energy of the TPA active states. For these states, B3LYP seems to perform less poorly than CAM-B3LYP but this may be due to cancellation of errors. Qualitative arguments based on resonance formulas suggest in fact that different states experience significant separation of charges. It is expected that these states may be not well described by B3LYP. An analysis of the charge separation of the OPA state based on the indices proposed in Ref. [63] on different squaraines including SQ0 was reported in Ref. [26], concluding that the CT character was only moderate. In the SI we extended this analysis to a larger number of states of SQ0. The amount of charge separation and the distance of the charge centroids for all considered states are in general moderate but they are quite different for different states. On the balance, we believe that these results do not allow to consider B3LYP results surely reliable and, in view of the clear error on $3A_g$, at least, in the following section we decided to explore the performance of different post-HF methods. When needed for comparison, we will focus on CAM-B3LYP results that should be free from an unbalanced treatment of CT contributions.

Before concluding this section, we mention further checks reported in the SI. As we recalled above, for computational convenience we substituted the long n-butyl substituents with methyls ones. Table S1 in the SI shows that this has very little effect on the electronic states (within 0.05 eV). The dependence of the transition energies reported in Table 1 on the functional and the basis set can be both direct, due to different stabilizations of the different states, and indirect, due to different ground state equilibrium geometries. In Table S2 in the SI, we checked the effect of the different geometries by repeating some of the calculations reported in Table 1 in the main text, using always the geometry optimized in gas phase at CAM-B3LYP/6-31G(d) level of theory. Results in the SI show that for CAM-B3LYP calculations both in gas-phase and in toluene this choice of geometry has very little effect on the vertical excitation energies (within 0.03 eV) and the effect is very moderate. Even in the worst case, i.e. changing both the functional, the treatment of the environment (from gas-phase to toluene) and using the 6-311+G(d,p) basis set the energy difference remains within 0.07 eV. Having shown that the effect of the geometry is small, for the

wavefunction methods discussed in the following sections, we always report transition energies at the equilibrium geometry obtained at CAM-B3LYP/6-31G(d) level in gas-phase.

Table 1: SQ0 excitation energies (eV) at TD-DFT level with CAM-B3LYP or B3LYP functionals. Calculations with different basis sets both in gas phase and in toluene (LR-PCM).

	CAM-B3LYP					B3LYP				Exp
State	GAS			toluene		GAS		toluene		
	6-31G(d)	diff ^a	diff2 ^b	6-31G(d)	diff ^a	6-31G(d)	diff ^a	6-31G(d)	diff ^a	
2A _g	4.16	4.14	4.15	4.00	3.97	3.50	3.48	3.40	3.37	2.95
3A _g	5.12	5.02	5.02	5.06	4.96	4.58	4.50	4.50	4.42	3.60
1B _{1u}	2.46	2.49	2.50	2.26	2.29	2.36	2.39	2.19	2.20	1.95
2B _{1u}	4.08	4.12	4.13	4.08	4.16	3.46	3.51	3.48	3.54	3.30
1B _{2u}	4.42	4.37	4.38	4.41	4.36	3.86	3.84	3.84	3.84	
1B _{3u}	3.47	3.59	3.60	3.65	3.80	2.94	3.05	3.13	3.26	
1B _{1g}	2.44	2.56	2.57	2.61	2.77	1.95	2.06	2.13	2.27	
2B _{1g}	6.62	5.62	5.30	6.58	5.74	5.61	4.91	5.83	5.14	
1B _{2g}	4.84	4.87	4.73	4.84	4.86	4.48	4.29	4.53	4.54	
1B _{3g}	4.42	4.37	4.38	4.41	4.36	3.85	3.84	3.84	3.83	
1A _u	5.41	5.44	5.33	5.48	5.53	4.58	4.60	4.75	4.79	

^a dif stands for 6-311+G(d,p). ^b dif2 stands for 6-311++G(2d,2p)

Table 2: TPA intensity^a (GM) for the lowest states of *gerade* symmetry computed at CAM-B3LYP and ADC(2) levels of theory in gas phase from quadratic response theory with the 6-31G(d) basis set.

State	ADC(2)	CAM-B3LYP
2A _g	1.1×10^5	2.1×10^3
3A _g	2.2×10^4	8.4×10^6
1B _{1g}	6.8×10^{-3}	1.1×10^{-3}
1B _{2g}	1.3	31
1B _{3g}	170	37

^a computed from the rotationally averaged TPA transition strength obtained for a single beam of linearly polarized light, with frequency equal to one half the excitation frequency of the excited state, assuming a Gaussian broadening with HWHM=0.1 eV. For further details see ref. [64]

3.2 Coupled Cluster, SAC-CI and ADC Calculations

In Table 3, we report the vertical excitation energies computed at the LR-CC2, EOM-CCSD, SAC-CI, ADC(2) and ADC(3) levels of theory. We focused on states that may be relevant for our discussion, skipping for computational convenience A_u symmetry and some higher energy-states of some other irreps. All calculations were performed with the 6-31G(d) basis set. At EOM-CCSD and ADC levels we used the frozen-core default option of Qchem [65], while for SAC-CI, both L2 and L3 options for double-excitations were used [52]. In the SI, we report some tests for LR-CC2, EOM-CCSD and ADC(2) with different basis sets. These data confirm that, as already for TD-DFT results, 6-31G(d) basis set provides fairly good results for SQ0. In particular for EOM-CCSD we also used a basis with a set of diffuse

functions (6-31+G(d)) finding that the largest change in the excitation energy is ~ 0.13 eV for $1B_{1g}$ state (Table S9 in the SI). Due to the large memory requirements, ADC(3) calculations were first performed with a slightly smaller basis set, 6-31G, and then refined only for few states with 6-31G(d). At ADC(2) level, the difference between 6-31G and 6-31G(d) results was found to be rather modest (see Table S8 in the SI).

As far as the bright $1B_{1u}$ state is concerned, all methods provide a good description with an accuracy comparable or better than TD-DFT ones. As already noticed by Jacquemin et al.[27, 28], ADC(2) is in excellent agreement with experiment, even considering the 0-0 vibronic transition. Interestingly, ADC(3) predicts a sensible blue-shift with respect to ADC(2). On the same foot, the L3 results are blueshifted with respect to the L2 ones for SAC-CI. The pair of states $1B_{2u}$ and $1B_{3g}$ are confirmed to be practically degenerate and significantly above 4. eV. The CC2 vertical transition energies are generally smaller than the EOM-CCSD ones, a rather typical trend. The $1B_{1g}$ and $1B_{3u}$ states are seen to be very sensitive to the level of theory. For CC2 and ADC(2), $1B_{1g}$ is the lowest excited state, but considering what happens for CAM-B3LYP predictions, it is plausible that the order would be reversed in toluene and with larger basis sets. Notwithstanding this, the differences between CC2 and EOM-CCSD results for these two states are rather remarkable. The same behaviour is observed comparing ADC(2) and ADC(3) results.

As far as the A_g states are concerned, CC2 and ADC (both second and third order) predict a remarkable stabilization of $2A_g$ with respect to what computed at CAM-B3LYP level, assigning it a value comparable to the B3LYP one. On the contrary, EOM-CCSD and SAC-CI(L3) place it at ~ 4 eV. For all methods except ADC(3), the $3A_g$ state is predicted to be very high in energy, close to ~ 5 eV, a value incompatible with the experimental TPA peaks. Actually, with the 6-31G(d) basis set, ADC(3) places $2A_g$ and $3A_g$ at 3.31 and 4.05 eV, respectively, indicating that they are the most likely candidates for the two experimental TPA peaks at ~ 2.95 and ~ 3.6 eV. Furthermore, considering that TD-DFT analysis suggests that for both states inclusion of solvent effects and extension of the basis set may lead to a red-shift of ~ 0.2 eV, the expected agreement of ADC(3) with experiments becomes remarkably good. The reason why ADC(3) yields such a lower energy for $3A_g$ is connected to the fact that it predicts a strong double-excitation HOMO $\rightarrow$ LUMO character (see Section 3.4), that is not accurately described by all other methods analyzed so far. In fact, although EOM-CCSD includes some double excitation character, it has been very recently shown that accurate transition energies for pure doubly-excited states with CC methods require the inclusion of triple and even quadruple excitations [66]. In this respect it is interesting to notice that inclusion of triples corrections with CCSDR(3) (calculations performed with Dalton [61, 62] and the 6-31G(d) basis set) improves but only moderately the excitation energies of $2A_g$

and $3A_g$, which are predicted to be respectively 3.74 and 4.81 eV.

Among the methods discussed in this section, we were able to compute TPA intensities only for ADC(2) with Qchem code. To the best of our knowledge, the Qchem results for the ADC(2) TPA cross section we report here were obtained based on the block-Lanczos ADC/ISR (Intermediate State Representation) methodology of Ref.[67]. The data reported in Table 2 complement those obtained at CAM-B3LYP level and support the assignment of the TPA experimental peaks to $2A_g$ and $3A_g$ states. In fact they are the only two states for which remarkable TPA intensities are predicted. In a sum-over-state expression for TPA, the transition dipole moments from the ground state to the B_{1u} states and from them to the $2A_g$ and $3A_g$ states are expected to play an important role in determining the TPA intensity from $1A_g$ to $2A_g$ and $3A_g$. CC2 and EOM-CCSD predict large values for these transitions dipoles (Table S3 in SI), exactly as CM-B3LYP, ADC(2), and multireference methods (see below). This finding is in line with the prediction that the $1A_g \rightarrow 2A_g$ and $1A_g \rightarrow 3A_g$ TPA are strong.

Table 3: SQ0 excitation energies (eV) with CC2, EOM-CCSD, SAC-CI, ADC(2) and ADC(3). All calculations with 6-31G(d) basis set except for ADC(3) where we used the 6-31G [G] one and refined only the energy of few states with 6-31G(d) [G(d)].

State	CC2	EOM-CCSD	SAC-CI ^a		ADC(2)	ADC(3)		Exp
			L2	L3		G	G(d)	
$2A_g$	3.55	4.08	3.48	3.91	3.32	3.20	3.31	2.95
$3A_g$	4.98	5.26	4.74	5.11	4.89	3.98	4.05	3.60
$1B_{1u}$	2.23	2.49	1.87	2.17	1.97	2.32		1.95
$2B_{1u}$	3.60	4.11	3.58	3.96	3.38	3.86		3.30
$1B_{2u}$	4.21	4.42	4.15	4.39	4.11	4.12		
$1B_{3u}$	2.98	3.71	3.31	3.73	2.73	3.97		
$1B_{1g}$	1.91	2.61	2.17	2.59	1.68	2.97	2.96	
$1B_{3g}$	4.21	4.42	4.13	4.37	4.11	4.13		

^a L2 and L3 stand for Level Two and Level Three options concerning double-excitation operators. L3 is the most accurate, L2 is intermediate.

3.3 Multireference Calculations

Multireference CI allows in principle to deal with all the challenges evidenced by SQ0, namely the partial biradical character and the relevant role of double-excitations in some of the excited states. CASSCF calculations (Table 4) were performed with a State Average (SA) approach, considering respectively 6, 4, 4, 4, 3 and 3 roots for A_g , B_{1u} , B_{2u} , B_{3g} , B_{3u} and B_{1g} irreps. After preliminary calculations, for A_g we considered a larger number of roots, i.e. 6, since these are the states that were found more relevant for TPA. However, we checked that averaging 4, 7 or 8 roots results were similar. The excitation energy for the OPA state $1B_{1u}$ is predicted to be to 2.95 eV, while $2A_g$ and $3A_g$ are respectively at 3.98 and 5.31 eV. At CASPT2 level, these energies decrease to 2.62, 3.51 and 4.22 eV with a SS approach, and at 2.28, 3.65 and 4.70 eV with the MS approach. At CASSCF level, the pair of states $1B_{2u}$ and $1B_{3g}$ is confirmed

to be almost degenerate at ~ 4.45 eV, whereas they exhibit a small gap according to CASPT2 and MS-CASPT2. SS-NEVPT2 and QD-NEVPT2 results follow the same trend observed for SS-CASPT2 and MS-CASPT2. Considering partially contracted (PC) data, $1B_{1u}$ is at 2.58 (SS) and 2.32 eV (QD), $2A_g$ at 3.53 (SS) and 3.63 eV (QD) and $3A_g$ at 3.95 (SS) and 4.40 eV (QD). The pair of quasi degenerate states $1B_{2u}$ and $1B_{3g}$ are at ~ 4.58 eV and ~ 4.83 eV, respectively for SS and QD calculations, confirming that $1B_{3g}$ cannot be relevant for the experimental TPA peaks.

The $2A_g$ state is well described by the MRPT2 approach: this is witnessed by the small variation on the energy differences when passing from CASSCF to CASPT2 and NEVPT2 (which indicates that the two zeroth order wavefunctions are described at a similar level of quality), and by the similarity of CASPT2 and NEVPT2 results and, within the latter, of Strongly contracted (SC) and partially contracted (PC) calculations. On the contrary, $3A_g$ is drastically stabilized by the PT2 correction. In similar cases, it is possible that the PT2 correction is too high, which makes the different roots too interacting in a MS-CASPT2 or QD-NEVPT2 scheme, possibly leading to an incorrect estimation of the splitting among $1A_g$, $2A_g$ and $3A_g$. Therefore, we will in the following mainly discuss SS data for the A_g states. Considering for example SS-NEVPT2 data, the energies for $2A_g$ and $3A_g$ are quite close to what predicted by ADC(3) and confirm that these states are the most reasonable candidates for the two experimental TPA peaks at ~ 2.95 and ~ 3.6 eV. The computational error would in fact be 0.5-0.6 eV, without considering vibronic and solvent effects. As for CC2 and EOM-CCSD, the transition dipole moments in Table S3 in the SI indicate that, also according to the CASPT2 and CI-MRPT2 methods, both $2A_g$ and $3A_g$ states should have a strong zz contribution to the two-photon transition tensor.

For a proper description on the $n\pi^*$ transitions, $1B_{1g}$ and $1B_{3u}$, we had to enlarge the AS up to (18o,16e). MS-CASPT2 predicts that $1B_{1g}$ is the second lowest excited state and that $1B_{3u}$ lies close to the $2A_g$ state. In the SI we show that the enlargement of the AS to (18o,18e) and the adoption of the CASPT2 GS geometry in place of the CAM-B3LYP one introduce only minimal changes in the excitation energies of the $\pi\pi^*$ states reported in Table 4.

CI-MRPT2 data in Table 4 confirm the picture arising from CASPT2 and NEVPT2 calculations. As described in the Computational Details section, we enlarged the variational space in three steps, reaching a maximum dimension of 181361 Configuration State Functions (CSFs). In the SI, we report a study of the convergence of the results with the dimensions of the space, while in Table 4 we only give the data obtained with the largest space. CI-MRPT2 places $1B_{1u}$ at 2.10 eV, while $2A_g$ and $3A_g$ are at 3.28 and 3.58 eV, in very nice agreement with experimental data. Moreover, the pair of quasi-degenerate states $1B_{2u}$ and $1B_{3g}$ are confirmed to be above 4 eV. It is interesting to highlight that, despite the large

variational space, the final diagrammatic PT2 correction on the energy differences is quite remarkable for these states, and bigger than for SA-CASSCF. Large PT2 corrections on the energy differences in general indicate that the zeroth order wave functions are not described at the same level of quality and in such a case one cannot be sure that the PT2 is able to entirely recover this differential effect. Moreover, the differences between CI-MRPT2 and SA-CASSCF can also find a partial explanation in the fact that the former method uses HF orbitals that are not optimal for the description of the excited states.

CI-MRPT2 places the dark state $1B_{1g}$ and $1B_{3u}$ very low in energy, at variance with what predicted by CASPT2 and MS-CASPT2. The latter however show that computations for these states are challenging since they are very sensitive to the AS (for MS-CASPT2 $1B_{1g}$ and $1B_{3u}$ are at 1.84 eV and 2.87 eV with a (16o,15e) AS). Preliminary CI-MRPT2 calculations suggest that extension of the basis set induces a relative destabilization of $1B_{1g}$ with respect to $1B_{1u}$ by ~ 0.4 eV and TD-DFT calculations show that a further destabilization occurs in toluene. The experimental observed fluorescence which is strong and mirror-symmetric with respect to the absorption of $1B_{1u}$ together with the high fluorescence quantum yield seems to indicate that $1B_{1g}$ is not the lowest excited state in toluene[34].

Table 4: SQ0 excitation energies (eV) with different CASSCF-MRPT2 methods, with CI-MRPT2 and with SAC-CI.

State	CASSCF	CASPT2	MS-CASPT2	NEVPT2 ^a		QD-NEVPT2 ^a		CI-MRPT2		Exp
				SC	PC	SC	PC	CI	+MRPT2	
$2A_g$	3.98	3.51	3.65	3.58	3.53	3.65	3.62	5.49	3.28	2.95
$3A_g$	5.31	4.22	4.70	4.12	3.95	4.46	4.40	7.19	3.58	3.60
$1B_{1u}$	2.95	2.62	2.28	2.62	2.58	2.45	2.32	3.63	2.09	1.95
$2B_{1u}$	4.14	3.64	4.17	3.56	3.48	3.95	4.02	6.05	3.29	3.30
$1B_{2u}$	4.43	4.23	4.28	4.48	4.44	4.49	4.45	6.59	4.19	
$1B_{3u}$	3.09	3.25	3.54					5.69	2.45	
$1B_{1g}$	2.36	2.14	2.43					4.38	1.49	
$1B_{3g}$	4.48	4.38	4.35	4.62	4.58	4.53	4.48	6.59	4.18	

^a SC and PC stand for strongly contracted and partially contracted. For $1B_{1g}$ and $1B_{3u}$ a (18e,16o) AS was employed, see SI.

3.4 Assignment of the Relevant States

Assignments of the states in terms of dominant electronic configurations are reported in Tables 5 and 6. The relevant MOs are sketched in Figures 2 (CASSCF/MS-CASPT2) and 3 (SAC-CI, CC2, ADC and CI-MRPT2). DFT Kohn-Sham MOs are reported in the SI. In most of the cases, CASSCF, HF and DFT orbitals are very similar. Therefore, to facilitate the comparison, we decided to label HF and DFT MOs, not only with the usual nomenclature HOMO−x and LUMO+y in order of increasing energy, but also with the labels given to the CASSCF MOs they resemble most. SS-CASPT2 and SS-NEVPT2 assignments coincide with CASSCF ones, while QD-NEVPT2 assignments are similar to MS-CASPT2 and are not

given for sake of brevity. In the SI we show that for EOM-CCSD a more refined assignment in terms of natural transition orbitals provides a very similar picture. The strong OPA state $1B_{1u}$ is always a HOMO→LUMO transition and is polarized along the long molecular axis. The weak $2B_{1u}$, with the same polarization is essentially a $5b_{3u} \rightarrow 5b_{2g}$ transition for CASSCF, while for all other methods it is mainly a $5'b_{3u} \rightarrow 5b_{2g}$ (HOMO−2→LUMO in terms of HF MOs). The weak-OPA $1B_{2u}$ state, polarized along the short molecular axis, is a $2a_u \rightarrow 5b_{2g}$ (HOMO−4→LUMO) transition. Finally, the weak-OPA $1B_{3u}$ is a $n\pi^*$, polarized along the direction orthogonal to the molecular plane, with strong component from $19b_{1u} \rightarrow 5b_{2g}$, where $19b_{1u}$ has large contribution from Oxygen lone pairs. The latter also contribute to the low-energy $1B_{1g}$, a second $n\pi^*$ to the LUMO, involving in this case a σ orbital with symmetry $13b_{3g}$. Finally, the state $1B_{3g}$, almost degenerate with $1B_{2u}$, has always a significant contribution from $6b_{3u} \rightarrow 7b_{3u}$ transition.

Concerning the $2A_g$ and $3A_g$ states, they are made up essentially from the $6b_{3u} \rightarrow 7b_{3u}$ (HOMO→LUMO+1) and $4b_{2g} \rightarrow 5b_{2g}$ (HOMO−1→LUMO) single-excitations, which however, according to CASPT2, ADC(3) and CI-MRPT2 are strongly mixed with the, $6b_{3u}^2 \rightarrow 5b_{2g}^2$ (HOMO² → LUMO²) double excitation. Such double-excitation character is missing in CAM-B3LYP, ADC(2) and CC2, and seems to be inaccurately treated by EOM-CCSD and SAC-CI level. This may explain the strong overestimation of the energy of one or both these states by the above methods.

Table 5: Description of states in terms of dominant electronic configurations/amplitudes (only the part differing from the GS or reference state is reported) is given for CAM-B3LYP, CC2, EOM-CCSD, ADC(2) and ADC(3). For all methods, assignments refer to HF MOs depicted in Figure 3 except for CAM-B3LYP for which we considered the Kohn-Sham MOs reported in the SI. To facilitate the comparison, MOs are labeled in analogy to what done for CASSCF MOs.

State	CAM-B3LYP	CC2	EOM-CCSD	ADC(2)	ADC(3)
2A _g	[4b _{2g}] ¹ [5b _{2g}] ¹ (97%)	[4b _{2g}] ¹ [5b _{2g}] ¹ (76%)	[4b _{2g}] ¹ [5b _{2g}] ¹ (83%)	[4b _{2g}] ¹ [5b _{2g}] ¹ (93%)	[6b _{3u}] ¹ [7b _{3u}] ¹ (15%) [6b _{3u}] ⁰ [5b _{2g}] ² (27%)
3A _g	[6b _{3u}] ¹ [7b _{3u}] ¹ (94%)	[6b _{3u}] ¹ [7b _{3u}] ¹ (77%)	[6b _{3u}] ¹ [7b _{3u}] ¹ (79%)	[6b _{3u}] ¹ [7b _{3u}] ¹ (90%)	[4b _{2g}] ¹ [5b _{2g}] ¹ (70%) [6b _{3u}] ¹ [7b _{3u}] ¹ (1%)
1B _{1u}	[6b _{3u}] ¹ [5b _{2g}] ¹ (97%)	[6b _{3u}] ¹ [5b _{2g}] ¹ (81%)	[6b _{3u}] ¹ [5b _{2g}] ¹ (81%)	[6b _{3u}] ¹ [5b _{2g}] ¹ (93%)	[6b _{3u}] ¹ [5b _{2g}] ¹ (81%)
2B _{1u}	[5'b _{3u}] ¹ [5b _{2g}] ¹ (93%)	[5'b _{3u}] ¹ [5b _{2g}] ¹ (78%)	[5'b _{3u}] ¹ [5b _{2g}] ¹ (80%)	[5'b _{3u}] ¹ [5b _{2g}] ¹ (93%)	[5'b _{3u}] ¹ [5b _{2g}] ¹ (78%)
1B _{2u}	[2a _u] ¹ [5b _{2g}] ¹ (69%) [6b _{3u}] ¹ [4b _{1g}] ¹ (23%)	[2a _u] ¹ [5b _{2g}] ¹ (61%) [6b _{3u}] ¹ [4b _{1g}] ¹ (19%)	[2a _u] ¹ [5b _{2g}] ¹ (49%) [6b _{3u}] ¹ [4b _{1g}] ¹ (25%)	[2a _u] ¹ [5b _{2g}] ¹ (70%) [6b _{3u}] ¹ [4b _{1g}] ¹ (22%)	[2a _u] ¹ [5b _{2g}] ¹ (34%) [6b _{3u}] ¹ [4b _{1g}] ¹ (29%)
1B _{3u}	[19b _{1u}] ¹ [5b _{2g}] ¹ (94%)	[19b _{1u}] ¹ [5b _{2g}] ¹ (82%)	[19b _{1u}] ¹ [5b _{2g}] ¹ (85%)	[19b _{1u}] ¹ [5b _{2g}] ¹ (81%)	[19b _{1u}] ¹ [5b _{2g}] ¹ (79%)
1B _{1g}	[1b _{3g}] ¹ [5b _{2g}] ¹ (95%) [3b _{1g}] ¹ [5b _{2g}] ¹ (70%)	[1b _{3g}] ¹ [5b _{2g}] ¹ (83%) [3b _{1g}] ¹ [5b _{2g}] ¹ (62%)	[1b _{3g}] ¹ [5b _{2g}] ¹ (86%) [3b _{1g}] ¹ [5b _{2g}] ¹ (51%)	[1b _{3g}] ¹ [5b _{2g}] ¹ (81%) [3b _{1g}] ¹ [5b _{2g}] ¹ (71%)	[3b _{1g}] ¹ [5b _{2g}] ¹ (35%) [6b _{3u}] ¹ [3a _u] ¹ (30%)
1B _{3g}	[6b _{3u}] ¹ [3a _u] ¹ (21%)	[6b _{3u}] ¹ [3a _u] ¹ (18%)	[6b _{3u}] ¹ [3a _u] ¹ (25%)	[6b _{3u}] ¹ [3a _u] ¹ (21%)	

^a Labeled according to the energy ordering.

Table 6: Description of states at CASSCF, MS-CASPT2, MRCI, and SAC-CI level of theory in terms of dominant electronic configurations (only the part differing from the GS or reference state is reported) with respect to the MOs depicted in Figure 2 (CASSCF/MS-CASPT2) or Figure 3 (CI-MRPT2 and SAC-CI). For all MOs labels analogous to those introduced from CASSCF MOs are used for easier comparison.

State	CASSCF		MS-CASPT2		CI-MRPT2		SAC-CI
1A _g	Ref. Conf. (76%) [6b _{3u}] ⁰ [5b _{2g}] ² (5%)		Ref. Conf. (82%) [6b _{3u}] ⁰ [5b _{2g}] ² (<1%)		Ref. Conf. (81%) [6b _{3u}] ⁰ [5b _{2g}] ² (1%)	–	
	[6b _{3u}] ⁰ [5b _{2g}] ² (28%)		[6b _{3u}] ⁰ [5b _{2g}] ² (43%)			[4b _{2g}] ¹ [5b _{2g}] ¹ (83%)	
	[6b _{3u}] ¹ [7b _{3u}] ¹ (18%)		[6b _{3u}] ¹ [7b _{3u}] ¹ (10%)			[6b _{3u}] ¹ [7b _{3u}] ¹ (3%)	
	[4b _{2g}] ¹ [5b _{2g}] ¹ (13%)		[4b _{2g}] ¹ [5b _{2g}] ¹ (10%)		[4b _{2g}] ¹ [5b _{2g}] ¹ (71%) [6b _{3u}] ⁰ [5b _{2g}] ² (9%)	[6b _{3u}] ⁰ [5b _{2g}] ² (2%)	
2A _g	[5b _{3u}] ¹ [6b _{3u}] ¹ [5b _{2g}] ² (8%)		[5b _{3u}] ¹ [6b _{3u}] ¹ [5b _{2g}] ² (6%)				
	[4b _{2g}] ¹ [5b _{2g}] ¹ (44%)		[4b _{2g}] ¹ [5b _{2g}] ¹ (49%)			[6b _{3u}] ¹ [7b _{3u}] ¹ (76%)	
	[6b _{3u}] ⁰ [5b _{2g}] ² (15%)		[6b _{3u}] ⁰ [5b _{2g}] ² (13%)		[6b _{3u}] ⁰ [5b _{2g}] ² (61%) [4b _{2g}] ¹ [5b _{2g}] ¹ (8%)	[6b _{3u}] ⁰ [5b _{2g}] ² (7%)	
	[5b _{3u}] ¹ [6b _{3u}] ¹ [5b _{2g}] ² (5%) Ref. Conf. (5%)		[5b _{3u}] ¹ [6b _{3u}] ¹ [5b _{2g}] ² (7%)		[6b _{3u}] ¹ [7b _{3u}] ¹ (7%)	[4b _{2g}] ¹ [5b _{2g}] ¹ (2%)	
1B _{1u}	[6b _{3u}] ¹ [5b _{2g}] ¹ (67%)		[6b _{3u}] ¹ [5b _{2g}] ¹ (69%)		[6b _{3u}] ¹ [5b _{2g}] ¹ (81%)	[6b _{3u}] ¹ [5b _{2g}] ¹ (90%)	
2B _{1u}	[5b _{3u}] ¹ [5b _{2g}] ¹ (47%)		[5b _{3u}] ¹ [5b _{2g}] ¹ (55%)				
	[6b _{3u}] ¹ [4b _{2g}] ¹ [5b _{2g}] ² (13%)		[6b _{3u}] ¹ [4b _{2g}] ¹ [5b _{2g}] ² (7%)		[5'b _{3u}] ¹ [5b _{2g}] ¹ (76%)	[5'b _{3u}] ¹ [5b _{2g}] ¹ (83%)	
	[6b _{3u}] ¹ [5b _{2g}] ¹ (7%)		[6b _{3u}] ¹ [5b _{2g}] ¹ (4%)				
	[2a _u] ¹ [5b _{2g}] ¹ (31%)		[2a _u] ¹ [5b _{2g}] ¹ (55%) [6b _{3u}] ¹ [5b _{1g}] ¹ (5%)				
1B _{2u}	[6b _{3u}] ¹ [5b _{1g}] ¹ (19%)		[6b _{3u}] ¹ [3b _{1g}] ¹ [5b _{2g}] ² (10%)				
	[6b _{3u}] ¹ [3b _{1g}] ¹ [5b _{2g}] ² (11%)		[6b _{3u}] ⁰ [5b _{2g}] ¹ [3a _u] ¹ (1%)		[2a _u] ¹ [5b _{2g}] ¹ (80%)	[2a _u] ¹ [5b _{2g}] ¹ (64%)	
	[6b _{3u}] ⁰ [5b _{2g}] ¹ [3a _u] ¹ (7%)					[6b _{3u}] ¹ [5b _{1g}] ¹ (19%)	
1B _{3u}	[19b _{1u}] ¹ [5b _{2g}] ¹ (57%)		[19b _{1u}] ¹ [5b _{2g}] ¹ (57%)		[19b _{1u}] ¹ [5b _{2g}] ¹ (78%)		
1B _{1g}	[13b _{3g}] ¹ [6b _{3u}] ¹ [5b _{2g}] ¹ [4b _{1g}] ¹ (14%)		[13b _{3g}] ¹ [6b _{3u}] ¹ [5b _{2g}] ¹ [4b _{1g}] ¹ (14%)				
	[13b _{3g}] ¹ [5b _{2g}] ¹ (65%)		[13b _{3g}] ¹ [5b _{2g}] ¹ (65%)				
	[19b _{1u}] ¹ [6b _{3u}] ¹ [5b _{2g}] ¹ [4b _{1g}] ¹ (8%)		[19b _{1u}] ¹ [6b _{3u}] ¹ [5b _{2g}] ¹ [4b _{1g}] ¹ (8%)		[13b _{3g}] ¹ [5b _{2g}] ¹ (79%)		
	[3b _{1g}] ¹ [5b _{2g}] ¹ (28%)						
1B _{3g}	[6b _{3u}] ¹ [3a _u] ¹ (19%)		[6b _{3u}] ¹ [3a _u] ¹ (53%) [6b _{3u}] ¹ [3a _u] ¹ (3%)				
	[6b _{3u}] ¹ [2a _u] ¹ [5b _{2g}] ² (10%)		[6b _{3u}] ¹ [2a _u] ¹ [5b _{2g}] ² (12%)		[3b _{1g}] ¹ [5b _{2g}] ¹ (80%)	[3b _{1g}] ¹ [5b _{2g}] ¹ (64%)	
	[6b _{3u}] ⁰ [5b _{1g}] ¹ [5b _{2g}] ¹ (5%)		[6b _{3u}] ⁰ [5b _{1g}] ¹ [5b _{2g}] ¹ (<1%)			[6b _{3u}] ¹ [3a _u] ¹ (19%)	

^a Labeled according to the energy ordering.

More in detail, according to CASSCF/MS-CASPT2, $2A_g$ and $3A_g$ share the double-excitation component, which is larger for $2A_g$ than for $3A_g$. In $2A_g$ it is mixed with both $6b_{3u} \rightarrow 7b_{3u}$ and $4b_{2g} \rightarrow 5b_{2g}$, while it mixes essentially with $4b_{2g} \rightarrow 5b_{2g}$ in $3A_g$. The double-excitation mainly enters in $2A_g$ also according to ADC(3), while $4b_{2g} \rightarrow 5b_{2g}$ excitation is dominant in $3A_g$. CI-MRPT2, on the contrary, apparently exchanges the characters of the two states. In fact, $2A_g$ is dominated by the single-excitation $4b_{2g} \rightarrow 5b_{2g}$ (71%) with a 9% contribution of the double-excitation $6b_{3u}^2 \rightarrow 5b_{2g}^2$. The latter, on the contrary, dominates $3A_g$ (61%), where it mixes with small contributions of both $4b_{2g} \rightarrow 5b_{2g}$ (8%) and $6b_{3u} \rightarrow 7b_{3u}$ (7%).

It is worth noticing that this analysis strongly resembles what has been observed for linear polyenes [68] and also carotenals [69] where the first excited state of the same symmetry as the GS is a combination of the double excitation $\text{HOMO}^2 \rightarrow \text{LUMO}^2$ and of the two single excitations $\text{HOMO}-1 \rightarrow \text{LUMO}$ and $\text{HOMO} \rightarrow \text{LUMO}+1$. Moreover, in these systems when the chain is increased this state becomes lower in energy than the bright $\text{HOMO} \rightarrow \text{LUMO}$ state.

3.5 An Analysis of the CASSCF Wavefunctions in Terms of Localized Orbitals

In order to get further insight into the nature of the excited states more involved in the OPA and TPA processes, we analyzed the CASSCF wave functions used in the CASPT2 and NEVPT2 calculations in terms of localized orbitals. This approach is based on the invariance of the CAS-CI wave function upon a unitary transformation within one of the three orbital spaces (doubly occupied, active, empty). A detailed description on how localized orbitals were built is given in the SI. In summary, we localized the active orbitals on the three fragments of the squaraine molecule, namely, the central “square” ($\text{C}_2(\text{CO})_2$) and the two aromatic rings, imposing that the new orbitals respect the molecular symmetry. The transformed (localized) orbitals reported in Figure 4 are those which resemble as much as possible the ground state CASSCF orbitals obtained from a calculation on the three separate fragments. They are localized but they are orthogonal, thus they show orthogonalization tails on the neighbor fragments. The numbering of the orbitals considered in this section is not related to the energy ordering and has no connection with that used in the previous sections. Wave functions fully equivalent (energy and any other property) to those obtained in the preceding standard calculation can be obtained diagonalizing the electronic Hamiltonian on the CAS-CI space built with these new orbitals. The benefit of the localization procedure is that the Slater determinants on which the wave function is expanded have a clear (intuitive and chemically meaningful) interpretation when the orbitals are localized. From a general point of view, such a procedure is called Orthogonal Valence Bond (OVB) reading of the CASSCF wavefunction [70] and has been used

recently to explain and unravel the nature of complex wave functions [71–75]. The OVB name places this strategy in the frame of the orthogonal variant of the VB approach on the H_2 molecule [76, 77].

Figure 4: CASSCF localized orbitals, isovalue= ± 0.03 au.

Tables 7-9 report the most important electronic configurations for the first three states belonging to the A_g irrep (those with a weight larger than 5 % for at least one of the three states), both in the CASSCF wave functions and for the wave functions obtained from the diagonalization of the effective Hamiltonian computed at the MS-CASPT2 (thus under the effect of electron dynamical correlation).

Table 7: Configurations with a weight larger than 5 % in the $1A_g$, $2A_g$, and $3A_g$ states. Part I.

State	Electronic configurations			
	$8b_{3u}$ ——— $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ ——— $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $4b_{2g}$	$8b_{3u}$ ——— $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\uparrow\downarrow$ $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $4b_{2g}$	$8b_{3u}$ ——— $\uparrow\downarrow$ $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\uparrow$ $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $4b_{2g}$	
	Reference structure	CT from the aromatic rings to the C atoms of the central square	Single excitation on the central ring coupled with a single excitation on the aromatic rings	
	SA-CASSCF wave functions			
$1A_g$	40.21 %	24.15 %	0.52 %	
$2A_g$	10.20 %	< 0.25 %	15.49 %	
$3A_g$	7.23 %	20.16 %	1.99 %	
	Wave functions after diagonalization of the MS-CASPT2 effective Hamiltonian.			
$1A_g$	33.14 %	33.43 %	< 0.25 %	
$2A_g$	4.45 %	< 0.25 %	15.94 %	
$3A_g$	18.59 %	11.32 %	1.09 %	

Let us first analyze the CASSCF wave functions. The most relevant structure (hereafter a synonymous for the term electronic configuration) for the ground state (indicated with “reference structure” in Table 7, with a weight of 40.21 %) considers doubly occupied the orbitals with the lowest energy. The other structures are here described as an excitation process on top of this structure. The second most important structure (24.15 %) describes a charge transfer (CT) from the donor aromatic rings to the C atoms of the central ring ($4b_{2g} \rightarrow 5b_{2g}$ excitation). Among the other structures (all with a weight lower than 5 %), it is relevant to consider the one with two electrons promoted from the $6b_{3u}$ orbital to the $5b_{2g}$ one. As explained in the SI, the ratio of the weight of this structure with that of the reference structure is related to the biradicaloid character of the GS: if the two weights are almost equal, one can expect a marked biradical nature of the wave function. In the present case (4.32/40.21) one can say that the biradicaloid character is rather small. The structures reported in Tables 7-9 describe together 76.47 % of the GS CASSCF wave function.

Table 8: Configurations with a weight larger than 5 % in the $1A_g$, $2A_g$, and $3A_g$ states. Part II.

State	Electronic configurations		
	$8b_{3u}$ ——— $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\uparrow\downarrow$ $6b_{3u}$ ——— $5b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $4b_{2g}$	$8b_{3u}$ ——— $\downarrow$ $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ ——— $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ $\uparrow$ $4b_{2g}$	$8b_{3u}$ $\downarrow$ ——— $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\downarrow$ $6b_{3u}$ $\uparrow$ $5b_{3u}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ $\uparrow$ $4b_{2g}$
	Double excitation from the π to the π^* MOs on the C atoms of the central square. The mixing of this structure with the reference one describes the biradical character of the wave function	Single excitation on the aromatic rings	Single excitation on the central ring coupled with a single excitation on the aromatic rings
	SA-CASSCF wave functions		
$1A_g$	4.32 %	1.17 %	3.41 %
$2A_g$	< 0.25 %	< 0.25 %	8.41 %
$3A_g$	13.03 %	7.88 %	0.59 %
	Wave functions after diagonalization of the MS-CASPT2 effective Hamiltonian.		
$1A_g$	1.30 %	2.65 %	3.15 %
$2A_g$	1.55 %	< 0.25 %	3.46 %
$3A_g$	13.92 %	6.98 %	< 0.25 %

The second A_g state is mainly expanded on the reference structure (10.20 %) and on a more complex $4b_{3u}6b_{3u} \rightarrow 5b_{2g}6b_{2g}$ structure (15.49 %) which can be seen as the product of the $6b_{3u} \rightarrow 5b_{2g}$ excitation with the $4b_{3u} \rightarrow 6b_{2g}$ excitation. The first is localized on the central ring while the second is on the external aromatic rings. The other structures have a weight lower than 10 %. In general this state is quite spread out over a large number of electronic distributions with the structures in Tabs 7-9 describing only 48.85 % of the CASSCF wave function.

The $3A_g$ state has a more compact expansions (the structures reported in Tabs. 7-9 describe 59.19 % of the CASSCF wave function). The main electronic contributions are the $4b_{2g} \rightarrow 5b_{2g}$ excitation (CT from the donor aromatic rings to the C atoms of the central ring, 20.16 %) and the $(6b_{3u})^2 \rightarrow (5b_{2g})^2$ double excitation (combination of the ionic and biradical components on the C atoms of the central ring, *vide supra*, 13.03 %). In this state the reference structure has a non negligible weight (7.23 %) and an opposite sign of the coefficient with respect to that of this structure, therefore the wave function has an increased biradicaloid character with respect to the GS (while still keeping a partial ionic nature). The other relevant structure, $4b_{2g} \rightarrow 6b_{2g}$ (7.88 %) describes a single excitation on the external rings.

Table 9: Configurations with a weight larger than 5 % in the $1A_g$, $2A_g$, and $3A_g$ states. Part III.

State	Electronic configurations		
	$8b_{3u}$ ——— $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\uparrow\downarrow$ $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow$ ——— $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ ——— $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ ——— $\uparrow\downarrow$ $4b_{2g}$	$8b_{3u}$ ——— $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\uparrow\downarrow$ $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow\downarrow$ ——— $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ ——— $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ $\uparrow\downarrow$ ——— $4b_{2g}$	$8b_{3u}$ ——— $\uparrow$ $6b_{2g}$ $5b_{1g}$ ——— $3a_u$ $7b_{3u}$ ——— $4b_{1g}$ $5b_{2g}$ $\uparrow$ $6b_{3u}$ $\uparrow\downarrow$ $5b_{3u}$ $\uparrow\downarrow$ ——— $\uparrow\downarrow$ $3b_{1g}$ $2b_{1g}$ $\uparrow\downarrow$ ——— $\uparrow\downarrow$ $2a_u$ $4b_{3u}$ ——— $\uparrow\downarrow$ $4b_{2g}$
	CT from the π MOs of CO and from the aromatic rings to the C atoms of the central square	Double CT from the aromatic rings to the C atoms of the central square	CT from the aromatic rings to the C atoms of the central square coupled with a single excitation on the aromatic rings
	SA-CASSCF wave functions		
$1A_g$	0.87 %	1.82 %	< 0.25 %
$2A_g$	7.76 %	0.69 %	6.30 %
$3A_g$	2.42 %	5.89 %	< 0.25 %
	Wave functions after diagonalization of the MS-CASPT2 effective Hamiltonian.		
$1A_g$	< 0.25 %	3.15 %	< 0.25 %
$2A_g$	11.95 %	0.93 %	9.48 %
$3A_g$	1.34 %	4.86 %	< 0.25 %

The introduction of dynamical correlation at the MS-CASPT2 level strongly modifies the nature of the wave functions. For the ground state, the two most relevant structures at the CASSCF level (with a weight of 40.21 % and 24.15 %) acquire the same weight ($\simeq 33$ %), while the other structures maintain low weights.

For the $2A_g$ state, the relaxation of the wavefunction induced by dynamic correlation leads to a reduction of the weight of the reference structure (from 10.20 % to 4.45 %) and of the product of local excitations $6b_{3u}4b_{2g} \rightarrow 8b_{3u}5b_{2g}$ structure (from 8.41 % to 3.46 %) and to an increase of the CT $4b_{3u}5b_{3u} \rightarrow 5b_{2g}5b_{2g}$ (from 7.76 % to 11.95 %) and of the $4b_{3u}4b_{3u} \rightarrow 5b_{2g}6b_{3g}$ (from 6.30 % to 9.48%) structures.

Finally, for the $3A_g$ state there is an opposite modification of the role of the reference and $4b_{2g} \rightarrow 5b_{2g}$ structures with respect to the GS, leading to a complete inversion of their weights (from 7.23 % to 18.59 % for the reference structure and from 20.16 % to 11.32 % for the $4b_{2g} \rightarrow 5b_{2g}$ excitation). The strong reduction of the weight of the reference structure combined with the almost invariance of the weight of the $(6b_{3u})^2 \rightarrow (5b_{2g})^2$ excitation has a great impact on the ratio between the weights of these two structures (now larger than 0.7) and can be interpreted as an increase of the biradical nature of this state.

For the sake of brevity, the Tables reporting the OVB reading of the strong OPA $1B_{1u}$ state are given in the SI and are only discussed here. The expansion of this state is quite compact (46.44 % of the CASSCF wave function with four electronic distributions). The most important structure is the $6b_{3u} \rightarrow 5b_{2g}$ singlet excitation (20.34 %) which describes the out-of-phase resonance between the two ionic configurations on the two opposite C atoms of the squarylium moiety (see above). The other three relevant structures reported in the Tables in SI have three electrons in the $6b_{3u}$ and $5b_{2g}$ orbitals, which in OVB terms indicates that one of the C atoms of the central ring bears two electrons and the other one. Therefore one C atom is negative and the other neutral. Starting from the biradical electronic structure, this electronic situation can be considered as an attachment of one electron to one of the C atoms. This electron is removed from the external rings for the $4b_{3u} \rightarrow 5b_{2g}$ (10.54 %) and $4b_{2g}6b_{3u} \rightarrow (5b_{2g})^2$ (6.3 %) structures, while it is removed from the π orbitals of the two CO groups for the $5b_{3u} \rightarrow 5b_{2g}$ (9.26 %) structure.

The relaxation of this wave function induced by the introduction of the electron dynamic correlation is, for this state, even more pronounced than in the GS. The order of the two most relevant structures ($6b_{3u} \rightarrow 5b_{2g}$ and $4b_{3u} \rightarrow 5b_{2g}$) is reversed, with a drastic modification of their weights. The $6b_{3u} \rightarrow 5b_{2g}$ structure passes from 20.34 % at CASSCF level to 11.20 % at MS-CASPT2, while $4b_{3u} \rightarrow 5b_{2g}$ structure goes from 10.54 % to 35.72 %. A similar marked modification is observed also for other three structures: the $5b_{3u} \rightarrow 5b_{2g}$ and the $6b_{3u}4b_{2g} \rightarrow (5b_{2g})^2$ structures show a reduction of their weight (from 9.26 % to 0.80 % and from 6.30 % to 2.06 %, respectively), while the $4b_{3u} \rightarrow 6b_{2g}$ structure shows an increase of its weight (from 3.69 % to 9.69 %). The effect is the marked modification of the nature of this excited state, which becomes much less expanded on local excitations within the central square ring and mainly described by a CT from the aromatic rings to the squarylium moiety, with a certain weight on a single excitation on the aromatic rings.

The analysis here reported corroborate the results obtained in previous studies. From a general point of view, as indicated in Refs. [21, 22], the CO groups of the central ring can act both donors (as happens in the $1B_{1u}$ state) and as acceptors (structures with a weight lower than 5 %, here not reported). For what concerns the bright $1B_{1u}$ state, our analysis of the CASSCF wave function confirms what usually reported in literature, namely that it has the nature of a $\pi \rightarrow \pi^*$ transition within the central ring[21] ($\pi \rightarrow \pi^*$ on the two C atoms, and a CT from the π orbitals of the CO to the C atoms[21]), even though we also observe that the CTs from the external rings to the squarylium moiety play a role, in agreement with the consideration that the donor groups are not involved in the $S_0 \rightarrow S_1$ transition [21, 22] (or only moderately involved [26]) and that, in case of weak side donor groups, the larger CT to the central acceptor ring takes place from the oxygen atoms[21]. As already observed [26], this result is in contrast

with what expected for a donor–acceptor–donor type structure where the charge depletion region in the excited state is expected on the aromatic rings.

On the other hand, the analysis of the MS-CASPT2 wave function shows a rather different scenario, with the $1B_{1u}$ state mainly described by CT from the external aromatic rings to the central square. This nature advocates again the donor–acceptor–donor structure of this molecule. It is rather difficult to assess the robustness of this result. Here we limit ourselves to observe that for both the A_g and B_{1u} irreps, the nature of the states arises from various different components (local excitations, on the fragments and on the central ring, and CTs), whose weights depend on the correct description of electron dynamic correlation. Therefore the composition of the wave functions is controlled by rather subtle effects. A complete analysis of this problem is beyond the scope of this paper and will be the subject of further studies.

4 Assignment of the Spectroscopic Signals

We are now in the position to discuss the main OPA and TPA spectroscopic signatures of SQ0 reported in Ref. [34]. All methods provide a reasonable description of the strong OPA signal observed experimentally at 1.95 eV in toluene and assign it to a HOMO→LUMO transition polarized along the long molecular axis. Figure 5 compares the experimental spectrum and the computed vibronic shape obtained in toluene at CAM-B3LYP/6311+G(d,p) level with AS model. The agreement is very good, in line with what already reported in literature [28]. We also computed the spectral shape in gas phase at CASPT2 and CAM-B3LYP levels of theory with the smaller 6-31G(d) basis set. The CASPT2 spectrum is in good agreement with experiment although it predicts an excessive enhancement of the 0-1 vibronic band at ~2.15 eV. Considering MS-CASPT2 vertical transition energies, the predicted blueshift with respect to experiment is only 0.18 eV. In Figure SI in the SI we report the assignments of the most intense vibronic transitions and in Figure S6 the most relevant normal modes are sketched. Analysis of these data show that while at CAM-B3LYP level the 0-1 band is essentially due to the excitation of mode 104, a benzyl collective CC stretching, the relative intensity of the band increases at CASPT2 as a result of additional excitations of benzyl CH bendings and of the CO stretchings. Comparison of the CAM-B3LYP results indicates that extension of the basis set and inclusion of the solvent effects changes only slightly the computed spectral shape (improving the agreement with experiment) and redshifts it by ~0.17 eV. Assuming similar effects for CASPT2 would bring the predicted CASPT2 maximum to overlap with the experiment. Although we used the AS model, for each stationary structure obtained with TD-DFT calculations we also computed

the corresponding excited-state Hessians. Therefore we could check that at CAM-B3LYP/6-31G(d) level we located a true minimum for $1B_{1u}$. SI shows that adoption of the Adiabatic Hessian (AH) model which also accounts for the effects of frequency changes and Duschinsky mixings predict an expected[78] small red-shift (~ 0.1 eV) while it modifies only very slightly the spectral shape. At variance, with CAM-B3LYP/6-311+G(d,p) level in toluene three very small imaginary frequencies (the largest being $i49\text{ cm}^{-1}$) are predicted for $1B_{1u}$ along b_{3g} modes whose analysis is beyond the scopes of the work. The Cartesian geometries of all optimized geometries have been reported in the SI.

Figure 5: The computed OPA spectrum for the transition $1A_g(\text{GS}) \rightarrow 1B_{1u}$ obtained with the AS vibronic model in gas phase at CASPT2 and CAM-B3LYP level with the 6-31G(d) basis set and in toluene with CAM-B3LYP/6-311+G(d,p) level are compared with the experimental spectrum in toluene taken from ref.[34]. Spectra have been normalized to a maximum intensity equal to 1 and phenomenologically broadened with a Gaussian with half width at half maximum equal to 0.03 eV. The computed spectra are shifted in order to best overlap with the experimental one and the shifts are reported in the insets. For CASPT2 results, the shift is computed considering the MS-CASPT2 vertical excitation energy.

In Figure 5 we reported normalised spectra, as done in Ref. [34] for the experimental spectrum. In the same work however the authors mention that the peak intensity is $3.6 \cdot 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Our predicted absorption maximum with CAM-B3LYP is in excellent agreement if gas-phase results are considered ($3.5 \cdot 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and slightly overestimated when toluene effects are described with LR-PCM (5.5

$10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

A low-lying dark state, $1B_{1g}$, is predicted at all level of computations and assigned to a $n\pi^*$ transition involving the Oxygen lone pairs. Although for some of the employed methods it is the lowest energy state in gas phase and with the 6-31G(d) basis set, extension of the basis set and consideration of the effect of toluene should bring it above the OPA state. These results are therefore in line with the fact that this state has not been experimentally observed in the OPA spectrum in toluene [34].

A second very weak OPA absorption is observed in the experiment at 3.3 eV. This could be assigned to the second state of B_{1u} symmetry that is at 3.64 and 3.48 eV according to SS-CASPT2 and SS-NEVPT2 (PC) and 3.29 eV for CI-MRPT2. However it should be noticed that its intensity seems remarkably overestimated by all methods.

The reproduction of the two intense TPA peaks at ~ 2.95 and ~ 3.6 eV (notice however that in Ref.[34] the spectrum is truncated, so 3.6 might be slightly underestimated) turned out to be very challenging. Methods that include a proper description of double-excitations, like CASSCF/MRPT2, CI-MRPT2 and ADC(3) allow us to confidently assign them to the two states $2A_g$ and $3A_g$, respectively. The predicted vertical excitation energies are in fact for both states within 0.4 eV for ADC(3) and CI-MRPT2 (much less actually for $3A_g$), within 0.6 ($2A_g$) and 0.4 ($3A_g$) eV for SS-NEVPT2 and within 0.6 eV for both the states according to SS-CASPT2. Inclusions of solvent effects and extension of the basis sets would probably further improve the agreement. These two states are made by essentially a HOMO $\rightarrow$ LUMO double excitation coupled with two single-excitations HOMO $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO, but some discrepancies exist on their relative weights in different methods. Methods that do not account for double-excitations or include them in a non accurate way, describe these two states essentially in terms of the two single-excitation components and, as a consequence, strongly overestimate their energy. In the SI we show that the lack of the double-excitation has also a drastic impact on the vibronic shapes that are predicted to be very different at CAM-B3LYP and CASPT2 level. The experimental spectrum shows in practice no vibronic resolution [34], a finding that seems more in line with the broad vibronic shape predicted by CASPT2.

Despite the large inaccuracy in the energy and the absence of the double-excitation components, the computation with CAM-B3LYP and ADC(2) level show that $2A_g$ and $3A_g$ are the only two excited states with remarkable TPA intensities, confirming the assignments of the observed experimental TPA bands. The large transition dipoles $1B_{1u}\rightarrow 2A_g$ and $1B_{1u}\rightarrow 3A_g$ predicted with all methods are coherent with this finding.

A significant involvement of states $1B_{2g}$ and $1B_{3g}$ in the observed TPA experimental features is ruled

out by the predicted excitation energies, well above 4 eV for all methods, and by the small TPA intensities predicted at CAM-B3LYP and ADC(2) level. The very weak TPA band observed at ~ 2.1 eV can only be due to either $1B_{1u}$ or $1B_{1g}$ states. The first is dark by symmetry and the second is predicted to be extremely weak. Therefore the observed intensity arises from a vibronically-induced intensity-borrowing mechanisms [79, 80]. They require the excitation of at least a vibrational mode, a fact in line with the observation that the TPA band is actually blue-shifted (by ~ 0.15 eV) with respect to the OPA one.

Finally, fluorescence anisotropy in THF reveals two dips in rough correspondence with the TPA maxima, i.e. at ~ 2.9 - 3.0 and 3.5 - 3.6 eV [34]. They indicate the existence of an OPA along a polarization perpendicular to the one of the fluorescence, i.e. along either the short molecular axis y or perpendicular to the molecular plane x . This phenomenon can take place either through a direct absorption of states of the corresponding symmetry, i.e. B_{2u} and B_{3u} states, or by a weak absorption of the A_{2g} and A_{3g} states, caused by a vibronically-induced mixing with these states. This second mechanism is plausible and, by definition, it would explain the coincidence of the position of the TPA peaks and the dips in the fluorescence anisotropy. As far as the first mechanism is concerned, a direct role of $1B_{2u}$ state seems ruled out, since it is placed by all methods well above 4 eV. On the contrary, predictions for $1B_{2u}$ show larger discrepancies so that, depending on the method, it may be compatible with one of the two absorptions. Further study, also extending the basis set, seems necessary to reach a robust conclusion on this point.

5 Concluding Remarks

In this contribution we presented an extensive computational study of the excited states of a prototypical symmetric squaraine dye, adopting both TD-DFT, with two different functionals, and a large variety of post-Hartree-Fock approaches. The prediction of the strong OPA band, a HOMO $\rightarrow$ LUMO transition, is reasonable with all methods and its vibronic shape is well reproduced by the two methods we tested, CAM-B3LYP and CASPT2. The errors in the position of the spectrum are ~ 0.3 eV for CAM-B3LYP in toluene and within 0.2 eV for MS-CASPT2 (so likely lower in toluene). CI-MRPT2, ADC(2) and CC2 vertical excitations in gas phase are within 0.2-0.3 eV from the experimental maximum and inclusion of vibronic and solvent effects is expected to further improve the agreement.

The analysis of the TPA was much more challenging. The two experimental peaks at 2.95 and 3.6 eV have been confidently assigned to the two $2A_g$ and $3A_g$ states, made up by the mixing of two single-excitations, HOMO $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO and a double excitation HOMO $\rightarrow$ LUMO. Only post-HF methods able to properly describe the double-excited character provide reasonable estimations

of the vertical excitation energy (within ~ 0.5 eV), whereas all other adopted methods, like TD-DFT, CC2, ADC(2) and EOM-CCSD, can be more than 1 eV off.

There has been a long debate on whether the low-energy strong OPA of squaraines arise more from CT transitions due to the donor-acceptor-donor structure, or from a biradicaloid behaviour [31]. Here we looked at the problem adopting a OVB reading of the CASSCF and MS-CASPT2 wavefunctions in terms of orbitals localized on the donor or the acceptor and, for the first time, we extended the analysis to the states responsible for the two-photon absorption. Our results confirm that the biradicaloid character of the ground state is only moderate. The excited states arise from the contribution of many different components with a delicate balance that is sensitive to the level of computations. At CASSCF level $1B_{1u}$, the state responsible for the strong OPA, is made up by local excitations on the central squarylium moiety and partial CT to the carbons of the square not belonging to the carbonyl groups, that accept charge from both the side rings and the carbonyl groups. At MS-CASPT2 level, the CT from the aromatic rings becomes much more important. Concerning $2A_g$ and $3A_g$, at CASSCF level they are made up by many contributions both local excitations on the central and side rings (mainly $2A_g$) and partial D $\rightarrow$ A CT states (mainly in $3A_g$). MS-CASPT2 strongly modifies the picture increasing the CT character of $2A_g$ and the biradical character of $3A_g$.

In conclusion, the results presented in this contribution point out that an accurate computational description of the the excited states involved in the OPA and even more in the TPA processes of this small squaraine challenges many popular theoretical methods of quantum chemistry. The nature itself of these states arise from a subtle balance of biradicaloid, charge transfer and double-excitation characters that is sensitive to the level of computations and likely can be shifted by environmental effects. Further work will be required in the next future to definitively clarify these aspects, a necessary premise to face a robust modelling of the linear and non-linear optical properties of these systems in aggregate form, a topics of large interest in the recent literature.[19]

Acknowledgment

We thank A. Painelli and C. Sissa at University of Parma for proposing us to study this squaraine and for many stimulating discussions. Furthermore, we thank I. Cacelli of University of Pisa for useful discussions on CI-MRPT2 calculations. F.J.A.F. thanks University of Málaga for the contract E-29-2018-0016654. S.C. acknowledges support from the Independent Research Fund Denmark, DFF-Forskningsprojekt2 grant no. 7014-00258B.

Keywords

Single and double excitations, biradicaloid and charge transfer character, TD-DFT and post HF calculations, OVB reading of CASSCF wave functions, vibronic spectra.

Single and double excitations. We performed a computational study of the excited states of a symmetric squaraine dye with TD-DFT and post-HF methods. A balanced treatment of single and double excitations is necessary for a coherent description of one-photon and two-photon absorption.

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