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Spectroscopic properties of chlorophylls and bacteriochlorophylls studied by molecular orbital CI methods

JM Linnanto and JEI Korppi-Tommola

Department of Chemistry, University of Jyväskylä, P.O.Box 35, FIN-40351 Jyväskylä, Finland, fax 358-14-2602553, email linnanto@jyu.fi

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Introduction

Systematic computational methods are needed for prediction of spectroscopic properties of photosynthetic chromophores in order to understand their function in specialised photosynthetic complexes. We have used quantum chemical MO/CI methods to study spectroscopic properties of chlorophylls *a*, *b*, c_1, c_2, c_3 and *d* and bacteriochlorophylls *a, b, c, d, e, f, g, h*. To test the usefulness of quantum chemical methods in characterisation of spectroscopic properties of photosynthetic pigments, absorption spectra of the chlorophylls (Chl's) and bacteriochlorophylls (BChl's) have been simulated. Both vacuum dyes and 1:1 solvent complexes were studied. Simulations included full energy minimisation at semiempirical PM3, ab initio 6-31G* and density functional (DFT) level of calculation. In particular it was shown that solvent interaction in the excited states induces red shifts of the lowest energy spectroscopic transitions of the dyes. It is demonstrated that chlorophylls and bacteriochlorophylls imbedded in a particular site of a protein are subject to similar interactions.

Results

As the first approach semiempirical PM3 method was used to optimise geometric structures of the Chl's (Linnanto 2000) and the BChl's (Linnanto 2001a), magnesium porphin, magnesium-chlorin and magnesium-bacteriochlorin. In all computed

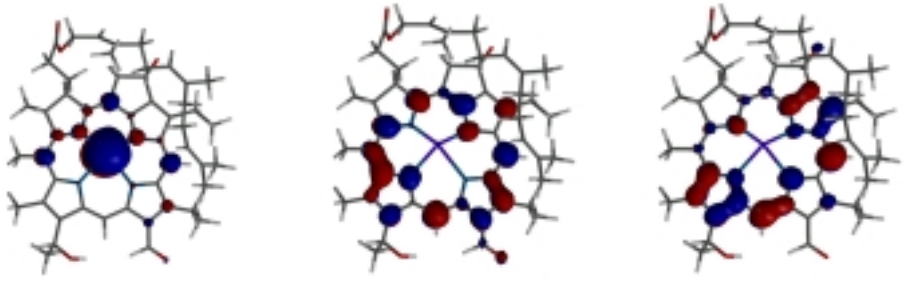

Fig. 1. *From left to right LUMO+2, LUMO+1 and LUMO orbitals of Bchle*

structures the magnesium atom was located off the centre and above the porphyrin ring and positive atomic charges on nitrogen atoms were obtained (**Fig.1.**). At PM3

minimum energy geometry *ab-initio* HF/ 6-31G* level calculation gives negative charges on nitrogen atoms. Surprisingly the HOMO states did not contain charge on magnesium atom, but the excited LUMO+1 and/or LUMO+2 states show considerable charge. Configuration interaction (CI) methods, the PM3 (5,5) CIS and CISD, ZINDO/S CIS (n,n) with 2<n<30 and *ab-initio* CIS (5,5)/6-31G* were used to estimate spectroscopic properties of the chromophores. Linear correlations between the experimentally observed and calculated transition energies were obtained in all cases. Such correlations were used to estimate transition energies for parent molecular systems. At semiempirical level best estimations of transition energies of the Q_y, Q_x and the Soret bands were obtained by using the PM3 (5,5) CISD method.

The ZINDO/S CIS (15,15) method turned out to perform best for overall simulation of absorption spectra of the Chl's and BChl's as this method gave reasonable oscillator strengths and transition energies. In fact relative positions of the Q_y bands of all Chl's and BChl's were correctly predicted. Calculations predicted also solvent induced spectroscopic shifts of the Q_x and Soret transitions of the chromophores leaving the Q_y transition almost unshifted, in accord with experimental findings. The spectroscopic shifts are due to solvent induced energy level shifts and redistribution of charge on the magnesium atom in the excited states. Computed spectra of 1:1 solvent complexes match the experimental spectra much better than spectra calculated in

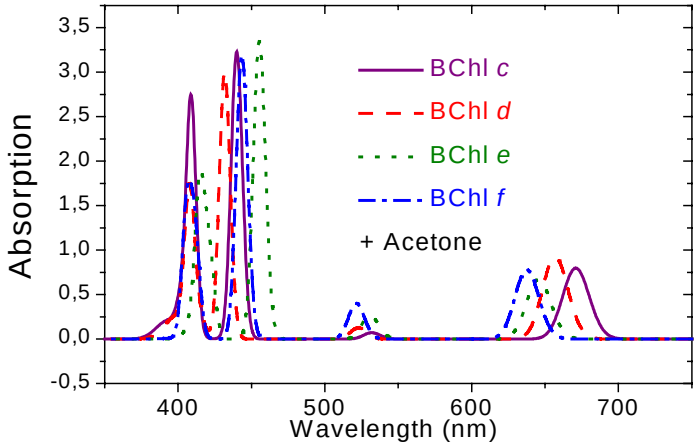

Fig. 2. *Computed absorption spectra of BChlc, d, e and f complexes with acetone*

vacuum (Fig.2). Geometry optimisations were made for all the mentioned chromophores and their solvent complexes also at ab initio 6-31G* and density functional (DFT, B3LYP/6-31G*) levels (Linnanto 2001b). The major difference as compared to the semiempirical results is that in the minimum energy geometry the magnesium atom is more or less centrally located and the charge densities on the magnesium atom and the nitrogen atoms become positive and negative, respectively, as expected.

The ab initio and DFT minimum energy structures were then used in subsequent CI calculations at ZINDO/S CIS (15,15) or HF CIS (5,5) levels. The DFT minimum energy geometries with single point ZINDO/S CIS (15,15) or HF CIS (5,5) calculations give best agreement between the experimentally observed and computed transition energies of Chl's and BChl's (**Table 1.**). Especially the Q_x transition

energies were much better predicted than with PM3 or HF 6-31G* minimisation. Yet linear scaling of semiempirical transition energies with experimentally measured transition energies turned out reasonable results and it is by all means the most economical method to predict spectral Q_y transition energies of Chl's and BChl's. This approach is almost the only way of calculation of nearest neighbour chromohore-chromophore and chormophore-protein interaction energies when much larger systems than a single chromophore has to be computed.

Table 1. Calculated transition energies of Chl *a* using PM3, HF 6-31G* and DFT (B3LYP 6-31G*) geometry optimisation and PM3 CISD(5,5), ZINDO/S (15,15) and HF CIS (5,5) configuration interactions

Chl *a*	Q_y (f)	Q_x (f)	Soret (f)
PM3 [a]			
ZINDO/S CIS (15,15)	666 (0.5)	534 (0.1)	439 (1.7)
PM3 CISD (5,5)	664 (7.1)	602 (4.8)	441 (1.8)
HF CIS (5,5)	681 (0.8)	532 (0.2)	439 (3.0)
HF 6-31G* [b]			
ZINDO/S CIS (15,15)	671 (0.4)	548 (0.1)	437 (1.9)
HF CIS (5,5)	678 (0.4)	541 (0.3)	441 (1.9)
B3LYP 6-31G* [b]			
ZINDO/S CIS (15,15)	669 (0.5)	560 (0.0)	434 (2.0)
HF CIS (5,5)	673 (0.6)	565 (0.0)	433 (3.1)
Exp.	662	578	430

a) Chl *a* b) Phytyl tail of Chl *a* has been substituted by a mehtyl group in in HF and B3LYP geometry optimisations.

Calculation of spectroscopic transitions in Chl- and BChl-solvent complexes gave an hint of what may take place when chromophores are imbedded in a protein site, transition energies will be changed due to chromophore-protein interaction. This effect was most clearly seen in simulation of site energies of the BChl *a* - B800 in *Rps. acidophila*. In the B800 ring the inter chromophore interaction energies are very small, yet the spectroscopic transition is substantially red shifted (about 30 nm) from the monomer value of 773 nm. The transition energies of the BChl *a* - B800 rings were estimated by including the nearby protein environment of the chromophore within 7Å radius in a semiempirical ZINDO/CI calculation. The calculations produced results that were consistent with the experimental spectrum. According to the results of the present study best site energies will be obtained by using fixed heavy atom co-ordinates of a chromophore present in a light harvesting complex and DFT optimisation of hydrogens. A large enough environment has to be included in the calculations to obtain correct site energies. The ZINDO/S CIS (15,15) configuration interaction will produce realistic spectroscopic transition energies. This result is general and applicable for prediction of site energies of any chromophore imbedded in protein the atomic structure of which is known. In particular, in the light harvesting antenna of cyanobacteria, algae and plants that contain large number of chlorophylls (Chl a and/or Chl b) at fairly large distances from each other, local protein interactions more than chromophore - chromophore interactions determine spectroscopic transition energies in these complexes. The assignment of spectroscopic transitions to chromophores located in a particular site of such a light harvesting complex is almost impossible without such systematic calculations.

Conclusions

Quantum chemical methods were tested for their predictive power in simulation of absorption spectra of photosynthetic pigments Chl's and BChl's. It was observed that solution spectra could be simulated much better by using transition energies of 1:1 solvent complexes than those obtained for vacuum molecules. It is concluded that DFT optimisation of hydrogens with heavy atom co-ordinates fixed to crystalline structure and single point ZINDO/S CIS (15,15) configuration interaction calculation give reasonable site and nearest neighbour interaction energies of chromopores imbedded in the protein.

References

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