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Ionization of chlorophyll-c_2 in liquid methanol

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ABSTRACT

The ionization of chlorophyll-c_2 in liquid methanol was investigated by a sequential quantum mechanical/Monte Carlo approach. Focus was placed on the determination of the first ionization energy of chlorophyll-c_2. The results show that the first vertical ionization energy (IE) is red-shifted by 0.47 ± 0.24 eV relative to the gas-phase value. The red-shift of the chlorophyll-c_2 IE in the liquid phase can be explained by Mg···OH hydrogen bonding and long-ranged electrostatic interactions in solution. The ionization threshold for chlorophyll-c_2 in liquid methanol is close to 6 eV.

1. Introduction

Photophysical properties of chlorophylls are of fundamental interest to understand the molecular mechanisms of energy and charge transfer in complex antenna and photosynthetic reaction centers. The ionization of photosynthetic chromophores is a central process in photosynthesis. The ionization process is closely related to the oxidation and light driven charge separation processes that take place in photosynthetical reaction centers after electronic excitation [1,2].

Several works were dedicated to the study of oxidation/ionization processes in photosynthetic chromophores including chlorophylls [3–8] and porphyrins [9–14,16]. Dupuis et al. [12] pointed out the possibility that the very low ionization energies (IEs) of porphyrins and the presence of Rydberg states could play a relevant role in photosynthesis. This Letter also reported IEs for a series of porphyrins with values in the 5.9–6.9 eV range. More recently, Shafizadeh et al. [8] reported a threshold value of 6.1 ± 0.05 eV for the ionization of chlorophyll-a in vacuo [8]. The importance of this Letter should be stressed because most of the available experimental information on the absorption and ionization spectra of photosynthetic chromophores relies on measurements carried out in solution. Actually, a relevant issue concerns the electronic properties of photosynthetic chromophores in solution or in interaction with hydrogen bonding species [5,6,17–21] or with the protein environment [22,23]. Two specific aspects deserve special attention. The dependence of the ionization energies on hydrogen bonding and the influence of long-ranged solute–solvent interactions on the electronic properties of the solvated chromophores.

In this Letter a theoretical analysis on the ionization of chlorophyll-c_2 in liquid methanol is reported. The choice of this specific system was driven by the importance of methanol as a hydrogen bonding solvent. Moreover, although experimental information on the absorption spectrum for chlorophyll-c_2 in liquid methanol is available, we are not aware of experimental or theoretical work on the ionization spectrum of this species. The theoretical procedure relies on a sequential quantum mechanical/Monte Carlo approach [24], in which a series of configurations generated by Metropolis Monte Carlo sampling [25] are selected for *a posteriori* quantum mechanical calculations. By adopting this approach, thermal effects on the electronic structure are implicitly taken into account. The correct description of these effects is important to assess the role played by thermal broadening [26] on the electronic properties.

The Letter is organized as follows. After presenting details on the computational procedures we report results for the gas-phase ionization energy of chlorophyll-c_2. Then, by adopting a microsolvation approach we discuss how hydrogen bonding of chlorophyll-c_2 to a few molecules of methanol and water modifies the gas-phase IE. In the last section we discuss results for the ionization energy and electronic density of states for chlorophyll-c_2 in liquid methanol with emphasis on the role played by long-ranged electrostatic interactions on the ionization process, and an estimate for the gas-to-liquid shift of the chromophore IE is reported.

2. Computational details

The gas-phase structure of isolated chlorophyll-c_2 (Chl-c_2) was determined by carrying out full geometry optimizations with the hybrid B3LYP functional [27,28] and the Pople's 6-31G(d,p) [29] basis-set. To assess the importance of local hydrogen bonding on the vertical ionization of Chl-c_2 a microsolvation approach was

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adopted and geometry optimizations for complexes of the chromophore with a few methanol and water molecules were carried out. As illustrated in Figure 1 these optimized structures involve hydrogen bonding formation between the Chl-c_2 metallic center (two solvent molecules) and also hydrogen bonding to the carboxyl groups (three solvent molecules). Full geometry optimizations for the Chl-c_2–$(CH_3OH)_5$ and Chl-c_2–$(H_2O)_5$ complexes were also carried out (see Figure 1).

We are not aware of experimental results for the ionization spectra of chlorophyll-c_2. Therefore, initially, we carried out calculations for related porphyrins. In this case, experimental [12] and theoretical [13–16] results are available. In the present Letter, vertical ionization energies were calculated with two recent exchange–correlation functionals proposed by Zhao and Truhlar [30] (M06-2X) and Chai and Head-Gordon [31] (wB97XD). The first one (M06-2X) was recently applied to calculate the ionization spectrum of porphyrin and Mg-porphyrin [16] and the results were in good agrement with those relying on electron propagator theory [32]. The second one (wB97XD) is a long-range corrected hybrid density functional with damped atom–atom dispersion corrections [31]. For comparison, results from Hartree–Fock (HF) and Möller–Plesset second order perturbation theory (MP2) calculations are, in some cases, presented. Open-shell calculations for the ionized species were carried out with restricted open HF (ROHF [33]) and restricted open MP2 (ROMP2 [34]) methodologies. For closed shell HF calculations the first vertical ionization energy was estimated by using the Koopmans' theorem [35]. The (minus signed) energy of the highest occupied molecular orbital (HOMO) was also used to estimate the first vertical ionization energy from the DFT calculations [44,45].

Basis-set dependence of the ionization energies was investigated by performing calculations with the Dunning's hierarchical basis-set family (cc-pVxZ, x = D;T;Q) [36]. The liquid phase configurations were generated by the Metropolis Monte Carlo (MC) method [25]. Metropolis MC simulation were carried out using one molecule of Chl-c_2 and 1500 methanol molecules in the *NPT* ensemble at room conditions in a parallelogram box of initial lengths $54 \times 54 \times 37$ Å and average lengths of $53.6 \times 53.6 \times 36.6$ Å. The average calculated density is 0.765 g/cm^3, in agreement with the experimental density of methanol (0.787 g/cm^3). The intermolecular interactions are described by the Lennard-Jones plus Coulomb potentials with the conventional three-parameters for each site i (ϵ_i, σ_i and q_i). For methanol and Chl-c_2, the ϵ_i and σ_i parameters of the potential were obtained from the optimized parameters for liquid simulation (OPLS) of Jorgensen and co-workers [37,38]. For Mg we used the parameters suggested by Aqvist [39]. The inclusion of the solute polarization is made using polarizable continuum model (PCM), as before [40]: we determine the atomic charges for the classical MC simulation from an electrostatic fit (CHELPG) [41] in a PCM-B3LYP/6-31G(d,p) calculation. The B3LYP/6-31G(d,p) dipole moment for gas-phase Chl-c_2 is 11.61 D, and in methanol, the resulting dipole moment is 15.20 D. The full set of interactions parameters can be found in our previous work [21]. All the MC simulations were performed with the DICE program [42] and consisted of a thermalization of 7.5×10^7 MC steps, followed by an averaging stage of 1.5×10^8 MC steps.

Two sets of structures were selected for the sequential QM calculations. In the first one the QM system is defined by the chromophore and the two nearest methanol molecules from the Mg atom of Chl-c_2. In the second set, the QM system previously defined was embedded in the electrostatic field of the remaining methanol molecules. In this way we can assess, separately, the role played by local Mg···OH hydrogen bonding and long-ranged interactions on the ionization energy of the chromophore. Quantum mechanical calculations were carried out with the GAUSSIAN09 program [43].

3. Results and discussion

3.1. Ionization of gas-phase and microsolvated chlorophyll-c_2

Results for the first vertical ionization energies (IEs) of gas-phase and microsolvated Chl-c_2 are presented in Table 1. Vertical IEs were calculated as the difference between the energy of the neutral and ionized structures in the geometry of the neutral (ΔE calculations) and also by using the (minus signed) energy of the highest occupied molecular orbital (HOMO) [44,45] (bracketed values in Table 1). As shown in Table 1, the result from the HOMO energy at the wB97XD/cc-pVQZ level for the gas-phase free base porphyrin (6.96 eV) practically coincides with the experimental value of 6.9 eV [12] (the first IE of D_{2h} H_2P corresponds to electron remotion from a MO of b_3u symmetry [13,15,16]). This value (6.96 eV from the HOMO energy) is quite similar to the ΔE estimate with the M06-2X functional (7.00 eV) a tendency that is also observed for the other calculations reported in Table 1. The present results for the first IE of H_2P are also in excellent agreement with predictions relying on the P3 approximation of the electron propagator theory (EPT) [15] (see Table 1). Moreover, the results also indicate that the IEs are near the convergence value or the basis-set limit for calculations with a cc-pVTZ basis-set. The differences between the results with the cc-pVQZ and cc-pVTZ calculations are below 0.05 eV. Therefore, calculations for the larger systems and also for the configurations generated by Monte Carlo for Chl-c_2 in liquid methanol were performed with a cc-pVTZ basis-set. The wB97XD/cc-pVDZ result for the first IE of isolated Chl-c_2 (7.14 eV from the HOMO energy) is in very good agreement with the result relying on the M06-2X functional (~7.1 eV from ΔE). We should stress that our predictions for the first IE of Chl-c_2 are very close to the results for Mg-porphyrin [15,16]. This is not surprising considering the similarities between the structures of Mg-porphyrin and Chl-c_2.

Gas-phase optimized structures [B3LYP/6-31G (d,p)] for complexes of Chl-c_2 with methanol and water are presented in Figure 1. The panel (A) shows the structure of Chl-c_2–$(CH_3OH)_2$ stabilized by Mg···OH hydrogen bond interactions. The structure of the Chl-c_2–$(CH_3OH)_3$ complex (panel (B) of Figure 1) illustrates hydrogen bond formation of methanol with the carboxyl groups of Chl-c_2. Panel (C) shows the structure of the Chl-c_2–$(CH_3OH)_5$ complex, which is characterized by hydrogen bonding to both the metal and carboxyl groups. Similar structures (panels (D–F)) for Chl-c_2–water complexes are also shown in Figure 1. Some recent works discussed the structure and energetics of Chl a–water complexes [17–19]. Here, our main interest is to investigate the influence of hydrogen bonding on the ionization of Chl-c_2 by using microsolvation models.

First, we will discuss the results for the gas-phase Chl-c_2–methanol complexes relying on ΔE calculations. The vertical ionization energies of Chl-$c_2(CH_3OH)_2$ are reported in Table 1. In comparison with the gas phase value, the first IE of the complex is red shifted by ~0.34 eV (wB97XD/cc-pVTZ) and 0.24 eV (M06-2X/cc-pVTZ). Quite similar values for this shift are predicted with cc-pVDZ basis-set (0.36 and 0.30 eV for wB97XD and M06-2X, respectively). The first IE for the Chl-$c_2(CH_3OH)_3$ complex (panel B of Figure 1) are 7.13 eV (M06-2X/cc-pVTZ) and 6.89 eV (wB97XD/cc-pVTZ). These values are very close to the predictions for isolated Chl-c_2 (7.08 and 6.86 eV) indicating that hydrogen bonding (HB) of methanol to the carboxyl groups do not modify the first IE of Chl-c_2. However, both functionals (wB97XD and M06-2X) predict a significant red-shift (0.69 and 0.65 eV, respectively) for the first IE of the Chl-$c_2(CH_3OH)_5$ complex relative to isolated Chl-c_2. This result seems to be an indication that the red-shift of the first IE of Chl-c_2 when the metal center is interacting with two methanol molecules is enhanced by HB to the carboxyl groups.

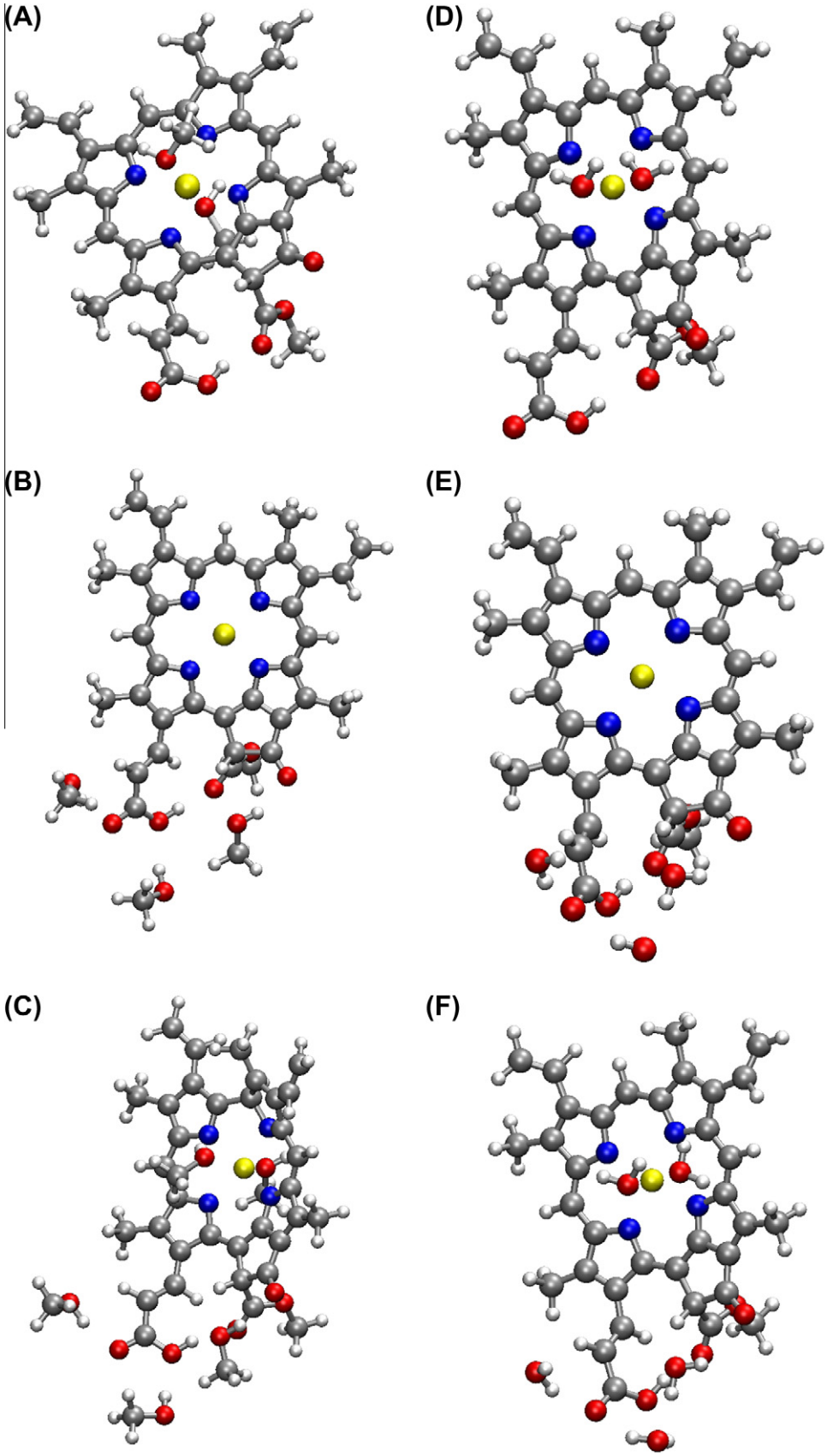

Figure 1. Gas-phase optimized structures [B3LYP/6-31G(d,p)]. (A) Chl-c_2–$(CH_2OH)_2$ with Mg···OH hydrogen bond interactions; (B) Chl-c_2–$(CH_2OH)_3$ with hydrogen bonding to carboxyl groups of chlorophyll-c_2; (C) Chl-c_2–$(CH_2OH)_5$ complex. (D) Chl-c_2–$(H_2O)_2$ with Mg···OH hydrogen bond interactions; (E) Chl-c_2–$(H_2O)_3$ with hydrogen bonding to carboxyl groups of chlorophyll-c_2; (F) Chl-c_2–$(H_2O)_5$ complex. Mg···OH distances are ~2.2 Å for methanol and water coordination.

Table 1
Gas-phase data (ΔE calculations) for the first vertical ionization energy (IEs in eV) of chlorophyll-c_2, complexes with methanol and water molecules, and free-base porphyrin (H_2P). Geometries optimized at the B3LYP/6-31G(d,p) level. Bracketed values are IEs from the (minus signed) HOMO energy.

	M06-2X	wB97XD	ROHF	ROMP2
Chlorophyll-c_2				
6-31G (d,p)	6.96 [6.45]	6.68 [6.92]	5.68 [6.29]	7.12
cc-pVDZ	6.98 [6.54]	6.78 [7.02]	5.75 [6.37]	7.33
cc-pVTZ	7.08 [6.68]	6.86 [7.10]	5.77 [6.42]	
cc-pVQZ	7.09 [6.69]	6.87 [7.14] (6.1 ± 0.05)[a]	5.79 [6.45]	
Chlorophyll-c_2–$(CH_3OH)_2$[b]				
cc-pVDZ	6.68 [6.29]	6.42 [6.82]	5.56 [6.19]	7.14
cc-pVTZ	6.84 [6.48]	6.52 [6.92]		
Chlorophyll-c_2–$(CH_3OH)_3$[c]				
cc-pVDZ	7.03 [6.60]	6.82 [7.09]	5.79 [6.43]	
cc-pVTZ	7.13 [6.74]	6.89 [7.17]		
Chlorophyll-c_2–$(CH_3OH)_5$				
cc-pVDZ	6.29 [5.91]	6.07 [6.48]	5.42 [6.27]	
cc-pVTZ	6.43 [6.09]	6.17 [6.59]		
Chlorophyll-c_2–$(H_2O)_2$[b]				
cc-pVDZ	6.87 [6.37]	6.52 [6.88]	5.65 [6.27]	7.20
cc-pVTZ	6.93 [6.56]	6.62 [6.99]		
Chlorophyll-c_2–$(H_2O)_3$[c]				
cc-pVDZ	6.92 [6.49]	6.71 [6.98]	5.69 [6.33]	
cc-pVTZ	7.03 [6.63]	6.79 [7.06]		
Chlorophyll-c_2–$(H_2O)_5$				
cc-pVDZ	6.77 [6.33]	6.47 [6.85]	5.61 [6.24]	
cc-pVTZ	6.93 [6.52]	6.57 [6.97]		
Porphyrin (H_2P)				
cc-pVDZ	6.89[6.28]	6.64 [6.83]	6.14 [6.10]	6.52
cc-pVTZ	7.00[6.44]	6.71 [6.91]; (7.00)[d]	6.21 [6.14]	
cc-pVQZ	7.02[6.46]	6.73 [6.96]	6.24 [6.18]	
Experimental [e]		6.9		

[a] Photoionization threshold for chlorophyll-a from Shafizadeh et al. [8].
[b] Coordination to Mg through Mg···OH hydrogen bond interactions.
[c] Hydrogen bonding to carboxyl groups of chlorophyll-c_2.
[d] Electron propagator theory calculation [P3/6-311+G(d,p)] from *Dolgounitcheva et al. [15].*
[e] Experimental value from Dupuis et al. [12].

In comparison with ΔE calculations, results from the HOMO energies show that the shift on the Chl-c_2 IEs due to complexation with methanol molecules follow similar trends. For example, in agreement with ΔE calculations, HB of methanol molecules only to the carboxyl groups do not modify the IE relative to the isolated chromophore (IE shifts are close to zero). In addition, a significant red-shift is observed for the Chl-$c_2(CH_3OH)_5$ complex (0.51 eV, wB97XD/cc-pVTZ and 0.59 eV, M06-2X/cc-pVTZ). Therefore, it seems reasonable to point out that although the absolute values of the ionization energies may show some differences when the calculations are performed with the two functionals and by using ΔE or the HOMO energies, their dependence with HB to the solvent molecules is quite similar.

For the Chl-c_2–water complexes the IE dependence on HB shows the same trends previously discussed for Chl-c_2–methanol although the magnitude of the red-shifts due to the interaction with water is small. Thus, from ΔE calculations the IE of Chl-$c_2(H_2O)_2$ is red-shifted by 0.24 eV (wB97XD/cc-pVTZ) and 0.15 eV (M06-2X/cc-pVTZ). In agreement with the results for methanol, HB of water to the Chl-c_2 carboxyl groups has no significant influence on the first IE. For Chl-$c_2(H_2O)_5$ and ΔE calculations the red-shifts are 0.29 eV (wB97XD/cc-pVTZ) and 0.16 eV (M06-2X/cc-pVTZ). Results from the HOMO energies show the same trends. Interestingly again, the shifts predicted by ΔE M06-2X calculations are in good agreement with those relying on the wB97XD HOMO energies. For the Chl-$c_2(H_2O)_5$ the shifts are 0.16 eV (M06-2X/cc-pVTZ, ΔE) and 0.13 eV (wB97XD/cc-pVTZ, HOMO).

Table 1 also presents a series of ab initio ROHF and ROMP2 results for the systems under study. Although ROMP2 calculations for the larger systems and basis-sets is beyond the scope of the present Letter, the ab initio calculations can be useful, in the case of the smaller systems, to discuss the behavior of the IEs with HB and thus provide a comparison with the two adopted functionals. Therefore, results for H_2P, Chl-c_2, and Chl-c_2 complexes with methanol and water molecules (with the cc-pVDZ basis-set) are reported. Firstly, it should be noticed that in comparison with experimental information for the free base porphyrin, ROHF predictions are underestimated in comparison with experiment (see Table 1). As expected, in comparison with ROHF, the ROMP2/cc-pVDZ result (6.52 eV) is in better agreement with experiment (6.9 eV) [12]. Although these discrepancies, it is important to observe that the dependence of the Chl-c_2 IEs with HB to methanol and water predicted by ROMP2 calculations seems to reproduced the trends already discussed for the DFT calculations. We should also notice the excellent agreement between the electron propagator theory (EPT) result for H_2P (7.0 eV) [14] and the experimental result is observed. It is known that EPT is a reliable theoretical approach to investigate the electronic spectra of complex systems. However, our results also indicate that a correct prediction of IEs and their dependence on HB can be provided by using recently proposed exchange–correlation functionals [30,31].

Although some differences are observed for IEs from DFT ΔEs and HOMO results, both routes lead to the same conclusion: the first vertical IE of Chl-c_2 is red-shifted by Mg···OH hydrogen bond interactions and this effect seems to be further enhanced by hydrogen bonding to the carboxyl groups. This conclusion is also supported by ab initio calculations. We believe that this tendency is important to analyse the role played by hydrogen bonding on the

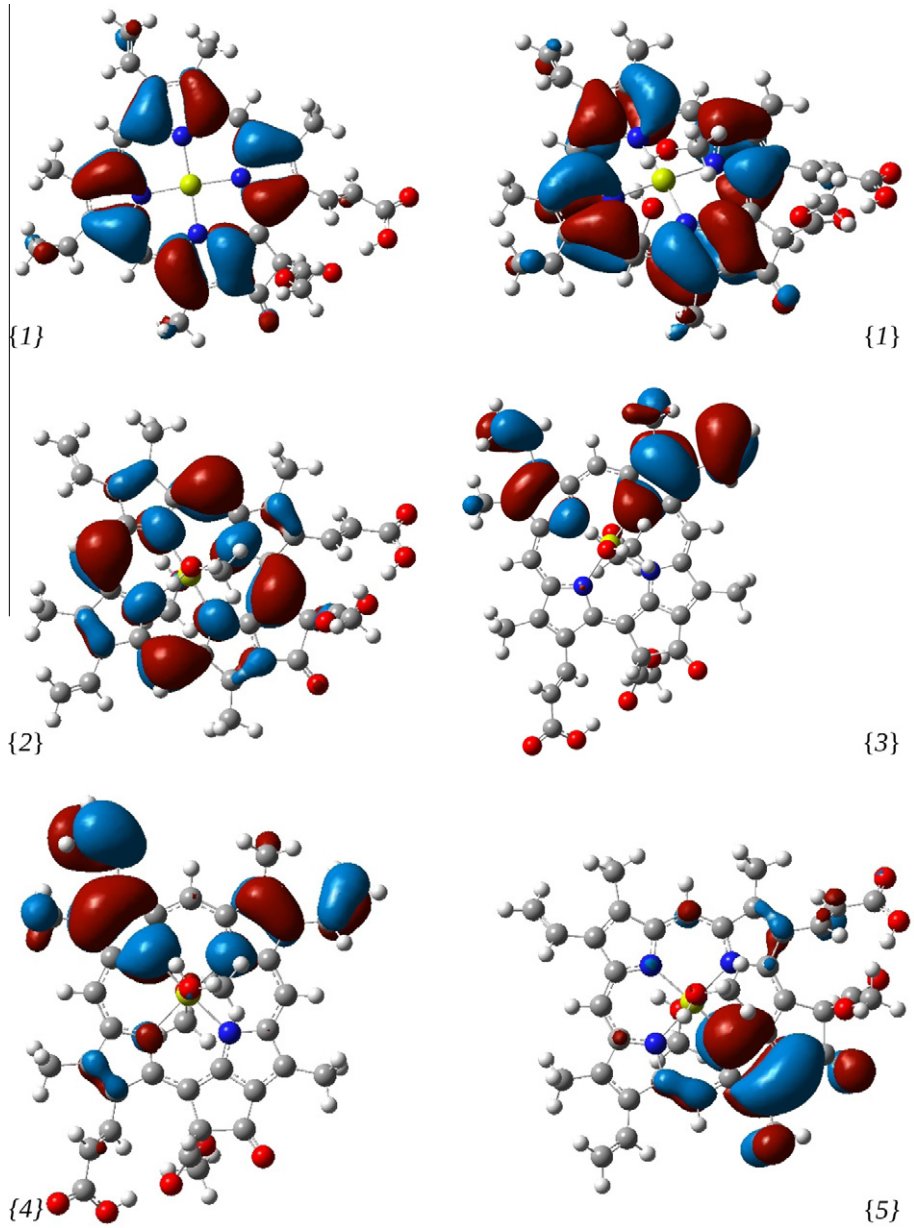

Figure 2. Gas-phase structures and highest occupied molecular orbitals {1} of Chl-c_2 (left top) and Chl-c_2–$(CH_3OH)_2$ (right top); the lower panels show the next four outer valence molecular orbitals of Chl-c_2–$(CH_3OH)_2$ {2–5}.

ionization and charge transfer processes in photosynthetic chromophores.

The experimental result for the first vertical ionization energy of gas-phase methanol is 10.94 eV [46]. Although hydrogen bonding in liquid methanol leads to a gas-to-liquid red-shift of 0.95 eV for the first ionization energy [46] the IE of the solvent is higher than the IEs corresponding to the outer valence bands of the photosynthetic chromophore. Molecular orbitals of Chl-c_2 and Chl-c_2–$(CH_3OH)_2$ are shown in Figure 2, where the top panels show the highest occupied molecular orbitals (HOMO or {1}) for these structures. The lower panels show the next four outer valence molecular orbitals of Chl-c_2–$(CH_3OH)_2$ {2–5}. The HOMO for both structures (Chl-c_2 and Chl-c_2–$(CH_3OH)_2$) is defined by contributions from the pyrrolic rings. As also illustrated in Figure 2, the next outer valence orbitals {2–5} may involve localization over specific rings or other peripherical groups.

Table 2
wB97XD results for the average first ionization energy (IEs in eV) of chlorophyll-c_2 in liquid methanol with and without (italics) electrostatic embedding. Bracketed values are IEs from the (minus signed) HOMO energy. Δ(G–S) is the shift of the first ionization energy from the gas-phase (G) to solution (S).

Chlorophyll-c_2–$(CH_3OH)_2$[a]	S	Δ(G–S)
cc-pVDZ	6.11 ± 0.24	0.67 ± 0.24
	[6.51 ± 0.23]	[0.51 ± 0.24]
	[*6.75 ± 0.02*]	[*0.27 ± 0.02*]
cc-pVTZ	6.15 ± 0.24	0.71 ± 0.24
	[6.63 ± 0.23]	[0.47 ± 0.24]
	[*6.86 ± 0.02*]	[*0.24 ± 0.02*]

[a] Coordination to Mg through Mg···OH hydrogen bond interactions.

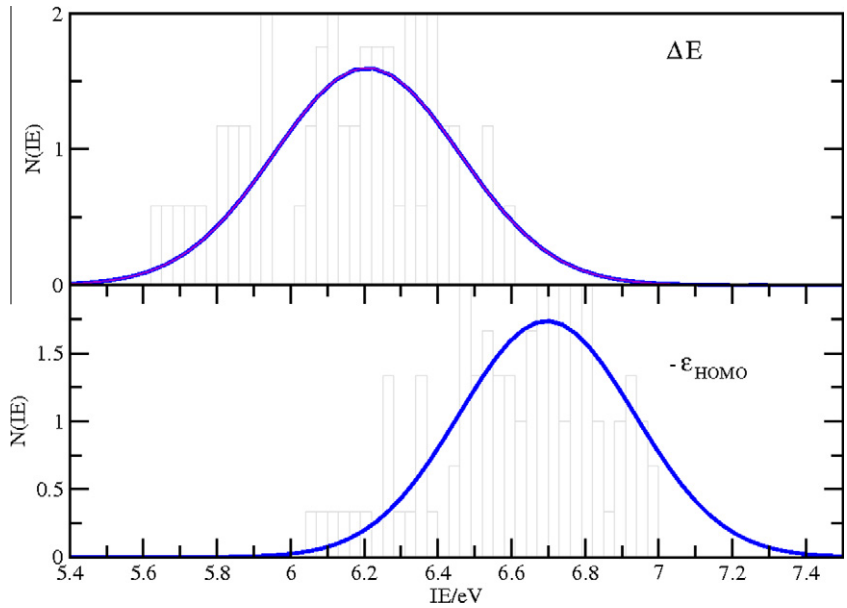

Figure 3. Ionization energy (IE) distribution (wB97XD/cc-pVTZ) of Chl-c_2 in liquid methanol. (Top) IE distribution from ΔE calculations; (Bottom) IE distribution from the (minus signed) HOMO energy. Curves are gaussian fits to the distributions.

3.2. Ionization of chlorophyll-c_2 in liquid methanol

Results for the ionization of Chl-c_2 in liquid methanol are reported in Table 2. These results rely on calculations using 100 Monte Carlo configurations for a complex of Chl-c_2 with the two nearest methanol molecules of the Mg atom (the QM system) embedded in the electrostatic background of remaining methanol molecules represented by point charges. Results for the QM system without the electrostatic embedding are also reported in Table 2 (values in italics). We defined Δ(G–S) as the shift of the first ionization energy of Chl-c_2 from the gas-phase (G) to solution (S). Our prediction for Δ(G–S) is 0.71 ± 0.24 eV (wB97XD/cc-pVTZ) by using IEs from ΔE calculations. Calculations by using the HOMO energy leads to 0.47 ± 0.24 eV. Similar values for Δ(G–S) from the HOMO energy differences are predicted by calculations carried out with the cc-pVDZ basis-set. For example, Δ(G–S) estimates are (0.51 ± 0.24) and (0.47 ± 0.24) eV for calculations with the cc-pVDZ and cc-pVTZ, respectively. Δ(G–S) from ΔE calculations are 0.67 ± 0.24 eV (cc-pVDZ) and 0.71 ± 0.24 eV (cc-pVTZ). However, the gas-phase calculations suggest that estimates from the HOMO energy with the wB97XD functional are in good agreement with experiment (see Table 1). Our results for the non-embedded configurations indicate the Mg···OH interactions lead to a red-shift of 0.24 ± 0.02 eV of Chl-c_2 in liquid methanol relative to the gas-phase value. This result is quite similar to the gas-phase estimate based on the microsolvation approach and it is ~0.2 eV smaller than the estimate for Δ(G–S) when the electrostatic background is included. Interestingly, our value for the IE of the Chl-c_2–$(CH_3OH)_5$ complex (6.59 eV with wB97XD/cc-pVTZ) is close to our estimate for the average IE in liquid methanol by using the quantum system (Chl-c_2 + the two closest methanol molecules) embedded in the electrostatic field of the remaining methanol molecules (6.63 ± 0.23 eV). This is not suprising because in this case, although not expliclty included, the methanol molecules interacting with Chl-c_2 carboxyl groups are represented by point charges. Therefore, the dependence of the IE with the number of methanol molecules is in keeping with our previous analysis on the electronic absorption spectrum of Chl-c_2 in liquid methanol [21] that pointed out the importance of the explicit consideration of the solvent molecules in close interaction with the solute.

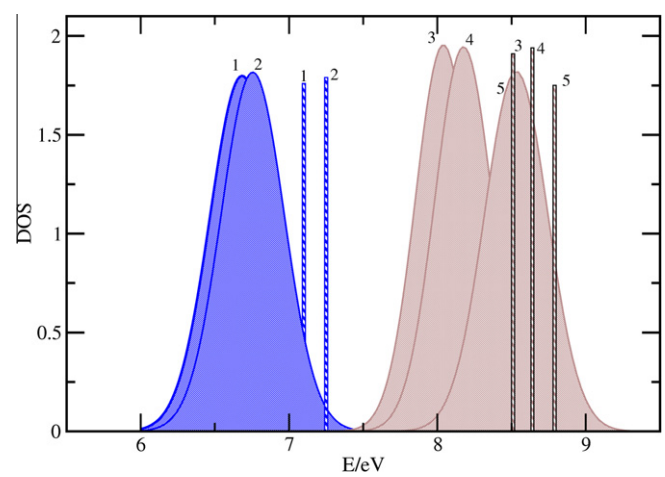

Figure 4. Electronic density of states (DOS) for the five outer valence states {1–5} of Chl-c_2 in liquid methanol from wB97XD/cc-pVTZ calculations. Vertical bars are gas-phase ionization energies.

A relevant aspect of the present analysis of the ionization energy of Chl-c_2 in liquid methanol concerns thermal induced fluctuations of IEs in the liquid. This is illustrated in Figure 3 that shows the distribution of IEs [N (IE)]. Our results indicate that the ionization threshold of Chl-c_2 in liquid methanol can be placed near 6.0 eV, which is ~1.0 eV below the gas-phase value. We stress the importance of this estimate considering that it illustrates the role played by thermal induced fluctuations in liquid phase on the ionization process of a solvated photosynthetic chromophore.

Although our calculations were focused on the estimate of the average first ionization energy of solvated Chl-c_2, it should be noticed that by using DFT orbital energies, the valence electronic density of states (DOS) for Chl-c_2 in liquid methanol can be determined. This is illustrated in Figure 4, where we present the wB97XD/cc-pVTZ DOS. The curves in Figure 4 are gaussian fits to the DOS. Vertical bars represent (minus signed) gas-phase orbital energies for the set of HOMO plus the four outer valence orbitals illustrated in Figure 1. These results indicate that this set of valence

orbital energies are red-shifted (by nearly the same value) relative to the corresponding gas-phase values. They also indicate the formation in solution of two energy bands (blue and brown in Figure 4 associated with different sets ({1–2} and {3–5}) of Chl-c_2 orbitals. Considering the difference between the first vertical ionization energies of Chl-c_2 and methanol previously referred, this DOS corresponds essentially to the energy distribution for the outer valence states of the chromophore.

4. Conclusions

Solvent effects on the ionization energy of Chl-c_2 in liquid methanol were investigated using a sequential QM/MM methodology. To assess the influence of hydrogen bonding on the Chl-c_2 IEs, a series of calculations relying on microsolvation models were also carried out. By performing calculations for a set of statistically uncorrelated configurations generated by Metropolis Monte Carlo sampling we predict that the first ionization energy of Chl-c_2 in liquid methanol is red-shifted by $\sim$ 0.5 eV relative to its gas-phase value. This estimate is in good agreement with results for a gas-phase optimized structure of the Chl-c_2–$(CH_3OH)_5$ complex. Moreover, our results also suggest that the ionization threshold for Chl-c_2 in solution is significantly red-shifted relative to the gas-phase value, a result that may be useful for understanding the electronic properties of photosynthetic chromophores in solution. The observed (red)-shifts can be explained by (local) hydrogen bonding and long-ranged electrostatic interactions. Our results indicate that the maxima of the outer valence orbital energy distributions of Chl-c_2 in liquid methanol are red-shifted by nearly the same value relative to the corresponding gas-phase orbital energies. The formation in solution of two energy bands related to a set of five outer valence orbitals of Chl-c_2 is also observed. In conclusion, this study provides relevant information to understand the role played by solvent effects on the ionization of a photosynthetic chromophore.

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