

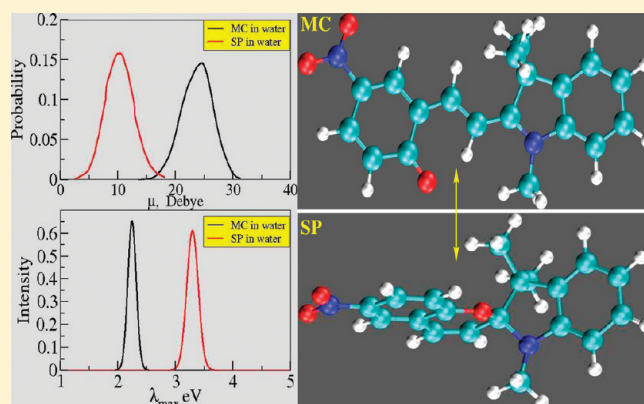
# Solvent Dependence of Structure, Charge Distribution, and Absorption Spectrum in the Photochromic Merocyanine–Spiropyran Pair

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**ABSTRACT:** We have studied the structures and absorption spectra of merocyanine, the photoresponsive isomer of the spiropyran (SP) –merocyanine (MC) pair, in chloroform and in water solvents using a combined hybrid QM/MM Car–Parrinello molecular dynamics (CP-QM/MM) and ZINDO approach. We report remarkable differences in the molecular structure and charge distribution of MC between the two solvents; the molecular structure of MC remains in neutral form in chloroform while it becomes charge-separated, zwitterionic, in water. The dipole moment of MC in water is about 50% larger than in chloroform, while the value for SP in water is in between, suggesting that the solvent is more influential than the conformation itself in deciding the dipole moment for the merocyanine–spiropyran pair. The calculations could reproduce the experimentally reported blue shift in the absorption spectra of MC when going from the nonpolar to the polar solvent, though the actual value of the absorption maximum is overestimated in chloroform solvent. We find that the CP-QM/MM approach is appropriate for structure modeling of solvatochromic and thermochromic molecules as this approach is able to capture the solvent and thermal-induced structural changes within the solute important for an accurate assessment of the properties.



## 1. INTRODUCTION

The term “photochromism”<sup>1</sup> denotes a special case of a photochemical reaction where a reversible molecular transformation takes place between two geometrical isomers with a significant change in the absorption spectrum upon exposure to electromagnetic radiation. The phenomenon of photochromism was discovered by Fischer and Hirshberg way back in 1952<sup>2</sup> and was then observed in both organic and inorganic molecules. Photochromism also finds its place in biology; e.g., our vision process is crucially guided by the photochromic transformation of the retinaldehyde molecule.<sup>3</sup> Besides the significant difference in the absorption spectra of the two isomers, several other molecular and bulk properties, like refractive index, dielectric constant, redox potential, are also different in the two forms.<sup>4</sup> One of the most common applications of photochromic materials is the color change of an eyeglass when exposed to sunlight. Apart from this simple application, photochromic materials have gained substantial research attention owing to their tremendous potential in various photonic devices such as erasable optical memory media in recordable compact disks, variable frequency filters, attenuators, phase shifters, and fast nonlinear optical switchers, to mention a few examples.<sup>4–8</sup> At present, a large

number of photochromic pairs of organic molecules is available which already have proved their value in various applications. These include spiropyran, spirooxazine, fulgide, diarylethenes, salicylideneimines, azobenzene, stilbene derivatives, etc.<sup>4</sup> Of the many classes of photochromic compounds identified so far, the spiropyran type of compounds have been studied most extensively both from the experimental and theoretical view points.<sup>9</sup> In the spiropyran type molecules, two planar cycles are attached by a common  $sp^3$  hybridized carbon atom which prevents the system from extensive  $\pi$  delocalization, and as a consequence, the lowest electronic transition in spiro isomer (SP) normally takes place in the near-ultraviolet region. Upon irradiation by ultraviolet light, the carbon–oxygen bond of the SP isomer is broken and subsequent rotation across the C–C bond leads to the formation of the photoresponsive merocyanine (MC) form.<sup>10</sup> The MC isomer has an intense color with an absorption maximum in the range of 500–700 nm<sup>9</sup> while the absorption maximum for the SP form has been recorded in the range of 300–400 nm.<sup>9,11</sup> The

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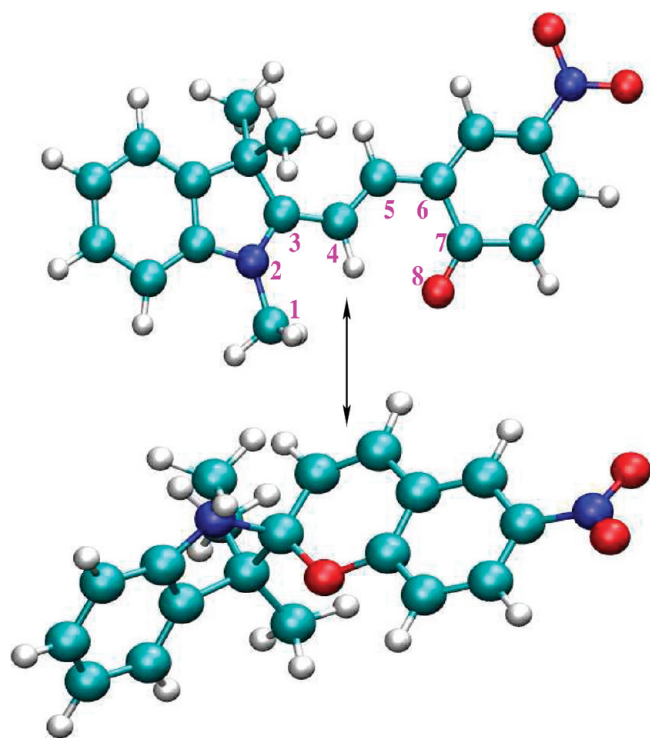


Figure 1. Molecular structure of the MC–SP pair.

photoinduced reversible transformation of the two isomers (SP and MC) is depicted in Figure 1. It is worthwhile to mention that the MC form is thermally unstable and rapidly turns back into the closed SP form and the appropriate substitution of electron withdrawing and donating groups in MC can stabilize this form. Several theoretical works have already been carried out to elucidate the thermal and light induced ring-opening and ring-closing of SP and MC, respectively.<sup>10</sup> Gómez et al.<sup>12</sup> performed *ab initio* calculations at the CASSCF/CASPT2 level of theory on the thermal and photochemical ring closing mechanism of MC and suggested that the  $S^2/S^1-S^1/S^0$  conical intersection is mainly responsible for the high speed of this reaction. On the other hand, Cottone and co-workers<sup>10</sup> in their thorough investigation on the SP  $\rightarrow$  MC isomerization mechanism at the level of density functional theory (DFT) proposed that the ring-opening does not occur in a synchronous one-step mechanism, but rather that the process is a multistep reaction with a conformational changeover of MC being the rate-determining step.

Apart from the isomerization mechanism, the solvatochromism of MC is an important aspect which is relatively unexplored at the theoretical level albeit a large body of experimental results is available in the literature.<sup>9</sup> Nadolski et al.<sup>13</sup> argued that in the MC form the ground state is more polar than the excited state and as result a polar solvent will stabilize the ground electronic state, resulting in a blue shift of the absorption maxima. Kinashi et al.<sup>14</sup> also monitored the absorption spectra of MC in various matrices and solvents and their findings were in line with those of Nadolski et al.<sup>13</sup> Baraldi and co-workers<sup>15</sup> explored the absorption and emission spectra of some MC dyes by means of theoretical calculations with a solvation CS INDO model and tried to interpret the experimental results. In all these calculations there is no explicit addition of solvent molecules, something that fails to provide the correct ground state geometry of the molecule

which is actually essential for getting the correct vertical transition energy and Franck–Condon distribution of the system under consideration. In this article, we have investigated the solvent effect on structure and absorption spectra using approaches where the solvents are treated explicitly in both the structure and spectra modeling.

For modeling the finite temperature absorption spectra and other electronic properties of organic molecules, a sequential approach is commonly employed where the first step is to obtain the finite temperature solute–solvent supermolecular structures and the next step is to calculate the absorption spectrum as an average property over these configurations.<sup>16–20</sup> Particularly, a sequential Monte Carlo/quantum mechanics (S-MC/QM) approach has been extensively used and reported to be successful in modeling the absorption spectra of many organic molecules in solvents.<sup>16</sup> In this approach, the solute–solvent structures at finite temperature are obtained from a Monte Carlo simulation, while the absorption spectra are obtained from the semiempirical INDO/CIS approach. There are also reports of absorption spectra using S-MD/QM where the structure for solute–solvent system is obtained from force-field molecular dynamics techniques.<sup>17</sup> Recently, in the place of MD and MC techniques, the Car–Parrinello hybrid QM/MM technique has been used to model the structure of solute–solvent systems.<sup>18–20</sup> We have shown that this technique is the most advantageous one when the solvent- and thermal-induced structural changes in the solute are significant. It is very common for the solvatochromic molecules to display different molecular structures, like neutral, cyanine-like and zwitterionic structures, depending upon the nature of solvents.<sup>21</sup> Accounting for such solvent-induced geometrical changes in the solute turn out to be most important for accurate property calculations. This follows simply from the fact that many of the properties such as absorption spectra, hyperpolarizability, two photon absorption cross sections, etc., are very sensitive to the molecular geometry.<sup>22</sup> For example, in the case of stilbazolium merocyanine dyes, the change in molecular geometry from zwitterionic to neutral geometry leads to a red-shift in the absorption spectra, instead of a blue-shift, with the increase in solvent polarity.<sup>20,23</sup> Moreover, the hyperpolarizability of the zwitterionic form has been reported to be many order larger than for the neutral form in compounds like phenol blue and dimethylamino nitrostilbene.<sup>22,24</sup>

In this article, we use a combined CPMD/QM-MM<sup>25–27</sup> and ZINDO/S<sup>28</sup> procedure to model the structure and absorption spectra of MC in polar and nonpolar solvents. We use the CPMD-QM/MM procedure to derive an ensemble of configurations for MC in chloroform and water solvents. The ZINDO/S scheme is then used to calculate the absorption spectra for MC in water and chloroform solvents by a judicious selection of configurations from the trajectory. The reasonable computational cost of ZINDO/S gives the possibility to include additional solvation shells in order to systematically analyze their contributions to the solvatochromic shift. We have used the solute–all-atoms and solvent center of mass radial distribution function to define different solvation shells around the MC molecule. We have also used the same sequential approach to model the structure and absorption spectra of SP form in water.

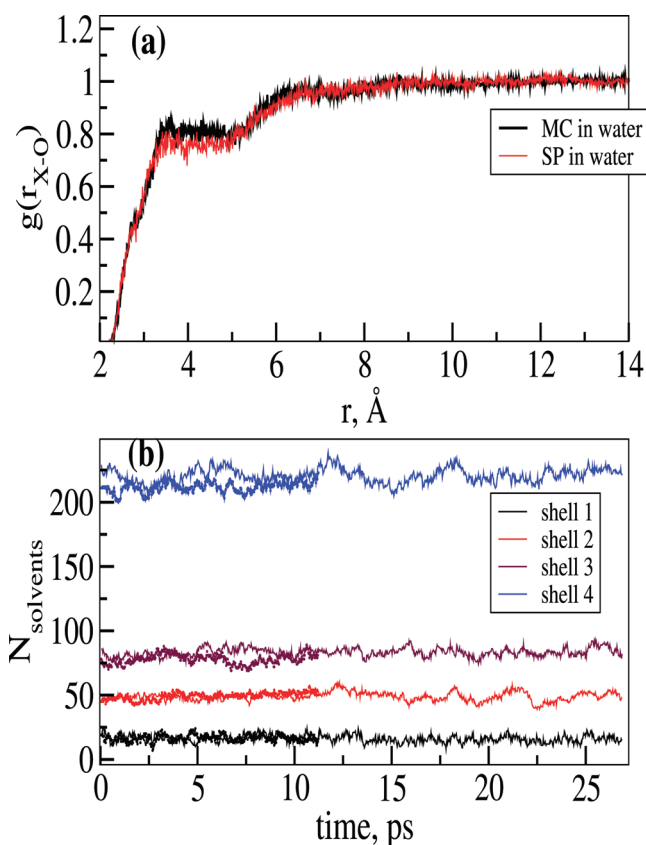
## 2. COMPUTATIONAL DETAILS

### 2.1. Car–Parrinello Molecular Dynamics Calculations.

The CP-QM/MM calculations for MC in chloroform and water

solvents have been carried out for the equilibrated structures of MC/CHCl<sub>3</sub> and MC/water solute–solvent systems obtained from molecular dynamics calculations. First, we have optimized a single molecule of MC at the HF level using the 6-31+G\* basis set using the Gaussian09 software.<sup>29</sup> The optimized structure along with the GAFF<sup>30</sup> force-field has been used to define MC for the initial molecular dynamics calculations. The MC molecule has been solvated with 11014 water molecules in an orthorhombic box with a size of approximately 75.3, 67.9, and 65.6 Å. The water molecules, described using the TIP3P force field,<sup>31</sup> were allowed to equilibrate under ambient condition using molecular dynamics (MD) calculations in an isothermal–isobaric ensemble for a time scale of 100 ps until the structural quantities such as density are converged. The MD calculations were carried out using the SANDER module of the Amber8 software.<sup>32</sup> A similar procedure has been followed to obtain the equilibrated structure for the MC/CHCl<sub>3</sub> system. In this case, the simulation box size was approximately, 75.2, 67.6, and 66.2 Å and contained a single MC molecule and 2456 solvent molecules. The final configurations obtained for MC/CHCl<sub>3</sub> and MC/water systems were used as input for the subsequent CP-QM/MM calculations. These calculations were carried out in a QM/MM setup,<sup>25–27</sup> where the MC molecule is treated using density functional theory, and the solvent molecules are treated with a molecular mechanics force field (TIP3P<sup>31</sup> for water and GAFF<sup>30</sup> for chloroform). The QM/MM implementation used here includes the coupling between the solute QM region and the instantaneous electrostatic field arising from the dynamic MM environment. The interaction between the QM and MM systems involves electrostatic, short-range repulsion, and long-range dispersion interaction terms and hence accounts for the polarization of the solute by solvent environment. We have used the Becke exchange functional and the Lee, Yang, and Parr correlation functional as expressed in the BLYP gradient-corrected functional<sup>33</sup> and the Troullier–Martins norm-conserving pseudopotentials.<sup>34</sup> The electronic wave function is expanded in a plane wave basis set. The energy cutoff employed was 80 Ry and the fictitious electronic mass used was 600 amu. We have used 5 au as the time step for the integration of the equation of motion. The CP-QM/MM calculations start with a quenching run that relaxes the initial structure to the Born–Oppenheimer surface within the QM/MM framework. The temperature scaling run was then carried out for 0.5 ps to rise the system temperature to 300 K. Finally, the system was allowed to sample in canonical ensemble by connecting it to a Nose–Hoover thermostat. The length of the production run was approximately, 28 ps. In order to investigate the molecular structure, charge distribution, dipole moment of the SP form in water we have also carried out CP-QM/MM calculations for SP molecular structure in water solvent. The simulation box size was approximately, 73.3, 67.6, and 68.1 Å. The SP/water system contained a single molecule of SP and 11102 water molecules and taken from the equilibrated MD simulation in NPT ensemble. Since during the CP-QM/MM simulation the SP molecule in water interconverts spontaneously to MC form at ambient temperature, we have constrained the C<sub>3</sub>–O<sub>8</sub> (see Figure 1) bond to the optimal value. The total time scale for the production run was in this case approximately 12 ps.

**2.2. Calculations of Absorption Spectra.** The absorption spectra calculations for MC and SP forms in solvents were performed using the semiempirical spectroscopic-ZINDO method<sup>28</sup> as implemented in Gaussian09.<sup>29</sup> This approach has been shown to be highly successful in computing absorption spectra of number of organic molecules in solvent and protein



**Figure 2.** (a) Solute-all-atoms and solvent center of mass rdf for MC and SP in water and (b) time evolution of the number of solvent molecules in different solvation shells for MC and SP in water.

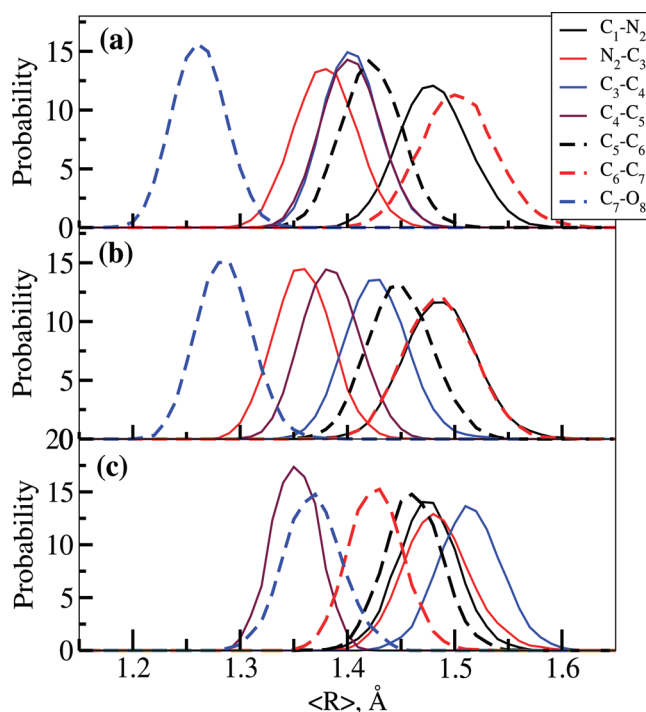
environments<sup>35</sup> and has on many occasions shown to outperform the TD-DFT and TD-HF methods.<sup>36</sup> Moreover, the absorption spectra calculations using INDO–CIS are not computationally expensive and can therefore be used to calculate the spectra for the solute molecule with explicitly including several solvation shells or the protein environment within the QM region.<sup>35</sup> It has often been reported in the literature that the explicit inclusion of solvents is important for accurately reproducing absorption spectra and other properties when the solute–solvent interaction is site-specific and involves charge transfer and hydrogen bonding interaction,<sup>16,37,38</sup> advocating the importance to treat water solvents explicitly within QM region as the solute. We have thus performed the calculations for MC and SP forms in water including different solvation shells as an attempt to investigate the convergence of absorption spectra with solvation shells. Overall, we have carried out five different sets of calculations which differ in the number of solvent molecules included. Different solvation shell structures have been characterized based on a solute-all-atoms and solvent center of mass minimum distance radial distribution function (rdf) which is referred to as  $g(r_{X-O})$ . For nonspherical molecules, this rdf has been reported to be more relevant than the solute and solvent center of mass rdf.<sup>39</sup> The  $g(r_{X-O})$  rdf computed for the MC and SP forms in water are shown in Figure 2a. On the basis of the shoulder and peaks seen in the  $g(r_{X-O})$  rdf, we have defined different solvation shells and for the property calculations we have then used solute and the solvents with these different solvation shells included. We see a shoulder appearing at



$r \approx 2.85 \text{ \AA}$  and attributes this to the first solvation shell. Usually, the solvent molecules in this shell contribute to the largest extent to the property since these solvent molecules are in direct contact with the solute and are involved in charge transfer and hydrogen bonding interaction. We define the solvent molecules up to a distance  $4.0 \text{ \AA}$  as the second solvation shell, while the third solvation shell includes solvent molecules in the distance range  $4 < r < 5.1$  from the solute atoms. We have also defined a fourth solvation shell that includes solvent molecules up to  $8 \text{ \AA}$ . Figure 2b shows the time evolution of solvent molecules in different solvation shells for the MC and SP in water systems. The fluctuation in the number of solvent molecules around a constant value shows that the solute–solvent structures are equilibrated in all the cases. The average number of solvent molecules in the first, second, third and fourth solvation shells are, respectively, 16, 49, 84, and 220 for the case of MC in water and 17, 49, 78, and 212 for the case of SP in water. This shows that the conformational change from spiropyran to merocyanine does not significantly affect the solvation shell structure and the number of solvent molecules in the solvation shells even though as will be discussed in section 3.1, it significantly affects the intramolecular structure. The calculations are referred to as MM-1 to MM-4 where the digit refers to the solvation shells included. For the solute (ie MC or SP form) alone, we have carried out absorption spectra calculations which are referred to as MM-0. The excitation energies are calculated for different solute–solvent supermolecular clusters using the ZINDO/S model. In these calculations, the MC molecule contributes to 122 valence electrons and each water molecule contributes to 8 valence electrons. For MC in chloroform solvent the absorption spectra calculation has been carried out again using ZINDO but with a polarizable continuum model for the solvent description since the chloroform solvent is not involved in site-specific interaction with the solute molecule.<sup>37,38</sup> This set of calculations will be referred as the MM-1 model while the calculations carried out solely for the solute molecular structures obtained from the CP-QM/MM simulations will be referred as MM-0.

### 3. RESULTS AND DISCUSSION

**3.1. Molecular Structure and Charge Distribution of MC and SP Forms in Solvents.** For the molecules that exhibit a large solvatochromic shift, the solvent-induced geometrical changes in molecular structure are quite significant.<sup>21,40</sup> Depending on the solvent polarity, these molecules have a tendency to prevail in different molecular structures, namely neutral, cyanine-like, and charge-separated zwitterionic. Many properties like absorption spectra, hyperpolarizability ( $\beta$ ) and TPA cross sections have a strong dependence on the nature of molecular structure.<sup>22</sup> There is a well-established relationship between the bond-length alternation parameter which defines the nature of molecular structure and  $\beta$ <sup>22</sup> which goes to zero for cyanine-like structures. Similarly, there are detailed theoretical studies on stilbazolium merocyanine where the zwitterionic structure absorb in the longer wavelength than the neutral structure. So, reproducing the molecular geometry is of primary importance for an accurate property calculation of these solvatochromic/thermochromic molecules. Accordingly, we have looked into the molecular geometry of MC in chloroform and water solvents and the SP form in water solvent. As discussed above the MC form refers to the open form of the spiropyran–merocyanine pair while SP refers to the closed form.<sup>41</sup> In particular, when there is



**Figure 3.** Bond length distributions of MC (a) in chloroform and (b) in water and SP in (c) water.

spiropyran–merocyanine interconversion larger changes in molecular geometry occurs around  $C_3$  (refer Figure 1) atom which becomes  $sp^2$ -hybridized from  $sp^3$ -hybridized. Interestingly, the MC form can exist in both neutral and charge-separated zwitterionic form depending upon the solvent polarity while for the SP form, no such solvent-induced geometrical change is feasible. So, the SP form has been studied only in water solvent. We have computed the distance distribution for bond lengths along the conjugation pathway since these are very sensitive to solvent polarity and conformational nature of the molecule (i.e., spiropyran or merocyanine). The distance distributions for various bonds along the conjugation pathway are computed for the entire trajectory of the CPMD-QM/MM simulations and are plotted in Figure 3. Parts a–c of Figure 3 correspond to the MC form in chloroform, the MC form in water, and the SP form in water, respectively. The MC forms in chloroform and in water differ considerably with respect to the spacer group (i.e.,  $CH-CH$ ) geometry between the donor and acceptor group substituted aromatic moieties. In the neutral form of MC, the  $C_3-C_4$  and  $C_5-C_6$  bonds have been proposed to have double bond character while the  $C_4-C_5$  bond has single bond character (see Table 1). The reverse has been proposed in the case of the zwitterionic form of MC. The present calculations suggest a slightly different behavior for the molecular structure of MC in chloroform and water solvents. For MC in chloroform,  $C_3-C_4$  and  $C_4-C_5$  bonds have equal bond lengths while  $C_5-C_6$  has a slightly larger bond length. Rather, for stilbazolium merocyanine in chloroform solvent, we have reported cyanine-like structure where all the bond lengths along the conjugation pathway are equal.<sup>20</sup> The difference arises due to the difference in the aromatic moieties attached at the either sides of the  $CH=CH$  group in MC. It is also interesting to note that the  $C_3-C_4$  and  $C_5-C_6$  bond lengths are not quantitatively equal as in stilbene or

Table 1. Average Bond Lengths

system	MC in chloroform	MC in water	SP in water
C <sub>1</sub> –N <sub>2</sub>	1.48	1.49	1.48
N <sub>2</sub> –C <sub>3</sub>	1.38	1.36	1.48
C <sub>3</sub> –C <sub>4</sub>	1.40	1.43	1.51
C <sub>4</sub> –C <sub>5</sub>	1.40	1.39	1.35
C <sub>5</sub> –C <sub>6</sub>	1.42	1.45	1.46
C <sub>6</sub> –C <sub>7</sub>	1.50	1.49	1.43
C <sub>7</sub> –O <sub>8</sub>	1.26	1.29	1.37

azobenzene backbones due to the difference in chemical nature of the groups connected to these bonds. As expected for the zwitterionic form of MC in water, the C<sub>4</sub>–C<sub>5</sub> bond length is shorter than the C<sub>3</sub>–C<sub>4</sub> and C<sub>5</sub>–C<sub>6</sub> bond lengths. Moreover, as expected for the zwitterionic form of MC in water, the C<sub>7</sub>–C<sub>8</sub> bond is slightly larger than in chloroform solvent. Overall, the solvent-induced geometrical changes are significant for the MC form where in chloroform solvent the molecular structure is in neutral form, while in water solvent the structure is closer to a zwitterionic form. It is instructive to compare the MC and SP forms in water solvent. As we mentioned earlier, there is a large difference in structure between these two forms which can be seen in Figure 3, parts b and c. In the SP form, C<sub>4</sub>–C<sub>5</sub> is proposed to have double bond character as in the zwitterionic form of MC. As expected, the C<sub>4</sub>–C<sub>5</sub> bond in SP form is smaller while the C<sub>3</sub>–C<sub>4</sub> and C<sub>5</sub>–C<sub>6</sub> bonds have larger bond lengths. Interestingly, in the case of SP form in water, the C<sub>4</sub>–C<sub>5</sub> bond seems to be the shortest in the conjugation pathway while for the MC form in both solvents, the C<sub>7</sub>–O<sub>8</sub> bond is the shortest.

In CPMD-QM/MM simulations, the chemical nature of the system can be traced from the D-resp charges defined for each of the atoms in the QM region. The D-RESP charges refer to dynamically restrained electrostatic potential fitted charges. These charges account for the effect of an instantaneous electric field due to the solvent on the electron density of the solute and so account for the solvent polarization of the solute. Moreover, the group charges are useful indicators to get insight into the charge-separated and neutral state of the molecule because in the charge-separated zwitterionic form of the molecule, the negative and positive charges are accumulated on the acceptor and donor groups while in the neutral form there is no significant charge separation. In the nonpolar solvents, the zwitterionic form cannot be stabilized and so the molecules remain in a neutral molecular structure while in polar solvents it tends to be in a zwitterionic molecular structure. We have computed the group charge distributions for MC in chloroform and in water solvent and for the SP form in water solvent; the results are shown in Figure 4a. The acceptor group and donor group charges were computed by summing the average atomic charges corresponding to atoms in either sides of the CH=CH (i.e., C<sub>4</sub>–C<sub>5</sub>) group of MC molecule. The aromatic moiety containing the NO<sub>2</sub> group refers to the acceptor group while the aromatic moiety with the *N*-methyl group refers to the donor group. The average acceptor and donor group charges for MC in chloroform solvent are respectively, –0.46 and 0.46 q/e while the values are respectively –0.76 and +0.76 q/e in the case of water solvent. This clearly shows that the molecular structure in water solvent is zwitterionic while in chloroform solvent it is closer to a neutral form. The acceptor and donor group charges computed for the SP form in water is –0.60 and +0.60 q/e, which are quantitatively larger than for the

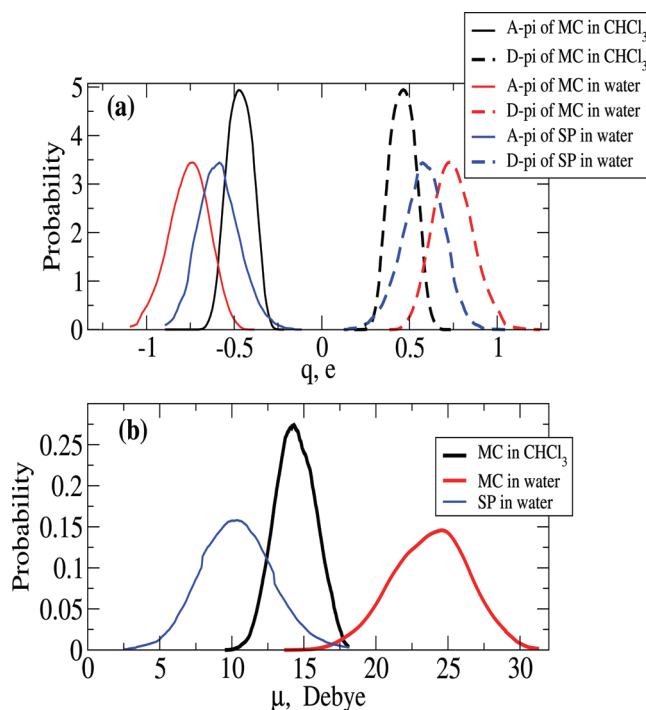
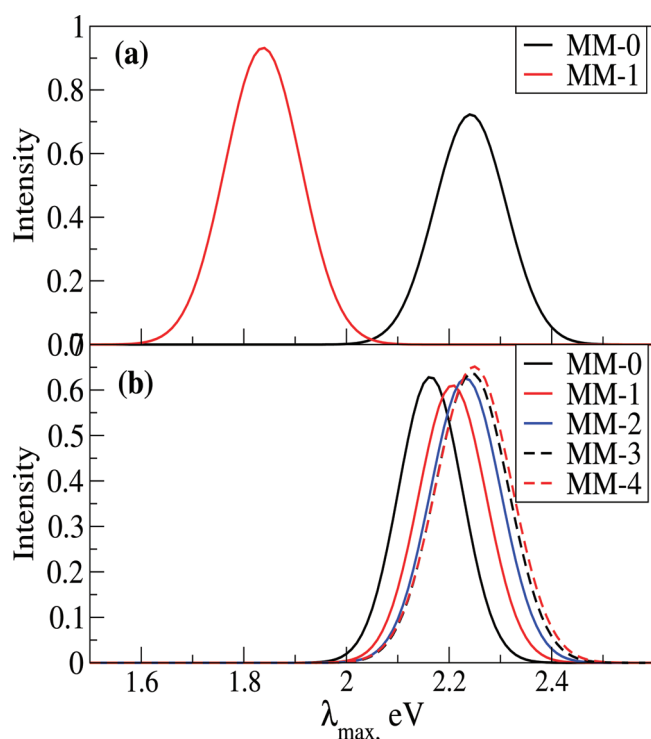


Figure 4. (a) Group charge distributions of MC in chloroform and in water and for SP in water. (b) Dipole moment distribution of MC in chloroform and in water and for SP in water.

MC form in chloroform solvent. The results clearly show that the solute molecule even in its SP form is considerably more polarized by the water solvent when compared to the chloroform solvent. We have also computed the dipole moment distribution for MC in chloroform and water solvents and for the SP form in water solvent and the results are presented in Figure 3b. The dipole moments of MC form in chloroform and in water solvents are respectively, 14.4 and 23.8 D while for the SP form in water the dipole moment is approximately, 10 D. These values confirm the zwitterionic nature in the water solvent. Interestingly, the value of the dipole moment of the MC form in chloroform is larger than the dipole moment of SP in water. Even though the group charges were larger for SP in water when compared to MC in chloroform the dipole moment of the former is smaller, something that has to be attributed to the twisted conformation of SP while a planar conformation is seen for the MC form (see Figure 1).

**3.2. Solvatochromic Shifts.** The absorption spectra of spiropyran and merocyanine have been studied extensively in nonpolar and polar solvents and in polymer matrices.<sup>9,11</sup> The closed spiropyran form is reported to be colorless and to absorb in the UV region (i.e., 300–400 nm),<sup>11</sup> while the open MC form absorbs in the visible region and the absorption maximum is in the range 540–610 nm.<sup>9</sup> The absorption spectrum reported for MC has two bands with one band appearing between 450 and 600 nm and one appearing between 300 and 450 nm. The first band is the one responsible for the negative solvatochromic effect of MC. Negative solvatochromic molecules have been proposed to have charge-separated ground and excited state;  $\mu_g > \mu_e$  where  $\mu_g$  and  $\mu_e$  refer to the ground and neutral excited state dipole moments. So, the ground state is stabilized in polar solvents relative to the excited state which brings a blue shift in the absorption spectra. The absorption spectrum of MC has a



**Figure 5.** Absorption spectra for MC in (a) chloroform and (b) in water.

maximum corresponding to 610 nm in cyclohexane, while in methanol it blue shifts to 580 nm and further blue shifts to 550 nm in water.<sup>9</sup> The ground state of the MC molecule has been proposed to be in charge-separated zwitterionic form while in the excited state there is intramolecular charge transfer leading to a neutral molecular form. So, the bipolar ground state is stabilized by polar solvents more than the neutral excited state resulting in a bathochromic or blue shift. The blue shift, or negative solvatochromic behavior, in absorption spectra is due to the relative stabilization of ground state by polar solvents when compared to its excited state. In fact, the analysis of molecular geometry (particularly along the conjugation pathway) and group charge distribution and dipole moment distribution suggests that the ground state molecular geometry of MC in water is closer to the zwitterionic form while in chloroform solvent it has a neutral form. A similar structural change from neutral to zwitterionic form due to change in solvents from chloroform to water has been proposed for Brooker's merocyanine dye.<sup>20</sup> We have computed the absorption spectra for MC in solvents as an average over many configurations; the results are presented in Figure 5. Panel a shows the absorption spectra calculated for MC in chloroform solvent while panel b corresponds to MC in water solvent. The calculated average excitation energies for the solvatochromic band obtained from the calculations for MC in chloroform and MC in water are reported in Table 2. The average  $\lambda_{\text{max}}$  calculated from the MM-0 model is 553 nm while the value from the MM-1 model is 676 nm. Interestingly, the inclusion of solvents through the CPCM model leads to a red shift in the absorption spectra by approximately 120 nm when compared to the MM-0 model. The MM-0 model for MC in water predicts  $\lambda_{\text{max}} = 574$  nm. The difference in the  $\lambda_{\text{max}}$  values for MM-0 models of MC in different solvents has to be attributed to the difference in molecular structure in these two solvents.

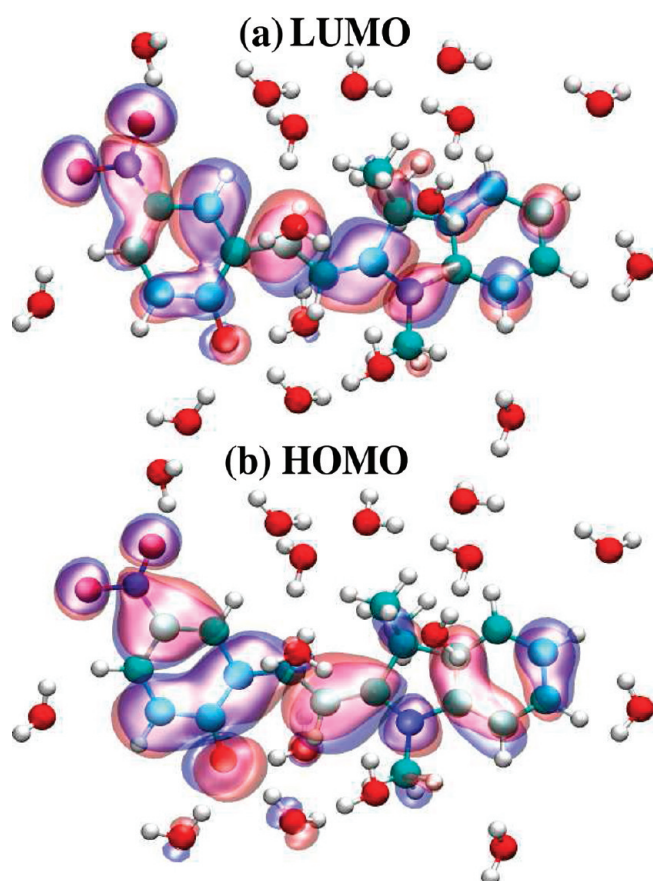
**Table 2.** Average Excitation Energies and Solvatochromic Shifts Obtained Using the Different Computational Models Described in This Paper

system	shell	$\lambda_{\text{max}}$ , nm
MC in chloroform	MM-0	553
	MM-1	676
	expt (cyclohexane)	610
MC in water	MM-0	574
	MM-1	562
	MM-2	556
	MM-3	553
	MM-4	552
SP in water	expt	550
	MM-0	310
	MM-1	345
	MM-2	355
	MM-3	380
	MM-4	385

Interestingly, contributions from the solvent-induced geometrical changes to the absorption spectra is only 20 nm in the case of MC while we have reported a quite large contribution in the case of nile red and stilbazolium merocyanine.<sup>19,20</sup> In contrast to the case of MC in chloroform, with the inclusion of different solvation shells we report a blue shift in spectra for MC in water. This indicates that, similar to stilbazolium merocyanine, MC exhibits a solvatochromic reversal behavior, thus calling for careful spectroscopic studies for MC in nonpolar solvents. It is relevant to unravel the contributions from different solvation shells of MC to the solvatochromic shift. The first solvation shell brings a dominant contribution to the solvatochromic shift, by 12 nm, while the contributions from the second, third, and fourth solvation shells bring 6, 3, and 1 nm, respectively. This series suggest convergence of the solvatochromic band with respect to solvation shells. The large solvatochromic shift is obtained from the first solvation can be rationalized by the hydrogen bonding interaction and intermolecular charge transfer which can be significant for polar solvents like water, as reported, e.g., in refs 37 and 38. Consequently, the relative contributions to the solvatochromic shift from the other solvation shells are not that significant. This is consistent with earlier results for systems such as acrolein, phenol blue, and nile red.<sup>42,19</sup> We have reported that in the case of phenol blue as much as 70% of the solvatochromic shift is obtained when only the first solvation shell is included. The MM/CPCM model of MC in chloroform predicts 676 nm while the MM-4 model of MC in water predicts 552 nm. Overall, the experimentally reported blue shift in absorption spectra with change from nonpolar to polar solvents is excellently reproduced. The solvatochromic band has  $\pi-\pi^*$  character as seen in Figure 6 depicting the HOMO and LUMO orbitals. As seen the electron density is spread over on all the atoms in the aromatic moieties.

We have also computed the absorption spectra for SP form in water as an average property over the configurations obtained from the trajectory. A similar procedure has been followed as in the case of MC in water where we use the solute-solvent radial distribution function to extract solute-solvent supermolecular structures for computing the spectra. The average excitation energy of the HOMO  $\rightarrow$  LUMO transition has been obtained for the MM-X, X = 1–4, models and are presented in Table 2.

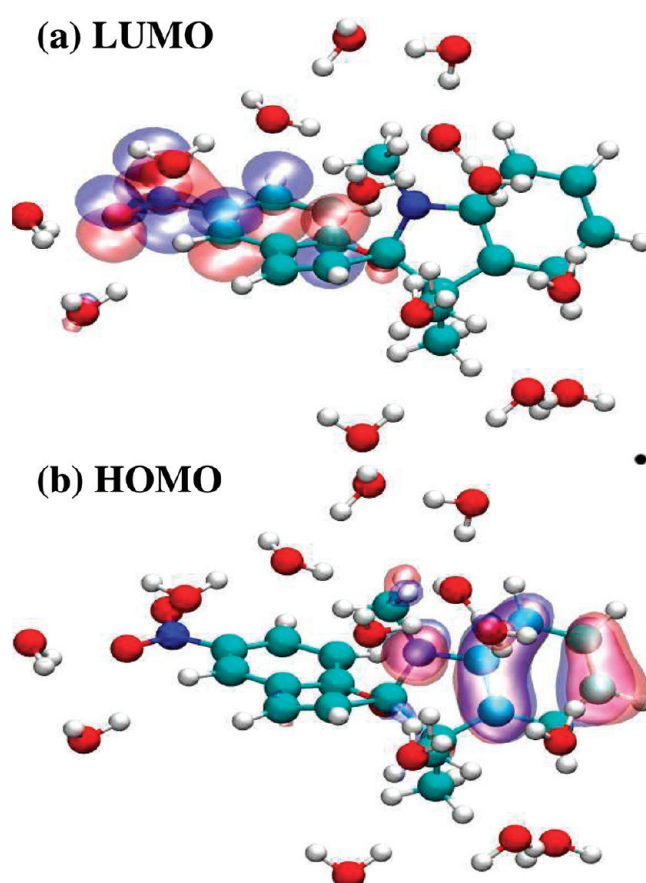




**Figure 6.** Frontier molecular orbitals for MC in water: (a) HOMO; (b) LUMO.

Interestingly, the solvent effect is much more dominant in the case of SP than for its photoreceptive counterpart. The MM-0 model predicts 311 nm for the excitation energy while the MM-4 model predicts 384 nm. In contrast to MC for which the electron density in HOMO and LUMO orbitals were occupied on both the aromatic moieties, the electron density in the HOMO of SP (see Figure 7a) is localized on the aromatic moiety connected to the *N*-methyl group (donor) while the electron density in the LUMO (See Figure 7b) is localized over the aromatic moiety connected to the NO<sub>2</sub> (acceptor) group. Because of sp<sup>3</sup> hybridization at C3 the hyperconjugation in the SP is not possible and the electron density in the frontier orbitals are localized on either side of this atom.

**3.3. Conclusions.** Using the hybrid QM/MM molecular dynamics approach, we have studied the structure of merocyanine in polar and nonpolar solvents and compared to the structure of spiropyran in water solvent. On the basis of the molecular geometry and charge distribution, we report that the merocyanine remains in a neutral form in chloroform solvent while it changes to a zwitterionic form in water solvent. The molecular dipole moment for MC-SP pair in solvents goes as MC in chloroform < SP in water < MC in water which suggest that the solvent nature is more influential than the conformation itself over the molecular dipole moment. The spectroscopic ZINDO calculations performed on MC in chloroform and water solvents could reproduce the experimentally reported blue shift in the absorption spectra with change in solvent from nonpolar to polar. The calculated absorption spectra for MC in water is in



**Figure 7.** Frontier molecular orbitals for SP in water: (a) HOMO; (b) LUMO.

good agreement with experimental value, while in chloroform solvent  $\lambda_{\text{max}}$  is overestimated.

Sequential approaches have shown to be very successful for modeling absorption spectra and other properties of organic molecules in solvents. However, the use of sequential approaches which employ MD or MC for modeling structure for solvatochromic molecules is questionable since these molecules display significant solvent-induced structural changes. Along this line, the present study shows that the combined CP-QM/MM and ZINDO approach can be used to explore the structure and absorption spectra of photochromic pair molecules in nonpolar and polar solvents. We also recommend the CP-QM/MM approach for structure modeling of the molecules that are solvatochromic and thermochromic since classical force-field based simulations might in those cases fail to capture the solvent and thermal-induced structural changes within the solute which would be important to reproduce the properties accurately.

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