

## Prediction of Vibronic Coupling and Absorption Spectra of Dimers from Time-Dependent Density Functional Theory: The Case of a Stacked Streptocyanine

Julien Guthmuller,<sup>\*,†</sup> Freddy Zutterman,<sup>‡</sup> and Benoît Champagne<sup>†</sup>

*Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium, and Agfa-Gevaert N.V., Septestraat 27, B-2640 Mortsels, Belgium*

Received July 29, 2008

**Abstract:** Methods based on density functional theory calculations have been used to simulate the absorption spectra of a streptocyanine and of its covalently bonded dimer. Two approaches, based on multimode Franck–Condon overlap integrals, have been employed. In the first approach the monomer and the dimer are treated as single molecules, and the Franck–Condon factors are determined for both systems. The second approach is based on the diagonalization of the dimer Hamiltonian which is constructed from the monomer Franck–Condon overlap integrals and quantities describing the intermonomer electronic coupling. Both approaches succeed in reproducing the hypsochromic shift of the maximum of absorption occurring upon dimerization with an accuracy of 0.05 eV. The vibronic structure of the monomer is also in good agreement with experiment and depends little on the inclusion of Duschinsky rotation effects. The shape and relative intensity of the dimer spectrum is qualitatively reproduced by the two methods, each of them being able to describe most of the vibronic features. Moreover, accounting for the solvent effects in the calculation of the intermonomer electronic coupling improves the agreement with experiment by reducing the intensity of the maximum and by enlarging the spectrum at longer wavelengths.

### 1. Introduction

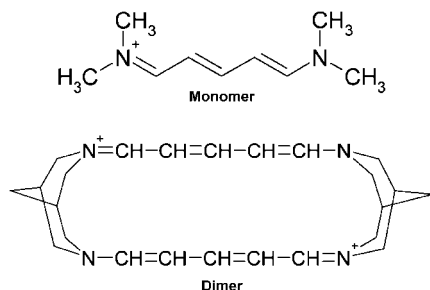
The description of the vibronic coupling in molecular aggregates and of the corresponding absorption spectrum have been the subject of many studies in the recent literature. For example, Einfeld et al.<sup>1</sup> have employed the so-called Coherent Exciton Scattering (CES) approximation<sup>2,3</sup> to rationalize the J and H bands of organic dye aggregates. Einfeld<sup>4</sup> has also recently proposed a simple method based on dipole–dipole coupled dimers to connect the absorption properties of the dimer to its conformation. The vibronic coupling in dimers has also been simulated from the diagonalization of the dimer Hamiltonian in a basis of monomer eigenstates.<sup>5–8</sup> This approach allows the investigation of the weak and strong electronic coupling limits and

enables the introduction of different approximations by eliminating some types of eigenstates from the basis set.<sup>6</sup> However, in the above-mentioned approaches<sup>5–8</sup> the absorption spectrum is usually described in terms of a single effective vibrational normal mode coordinate, while the electronic coupling parameters - representing the intermonomer interaction - are adjusted to reproduce the experimental spectrum. Moreover, a multimode vibronic treatment of coupled molecular dimers has been presented by Myers Kelley<sup>9</sup> and has been applied to the absorption, resonance Raman scattering, and hyper-Rayleigh scattering of molecular dimers.<sup>9,10</sup> In this approach the multimode vibronic properties are deduced from the analysis of the experimental resonance Raman intensities, and the strength of the intermonomer coupling is treated as an empirical parameter chosen to reproduce the experimental absorption spectrum. Finally, quantum chemical calculations describing the dimer as a supermolecule have been reported.<sup>11,12</sup> These methods allow

\* Corresponding author e-mail: julien.guthmuller@fundp.ac.be.

<sup>†</sup> Facultés Universitaires Notre-Dame de la Paix.

<sup>‡</sup> Agfa-Gevaert N.V.



**Figure 1.** Structure of the streptocyanine monomer and its covalently bonded dimer.

a direct evaluation of the intermonomer interaction, but their application has so far been limited to strongly coupled dimers in which the absorption spectrum can be represented as a single allowed electronic transition.

The aim of the present study is to investigate the ability of first principles theoretical schemes to predict the vibronic coupling and absorption spectrum of dimers. Two approaches based on time-dependent density functional theory (TDDFT) calculations are considered. In the first approach, similarly to our previous studies,<sup>13–15</sup> the absorption spectra of the monomer and of the dimer are simulated using DFT/TDDFT calculations treating the monomer and the dimer as simple molecules. In this approach, the geometrical relaxation and harmonic frequencies in the excited-state are computed for the state with the largest oscillator strength. Then, the absorption spectrum is constructed from the Franck–Condon (FC) factors, which are determined using a recursive scheme. In a second approach, the multimode vibronic treatment of coupled molecular dimers<sup>9</sup> is employed. In this method, the absorption spectrum of the dimer is obtained from the vibronic structure of the monomer and from intermonomer electronic coupling parameters. Furthermore, the amplitude of the coupling is evaluated from TDDFT calculations, which are performed at the dimer geometry. The two approaches are applied to the absorption properties of a streptocyanine dye and of its covalently bonded stacked dimer (Figure 1). These systems have been previously studied experimentally in methanol solution and theoretically at the INDO/S–CI level by Katoh et al.<sup>16</sup> The covalently bonded stacked dimer is particularly suitable because its geometry is well defined and does not require assuming the relative position of its chromophoric moieties which can be the case for many aggregates in solution.

## 2. Theoretical Method

**2.1. Vibronic Coupling and Franck–Condon Factors for a Single Molecule.** Quantum chemical calculations were carried out using the TURBOMOLE package.<sup>17</sup> The geometries and harmonic frequencies of vibration in the ground-state were calculated at the density functional theory (DFT) level by employing the B3LYP exchange–correlation (XC) functional and the TZVP basis set. The vertical transition energies  $E_{vert} = E_e - E_g$  were obtained from TDDFT with the same XC functional and basis set. In order to investigate the absorption properties, the geometry of the excited-state with the largest oscillator strength was optimized. The simulation of the absorption spectrum requires the determination

of multidimensional FC overlap integrals  $\langle \theta_{g0} | \theta_{ev} \rangle$ . In this notation  $|\theta_{g0}\rangle$  is the vibrational wave function of the electronic ground state (g) in its vibrational ground state (0), and  $|\theta_{ev}\rangle$  is the vibrational wave function of the electronic excited state (e), where  $\nu$  is a multi-index representing the harmonic quantum numbers of the 3N-6 vibrational normal modes. The FC overlap integrals were calculated with a homemade program (MultiFC), which makes use of the recursive relations given by P. T. Ruhoff.<sup>18</sup> The FC integrals were first calculated within the independent mode displaced harmonic oscillator model (IMDHOM), which only takes into account the geometrical differences between the ground and excited states. The absorption spectrum at 0 K is then obtained from eq 1:

$$A(\omega) \propto \omega \sum_{\nu} \frac{\Gamma}{\pi} \frac{\mu_{ge}^2 \langle \theta_{g0} | \theta_{ev} \rangle^2}{(\omega - E_{ev})^2 + \Gamma^2} \quad (1)$$

The summation is taken over all vibronic levels in the excited-state and the FC amplitudes are broadened by a Lorentzian function describing the homogeneous broadening with a full width at half-maximum (fwhm) equal to  $2\Gamma$ .  $\mu_{ge}$  is the dipole transition moment, and  $E_{ev}$  is the excitation energy accounting for both the electronic and vibrational levels. Typically, several thousands of FC overlap integrals are considered in order to get converged spectra. This method will be referred to in the following as the single molecule approach. Within this single molecule approach, the impact of the Duschinsky<sup>19</sup> rotations was investigated for the monomer. In that case, the determination of the FC overlap integrals requires the evaluation of the excited-state normal coordinates of vibration.

**2.2. Multimode Vibronic Theory of Coupled Monomers.** The absorption spectrum of the dimer was also simulated using a second approach based on the multimode vibronic theory of coupled identical monomers.<sup>9</sup> This approach allows the calculation of the dimer absorption spectrum only from the knowledge of the monomer properties and from the electronic coupling between both monomers. In addition to the ground state (g), only the single excited electronic state (e) - with the largest oscillator strength - is taken into account, and the two monomers (A and B) are coupled by an intermonomer electrostatic interaction. In the present treatment the dimer is initially in its ground state  $|(g0)_A(g0)_B\rangle$ , and the final excited states are sought as linear combinations of the basis vectors  $|(g0)_A(ev)_B\rangle$ ,  $|(ev)_A(g0)_B\rangle$ , in which  $\nu$  is again a multi-index representing the vibrational quantum numbers. For example, in this notation  $(g0)_A$  denotes the ground electronic and vibrational state of monomer A, while  $(ev)_B$  is a vibronic state of monomer B corresponding to the vibrational excitation  $\nu$  of the electronic excited state (e). Then, the dimer vectors  $|(g0)_A(ev)_B\rangle$  are constructed as products of the monomer states  $|(g0)_A\rangle$  and  $|(ev)_B\rangle$ . It is assumed in this basis that the vibrational excitation always strictly accompanies the electronic excitation. This approach has been referred to by Andrzejak and Petelenz<sup>6</sup> as the modified strong coupling (MSC) approach and will be referred to as so in the following. It is convenient to introduce the symmetric and antisymmetric dimer states

$$|g0, ev\rangle_{\pm} = \frac{1}{\sqrt{2}}(|(g0)_A(ev)_B\rangle \pm |(ev)_A(g0)_B\rangle) \quad (2)$$

In this basis the dimer Hamiltonian  $H = H_0 + V$  is block diagonal and is given by

$$\pm \langle g0, ev | H | g0, ev' \rangle_{\pm} = E_{ev} \delta_{vv'} + \Delta \delta_{vv'} \pm E_{exc} \langle \theta_{g0} | \theta_{ev} \rangle \langle \theta_{ev'} | \theta_{g0} \rangle \quad (3)$$

where  $E_{ev}$  are the monomer excited-state energies,  $E_{exc}$  is the exciton shift responsible for the splitting of the zero-order excited states,  $\Delta$  is a dimerization shift<sup>4</sup> describing both the modification of the initial and final state energies due to the intermonomer interaction, and  $\langle \theta_{g0} | \theta_{ev} \rangle$  are the monomer FC overlap integrals evaluated as discussed in section 2.1. The two blocks of eq 3 can be diagonalized separately and lead to the true eigenvalues  $E_{s\pm}$  and eigenvectors of the dimer excited states<sup>9</sup>

$$|\psi_{s\pm}\rangle = \sum_v C_{s\pm;0,v} |g0, ev\rangle_{\pm} \quad (4)$$

The calculation of the absorption spectrum of the dimer is then straightforward and can be performed by calculating the matrix elements of the dipole operator  $\vec{\mu}^A + \vec{\mu}^B$  between the ground-state and the excited vibronic states. For parallel H-dimers ( $\vec{\mu}_{ge}^A \cdot \vec{\mu}_{ge}^B = -\mu_{ge}^2$ ), these matrix elements are only nonzero for the (-) block. In this case, the absorption spectrum is given by<sup>9</sup>

$$A(\omega) \propto \omega \sum_s \frac{\Gamma}{\pi} \frac{2\mu_{ge}^2 (\sum_v C_{s-;0,v} \langle \theta_{g0} | \theta_{ev} \rangle)^2}{(\omega - E_{s-})^2 + \Gamma^2} \quad (5)$$

Adopting this MSC approach requires the knowledge of  $E_{exc}$  and  $\Delta$ . These quantities have often been used as parameters<sup>1-3,5-8</sup> tuned to fit to experiment. In this work they were evaluated from the vertical excitation energies of the monomer ( $E_{vert}^M$ ) and dimer ( $E_{vert}^D$ ) following eqs 6 and 7.

$$E_{exc} = \frac{E_{vert}^D(S_2) - E_{vert}^D(S_4)}{2} \quad (6)$$

$$\Delta = \frac{E_{vert}^D(S_4) + E_{vert}^D(S_2)}{2} - E_{vert}^M(S_1) \quad (7)$$

The electronic excited states  $S_2$  and  $S_4$  are the two excitonic components of the dimer, while  $S_1$  is the monomer excited-state with the largest oscillator strength (see section 3.1).

**2.3. Other Theoretical and Computational Aspects.** The effect of the solvent (methanol) on  $E_{exc}$  and  $\Delta$  was determined by using the program GAUSSIAN 03<sup>20</sup> (G03) and the integral equation formalism of the polarizable continuum model<sup>21</sup> (IEFPCM). The ground-state geometries and vertical transition energies of the monomer and dimer were calculated at the DFT/TDDFT/B3LYP/6-311G\* level of approximation. The calculations were also performed in vacuum and showed similar results to the one obtained with TURBOMOLE at the B3LYP/TZVP level ( $E_{exc}$  and  $\Delta$  differ at most by 0.01 eV between the two approaches).

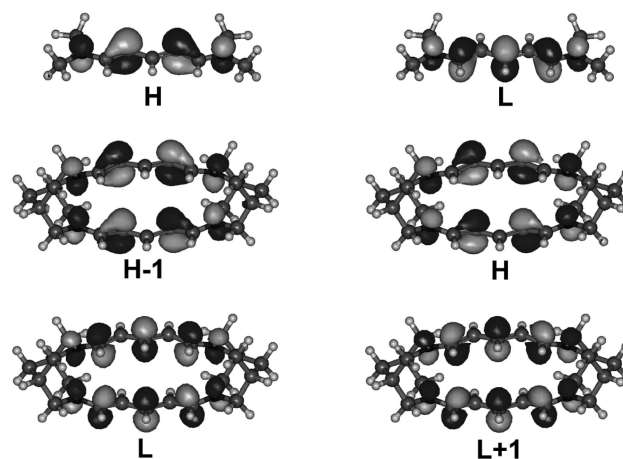
### 3. Results

**3.1. Excited States.** Table 1 presents the vertical transition energies and oscillator strengths of the monomer and dimer

**Table 1.** Vertical Excitation Energies, Oscillator Strengths, and Singly-Excited Configurations for the Lowest Energy Singlet Excited States of the Monomer and the Stacked Dimer<sup>a</sup>

	state	transition	wt (%)	B3LYP/TZVP (vacuum)		B3LYP/6-311G* (methanol)	
				$E_{vert}$ (eV)	f	$E_{vert}$ (eV)	f
monomer	$S_1$	H→L	99	3.77	1.410	3.65	1.487
dimer	$S_1$	H→L	98	2.41	<5.10 <sup>-4</sup>	2.46	<5.10 <sup>-4</sup>
	$S_2$	H→L+1	55	2.91	0.006	2.97	0.011
		H-1→L	45				
	$S_3$	H-1→L+1	97	3.74	<5.10 <sup>-4</sup>	3.77	<5.10 <sup>-4</sup>
	$S_4$	H-1→L	54	4.03	2.827	3.86	3.115
		H→L+1	44				

<sup>a</sup> The results in vacuum are calculated with TURBOMOLE at the TDDFT/B3LYP/TZVP level of approximation, and the effect of the solvent (methanol) is described using G03 with the IEFPCM approach at the TDDFT/B3LYP/6-311G\* level of approximation. H and L correspond to the highest occupied and lowest unoccupied molecular orbitals, respectively.



**Figure 2.** Molecular orbitals involved in the dominant configurations of the monomer and dimer low-energy excited states. H and L correspond to the highest occupied and lowest unoccupied molecular orbitals, respectively.

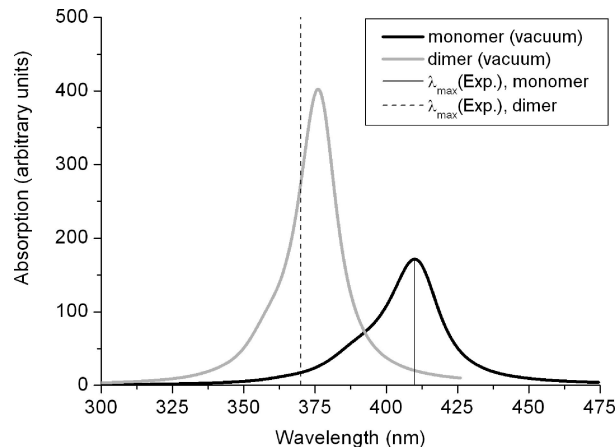
calculated in vacuum and methanol solution. The orbitals involved in the transitions are depicted in Figure 2 and have similar shapes in vacuum and methanol. The first excited-state of the monomer  $S_1$  is associated with a H→L configuration and presents a large oscillator strength of 1.410. Therefore, this state is responsible for the absorption properties of the molecule in this energy domain. Indeed, the next excited-state of the monomer,  $S_2$ , is calculated with a higher energy of 5.44 eV and a much smaller oscillator strength of 0.023. For the dimer, state  $S_4$  possesses the largest oscillator strength (2.827). This value is exactly twice larger than the  $S_1$  oscillator strength of the monomer. Therefore, state  $S_4$  corresponds to the allowed ( $\psi_{s-}$ ) component of the molecular exciton theory. Going from the monomer to the stacked dimer, the transition energy to this strongly dipole-allowed state shows a hypsochromic shift of 0.26 eV, which is characteristic of H-dimers. State  $S_2$  presents a small oscillator strength of 0.006 and is composed of comparable configura-

tions,  $H \rightarrow L+1$  and  $H-1 \rightarrow L$ , to  $S_4$ . Therefore,  $S_2$  can be associated to the forbidden ( $\psi_{s+}$ ) component of the molecular exciton theory. Two additional states,  $S_1$  and  $S_3$ , are also calculated, but they do not contribute to the absorption spectrum owing to their negligible oscillator strengths. Finally, note that the TDDFT results are in agreement with the molecular exciton theory, showing that only one electronic state is responsible for the absorption properties of the stacked H-dimer.

The inclusion of the solvent effects within the IEFPCM approach leads to non-negligible modifications of the vertical transition energies. On the one hand, a bathochromic shift is found for the allowed states  $S_1$  and  $S_4$  of the monomer and dimer, respectively. On the other hand, the  $S_2$  state of the dimer is hypsochromically shifted in methanol solution.

The exciton and dimerization shifts can then be evaluated in both environments from the energies of these states using eqs 6 and 7. In vacuum,  $E_{exc}$  and  $\Delta$  amount to  $-0.56$  eV and  $-0.30$  eV and to  $-0.45$  eV and  $-0.24$  eV in methanol, respectively. Thus, accounting for the effects of the solvent leads to a reduction of the absolute values of both  $E_{exc}$  and  $\Delta$ , which will be reflected in the simulated absorption spectra.

When comparison is performed with the experimental absorption maxima in methanol,<sup>16</sup> it appears that the calculated vertical transition energies of the monomer and dimer are overestimated. Indeed, the theoretical value of 3.77 eV for the monomer is 0.75 eV above the experimental maximum of 3.02 eV. Similarly, the calculated value of 4.03 eV for the dimer is 0.68 eV higher than the experimental value of 3.35 eV. In the case of the monomer, the inclusion of the geometry relaxation in the excited-state and of the vibrational structure leads to a theoretical maximum of 3.55 eV, which is still 0.53 eV above the experimental value. Additional corrections can be included by taking into account the interactions with the solvent. The calculations performed with the IEFPCM model and the program G03 for the vertical transition energies suggest that the solvent effect leads to a bathochromic shift of about 0.15 eV. Therefore, a value of 3.40 eV is our best theoretical estimate for the absorption maximum of the monomer in methanol. The remaining deviation of 0.38 eV with respect to experiment can be attributed to the limitations of the theoretical method. These limitations arise from the approximate XC functional (B3LYP) and from the treatment of the solvent. In the later, specific interactions with solvent molecules and, in the present case, counterions are not taken into account. In the former, one can distinguish between the limitations of both the exchange and correlation parts of the functional. For instance, Peach et al.<sup>22</sup> related the excitation energy underestimations to the charge transfer character of the transition. The situation is nevertheless more complicated here and involves correlation effects since the excitation energy is overestimated. However, in previous studies on structurally related cyanine dyes<sup>13,14</sup> it has been shown that these errors are rather systematic and positive. Consecutively, it has been shown that the overestimation of the excitation energies for compounds belonging to the same family can be corrected by applying a linear scaling procedure, which reduces the deviations within 0.1 eV.

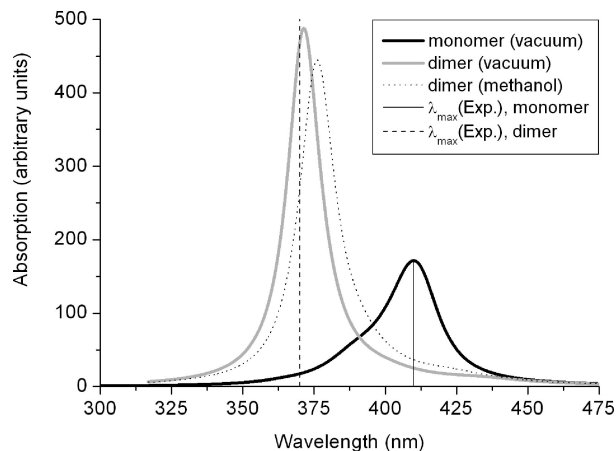


**Figure 3.** Absorption spectra of the monomer and stacked dimer within the IMDHOM. The results are obtained from a single molecule calculation at the TDDFT/B3LYP/TZVP level of theory in vacuum. The theoretical  $\omega_{e0,g0} = E_{e0} - E_{g0}$  origins have been shifted so that the experimental and theoretical absorption maxima of the monomer coincide. The broadening is described by a fwhm set to  $1000\text{ cm}^{-1}$ . The experimental maxima in methanol<sup>16</sup> (410 nm and 370 nm) are represented by vertical lines.

**3.2. UV/Visible Absorption Spectra.** Figure 3 presents the absorption spectra of the monomer and stacked dimer obtained from the single molecule approach within the IMDHOM. In order to correct the spectra for the systematic excitation energy overestimation, they were shifted so that the experimental and theoretical absorption maxima of the monomer coincide. Each vibronic transition was broadened by a Lorentzian function (see eq 1) with a fwhm of  $1000\text{ cm}^{-1}$ . The value of the fwhm was chosen in order to reproduce the experimental broadening of the spectra.<sup>16</sup> Due to the rather low resolution of the experimental spectra, only homogeneous broadening was assumed and appears adequate to simulate the observed broadening of the spectra. The spectrum of the monomer shows a vibronic shoulder between 375 nm and 400 nm. The spectrum of the dimer displays a narrower shape with a rather weak vibronic shoulder at shorter wavelengths. The ratio between the dimer and the monomer intensities at the maximum is equal to 2.35. The position of the dimer maximum with respect to the monomer is accurately predicted by the theory. An underestimation of 0.05 eV is found in comparison to experiment. The theoretical spectra also show a general good agreement with the experimental spectra reported by Katoh et al.<sup>16</sup> for both the intensities and the shapes. Indeed, for the monomer and dimer the shoulders at shorter wavelengths are properly reproduced by the calculation. Nevertheless, the experimental shoulder at larger wavelength for the dimer is not present in the calculated spectrum.

Figure 4 compares the monomer spectrum with the absorption spectra of the model dimer obtained from the diagonalization approach in the MSC basis set, where the (monomer) FC overlap integrals are evaluated within the IMDHOM. The spectra in vacuum and methanol were simulated using the exciton and dimerization shifts given in section 3.1. It should be mentioned that the spectrum in methanol was calculated using the monomer overlap integrals

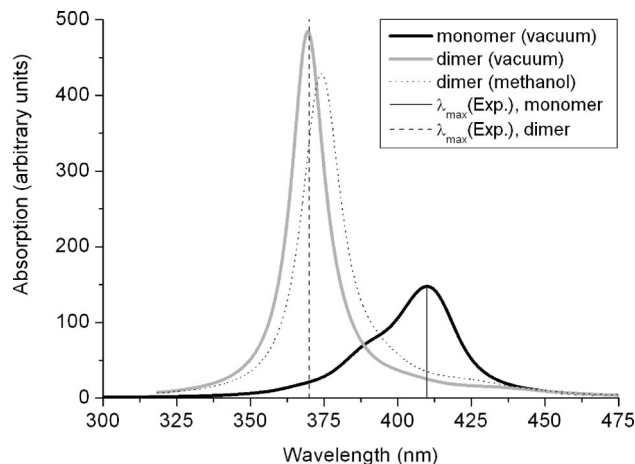




**Figure 4.** Absorption spectra of the monomer and dimer. The monomer spectrum is obtained within the IMDHOM while the dimer spectra are obtained from eq 5 after diagonalization of eq 3, of which the different quantities are evaluated at the TDDFT/B3LYP level of theory. The theoretical  $\omega_{e0,g0} = E_{e0} - E_{g0}$  origins have been shifted so that the experimental and theoretical absorption maxima of the monomer coincide. The broadening is described by a fwhm set to  $1000\text{ cm}^{-1}$ . The experimental maxima in methanol<sup>16</sup> (410 nm and 370 nm) are represented by vertical lines.

in vacuum and therefore that the effects of the solvent are only included in the exciton and dimerization shifts. This is however a good approximation since the shape of the theoretical monomer spectrum in vacuum is in good agreement with the experimental spectrum in methanol.<sup>16</sup> The positions of the absorption maxima for the dimer spectra are in very good agreement with experiment. The calculated values are underestimated by 0.01 eV and 0.05 eV in vacuum and methanol, respectively. The ratios between the dimer and monomer intensities are larger with values of 2.85 and 2.59 in vacuum and methanol, respectively. The dimer spectrum in vacuum shows a rather single band shape, whereas the spectrum in methanol displays a weak shoulder at larger wavelengths. The presence of this shoulder is connected to the smaller value of the exciton shift in methanol and is in agreement with the experimental spectrum reported by Katoh et al.<sup>16</sup>

Figure 5 shows similar spectra to Figure 4 obtained by including the Duschinsky rotation effect. On the one hand, the monomer spectrum displays a larger vibronic shoulder and a decreased intensity at the maximum in comparison to the IMDHOM scheme (Figures 3 and 4), which neglects Duschinsky rotations. On the other hand, the intensities of the dimer spectra are almost similar to those obtained from the monomer FC overlap integrals calculated within the IMDHOM approximation. This leads to larger dimer/monomer intensity ratios of 3.28 and 2.90 in vacuum and methanol, respectively. Moreover, the absorption maximum in vacuum is overestimated by 0.005 eV, whereas it is underestimated by 0.04 eV in methanol. In general, one can conclude that for this compound, the Duschinsky effect has a small impact on the shape and position of the dimer spectra. In agreement with previous studies dealing with absorption and resonance Raman spectra,<sup>23,24</sup> this shows that the



**Figure 5.** Absorption spectra of the monomer and dimer. The monomer spectrum is obtained including Duschinsky rotation effects, while the dimer spectra are obtained from eq 5 after diagonalization of eq 3, of which the different quantities are evaluated at the TDDFT/B3LYP level of theory. The theoretical  $\omega_{e0,g0} = E_{e0} - E_{g0}$  origins have been shifted so that the experimental and theoretical absorption maxima of the monomer coincide. The broadening is described by a fwhm set to  $1000\text{ cm}^{-1}$ . The experimental maxima in methanol<sup>16</sup> (410 nm and 370 nm) are represented by vertical lines.

IMDHOM can be considered as a good first approximation for the determination of the vibronic structure of excited states.

**3.3. Further Discussion.** As presented in the previous section, general agreement is found between both approaches and the experimentally reported spectra: i) the position of the dimer maximum with respect to the monomer is predicted with an accuracy of about 0.05 eV and ii) the global vibronic structure and shapes of the spectra are reproduced. Nevertheless, some remarks can be drawn concerning the differences and limit of applicability of both approaches. The comparison between the single molecule approach on the stacked dimer and the MSC results on the model dimer reveals some differences. The single molecule calculation shows a shoulder at shorter wavelengths, whereas the MSC method in methanol produces a shoulder at larger wavelengths. Subsequently, the second approach leads to a further increase of the intensity of the absorption maximum.

On the one hand, the single molecule calculation on the stacked dimer is based on the assumption that the Born–Oppenheimer approximation is valid for the dimer as a whole. As a consequence, the dimer displays a spectrum comparable to the monomer with a regular FC progression at shorter wavelengths. On the other hand, as discussed recently by Andrzejak and Petelenz,<sup>6</sup> the MSC approach is truly valid for weak electronic coupling (exciton shift small with respect to the monomer bandwidth) and can be considered as a good approximation for intermediate electronic coupling (exciton shift comparable to the monomer bandwidth). This approach is able to describe the complex interactions between the vibronic states in the intermediate coupling regime, which lead to a vibronic shoulder at longer wavelengths. However, when the exciton shift becomes large the intensity is mainly transferred to a single band, and the

method is unable to reconstruct the regular FC progression at shorter wavelengths. For the dimer investigated in this study the ratio between the exciton shift and the monomer bandwidth indicates a coupling lying between the intermediate and strong coupling limits. This is also suggested by the rather short optimized intermonomer spacing of 4.07 Å. Anyway, each method appears to be able to reproduce most features of the dimer absorption spectrum, partly due to the rather low resolution of the spectra. Improvements can however be achieved within the second approach by including in the dimer basis set vectors where both monomers are vibrationally excited. In this situation, it has been shown<sup>5,6</sup> using the monomode dimer model that the inclusion of these states strongly improves the description of the absorption spectrum for large exciton shifts. In particular, the regular FC progression is reproduced in the strong electronic coupling limit. The inclusion of such effects in a multimode approach has been presented by Myers Kelley<sup>9</sup> by employing experimentally determined quantities. In the future, an efficient implementation of such a scheme based on theoretical quantum chemistry approaches is expected to lead to more accurate predictions of the dimers and aggregates absorption spectra. Nevertheless, the use of the MSC approximation is still meaningful in situations like here and can lead to quantitative predictions for the apparent energy shift arising upon dimerization.

#### 4. Conclusions

DFT and TDDFT schemes have been used to simulate the absorption spectra of a streptocyanine and of its covalently bonded dimer. Two approaches, based on multimode FC overlap integrals, have been employed. The first approach corresponds to a single molecule calculation where the FC factors are determined for the monomer and the stacked dimer separately. The second approach is based on the diagonalization of the dimer Hamiltonian, which is constructed from the monomer FC overlap integrals and quantities ( $E_{exc}$  and  $\Delta$ ) describing the intermonomer electronic coupling. Both approaches succeed in reproducing the hypsochromic shift of the maximum of absorption occurring upon dimerization with an accuracy of 0.05 eV. The vibronic structure of the monomer is also in good agreement with experiment and depends little on the inclusion of Duschinsky rotation effects. The shape and relative intensity of the dimer spectrum is qualitatively reproduced by the two methods, each of them being able to describe most of the vibronic features. Moreover, accounting for the solvent effects in the calculation of the exciton and dimerization shifts improves the agreement with experiment by reducing the intensity of the maximum and by enlarging the spectrum at longer wavelengths. Finally, this study illustrates the efficiency of quantum chemical calculations for the prediction of dimer absorption spectra and can be seen as a first step toward first principles description of vibronic coupling in molecular aggregates.

**Acknowledgment.** One of the authors (J.G.) thanks the Fund for Scientific Research (F.R.S.)-FNRS for his post-

doctoral grant under the convention No. 2.4.509.04.F. The other author (B.C.) thanks the F.R.S.-FNRS for his research director position. The authors thank the IWT (Instituut voor Innovatie door Wetenschap en Technologie) for financial support. 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.

#### References

- (1) Eisfeld, A.; Briggs, J. S. *Chem. Phys.* **2006**, 324, 376.
- (2) Eisfeld, A.; Briggs, J. S. *Chem. Phys.* **2002**, 281, 61.
- (3) Eisfeld, A.; Briggs, J. S. *Phys. Rev. Lett.* **2006**, 96, 113003.
- (4) Eisfeld, A. *Chem. Phys. Lett.* **2007**, 445, 321.
- (5) Eisfeld, A.; Braun, L.; Strunz, W. T.; Briggs, J. S.; Beck, J.; Engel, V. J. *Chem. Phys.* **2005**, 122, 134103.
- (6) Andrzejak, M.; Petelenz, P. *Chem. Phys.* **2007**, 335, 155.
- (7) Fulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1964**, 41, 2280.
- (8) Kopainsky, B.; Hallermeier, J. K.; Kaiser, W. *Chem. Phys. Lett.* **1981**, 83, 498.
- (9) Kelley, A. M. *J. Chem. Phys.* **2003**, 119, 3320.
- (10) Leng, W.; Würthner, F.; Kelley, A. M. *J. Phys. Chem. B* **2004**, 108, 10284.
- (11) Gavrilenko, V. I.; Noginov, M. A. *J. Chem. Phys.* **2006**, 124, 044301.
- (12) Clark, A. E.; Qin, C.; Li, A. D. Q. *J. Am. Chem. Soc.* **2007**, 129, 7586.
- (13) Guillaume, M.; Champagne, B.; Zutterman, F. *J. Phys. Chem. A* **2006**, 110, 13007.
- (14) Champagne, B.; Guillaume, M.; Zutterman, F. *Chem. Phys. Lett.* **2006**, 425, 105.
- (15) Guillaume, M.; Liégeois, V.; Champagne, B.; Zutterman, F. *Chem. Phys. Lett.* **2007**, 446, 165.
- (16) Katoh, T.; Inagaki, Y.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1997**, 70, 2279.
- (17) *TURBOMOLE, Program Package for ab initio Electronic Structure Calculations*; University of Karlsruhe: Germany, Ver. 5.71.
- (18) Ruhoff, P. T. *Chem. Phys.* **1994**, 186, 355.
- (19) Duschinsky, F. *Acta Physicochim. URSS* **1937**, 7, 551.
- (20) *Gaussian 03, Revision C.02*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghava-

- chari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Wallingford CT, 2004.
- (21) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.
- (22) Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J. *J. Chem. Phys.* **2008**, *128*, 044118.
- (23) Guthmuller, J.; Champagne, B. *J. Chem. Phys.* **2007**, *127*, 164507.
- (24) Guthmuller, J.; Champagne, B. *J. Phys. Chem. A* **2008**, *112*, 3215.

CT8003047