Free energies for the coordination of ligands to the magnesium of chlorophyll-a in solvents

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Abstract. The coordination of bases to chlorophyll magnesium modifies spectroscopic properties in solution as well as *in situ* in reaction centres. We evaluate the free energies of complexation of one or two pyridine, 1-propanol, diethyl ether or water solvent molecules at 298 K and at 150 K to rationalize observed phenomena. Various *a priori* dispersion-corrected density-functional theory calculations are performed as well as 2nd-order Møller-Plesset calculations, focusing on the effects of dispersion modifying the intermolecular interactions, of dispersion modifying solvation energies, of entropy, and of basis-set superposition error. A process of particular interest is magnesium complexation in ether at low temperature that is often exploited to assign the Q-band visible absorption spectrum of chlorophyll. Recently, we demonstrated that trace water interferes with this process, but the nature of the resulting complex could not be uniquely determined; here it is identified as ether.Chlorophyll-a.H_2O, consistent with interpretations based on our authoritative 2013 assignment.

1. Introduction

Much progress has been made in the last 5 years concerning accurate cost-effective methods of including dispersion interactions in the evaluation of chemical reaction energies using *a priori* electronic-structure computation methods [1-5]. Still being understood is the importance of dispersion interactions between reactants and products and their solvation environment [6]. Here we consider complexation reactions of chlorophyll-a (Chl-a) with ligand bases. For gas phase reactions, Ben Fredj *et al.* [7] have demonstrated the importance of dispersion to the binding, as well as the role of entropy effects. They also considered binding in various solvents focusing on water complexation, but did not include the dispersive contributions to solvation [8]. The results obtained showed qualitative trends that allowed many observed chlorophyll solvation processes to be rationalized, but in absolute magnitude the calculated ligation free energies ΔG were too negative by ca. 5 kcal mol^{-1}, a significant amount when it comes to the *a priori* prediction of species concentrations aiding experimental investigations. We hypothesize that the neglect of the dispersion interactions with solvent forms a major component of this discrepancy.

A problem of this type of current interest is the complexation of trace water to Chl-a magnesium in diethyl ether (DEE) solution at ~ 150 K [9]. This issue directly affects the assignment of the visible-absorption Q-band spectrum of Chl-a and therefore relates to our basic understanding of most natural photosynthetic processes [10]. Low-temperature spectra measured in ether have traditionally been very important for the determination of this assignment [11-13], leading to rejection of the 1960's "traditional" assignment [14-18] and its replacement by the "modern" 1980's one [11-13,19-22]. Nevertheless, the "traditional" assignment remained in general use for the interpretation of photosynthetic function [23-26], while recent experiments continued to be interpreted as supporting either one assignment or the other [25,27]. In 2013 we resolved this 50-year-old riddle by noting that

the “traditional” and “modern” assignments represented the molecular excited state using two feasible Born-Oppenheimer potential-energy surfaces that in reality were strongly mixed by vibronic coupling [10], voiding the Born-Oppenheimer approximation. This allowed an extremely wide range of spectroscopic and kinetic data for Chl-a and 31 other chlorophyllides to be understood in a range of solvents as well as *in situ* in reaction centres. One significant anomaly remained, however: the nature of the spectra observed in DEE at low temperature, spectra critical to the historical development of the spectral assignment.

Complexation of chlorophyll magnesium can lead to significant shifts in the Q-band spectra, and it was this feature that was exploited in many early assignment studies [11-13,19-22]. Either one or two ligands may bind, leading to progressively larger effects [28]. Our assignment of the spectra of the chlorophyllides was strongly supported by time-dependent density functional theory (TDDFT) calculations using the CAM-B3LYP [29] method, the first such method demonstrated to be descriptive of the spectra of chlorophyllides [30]. However, these calculations gave results inconsistent with the standard interpretation of the experimental spectra assuming that DEE.Chl-a.DEE double adducts form at low temperature. Subsequent experiments in rigorously dried solvent showed that the critical observed bands only appeared when trace water was added to the solvent, indicating instead that water is involved in the complexation [9]. However, insufficient experimental and/or spectroscopic computational data was available to discriminate between two possible scenarios for the adduct, either DEE.Chl-a.H_2O or else H_2O.Chl-a.H_2O. Here we employ free-energy of ligation calculations to answer this question. To calibrate the methods used, reactions in liquid water, pyridine (PY), 1-propanol (PRO), and DEE are examined.

2. Methods

Following the basic methodology of Ben Fredj *et al.* [8], the ligation free energies in solution of Chl-a with explicit solvent molecules were calculated using a composite approach. Geometries for Chl-a complexed in the gas phase with various ligands in axial and diaxial coordination were optimized using GAUSSIAN-09 Revision D.01 [31]. This was done at the Møller-Plesset 2nd-order (MP2) level of theory [32] with 6-31G(d) basis, and alternatively using the density functional methods ωB97X [33], ωB97XD [34], PBE [35] and PBE corrected using Grimme's D3 method, PBE-D3 [4], with 6-31+G(d) basis set. Correlated methods are still believed to provide the most reliable *ab initio* calculations but they proved too costly to carry out beyond the MP2 6-31G(d) level. The ωB97XD density functional approach utilizes a later generation functional that includes range separation combined with Grimme's D2 dispersion model; it is known to be generally reliable [5]. The PBE-D3 method adds dispersion capability to a traditional quality density functional and has been shown to give excellent results for a range of properties [5]. Single-point energies were then obtained at the 6-31+G(d) geometries using the 6-311++G(2d,2p) basis sets and corrected for basis-set superposition error (BSSE) using the counterpoise correction method [36]. Its application here is slightly different to that employed by Ben Fredj *et al* [7,8], however, defining the energy of the second adducts using a simple complexation reaction for the first adduct. Thermodynamic effects were estimated by vibrational frequency calculations at the 6-31G(d) level using the various density functionals. Implicit solvation effects were determined using the PCM model of Tomasi *et al.* [37] considering also the effects of the dispersion solute-solvent interaction energy using the model of Floris *et al.* [38]. This treatment requires the specification of the solvent density which is not automatic in GAUSSIAN-09 for PRO and PY; for them, values of 0.008040 and 0.007470 molecules per Å^3 were used, respectively.

Use of PBE-D3 provides a technical advantage in that results can be obtained using extensive plane-wave basis sets as well as with atomic basis sets, allowing the errors associated with incomplete atomic basis sets to be investigated. The plane-wave calculations are performed by VASP [39] using the PAW method to treat core electrons [40]. High precision default cutoffs were used, the molecules being placed in periodic cubic boxes of length 20 Å; all structures were fully optimized.

Chla-a is modelled replacing its phytyl chain with methyl. This is not expected to have significant consequences as the adduct ligands are too small to interact with the phytyl chain and its inductive effect on the macrocycle is negligible.

3. Results

Figure 1 shows the PBE-D3 calculated geometries for the adducts, while Supporting Information (SI) lists all coordinates optimized at this level. Results obtained using other methods are not significantly different, as indicated by the calculated Mg to ligand distances shown in SI in Table S1. Note that the two sides of the macrocycle plane are different, not particularly because of the chiral centre present but more related to how the side chains orient themselves. In enhanced calculations, averaging over such reorientational motions would need to be included. A consequence of the difference in macrocycle face is that adducts expressed as X.Chl-a and Chl-a.X are different from each other, often by significant amounts. In SI, Table S3 provides a full set of calculated energies for all possible reactions. These results are abbreviated in Tables 1 and 2 which show the calculated contributions to the purely electronic energy plus temperature-related corrections and free-energies, respectively; in these tables only the most stable mono adducts and their subsequent reactions are

shown. Of particular note is the observation that water prefers to bind on the opposite side than does PY, PRO, and DEE, an effect that is paralleled in the bond-length data from Table S1.

Ben Fredj *et al.* [7,8], have previously shown that BSSE contributions to ligation energies are significant. For large basis sets, the wisdom of this approach for hydrogen-bond and ligation interactions has been questioned as often the increase in the correlation energy with increasing basis exceeds the BSSE [41,42]. To determine the most appropriate procedure, PBE-D3 interaction energies were evaluated both using our standard approach and using a plane-wave basis set. These basis sets are sufficiently large as to be at the complete basis set limit. As shown in Table 1, the resulting interaction energies ΔE (for all reactions) differ by at most 1 kcal mol^{-1} with a RMS difference of 0.54 kcal mol^{-1}, indicating that BSSE corrections indeed should be applied when studying magnesium ligation. Note that part of these small differences could arise from the use of the PAW method to approximate the effects of the core electrons during the plane-wave calculations.

Very similar results are obtained from the PBE-D3 and ωB97XD methods. In general PBE-D3 is slightly less bound, with a RMS difference of just 1.5 kcal mol^{-1}. MP2 is noticeably more attractive, however, with a RMS difference to PBE-D3 of 3.1 kcal mol^{-1}; this result is expected as MP2 by its nature is guaranteed to overbind by a small amount. It is an *ab initio* method, however, and this result allows the DFT values to be interpreted with confidence.

SI Table S2 shows the contributions to the interaction energies coming from the dispersion components of ωB97XD and PBE-D3 as well as the dispersion-dominated total correlation energy from the MP2 calculations. These are largest for PY and DEE and smallest for water, but their magnitudes double from ωB97XD to PBE and then again to MP2. They are indicative of the extent to which dispersion is implicitly treated in the base DFT methods.

The average solvation energy correction for all reactions is 4.9 kcal mol^{-1} when only electrostatic contributions are included, and its variation between reactions is small. Hence, as Ben Fredj *et al.* concluded [8], this term does not appear of great significance in terms of relative chemical property analysis. However, when the solvent dispersion correction [38] is added, the average correction increases to 12.4 kcal mol^{-1} with a spread of 9 kcal mol^{-1}. This term therefore significantly modifies calculated reaction free energies. Its effect is largest when ligands have sufficient bulk to sit in van der Waals contact with the Chl-a side chains.

These solvation energy changes include mostly enthalpic contributions and do not include the effect on the entropy of bringing molecules from the gas phase into solution. The entropy in the gas phase can be directly calculated but the entropy in solution is a complex property of the solution structure. As a result, we utilize experimental measurements of the entropy of vaporisation of the various solvents considered, showing their contributions to free-energy changes at 298 K and at 150 K in Table 1 and Table S3. At 298 K, these vary from -6.8 to -9.2 kcal mol^{-1}; using Trouton's rule [43], this value is expected to be close to -6.1 kcal mol^{-1}, but the solvents considered have internal structure.

As Ben Fredj *et al.* [7,8] showed, the free energy corrections associated with complexation reactions in the gas phase are large and variable, playing a key role in the ligation process. At 298 K, the average correction is 12.6 kcal mol^{-1}, but to some extent these are cancelled by the vaporisation entropy loss when gas-phase molecules are taken into solution and the combined contribution, on average, is just 4.6 kcal mol^{-1}.

Table 1 and Table S3 show that for the first ligation process the calculated interaction energies ΔE are ca. -25 kcal mol^{-1} for PY and DEE, -20 kcal mol^{-1} for PY and -15 kcal mol^{-1} for water. These are paralleled by proportionally smaller values for the second ligation process, ca. -17 kcal mol^{-1} for PY and DEE, -14 kcal mol^{-1} for PY and -11 kcal mol^{-1} for water. The reduced values for water are

consistent with the observation that Chl-a is insoluble in water but the similar values for PY and DEE are unintuitive as PY is a strong coordinating solvent that forms double adducts at room temperature [6,44] whilst, unlike PRO [27], DEE is now not believed to form double adducts even at low temperature [9].

The net effects of the thermal, solvent entropy, and vaporisation entropy corrections at 298 K (Table S3) introduce significant differences between the two possible first-ligation processes, but the relative ordering seen for ΔE is maintained, with ΔG for the lowest-energy process (Table 2) being ca. -7 kcal mol^{-1} for PY and DEE, -2.4 kcal mol^{-1} for PY and -2.0 kcal mol^{-1} for water. For PY, DEE, and PRO, these values are consistent with the observation that adducts form in pure-liquid solution, requiring ca. $\Delta G < 0$ kcal mol^{-1}. However, when the second ligation processes is considered, the differences between the coordination environments on each side of the macrocycle plane become dominant. For PY, ΔG is calculated to be 2 and 3 kcal mol^{-1} by PBE-D3 and ωB97XD, respectively, near the limit $\Delta G < 0$ kcal mol^{-1} required for double adducts to form in liquid solution, as observed. For DEE, these values increase to $\Delta G = 6$ and 5 kcal mol^{-1}, respectively, consistent with the observation that double adducts do not form. Intrinsically, the attractions between Chl-a and either PY or DEE are similar but dispersive interactions and entropy effects make the two sides of Chl-a look quite different to DEE. This is why these solvents take on a qualitatively different nature [44]. The calculations predict intermediary values of $\Delta G = 3$ and 2 kcal mol^{-1}, respectively, for PRO, in agreement with the observation that double adducts do not form at 298 K and with the qualitative notion that PRO is intermediate in its coordinating ability between PY and DEE.

Having established that the calculations depict key qualitative observations, we come to the critical issue of the ligation of Chl-a in DEE solution at low temperature. A new species starts to appear in spectra as the temperature is lowered below 190 K, increasing steadily in concentration until

the freezing temperature of DEE is reached at 156 K [9,11-13,27]. This species is a water adduct but its composition as inherently either H_2O.Chl-a.DEE or H_2O.Chl-a.H_2O is unclear [9]. If it were H_2O.Chl-a.H_2O, then other water molecules would also have to add in order to complete intramolecular hydrogen-bonding networks [8], but such microheterogeneity is commonly observed in binary mixtures of liquids [45]. Table 2 (and Table S3) show also free-energy changes evaluated at 150 K. First we consider the simpler process of solvation in PRO. At low temperatures double adducts form [27], a result understandable from the PBE-D3 and ωB97XD predictions of ΔG = 2 and 1 kcal mol^{-1}, respectively. For the addition of a second DEE ligand to Chl-a.DEE, both methods predict similar values of ΔG = 2 and 1 kcal mol^{-1}, respectively, suggesting that double DEE adducts may be feasible. Alternatively, for the addition of water to Chl-a.DEE, these methods predict ΔG = -2 and -1 kcal mol^{-1}, respectively. As water is dilute in these experiments, a value of ca. -2 kcal mol^{-1} would seems to be the maximum that could account for the observations. Therefore, we see that the calculated results can account for all experimental observations and predict that H_2O.Chl-a.DEE is preferred to DEE.Chl-a.DEE whilst H_2O.Chl-a.H_2O is uncompetitive. Hence the observed species is identified as being H_2O.Chl-a.DEE.

4. Conclusions

The accurate *a priori* prediction of free energy changes for reactions of large molecules in solution is a difficult task as many competing effects must be taken into account, all of which are problematic to evaluate reliably. Either computational methods like coupled-cluster theory or advanced density functionals with either very large basis sets in atomic-orbital calculations or else the inclusion of core electrons in plane-wave calculations are required to get accurate interaction energies. This must include accurate treatment of dispersion interactions. Free-energy corrections to gas-phase

reactions are also troublesome as many low-frequency modes are implicated and these may not be treated properly using the harmonic-oscillator approximation usually employed in evaluating zero-point energies and entropies. Finally, the solvation entropy and enthalpy terms are also both difficult to evaluate and now represent bottlenecks to accurate calculations. While treatment of electrostatic solvent interactions using dielectric-continuum models is at an advanced stage, the same is not true for dispersion interactions with the solvent. For large molecules and solvents, these interactions can dominate, as we see here even for just small solvent molecules interacting with Chl-a. While much more development is required in this area, we have also obtained excellent results using the 1991 method of Floris *et al.* [38] for free-energy calculations of self-assembled monolayers of very large meso-tetraalkylporphyrins on graphite [6]. *A priori* evaluation of the entropy of vaporisation of solute reactants and products presents a critical challenge, however. While approximations like Trouton's rule are general and useful, the errors associated with this are of the order of a few kcal mol^{-1} and are now significant compared to other calculation errors.

Available methods are shown to give results that are useful in interpreting subtle observed chemical ligation processes of the type that are critical for photosynthetic function in plants and bacteria. In particular, they have been applied to identify the nature of an important species seen for over 30 years in the spectra of Chl-a in DEE whose properties overturned the existing understanding of chlorophyll's critical low-energy Q-band, leading eventually to an authoritative assignment of the excited-state properties of Chl-a [10].

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Table 1. Electronic interaction energies ΔE from either plane-wave calculations or else atomic basis-set calculations with BSSE correction for ligands binding to Chl-a, along with enthalpic solvation corrections[a] evaluated using electrostatic plus dispersive contributions and those involving just electrostatic terms, all in kcal mol^{-1}.

Reaction[b]	ΔE PAW	ΔE 6-311++G** with BSSE			Full Solvent Correction 6-311++G** no BSSE		Electrostatic Solvent Correction 6-311++G** no BSSE	
	PBE-D3	PBE-D3	ωB97XD	MP2	PBE-D3	ωB97XD	PBE-D3	ωB97XD
Chl-a + PY → Chl-a.PY	-24.1	-23.5	-24.5	-27.6	13.6	13.8	5.9	5.9
Chl-a.PY + PY → PY.Chl-a.PY	-16.3	-17.3	-18.2	-21.8	12.6	12.8	3.5	3.9
Chl-a + H_2O → H_2O.Chl-a.	-15.0	-15.1	-14.9	-15.3	10.8	11.0	6.5	6.7
H_2O.Chl-a + H_2O → H_2O.Chl-a.H_2O	-11.2	-10.9	-10.5	-9.9	9.6	9.7	5.3	5.3
Chl-a + PRO → Chl-a.PRO	-19.8	-19.5	-20.4	-20.6	13.4	13.5	5.9	6.0
Chl-a.PRO + PRO → PRO.Chl-a.PRO	-14.5	-14.7	-15.5	-16.9	13.8	13.4	5.0	4.6
Chl-a + DEE → Chl-a.DEE	-24.3	-23.7	-26.5	-27.5	13.0	13.2	4.2	4.3
Chl-a.DEE + DEE → DEE.Chl-a.DEE	-14.9	-15.2	-17.6	-19.4	12.1	12.0	2.7	2.8
DEE.Chl-a + H_2O → DEE.Chl-a.H_2O	-10.6	-10.4	-9.4	-10.4	6.1	6.8	3.0	3.1

[a] The solvent is the liquid of the adduct except for the mixed water-DEE adducts for which the solvent is DEE.
[b] The two sides of the Chl-a molecule are defined as in Fig. 1.

Table 2. The free energy of ligation to Chl-a in solvents[a] and its components at 298 K and 150 K, in kcal mol^{-1}.

Reaction	Vaporization Entropy correction[b]		thermal corr. 298 K 6-31+G*		thermal corr. 150 K 6-31+G*		ΔG 298 K with solvent corr.			ΔG 150 K with solvent corr.		
	298 K	150 K	PBE-D3	wB97XD	PBE-D3	wB97XD	PBE-D3	wB97XD	Exp.	PBE-D3	wB97XD	Exp.
Chl-a + PY → Chl-a.PY	-7.5	-3.8	11.7	10.2	6.4	5.7	-5.7	-8.0	< 0	-7.2	-8.8	< 0
Chl-a.PY + PY → PY.Chl-a.PY	-7.5	-3.8	14.0	16.3	7.6	8.9	1.8	3.4	< 0	-0.8	-0.2	< 0
Chl-a + H_2O → H_2O.Chl-a.	-8.5	-4.3	10.6	10.5	6.0	5.7	-2.2	-1.8		-2.5	-2.4	
H_2O.Chl-a + H_2O → H_2O.Chl-a.H_2O	-8.5	-4.3	10.6	10.1	6.0	6.2	0.8	0.7		0.5	1.1	
Chl-a + PRO → Chl-a.PRO	-9.2	-4.6	12.8	13.8	7.1	7.7	-2.5	-2.3	< 0	-3.6	-3.8	< 0
Chl-a.PRO + PRO → PRO.Chl-a.PRO	-9.2	-4.6	13.2	13.4	7.2	7.3	3.1	2.2	> 0	1.8	0.7	~ 0
Chl-a + DEE → Chl-a.DEE	-6.8	-3.4	11.3	12.9	6.3	7.1	-6.2	-7.2	< 0	-7.9	-9.6	< 0
Chl-a.DEE + DEE → DEE.Chl-a.DEE	-6.8	-3.4	16.0	17.2	8.7	9.6	6.1	4.8	> 0	2.2	0.6	> 0
Chl-a.DEE + H_2O → H_2O.Chl-a.DEE	-10.1[c]	-5.1[c]	12.9	11.1	7.2	6.3	-1.5	-1.6	>-2	-2.1	-1.3	~ -2

[a] The solvent is the liquid of the adduct except for the mixed water-DEE adducts for which the solvent is DEE.

[b] See SI

[c] with other corrections, see SI

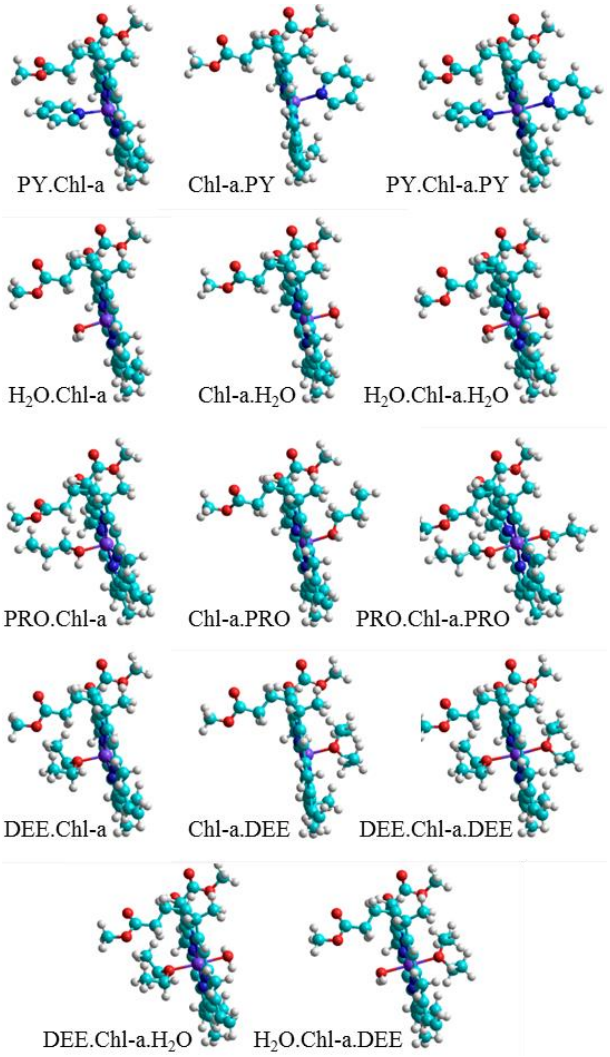

Figure 1. PBE-D3/6-31+G(d) optimized structures of Chl-a adducts with one or two PY, water, PRO, and DEE molecules. The coordination environments on each side of the macrocycle plane are different.