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Theoretical study of the absorption and emission spectra of 1,2-Bis(9-anthryl)acetylene in cyclohexane and acetonitrile

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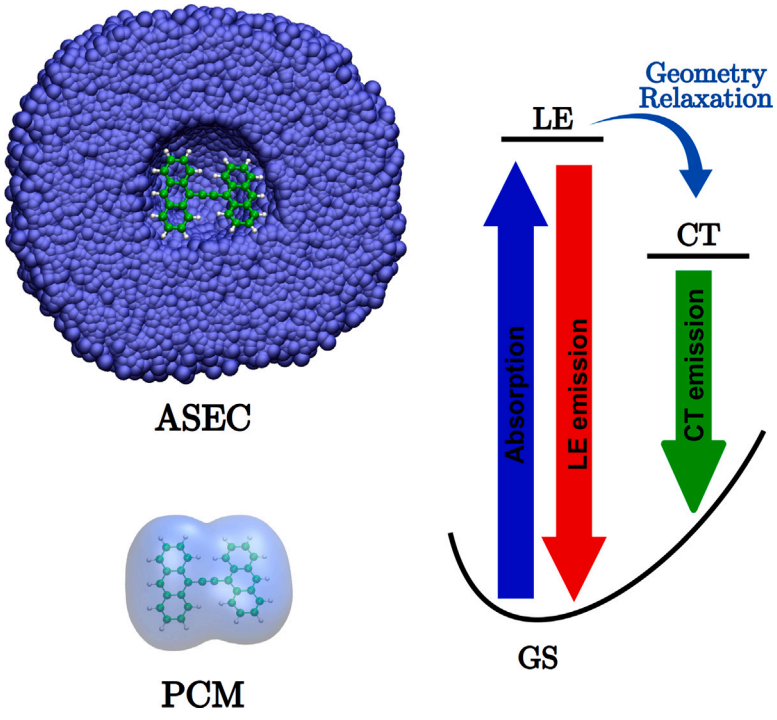
HIGHLIGHTS

- The excited states of 1,2bis(9-anthryl) acetylene are calculated in two solvents.
- Calculations are made using TD-DFT combined with two solvent models, PCM and QM/MM.
- The intense absorption band is composed by several electronic transitions.
- The emission at 510 nm in acetonitrile is due to a fully relaxed CT excited state.
- A symmetry break in the excited state is obtained in due agreement with experiment.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we use TD-DFT combined with Polarizable Continuum Method and QM/MM approach to analyze the absorption and emission spectra of 1,2-bis(9-anthryl)acetylene in cyclohexane and acetonitrile. The absorption band located at 250 nm is found to be composed by several absorption transitions contributing to its high intensity. Solvent effects are found to be mild in the positions of the absorption and emission bands but influence the relaxation of the excited state. We thus corroborate the experimental contention of a charge-transfer excited state with symmetry-break after the absorption in polar acetonitrile and leading to an emission transition at 510 nm.

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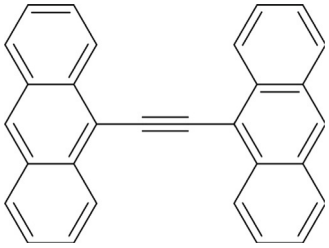

Fig. 1. Molecular structure of 1,2-bis(9-anthryl)acetylene (BisAA).

1. Introduction

1,2-bis(9-anthryl)acetylene (BisAA, Fig. 1) is a molecule formed by two anthracenes attached by an acetylenic bridge that provides a possible electronic coupling along the molecule allowing the charge redistribution after the absorption process [1]. The absorption spectrum of BisAA in non-polar solvents is very similar to the spectrum of BisAA in polar solvents, and the emission spectrum shows a redshift with increasing solvent polarity [1]. The emission spectrum in cyclohexane is similar to the spectrum of anthracene [2], showing two maxima: one more intense (470 nm), coming from a locally-excited state (LE), defined as a state with the same geometry as the ground state (GS) but in equilibrium with the solvent [3]; and another with lower intensity (510 nm) suggested to be due to the emission of a partial charge transfer (PCT) state [1]. In polar acetonitrile, the spectrum of BisAA has a single broadband (centered at 510 nm) that has been attributed [1] to an emission from a charge-transfer (CT) relaxed state.

In this work, we perform a theoretical study of the absorption and emission process of BisAA, focusing on the analysis of the LE and CT states in solvent environment. The formation of a CT state of BisAA in polar solvents was previously predicted by the experiments of Peon and co-workers [1], and here we attempt to theoretically analyze and possibly support this contention.

The theoretical modeling of solvent effect on absorption and emission spectra in the UV/Vis region is an extensively studied topic [4–19]. Solvent interactions play a crucial role also in stabilizing the geometries and charges of a molecular system [20]. Charge-separated states on symmetrical systems have been theoretically [2,21] and experimentally [1,22–24] studied, improving the understanding of the role of the solvent and/or geometry in the charge-transfer process upon electronic excitation. In this line, 1,2-Bis(9-anthryl)acetylene (BisAA) is a symmetric molecule recently synthesized [1], to characterize the process of symmetry reduction in an excited state involving the solvent.

The methodology adopted here is based on two different solvent models: (i) a polarizable continuum model (IEF-PCM) [25] and (ii) a discrete model based on the sequential use of the Monte Carlo and Quantum mechanical calculations (s-MC/QM) [26]. Particularly, the s-MC/QM method has been successfully used in different solvation problems including absorption and emission spectra [27–31]. In this work, we thus calculate the absorption and emission transition energies from LE and CT states using different levels of QM calculations and solvent models.

2. Methodology

The UV–Vis absorption and emission energies were calculated using the sequential Monte Carlo (MC) and quantum mechanical (QM) multiscale methodology (s-MC/QM) [26,27]. This approach combines MC simulations followed by QM calculations in which the classical simulations generate accessible configurations of the solute molecule surrounded by the liquid system in a given thermodynamic condition. Then, selected solute–solvent configurations are used to perform quantum mechanical calculations on statistically uncorrelated configurations [9,27].

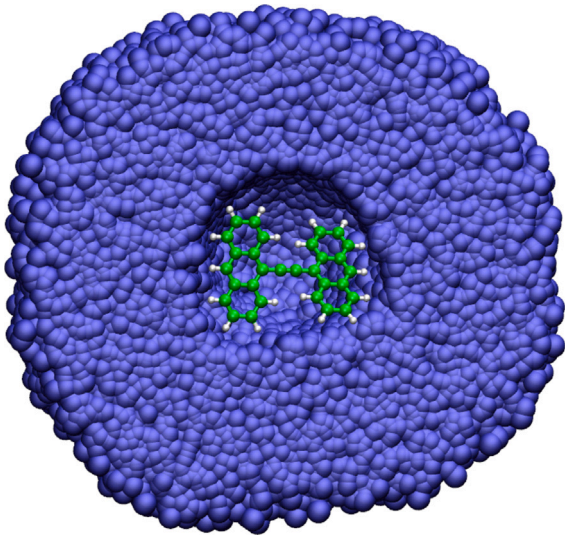

Fig. 2. Illustration of the ASEC configuration. BisAA is surrounded by the nearest 300 solvent molecules of 100 configurations represented by its atomic point charges.

Monte Carlo (MC) simulations were performed using the Metropolis sampling technique in the NPT ensemble using the DICE program [32]. One solute molecule (BisAA), surrounded by 800 or 1000 molecules of cyclohexane or acetonitrile, was used to simulate the solute–solvent systems at 1 atm and 298 K. As it is common practice [12,33,34] all solute and solvent geometries are kept fixed in the MC simulations. The solvent effect on BisAA geometries was included by optimizing the geometries in the solvent environment described by the integral equation formulation of the polarizable continuum model (IEF-PCM) [25]. These calculations were performed at TD CAM-B3LYP/6-311+G(d,p) level of theory. The Coulomb potential plus standard Lennard-Jones (LJ) parameters were used to model the interaction potential used in MC simulations. In particular, the BisAA atomic charges were obtained using the Charges from Electrostatic Potentials with the Grid-based (CHELpG) scheme [35] with the CAM-B3LYP/6-311+G(d,p) level considering the reference state (GS, LE or CT) including cyclohexane or acetonitrile as solvent. The atomic charges of cyclohexane and acetonitrile are those of Refs. [36,37], respectively. The set of LJ parameters of BisAA, cyclohexane, and acetonitrile were obtained from Refs. [36–38], respectively. All geometries, atomic charges, LJ parameters used in MC simulations are shown in Supporting Information.

The QM calculations of the transition energies of BisAA in each solvent considered were performed using time-dependent (TD) DFT with CAM-B3LYP/6-311+G(d,p) and the solute–solvent interaction in the electrostatic approximation within the average solvent electrostatic configuration (ASEC) [39]. ASEC is a model that by using only one single configuration gives the same result as the statistically converged average obtained using all MC configurations, thus providing considerable computational savings [40]. The MC simulations were made using 600 000 MC steps per molecule (or total 4.8×10^8 MC steps in the case of cyclohexane and for 6.0×10^8 in acetonitrile). The production stages of MC simulations were performed after the thermalization process. The ASEC includes 300 solvent molecules closest to the BisAA molecule (see Fig. 2) treated as point charges centered at the atomic positions of the corresponding solvent molecules. The nearest solvent molecules are selected from a minimum distance distribution function [33]. The

sampled configurations were used for BisAA absorption and emission calculations using the GAUSSIAN 09 [41] program.

We are concerned with two possible geometric arrangements of the excited state, whether including or not the possible relaxation. The Franck–Condon transition leads to what we call the LE state. After reaching this we allow for the geometry relaxation until reaching the geometry optimized excited state in equilibrium with the solvent and we will note the possible existence of the charge transfer in this fully relaxed excited state. So, the LE state corresponds to the vertical transition with the geometry of the ground state and its emission is calculated after obtaining the electrostatic equilibrium with the solvent in this state. The corresponding atomic charges are given in the Support Information. The geometry of the CT state, instead, corresponds to the fully relaxed geometry of the first excited state and equilibrated with the solvent. The absorption energies were calculated using the linear response theory [42]. The emission energies were calculated using linear response theory. In addition, the LE and CT emission energies were obtained using the state-specific approach [43] for the calculations performed with the solvent modeled with IEF-PCM. To verify the adequacy of the DFT method at some points a Multistate Multiconfigurational complete-active-space second-order perturbation theory (CASPT2) [44] was also performed. This used the Cholesky decomposition technique, including the solvent modeled using IEF-PCM. The multi-state CASPT2 used the CASSCF(12,12) Ref. [45]. The selection of an active space with 12 π electrons distributed among six bonding π orbitals plus six antibonding π^* orbitals is motivated by the consistent prediction of the anthracene absorption spectra [46] obtained using this active space. Figure S1 of Supporting Information shows the spatial configurations of active space's molecular orbitals. Intruder states were avoided by applying a level shift of 0.25 hartree in CASSCF calculations and an imaginary shift of 0.2 hartree in CASPT2 calculations. CASSCF and CASPT2 calculations were performed with the ANO-L-VDZ basis set [47] using the MOLCAS 8 program [48].

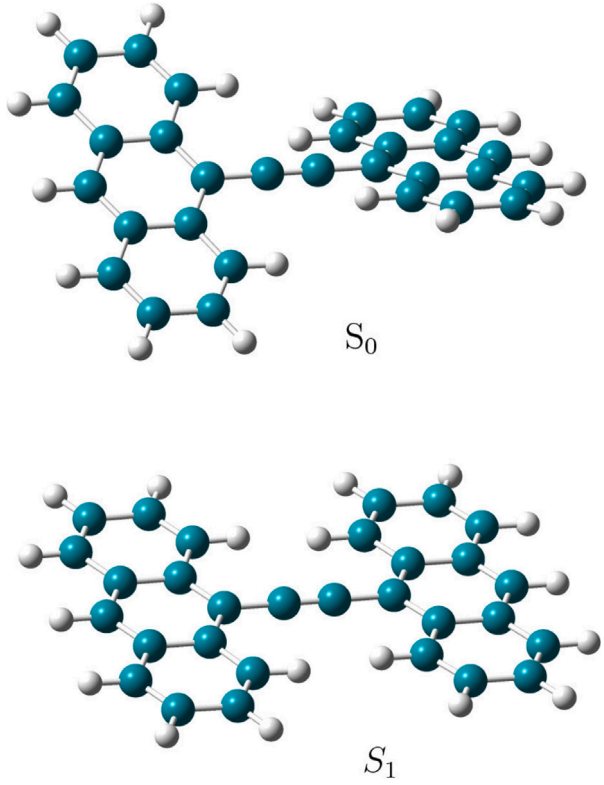

Fig. 3. Molecular geometries of GS (S_0) and the first excited state S_1 that has a charge transfer nature (CT) of BisAA in acetonitrile obtained at CAM-B3LYP/6-311+G(d,p) level.

3. Results

Geometries of the ground and charge transfer states.

The calculated twist angle between the two anthracenes groups of BisAA in the optimized GS geometry in cyclohexane and acetonitrile are around 43° and 38°, respectively. These non-zeros twist angles are similar to the previous results [1] and are consistent with the expectation that the lowest energy absorption transition of BisAA must occur as a localized transition in one of the two anthracenes moieties of the molecule [1,2].

In the energy optimized geometry of the first excited state (CT), the twist angle between the two anthracene groups of BisAA in cyclohexane and acetonitrile are around 14° and 11°, respectively. These values are smaller than the angles obtained for the GS. The geometries of the GS and CT states are similar to those previously obtained [1] and are shown in Fig. 3.

Absorption spectra

The calculated two lowest absorption excitation of BisAA in cyclohexane and acetonitrile are shown in Table 1 (for each band only the transition with the highest oscillator strength is shown). The calculations performed with TD-DFT CAM-B3LYP/IEF-PCM show that the first absorption transitions are located at 424 nm and 421 nm in acetonitrile and cyclohexane, respectively. These results are close to the respective values of 411 nm and 410 nm obtained by the CASPT2/IEF-PCM calculations. These CASPT2/IEF-PCM results are even closer to the results obtained with TD-DFT CAM-B3LYP/ASEC. In addition, it is clear that all theoretical models considered are consistent with the experiment because these theoretical values are located in the region of the very broad experimental absorption band. The two experimental maxima observed in the region around 450 nm correspond to one electronic transition and a vibrational progression of anthracene, as documented [49] and corroborated recently [1]. For the second transition, the TD-DFT CAM-B3LYP/IEF-PCM gives a transition with high intensity located at 245 nm for acetonitrile and 246 nm for cyclohexane. This result gives a small difference of 10 nm compared with CASPT2/IEF-PCM for both solvents. The results obtained with TD-DFT CAM-B3LYP/ASEC are 236 nm for both solvents. But again, all theoretical methods used here give results within the experimentally observed band in the region of 230–280 nm. Overall the results obtained with CASPT2 are similar to the results obtained with TD-DFT and we now limit the calculation to the TD-DFT model. The absorption band located in the region of 230–280 nm is more intense than that observed at 400–480 nm, in due agreement with experiment. However, at this point we note that the calculated high energy transition is only a factor of two more intense, where in the experiment it is about five times [1]. This is indicative that the intense band is in fact composed by several electronic transitions. Several transitions with smaller oscillator strength are obtained and will now be considered (Table 2). The spectrum is now obtained convoluting lorentzian functions for the calculated intensities of 30 lowest energy transitions. The convolutions are made for the calculated excitation energies with an individual line width of 0.15 eV. For comparison with experiment they are transformed to wavelength and shown in Fig. 4. The inset shows the additional calculated states. The convoluted spectra shown in Fig. 4 for the absorption of BisAA in both cyclohexane and acetonitrile are very similar for the two theoretical models used. In spite of small differences in the absorption maxima they all give a similar description, an intense absorption band in the region of 250 nm and a broad less intense band in the 400–480 nm region. The relative calculated intensities between the first and second bands now agrees with the experimental spectrum [1] in that the high energy band is five times more intense. The considerable

Table 1
First and second absorption bands maximum and the respective oscillator strengths (f) obtained using TD-DFT CAM-B3LYP/6-311+G(d,p) and CASPT2/ANO-L-VDZ calculations in acetonitrile and cyclohexane. Also, are shown the respective experimental results extracted from Ref. [1].

Solvent	QM method	Solvent model	Wavelength [nm]	f	Wavelength[b] [nm]	f
Acetonitrile	CASPT2	IEF-PCM	411	0.64	255	1.15
	CAM-B3LYP	IEF-PCM	424	0.67	245	1.90
	CAM-B3LYP	ASEC	415	0.56	236	1.55
Cyclohexane	CASPT2	IEF-PCM	410	0.68	256	1.20
	CAM-B3LYP	IEF-PCM	421	0.67	246	1.64
	CAM-B3LYP	ASEC	412	0.55	236	1.63
Experiment[a]			400–480		230–280	

[a]The experimental bands are located in the same region for acetonitrile and cyclohexane.
[b]Only the transitions with the highest oscillator strength located in the second absorption band are shown for comparison with experiment.

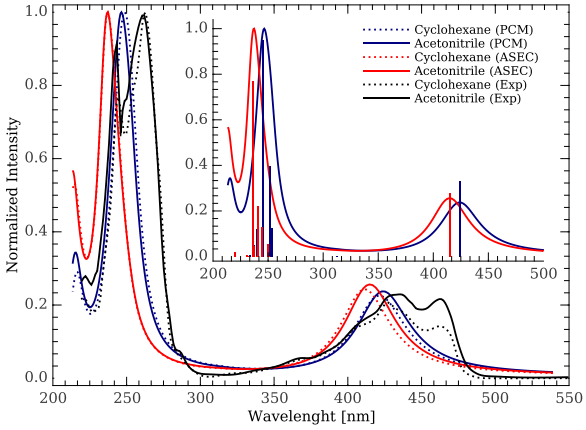

Fig. 4. Absorption spectrum of BisAA in cyclohexane and acetonitrile. Also, the experimental absorption spectrum extracted from Ref. [1] are shown. The inset highlights the absorption spectrum of BisAA in acetonitrile with the spectral lines used in the convolution. For better visualization, the spectral lines (oscillator forces) were rescaled by a multiplicative factor of 0.5.

Table 2
Absorption transitions and the respective oscillator strengths (f) that composes the second absorption band. The calculations are performed using TD-DFT CAM-B3LYP/6-311+G(d,p) in acetonitrile and cyclohexane as solvents. Only transitions with oscillator strength greater than 0.1 are shown.

Solvent	Solvent model	Wavelength [nm]	f
Acetonitrile	IEF-PCM	253	0.25
		252	0.80
		245	1.90
		240	0.24
	ASEC	250	0.11
		244	0.26
		241	0.44
		236	1.55
Cyclohexane	IEF-PCM	253	0.40
		252	1.25
		246	1.64
		240	0.14
	ASEC	248	0.13
		244	0.35
		241	0.34
		236	1.63

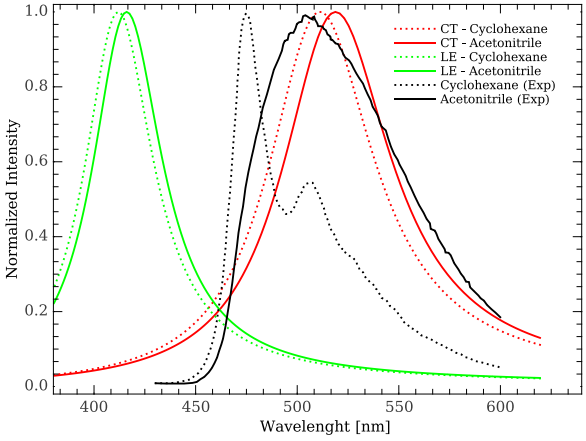

Fig. 5. Emission spectra of BisAA in cyclohexane and acetonitrile calculated with TD-DFT CAM-B3LYP/6-311+G(d,p) using ASEC to model the solvent. The CT and LE emissions are shown. The experimental emission spectra extracted from Ref. [1] are shown.

increase of the intensity of the high energy state derives from the existence of several electronic transitions with small oscillator strengths. Only one transition is calculated in the lower energy region around 400–480 nm but several are seen to compose the high energy band. It is interesting to note that only after considering the existence of different transitions beneath the band in the region of 250 nm gives the appropriate relative intensity. Furthermore, the absence of more than one transition state in the first absorption band (400–480 nm) corroborates previous results [1,49].

Emission spectra

Table 3 shows the calculated LE and CT emission transitions. The LE transition is obtained from an excited state where the BisAA electronic structure is equilibrated with the solvent. Also, the LE state geometry is not relaxed, remaining fixed at the same molecular geometry of the GS. The relaxed atomic charges are insufficient to cause significant changes in the electronic distribution of the LE state compared to the GS. Consequently, the calculated emission energy equals the calculated absorption energies in both solvents. On the other hand, the geometry relaxation of the first excited state induces geometry changes (cf. Fig. 3) and the optimized CT state modifies the emission transition.

Fig. 5 shows the emission spectrum of BisAA in cyclohexane and acetonitrile. The transition energies obtained modeling the solvent with IEF-PCM are the same as using ASEC and are not displayed in Fig. 5. The calculated emission bands change by 10 nm with change in the solvent. But the relaxed CT state in acetonitrile is calculated to emit around 510 nm, in agreement with the CT state experimentally defined [1]. In cyclohexane, the theoretical emission obtained for the relaxed state occurs in the same position of the lowest maximum of the experimental spectrum that is consistent with the state defined as partial charge transfer state (PCT) by Peon and co-workers [1]. However, the calculated dipole of BisAA in cyclohexane at the first excited state with relaxed geometry is zero, both with solvent modeled with IEF-PCM and ASEC. This result implies the absence of charge transfer in the electronic absorption followed by the geometric relaxation process of BisAA in cyclohexane. Therefore, this absence of charge transfer in the first relaxed excited state of BisAA in cyclohexane indicates that this state is not characterized as a relaxed charge transfer (CT)

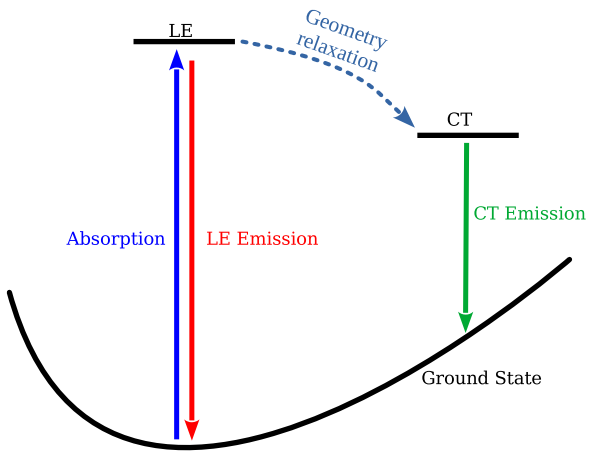

Fig. 6. Illustration of the energy diagram with a summary of the absorption and emission process due to the stabilization of the LE, and CT states of BisAA.

Table 3
LE and CT emission transitions calculated using TD-DFT CAM-B3LYP/6-311+G(d,p) in acetonitrile and cyclohexane modeled with IEF-PCM and ASEC.

Solvent	Solvent model	LE [nm]	CT [nm]
Acetonitrile	IEF-PCM	415	519
	ASEC	415	521
Cyclohexane	IEF-PCM	412	510
	ASEC	412	510
Experiment[a]		470[b]	510[c]

[a]The emission from LE state is not observed in acetonitrile even after a delay time of 100 ps in the measurement.
[b]In cyclohexane.
[c]In acetonitrile.

state. The calculated emissions of relaxed states agree with the lower energy emission for acetonitrile and cyclohexane, although the small polarization process expected (PCT state) of BisAA is not obtained in cyclohexane. The results of these calculations support the charge transfer excited state emitting in the region of 510 nm in acetonitrile only. Fig. 6 illustrates the absorption and emission process of BisAA in acetonitrile.

Symmetry break in acetonitrile

The theoretical results reveal that the charge transfer in BisAA in the relaxed first excited state could not be obtained with the PCM model indicating that a discrete solvent model is needed to reproduce the symmetry breaking of the CT state in acetonitrile.

The inclusion of acetonitrile as a discrete solvent environment (ASEC) leads to a symmetry break in the charge distribution of the relaxed CT excited state of BisAA, inducing a non-zero dipole moment of 1.8 D, obtained with CAM-B3LYP/6-311+G(d,p). Additional calculations with CASSCF/6-311+G(d,p) and B3LYP/6-311+G(d,p) obtained the values of 2.52 D and 2.54 D, respectively. This is consistent with the small solvatochromic effect theoretically obtained for the CT state. By combining experimental Stokes shifts with the dielectric approximation of Kawski and co-workers [50] the dipole moment of 9.7 D was estimated [1] for the CT state of BisAA in acetonitrile, assuming that the Onsager cavity radius is 5.95 Å. This is a very large value compared to the QM explicit calculations. The dependence of the dipole moment with the Onsager cavity radius can be severe and a decrease in this radius considerably decreases the resulting estimated dipole moment of the excited state. The selection of the cavity radius is somewhat arbitrary and influences the final dipole moment. In any case, both the theoretical and experiments results are consistent with the symmetry break in the fully relaxed excited state. Our theoretical results using explicit quantum mechanical calculation suggest indeed a symmetry break in the excited state but a relatively small dipole moment.

4. Summary and conclusions

1,2-Bis(9-anthryl)acetylene (BisAA) is an interesting model compound to study the time-scales for the formation of charge-separated electronically excited states starting with an originally symmetric electron distribution in the ground state. The absorption and LE and CT emission transitions of BisAA in cyclohexane and acetonitrile were theoretically studied. The main focus was on the theoretical description of the LE and CT states in solvent previously predicted experimentally [1]. The theoretical modeling of the solvent effect was performed using two distinct approaches: (i) a continuum model (IEF-PCM) and (ii) a QM/MM using the average solute–solvent electrostatic interaction (ASEC). These two approaches reproduce the qualitative aspects of the experimental absorption spectra very well. The more intense absorption band derives from a set of distinct states contributing to the absorption band, one aspect not previously discussed and important for understanding the relative intensities of the absorption bands. On the other hand, the lowest energy band at 400–480 nm corresponds to a single electronic transition. With respect to the emission process, we analyze two distinct possibilities: (i) a LE emission that occurs from an excited state equilibrated with the solvent but still in the ground state geometry; and (ii) a CT emission that derives from the first excited state with fully relaxed geometry and equilibrated with the solvent. This relaxation leads to sizeable changes generating a CT state with a nonzero dipole moment in acetonitrile. This emission is calculated in good agreement with the observed emission in 510 nm in acetonitrile, corroborating the experimental contention.

CRediT authorship contribution statement

Vinícius Manzoni: Conceptualization, Methodology, Data curation, Investigation, Writing – review & editing. **Yoelvis Orozco-Gonzalez:** Multiconfigurational calculations and analysis, Review. **Jorge Peon:** Conceptualization, Review & editing. **Sylvio Canuto:** Conceptualization, Methodology, Investigation, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.cplett.2023.140775.

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