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Born-Oppenheimer molecular dynamics and electronic properties of chlorophyll-c₂ in liquid methanol

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First principles Born-Oppenheimer molecular dynamics of chlorophyll- c_2 (chl c_2) in liquid methanol is reported. The structure of the chromophore-methanol solution is characterized by non-symmetric solvation and by the displacement of a pentacoordinated Mg atom from the π macrocycle plane of chl c_2 . Non-symmetrical solvation is in keeping with experimental data reported for chlorophylla and bacteriochlorophyll-a indicating a preferential side of the π macrocycle for binding a fifth ligand. The average displacement of the Mg atom (0.38 Å) is similar to X-ray data on magnesium phthalocyanine (~0.45 Å) and ethyl chlorophyllide-a dihydrate crystals (0.39 Å). The displacement of Mg from the macrocycle plane influences the orientational order of the methanol molecules in the axial region and the results indicate that the face defined by the methoxycarbonyl moiety exhibits a solvatophobic behavior. The maximum of the Soret (B) band for chl c_2 in liquid methanol (464 nm) is in good agreement with the experimental value (451 nm) and it is also very close to a recent result for chl c_2 in liquid 2-methyl tetrahydrofuran (466 nm). Intramolecular hydrogen bonding involving the carboxyl and methoxycarbonyl moieties of chl c_2 leads to a blueshift of ~20 nm of the B band maximum. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4808177]

I. INTRODUCTION

Electronic properties of chlorophylls and related systems are of fundamental interest to understand the molecular mechanisms of energy and charge transfer in complex antenna and photosynthetic reaction centers.¹ Several studies were dedicated to investigate the electronic absorption spectra of photosynthetic chromophores (see König and Neugebauer² for a recent review). Most of the available experimental information on the electronic properties of chlorophylls is determined in solution. This feature fostered theoretical studies on the electronic properties of photosynthetic chromophores in solution,^{3–10} or in interaction with hydrogen bonding species,^{10–18} or with the protein environment.^{19, 20}

Some specific aspects for understanding electronic properties of solvated chromophores are of general interest and include, for example, the dependence of these properties on hydrogen bonding, and the influence of long-range solutesolvent interactions on the absorption spectra. In addition, the relationship between the dynamics of a photosynthetic chromophore in solution and its electronic structure is also of great relevance. Recently, some works pointed out the importance of new photosynthetic species that show an absorption spectrum at lower energies, specifically in the 700–750 nm region or beyond.²¹ This is related to the role that may be played by new chromophores in artificial photosynthesis, by expanding the spectral absorption region, as well as in photoprotection, by increasing photoabsorption at lower energies. A close related issue concerns the role played by hydrogen bonding on the structural mechanisms and photoprotective function of water-soluble chlorophyll-binding proteins²² and synthetic analogues of natural chlorophylls aggregates in aqueous media.²³

In this sense, the study of the influence of the environment on the electronic absorption spectra of chlorophylls may also provide useful information for the design of new and more efficient chromophores in artificial photosynthesis.²¹ The present work is focussed on the analysis of the dynamics and electronic properties of chlorophyll- c_2 (chl c_2) in a hydrogen bonding system (liquid methanol). In contrast with other chlorophylls, $chlc_2$ (Fig. 1) is characterized by the absence of the isoprenoid tail and the similarity with porphyrins (no reduction of the D ring). Although chlc₂ is not soluble in water it is soluble in methanol and the absorption spectrum of chlc₂ in liquid methanol is known.²⁴ The interest in the analysis of the role played by hydrogen bonding on the electronic properties of photosynthetic chromophores and the availability of experimental information for the electronic absorption spectrum of chlc₂ in liquid methanol were the main motivations to study a chlc2-methanol solution. Recently, investigations on the electronic absorption⁹ and ionization spectra of chlorophyll- c_2^{10} in methanol were reported. These studies were based on the sequential Monte Carlo (MC)/quantum mechanics (QM) approach²⁵ and the calculations were carried out with the gas-phase optimized structure of chlc₂ (that was kept rigid during the MC sampling) and a classical force-field to represent the interactions in the chlc2-methanol system.⁹ Here, our main emphasis is on the dynamics of the

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FIG. 1. Gas-phase optimized structure [B3LYP/6-31G(d,p)] of chlc2.

chromophore in solution and its relationship with the absorption spectrum. The present theoretical analysis relies on the generation of the dynamics by Born-Oppenheimer Molecular Dynamics $(BOMD)^{26}$ and by the *a posteriori* calculation of the electronic properties for a selected set of BOMD configurations.

The article is organized as follows. After presenting computational details, the structure and the absorption spectra of gas-phase complexes of chlc₂ with methanol molecules are discussed. Results for the structure and dynamics of chlc₂methanol solution are then reported. This is followed by an analysis of the absorption spectrum of chlc₂ in liquid methanol. We conclude by stressing the importance of a sequential BOMD/quantum mechanical approach to investigate the electronic properties of a photosynthetical chromophore in solution.

II. COMPUTATIONAL DETAILS

Born-Oppenheimer molecular dynamics was carried out for a system with one chlorophyll- c_2 and 128 methanol molecules in a parallelepiped cell with periodic boundary conditions. The edges of the cell are 23.41 Å (*x* and *y*) and 18.04 Å (*z*). The hybrid Gaussian and plane-wave method GPW²⁷ as implemented in the QUICKSTEP module²⁸ of the CP2K program²⁹ was adopted. Goedecker, Teter, and Hutter³⁰ (GTH) norm-conserving pseudopotentials were used for representing the core electrons and only valence electrons were explicitly included in the quantum mechanical density functional theory (DFT) calculations of the forces to generate the dynamics. In the GPW approach, Kohn-Sham orbitals are expanded into atom-centered double-zeta-valence-polarization (DZVP) Gaussian-type orbital functions, whereas the electron density is represented with an auxiliary plane-wave basis-set. A charge density cutoff of 280 Ry was used for the auxiliary basis-set and the self-consistent-field energy threshold for calculating the electronic density was 10^{-6} hartree. DFT calculations were performed with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.³¹ PBE was adopted in BOMD because its predictions for the structure of hydrogen bonding liquids are in good agreement with experiment and theoretical results based on classical simulations.^{33–35}

A time step of 0.5 fs was used in all the MD runs. The BOMD was performed in the *NVT* canonical ensemble at a number density of 0.0130 Å⁻³. The canonical sampling has been carried out with a velocity scaling thermostat³⁶ and a target temperature of 300 K. The initial configuration for the BOMD simulation corresponds to an equilibrium configuration from a previous Monte Carlo simulation.⁹ The total time of the simulation was 20 ps (40 000 steps). Averages were calculated over the last 15 ps of the BOMD run. The final average temperature of the BOMD was 298 ± 4 K.

The gas-phase structures of chlc₂ and complexes of chlc2-methanol were determined by carrying out full geometry optimizations with the hybrid B3LYP functional^{37,38} and the Pople's $6-31G(d,p)^{39}$ basis-set. Very similar structures are predicted by using the PBE functional.³¹ Geometry optimizations for the gas-phase complex were carried out with the GAUSSIAN 03 program.³² The optimized structures are local minima on the surface energy and all the calculated frequencies are real. A posteriori calculations of the absorption spectrum are based on time dependent density functional theory (TDDFT).⁴⁰ The absorption spectra in the gas-phase and solution were calculated with the hybrid B3LYP^{37,38} and the 6-31G(d) basis-set. The choice of the hybrid B3LYP functional has been driven by previous calculations on the absorption spectra of chlorophylls indicating a good agreement between theoretical and experimental results.^{6,9}

For the calculations of the electronic properties of chlc₂ in liquid methanol, 100 configurations from the last 15 ps of the BOMD run were selected. The quantum mechanical calculations for these configurations were performed with a quantum system defined by (a) chlc₂ embedded in the electrostatic field of 128 methanol molecules represented by point charges corresponding to the three-site optimized potential for liquid simulation (OPLS).⁴¹ Some calculations with a sixsite OPLS-AA model⁴² were also carried out; (b) chlc₂ plus a given number of explicit methanol molecules (10 and 20) nearest to chlc₂, the whole system being embedded in the charge background of the remaining methanol molecules. The sequential quantum mechanical calculations were carried out with the GAUSSIAN 03 suite of programs.³²

III. RESULTS AND DISCUSSION

A. Structure and absorption spectra of gas-phase chlorophyll-c₂-methanol complexes

The structure of gas-phase chlorophyll- c_2 is shown in Fig. 1. Two main features characterizing the gas-phase structure are: the position of the Mg atom coincides with the π macrocycle plane; the presence of a OH···OC intramolecular hydrogen bond (HB) related to the interaction between the

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FIG. 2. Gas-phase optimized structures [B3LYP/6-31G(d,p)] for chlc₂-methanol complexes. (a) $chlc_2-(CH_2OH)_2$ with diaxial coordination of two methanol molecule to Mg; (b) $chlc_2-(CH_2OH)_2$ with axial coordination of one methanol molecule; (c) $chlc_2-(CH_2OH)_3$ complex illustrating hydrogen bonding of methanol to COOH and COOCH₃ moieties; (d) $chlc_2-(H_2O)_5$ complex with diaxial coordination of methanol to Mg and hydrogen bonding to COOH and COOCH₃ species.

OH of the carboxyl (COOH) moiety attached to ring D and the CO from the metoxycarbonyl (COOCH₃) moiety connected to ring E.

To investigate the role played by specific interactions (coordination to Mg or hydrogen bonding) on the absorption spectrum of $chlc_2$, we carried out geometry optimizations for small complexes of $chlc_2$ with methanol. Optimized structures of $chlc_2$ -methanol complexes are presented in Fig. 2. The first two structures (A and B) are complexes of $chlc_2$ with two methanol molecules. In the first one (A), the two methanol molecules are interacting directly with the Mg atom (diaxial coordination), whereas in the second (B) the molecule interacting directly with Mg is hydrogen bonded to other methanol molecule. Thus, for structure A the coordination number (Nc) of Mg is six (four nitrogen atoms + two

methanol molecules), whereas for structure B the coordination number of Mg is five. For structure A, the distance between the Mg atom and the methanol oxygen atom is 2.24 Å. For structure B, this distance is 2.09 Å indicating an enhancement of the Mg–O interaction strength for the first methanol molecule due to hydrogen bonding to the second one. In addition, for structure B the Mg atom is displaced by 0.39 Å from the center of mass of the N atoms. Displacement of the Mg atom from the macrocycle plane is also observed in the complex of chlc₂ with one methanol molecule coordinated to Mg. In this case, the displacement from the macrocycle plane is 0.29 Å and the Mg–O distance is 2.14 Å. Hydrogen bonding of methanol molecules to both the COOH and COOCH₃ moieties of chlc₂ is illustrated by structure C, which is a complex of chlc₂ with three methanol molecules playing the role



FIG. 3. Absorption spectra [B3LYP/6-31G(d)] for chlc2-methanol complexes.

of proton donors to $chlc_2$. HB distances for this structure are close to 2.0 Å. Structure D is the complex of $chlc_2$ with five methanol molecules and illustrates both coordination to Mg as well as HB with the COOH and COOCH₃ moieties of $chlc_2$. It should be noticed that due to the competing interactions with the methanol molecules there is no intramolecular HB in structure D.

The TDDFT excitation energies and oscillator strengths for the optimized gas-phase structures were convoluted by a Lorentzian distribution of 0.10 eV width and the simulated spectra are shown in Fig. 3. Comparison of the spectra for the A and B structures of Fig. 2 suggests that axial or diaxial coordination has a small effect on the Soret band peak position. For the complex of chlc₂ with five methanol molecules (structure D), the peak of the Soret band at 438 nm is redshifted by ~27 nm relative to the peak position of isolated chlc₂ (411 nm). The results also indicate that in comparison with the spectra of gas-phase chlc₂, for which the Q_x and Q_y excitations are nearly degenerate, HB to methanol leads to a split and shift to lower energies of the Q bands.

B. Structure and dynamics of chlorophyll-c₂ in liquid methanol

The structure of chlc₂ in liquid methanol, specifically the coordination of the chromophore metallic center to the methanol molecules can be discussed by representing the radial distribution function [RDF(r)] related to Mg-O interactions. The Mg-O RDF is presented in Fig. 4 and exhibits a first maximum (\sim 4.5) at 2.2 Å. The second maximum at 4.2 Å is related to the presence of a second methanol molecule hydrogen bonded to the first one. Integration of the Mg-O RDF up to the first minimum (\sim 3 Å) (see inset of Fig. 4) leads to a value of 1. Thus, the BOMD results for the structure indicate that the Nc for Mg of chlc₂ in liquid methanol is five. Several works discussed the coordination of the central Mg atom of porphyrins and chlorophylls in different solvents and environments.^{9, 14, 43–48} A recent work by Ben Fredj et al.¹⁴ pointed out the role played by dispersion interactions of chlorophylls with pyridine and water. The results



FIG. 4. Mg–O radial distribution function [RDF(r)] for chlc₂ in liquid methanol. Inset panel shows the coordination number Nc(r).

of this work indicate that coordination numbers of Mg for chlorophylls interacting with pyridine and water are, respectively, six (or diaxial coordination) and five (axial coordination). In addition, the difference between pyridine and water was related to a larger dispersion interaction in the case of pyridine.¹⁴ We notice that in the present case, it is reasonable to assume that the metal coordination to the solvent is mainly determined by hydrogen bond interactions and that an adequate description of these interactions is provided by the PBE functional.

Another relevant issue concerns the relationship between the non-symmetric structure of the π macrocycle and the metal center coordination. Our results also show that the Mg atom is displaced from the π macrocycle plane. This is illustrated in Fig. 5 where the left panel shows $\rho(\mathbf{r})$, which is the distribution of the distance r(Mg-X) between the Mg atom and the center of mass of the N atoms (X). The right panel shows the distribution $\rho(\phi)$, where $\phi(N-N-N-Mg)$ is the dihedral angle defined by the N–N–N plane and the Mg atom. The average value of ϕ is $15 \pm 5^{\circ}$ and the average deviation of Mg from the N₄ center of mass is 0.38 Å, which is practically the same displacement observed in the optimized gas-phase structure B previously discussed (see Fig. 2).



FIG. 5. (Left) ρ (r) is the distribution of the distances between the Mg atom and the center of mass of the N atoms r(Mg–X); (right) $\rho(\phi)$ is the distribution of the dihedral angle ϕ (N–N–N–Mg).

The displacement of the Mg from the macrocycle plane is dependent on the interaction of the metal with the methanol molecules. The solvent (liquid methanol) is characterized by a hydrogen bonding network whose structure is determined by many-body polarization effects. It seems reasonable to assume that these effects are important to define the nature and strength of the Mg-interaction with the environment. Deviation of Mg from the macrocycle plane has been experimentally observed in magnesium phthalocyanine crystals⁴⁹ and an aqua(phthalocyanine)magnesium compound.⁵⁰ X-ray single crystals studies indicate that Mg can be significantly displaced from the macrocycle plane and that the deviation increases with decreasing temperature.⁴⁹ For the aqua(phthalocyanine)magnesium, deviations of ~0.45 Å of Mg from the N₄ plane were observed.⁵⁰ Another related system is ethyl chlorophyllide-a dihydrate for which the crystal X-ray structure was reported.⁵¹ In this case, the displacement of the Mg atom from the N atoms plane is 0.39 Å.⁵¹ Our prediction for chlc₂ in liquid methanol (0.39 Å) coincides with this value. Thus, the present results also indicate that the interactions with the environment/solvent induces important structural changes on the macrocycle, specifically, by displacing the metal center from the N_4 plane.^{49–51}

Further analysis on the orientation of the methanol molecules in the chlc2 axial region indicates that the displacement of the Mg atom from the macrocycle plane significantly influences the orientational order of the methanol molecules. This is illustrated in Fig. 6 where the distribution of the θ (Mg–C–O) angle between the Mg atom and the methanol O–C vector is represented. Thus, θ close to 0° means that C-O is oriented towards Mg, whereas θ close to 180° means that the methyl group is oriented towards Mg. For the methanol molecules in the axial region corresponding to the face of the macrocycle defined by the "protruding" Mg atom (or the face opposite to the methoxycarbonyl moiety), the θ distribution (peaked at $\sim 30^{\circ}$) shows that the oxygen atoms are oriented towards Mg and therefore these molecules define the Mg (penta)coordination. On the other hand, the θ distribution also shows that the methanol molecules in the axial region on the same side of the methoxycarbonyl moiety are present in 47% of the configurations and have preferentially a methyl group pointing towards the macrocycle plane. The inset of Fig. 6 illustrates these features.

Recently, we reported Monte Carlo simulation results for the structure of a chlorophyll- c_2 methanol solution relying on a force field for chlorophyll-methanol interactions that indicated a diaxial coordination of Mg.⁹ We have verified that if the MC simulation is carried out for a chlc₂-methanol system where the Mg atom is displaced from the Mg center from 0.39 Å, a value that corresponds to the average displacement predicted by BOMD (or to the displacement observed in the optimized complex of chlc₂ with two methanol molecules), then the coordination number of Mg is five. More interestingly, the orientational order of the methanol molecules in the axial region for the two faces of the macrocycle is in good agreement with the BOMD results.

There is some experimental evidence that chlorophylls show a preferential side of the π macrocycle for binding a fifth ligand to Mg.^{45,48,52–54} As pointed out by Balaban,⁵⁴ this



FIG. 6. Distribution of the angle θ (Mg–O–C) for the methanol molecules in the axial region of the macrocycle plane. The inset shows a superposition of configurations illustrating the orientation of the methanol molecules relative to Mg in the opposite faces of the macrocycle.

feature may have implications on the electronic properties of (bacterio)chlorophyll dimers. The present BOMD results also suggest a preferential side for the binding of the methanol molecule (fifth ligand) to Mg that corresponds to the opposite side of the methoxycarbonyl moiety. Therefore, the fifth ligand in our case can be compared with the α ligand reported by Balaban *et al.*⁵² Figure 7 shows a snapshot of the BOMD run illustrating the orientation of the ligand relative to the methoxycarbonyl moiety.

The time evolution of the Mg–O distance to the closest methanol molecule is illustrated in Fig. 8 for a 6 ps window. The average distance is 2.2 ± 0.2 Å (this is the value of distance corresponding to the Mg–O RDF maximum presented in Fig. 4). The inset in Fig. 8 shows the distribution of the vibrational frequencies related to the Mg–O interaction with the closest solvent molecule. Vibrational frequencies were calculated by the Fourier transform of the average autocorrelation function $C_{AA}(t) = \langle A(t)A(t_i)/A(t_i)A(t_i) \rangle$, where $A = \frac{dx}{dt}$, t_i a time origin, and x = r(Mg–O) or x = r(O–H). A similar procedure was recently applied to calculate the vibrational modes of methane in a clathrate hydrate.⁵⁵



FIG. 7. Configuration of the BOMD run illustrating the orientation of the ligand (methanol) relative to the methoxycarbonyl moiety and the displacement of Mg from the macrocycle plane.



FIG. 8. Time evolution of the Mg–O distance (Å). (Inset) ν (Mg-O) stretch frequency (cm⁻¹).

A broad distribution in the 100–400 cm^{-1} range with maxima values close to 400 cm⁻¹ is observed. The experimental frequency for the gas-phase Mg-O diatomic molecule is 391.4 cm⁻¹.⁵⁶ The redshift of the Mg–O stretch frequency relative to the gas-phase value for the Mg-O molecule reflects, as expected, coupling of Mg to N atoms of the chlc2 macrocycle as well as the HB interaction of the closest methanol molecules with other molecules of the solvent. However, the presence of frequencies similar to those of the diatomic Mg-O molecule provides further indication on the formation of a chlc₂-methanol complex in the liquid phase. The dynamics of chlc₂ in liquid methanol suggests a strong coupling of Mg to the fifth ligand during all the BOMD run (see Fig. 8). The conventional picture that neglects the presence of a fifth ligand on the magnesium atom in the representation of chlorophylls has been questioned by recent works.^{47,52} The present results for the structure of the chlc₂methanol solution seem to be in agreement with this new perspective.

Analysis of the BOMD trajectories suggests that for chlc2 in liquid methanol the dynamics of intramolecular OH···OC HB (see Fig. 1) is correlated with the internal rotation of the COOH (attached to ring D) and COOCH₃ (attached to ring E) moieties. This is illustrated in Fig. 9 that shows the time evolution of the $R(OH \cdot \cdot \cdot OC)$ distance (bottom panel) and also of the H–O–O angle (top panel). The distribution for the ν (O–H) stretch frequency of the O-H COOH moiety related to the intramolecular HB interaction with the COOCH₃ is also shown in Fig. 9. This distribution is defined in the $3000-3600 \text{ cm}^{-1}$ range. The region for ν (O–H) below 3300 cm⁻¹ can be compared, for example, with the experimental value of ν (O–H) for dimers of formic acid, 3100 cm⁻¹, or benzoic acid, 3350 cm⁻¹ (see Florio et al.⁵⁷ and references therein). The blueshifted frequencies of the second region above 3300 cm⁻¹ can be compared with the frequencies for a quasi-free O-H group with some coupling to the methanol molecules. The ν (O–H) stretch frequency of gas-phase formic acid is 3569 cm⁻¹.⁵⁷

C. Absorption spectrum of chlorophyll-c₂ in liquid methanol

The absorption spectrum of $chlc_2$ in liquid methanol is shown in Fig. 10. The different curves of this figure cor-



FIG. 9. (Bottom) Time evolution of the R(OH···OC) distance (Å); (top) time evolution of the \angle H–O–O angle (degrees); (inset) ν (O-H) stretch frequency (cm⁻¹).

respond to calculations with (a) only the electrostatic environment of $chlc_2$ or charge embedding $(chlc_2 + CE, black$ curve) and (b) with the explicit inclusion of the nearest 10 and 20 methanol molecules to chlc₂, the whole system in this case is embedded in the electrostatic field of the remaining methanol molecules. The spectra for the systems with 10 and 20 methanol molecules explicitly included in the QM calculations correspond to the red and blue curves, respectively. The comparison between results predicted by these different representations of the solvent is useful because it allows to assess the reliability of the charge representation for the electrostatic environment (OPLS charges for methanol) as well as the importance of including explicitly a given number of methanol molecules in the calculations. The results indicate that explicit inclusion of a given number of methanol molecules plus the charge background leads to redshift of the absorption energy maxima for both the Soret (B) and Q bands as noted before.⁹ In addition, the spectra for the calculations with 10 and 20 methanol molecules are quite similar and this feature is an indication that an adequate representation of the environment is possible by the explicit inclusion of a relatively small number of methanol molecules plus the electrostatic background. In



FIG. 10. Absorption spectrum of chlorophyll- c_2 in liquid methanol: influence of embedding and explicit inclusion of methanol molecules.

TABLE I. Transition wavelengths (nm) and oscillator strengths (in parenthesis) of $chlc_2$ in the gas-phase and liquid methanol from time dependent B3LYP/6-31G(d) calculations.

	Gas-phase	CE	20 methanol + CE	Experimental
1	566 (0.03)	617 (0.02)	624 (0.02)	$633;^{a} 640^{b} (Q_{y})$
2	563 (0.00)	605 (0.02)	609 (0.01)	586; ^a 593 ^b (Q_x)
3	419 (0.29)	471 (0.24)	477 (0.22)	
4	413 (0.46)	457 (0.35)	464 (0.31)	451; ^a 462; ^b 466 ^c (B)
5	409 (0.51)	446 (0.27)	452 (0.24)	
6	398 (0.06)	434 (0.15)	440 (0.13)	
7	389 (0.04)	423 (0.10)	427 (0.09)	

^aChlorophyll-*c*₂ in liquid methanol.²⁴

^bChlorophyll-c1 in pyridine from Blankenship.¹

^cChlorophyll-c₂ in 2-methyl tetrahydrofuran (77 K).⁵⁹

agreement with a previous work,⁵⁸ the results are not particularly dependent on the choice of the electrostatic background and very similar spectra are generated by adopting charge representations corresponding to different intermolecular models for liquid methanol. This is illustrated in Fig. 10 where the absorption spectra corresponding to the charge background of the OPLS⁴¹ (full line) and OPLS-AA⁴² (diamonds) force fields are compared.

Table I presents the results for the absorption of chlc₂ in liquid methanol from the present calculations and other results from different experimental works on chlc₂ or for the closely related system (chlc₁). Mean squared deviations for the average wavelengths (100 BOMD configurations) are less than 2 nm. The maxima of the Soret (B) band are at 457 and 464 nm, respectively, for the calculations with CE and charge embedding plus 20 explicit methanol molecules (CE + 20 methanol). The first result is in good agreement with the experimental data reported by Jeffrey and Shibata²⁴ (451 nm). The result based on the (CE + 20 methanol) approach is redshifted by 13 nm relative to this experimental value. It is, however, in good agreement with the experimental value for chlc₁ in pyridine $(462 \text{ nm})^1$ and for chlc₂ in 2methyl tetrahydrofuran at 77 K (466 nm).⁵⁹ A good agreement can also be observed between the present predictions and data from the literature for the Q_x and Q_y bands. For the Q bands, calculations with the explicit inclusion of methanol molecules are in better agreement with experiment.

The analysis of the role played by intramolecular hydrogen bonding and displacement of the metal center from the π macrocycle plane on the absorption spectrum can be carried out by selecting configurations satisfying the adequate criteria. To analyze the role played by intramolecular HB formation, we have selected a set of configurations for which the R(HO···OC) distance is less than 1.8 Å (the time evolution of this distance is illustrated in Fig. 9). It will also be assumed that if the dihedral angle ϕ (N–N–N–Mg) > 15°, then there is a significant displacement of the metal center from the π macrocycle plane. The absorption spectra for configurations satisfying one of these criteria are presented in Fig. 11, where they are compared with the average spectrum calculated with the CE approach for the whole set of selected configurations. The results indicate that intramolecular hydrogen bonding in chlc₂ leads to a blueshift of the peak associated



FIG. 11. Absorption spectrum of chlorophyll- c_2 in liquid methanol: influence of intramolecular hydrogen bonding and displacement of Mg from the π macrocycle plane.

with the Soret (B) band by ~ 20 nm. In addition, for configurations where the metal center is displaced from the π plane a small blueshift of the B band peak is observed. This analysis illustrates the importance of taking into account the structural changes of the chromophore macrocycle in interaction with a solvent to investigate its electronic properties. The influence of the intramolecular HB and displacement of Mg from the macrocycle plane seems to concern essentially the Soret (B) band. No significant changes are observed for the Q bands.

IV. CONCLUSIONS

BOMD for chlorophyll- c_2 in methanol provided a series of fundamental information on the structure and dynamics of a photosynthetic chromophore in solution and their relationship with the absorption spectrum. First, the results strongly indicate that the solvation of chlc₂ in methanol is non-symmetric and it is characterized by non-planarity of the macrocycle framework and by a displacement of Mg from the macrocycle π plane. This leads to a pentacoordination for Mg and has implications on the orientational order of the methanol molecules in the axial region for the two faces of the macrocycle, where the face defined by the methoxycarbonyl moiety exhibits a solvatophobic behavior.

A complex intramolecular hydrogen bonding dynamics (coupled to the hydrogen bonding solvent) and involving the peripheral carboxyl and metoxycarbonyl moieties has been identified and may modify in a significant way the electronic absorption spectrum of the chromophore. Specifically, it was found that intramolecular hydrogen bonding in chlc₂ leads to a \sim 20 nm blueshift of the Soret (B) band peak position.

The results concerning the non-symmetric solvation are in keeping with several experimental works.^{45,48,53,54} The displacement of the Mg atom from the π macrocycle plane is supported by X-ray experiments.^{49–51} The coupling of Mg to a methanol molecule in liquid phase emphasizes the importance of taking into account the presence of a fifth ligand for representing a chlorophyll molecule in interaction with the environment.⁵² The good agreement between the present theoretical results relying on sequential BOMD/QM calculations and experimental data for the absorption spectrum of chlc₂ in liquid methanol illustrates the adequacy of the adopted approach to investigate electronic properties of complex supramolecular structures in condensed phase.

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