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ARTICLE *in* CHEMICAL PHYSICS LETTERS · SEPTEMBER 2007

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Time-dependent density functional theory investigation of the absorption and emission spectra of a cyanine dye

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Received 28 March 2007; in final form 27 July 2007

Available online 11 August 2007

Abstract

Density and time-dependent density functional theory have been used to simulate the vibronic structure of the emission and absorption spectra of a typical trimethine cyanine dye. This approach combines the BH and HLYP exchange-correlation functional with the Doktorov scheme to evaluate the Franck–Condon factors. The absorption and emission spectra present a dominant band and a shoulder, which nicely reproduce the experimental data. The theoretical calculations demonstrate that the simplicity of the shape results from rather small geometry relaxations in the first excited state, though many vibrational normal modes contribute to it.

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1. Introduction

Cyanine dyes are versatile compounds, which were primarily employed extensively as spectral sensitizers for silver halide photography [1]. As a function of the nature of the surrounding, they undergo different types of self-aggregation, displaying specific signatures on the absorption bands [2]. Recent studies have shown that they present large negative third-order nonlinear optical properties [3,4]. Moreover, cyanine dyes constitute a well-known class of fluorescent molecules, which have been extensively studied for their interest as label molecules in biochemistry due to their sensitivity to environmental conditions. For instance, interactions between cyanines and nucleic acids can increase their quantum yields by two orders of magnitude, so that these molecules are of particular interest as biopolymer markers [5]. The major part of the studies concerning the emission properties of cyanines are experimental spectroscopic investigations aiming at optimizing the wavelength of emission, the fluorescence quantum yields, and

the lifetime. To our knowledge, very few theoretical works on this subject have been reported while they appear of interest to help in deducing structure–property relationships, and therefore to optimize the structure of these compounds.

Notwithstanding the numerous aspects to consider in the theoretical simulations – optimization of the geometry of the ground and dominant excited states as well as the determination of their vibrational normal modes and frequencies to evaluate the Franck–Condon factors – several groups have simulated and interpreted emission spectra with success. For instance, Negri and Zgierski reported the emission spectra of naphthalene from three excited states and showed the impact of Dushinsky rotation on the redistribution of vibronic intensities [6]. Several studies addressed the absorption and emission spectra of π -conjugated polymers [7,8]. Usually, simplified, though reliable, schemes are sufficient to reconstruct the features of the experimental spectra, to analyze the vibronic structure in terms of torsional versus backbone vibrational modes, as well as to assess temperature effects. Baraille and co-workers [9] investigated HPCl by employing highly-correlated CASPT2 and CCSD(T) methods, which are however computationally too expensive for studying compounds like

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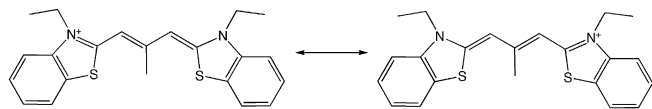


Chart 1. Sketch of the resonance forms of the trimethine cyanine characterized in Ref. [12].

cyanines. Baraldi and co-workers [10] studied both experimentally and theoretically the emission properties of two different merocyanines using a semi-empirical model, called solvation conformations spectra-intermediate neglect of differential overlap (CS-INDO), taking into account solvent effects.

In this Letter, density and time-dependent density functional theory (DFT and TDDFT) methods are applied to simulate the emission spectrum of a cationic trimethine (Chart 1) and to analyze it in comparison with its absorption spectrum [11] as well as with respect to the experimental spectra reported by Nakashima and Kunitake [12]. The latter study investigated the fluorescence enhancement induced by binding the cyanine to a bilayer membrane. Since this compound is a good representative of dyes and fluorescent probes [11], our results are significant for future molecular design because they show it is possible to proceed rapidly, without the costly synthesis step. Moreover, in addition to its success for determining the excitation energies of organic and transition-metal containing compounds [13–18] and furthermore, for simulating the vibrational structure of the absorption bands [19–22], these results bring additional support for using the TDDFT method for investigating optical properties.

2. Computational details

The geometry of the ground state was optimized at the DFT level with convergence criterions of 10^{-3} on the Cartesian gradients and 10^{-6} on the energies. The calculation of the ten first vertical excited states was carried out using TDDFT, then for the first dominant singlet excited state – the excited state presenting the largest oscillator strength – the geometry was optimized. The TDDFT geometry gradients were determined following the scheme due to Furche and Ahlrichs, implemented in the EGRAD algorithm of the TURBOMOLE package [23]. We applied the same gradient and energy convergence criteria as for the ground state. In all cases, the BH and HLYP exchange-correlation (XC) functional, including 50% of Hartree–Fock exchange, was employed in combination with the SV(P) basis set. Finally, the vibrational normal modes and frequencies were determined for the ground and the dominant excited states at the same level of approximation. The choice of the BH and HLYP XC functional is based on studies due to Dierksen and Grimme [21] and more recently, Magyar and Tretiak [24]. It is further substantiated by our previous investigations [11,22]. On the one hand, for π -conjugated systems, Dierksen and Grimme recommended the use of XC functionals contain-

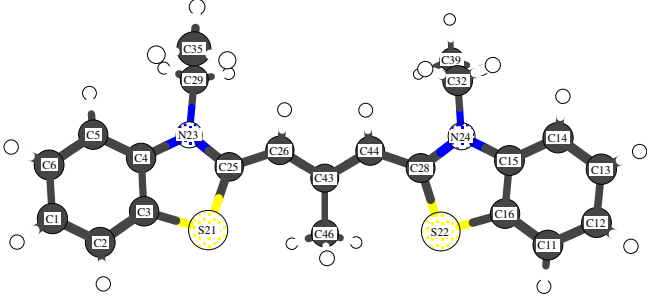
ing between 30% and 60% of Hartree–Fock exchange to reproduce the experimental vibronic structures. Magyar and Tretiak also pointed out the key role of Hartree–Fock exchange when studying large molecules and clusters to avoid level crossings in the optimization of excited states geometries, which result from *ghost* low-energy charge transfer excited states. Following these works the use of 50% of Hartree–Fock exchange appears as a good compromise ensuring the quality of TDDFT to determine excited state geometries and the corresponding vibrational modes. All calculations were performed using the TURBOMOLE package [25], adopting a recent algorithm for determining the force constants of the excited states [26]. The Franck–Condon factors were determined using the recursive Doktorov scheme [27] as described by Spangenberg et al. [28], in which the overlap between two vibrational functions of the ground and excited states are determined including relaxation and Duschinsky rotation effects within the harmonic approximation. This procedure was implemented in a homemade program, which has been elaborated in order to determine both absorption and emission transition spectra on the basis of vibrational modes of the two electronic states, the intensity of which being given by the amplitude of the FC factors. The vibrational normal modes are drawn by adopting the representation of Hug [29] and the VOAVIEW graphical package developed in Fribourg [30], where the direction of atomic displacements is perpendicular to the junction plane between the two hemispheres of distinct color while their amplitudes are proportional to the sphere surface.

3. Results and discussion

At the ground state optimized geometry, the dominant absorption band is associated to the first excited state and is located 3.01 eV ($\lambda = 412$ nm) above the ground state. Since, all the other excited states present much smaller oscillator strengths, simulations of the absorption and emission spectra reduce to the determination of the vibronic structure of that dominant excited state. After relaxation of the excited state geometry, the excitation energy reduces to 2.93 eV (423 nm) while a further decrease to 2.84 eV (437 nm) is obtained upon accounting for the zero-point vibrational energy. The remaining difference with respect to experiment (542 nm in methanol [11] and 565 nm in bilayer membrane [12]) comes from the effects of the surrounding as well as the limitation of the XC functional. The most important bond lengths (R), bond angles (α), and dihedral angles of both states are listed in Table 1 as well as their differences. Since the molecule is symmetric, only the non-redundant geometrical parameters are listed. The molecule is mostly planar in both states, though departure from planarity is more important for the excited state. Most of the geometry relaxation occurs along the conjugated path joining the two N atoms and corresponds to an elongation of the CN and CC bonds. It is accompanied by a shortening of the bonds between the N atoms and the

Table 1

Main optimized geometrical parameters (bond lengths in Å, bond and torsion angles in degrees) of the ground and first excited states of the trimethine cyanine determined at the BH and HLYP/SV(P) level of approximation



	Ground state	Excited state	Difference
<i>External benzene ring</i>			
C1–C2	1.386	1.385	–0.001
C2–C3	1.387	1.388	0.001
C3–C4	1.392	1.405	0.013
C4–C5	1.392	1.398	0.006
C5–C6	1.386	1.383	–0.003
C6–C1	1.394	1.399	0.005
<i>Conjugated path</i>			
C4–N23	1.394	1.376	–0.018
N23–C29	1.460	1.456	–0.004
N23–C25	1.354	1.376	0.022
C25–S21	1.744	1.748	0.004
C25–C26	1.397	1.393	–0.004
C26–C43	1.402	1.415	0.013
<i>Bond angles</i>			
C4–N23–C25	115.1	114.6	–0.5
N23–C25–C26	123.2	124.2	1.0
C25–C26–C43	130.3	130.0	–0.3
C26–C43–C44	116.6	115.1	–1.5
<i>Dihedral angles</i>			
C4–N23–C25–C26	–175.7	–174.3	1.4
N23–C25–C26–C43	–174.8	–172.5	2.3
C25–C26–C43–C44	–173.0	–167.0	6.0
C28–C44–C26–C25	2.8	5.6	2.8

benzene rings and by a bending of the angles along the central conjugated path. Nevertheless, these relaxations are rather small: $\Delta R < 0.02$ Å and $\Delta\alpha < 2^\circ$

The individual vibronic contributions to the absorption and emission intensities are represented in Fig. 1 as well as the resulting spectra obtained by associating to each transition a Gaussian distribution of full width at half magnitude of 0.1 eV. The absorption and emission spectra are dominated by a large band corresponding to the (0,0) transition while they exhibit a shoulder (35% of the intensity of the dominant band) and a second harmonic of smaller intensity (about 5% of the dominant band). Choosing the representation in the energy space enables to evidence that the two spectra are almost mirror image of each other. The small differences between the individual contributions, particularly in what concerns the first and second shoulders, comes from the fact the shape of the emission and absorp-

tion bands are related to the vibrational modes of the ground and excited states, respectively and from the fact these two sets of modes are different since the geometries and force constants are different. Differences between the modes are illustrated in Fig. 1 for the modes, which contribute most to the shoulder.

Contrary to what is usually assumed when adopting simple schemes such as the Huang-Rhys approximation, the shoulders are not determined by a unique, dominant, vibrational normal mode but rather by a collection of singly-excited vibrations. This results from the complex geometry relaxation upon excitation and the Dushinsky rotations, which lead to a large number of overlapping vibrational wavefunctions. In the case of the absorption, the most important excited vibrational states contributing to the first shoulder are associated with the vibrational normal modes #77 and #84 of the electronic excited state. These modes correspond to vibrational frequencies of 1195 and 1302 wavenumbers and are represented in Fig. 1. In addition to H bending, twisting, and rocking motions, these modes involve motions of the molecular backbone that are similar to the changes of optimized geometry upon excitation. The shoulder around 3.25 eV has been identified in turn to be dominated by the same vibrational modes excited at the second harmonic.

In the case of the emission spectrum, the main vibronic transitions contributing to the shoulders are related to the vibrational normal modes of the electronic ground state and of their successive excitations. Single excitations of vibrations #83 (1311 cm^{-1}) and #114 (1668 cm^{-1}) give rise to the largest Franck–Condon contributions to the first shoulder while their double excitations – corresponding to the second harmonic – dominate the second shoulder. These modes also contain backbone displacements. With respect to π -conjugated systems like the oligomers of polyacetylene, polydiacetylene, and polyparaphenylenevinylene, the geometry relaxations in the excited state of the trimethine cyanine are small and thereof the vibronic structure is reduced to a shoulder adjacent to a dominant band while, for the former, the absorption and emission spectra exhibit several bands associated with a few vibrational coordinates [7,8,21].

In addition to the fundamental transition, the shape and width of the dominant band are associated with mode #19 for both absorption (261 cm^{-1}) and emission (266 cm^{-1}). This mode combines a global bending of the backbone with bending and twisting motions of the Me and Et groups, and with in-phase circular rotations of the C and H atoms of the benzene ring, like a modified ν_3 mode of benzene [31] where the H and C atoms move in the same direction (Fig. 2).

Fig. 3 reproduces the absorption and emission spectra in the wavelength space. Due to the change of abscissa, the two spectra are no more mirror image of each other, the emission spectrum being broader because it extends towards the larger wavelengths. The Stokes shift is small and amounts to 5 nm (0.036 eV in the energy space). The

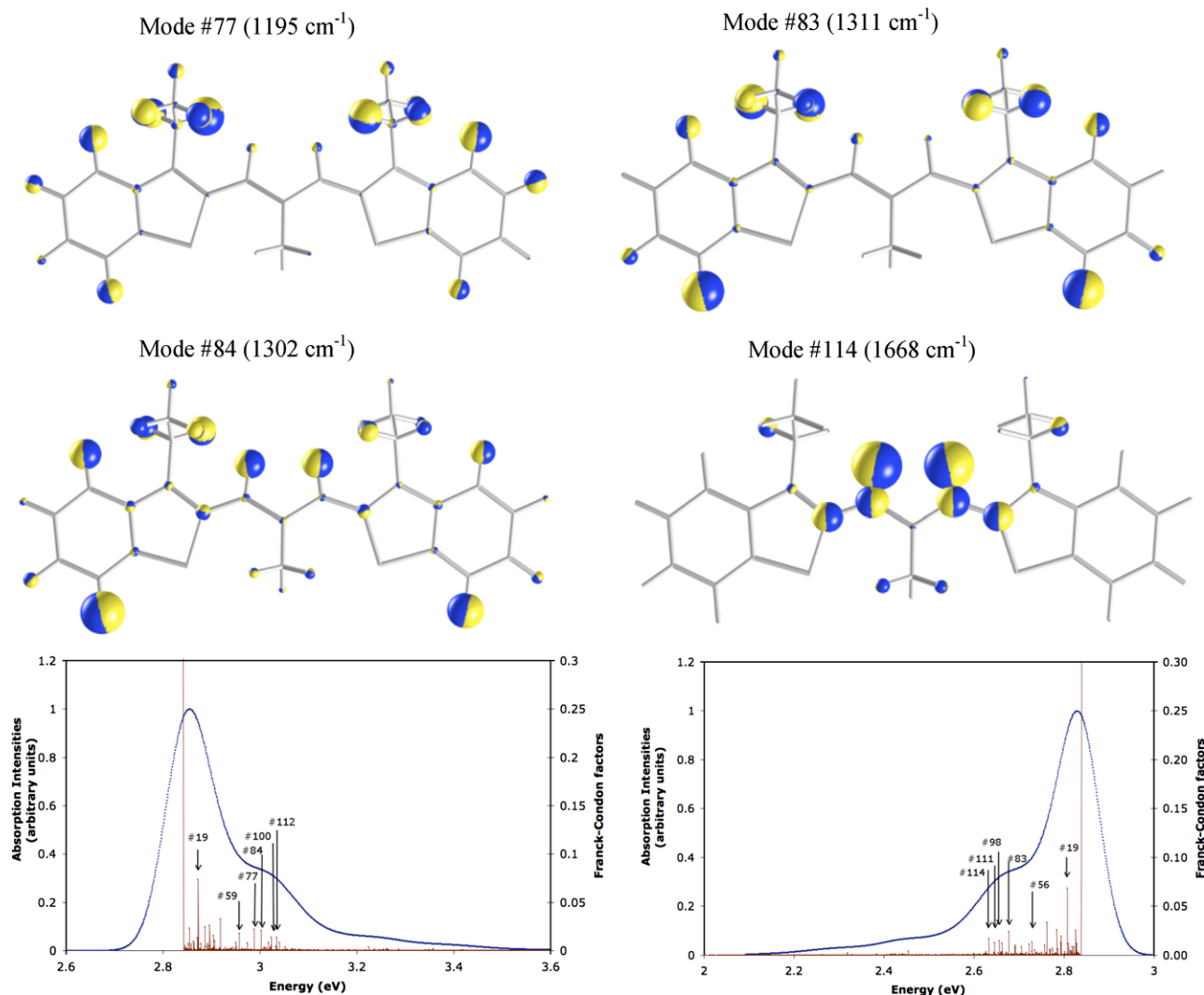


Fig. 1. (Bottom) Individual vibronic transitions to the absorption (left) and emission (right) spectra simulated at BH and HLYP/SV(P) level of approximation. Selected contributions are marked with arrows and numbered according to the vibrational normal modes of the electronic state. (Top) Representation of the vibrational normal modes mostly responsible for the vibronic structure of the shoulder. The surface of the spheres on the four top figures is proportional to the atomic displacements while the direction of atomic displacements is perpendicular to the color separation planes of the two hemispheres.

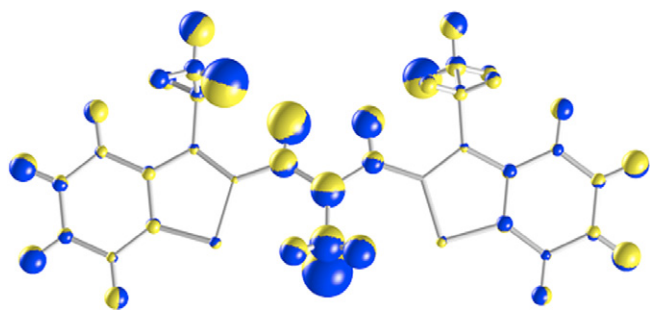


Fig. 2. Representation of the vibrational normal mode #19 of the electronic excited state. The surface of the spheres is proportional to the atomic displacements while the direction of atomic displacements is perpendicular to the color separation planes of the two hemispheres.

theoretical simulations nicely reproduce the shape of the experimental spectra of Nakashima and Kunitake [12].

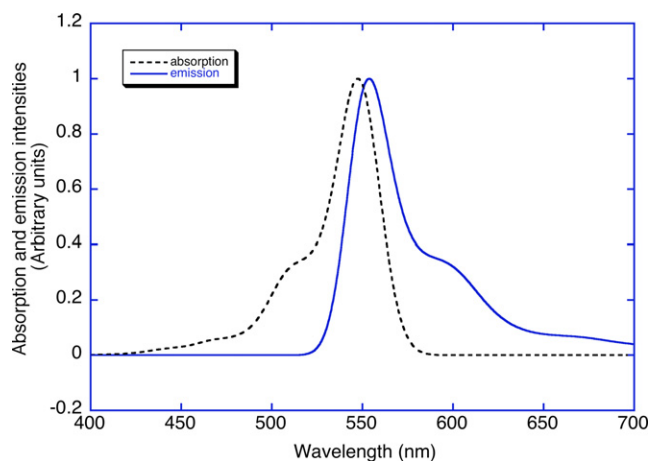


Fig. 3. Absorption (dashed) and emission (solid) spectra simulated at BH and HLYP/SV(P) level of approximation. A shift of 0.59 eV has been applied on the two theoretical spectra.

4. Conclusions

DFT and TDDFT schemes using the BH and HLYP exchange-correlation functional and the Doktorov approach to determine the Franck–Condon factors have been used to simulate the vibronic structure of the emission and absorption spectra of a typical trimethine cyanine dye. The results, which closely reproduce the shape of the experimental spectra, show that the geometry relaxations in the first dominant excited state are rather small with respect to other π -conjugated systems, which explains that the spectra are composed of a dominant band, one main shoulder, and small harmonic shoulders. The vibrational analysis of the simulated spectra have shown that the shoulders were not due to one specific normal mode but to a combination of a large number of transitions, the intensities of which being distributed due to the Duschinsky rotation effects. Based on this good reliability of this DFT/TDDFT method, future investigations will consider the absorption and emission spectra of aggregates of cyanine dyes.

Acknowledgement

This work is supported by the ‘Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT)’. V.L. and B.C. thank the FNRS for their Research Fellow and Research Director positions, respectively. The calculations have been performed on the Interuniversity Scientific Computing Facility (ISCF), installed at the Facultés Universitaires Notre-Dame de la Paix (Namur, Belgium), for which the authors gratefully acknowledge the financial support of the FNRS-FRFC and the ‘Loterie Nationale’ for the convention no. 2.4578.02, and of the FUNDP.

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