TDDFT Study of the Electronic Excitation Spectra of Chlorophyllide *a* and Pheophorbide *a* in Solvents

Zheng-wang Qu
Humboldt Universität zu Berlin, Institut für Physik,
AG Photobiophysik, Newtonstr. 15, Berlin
E-mail: zheng@physik.hu-berlin.de
SFB450 subproject C3

Motivated by recent efforts in our group on:

- Laser pulse control of exciton transfer in light harvesting complexes
- Optical properties of supermolecular chromophore complexes
- Mixed quantum-classical description including vibronic structures

Outline

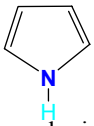
1. Introduction: molecular structures, remaining problems
2. Density Functional Theory (DFT) and Time-Dependent DFT
3. Polarizable Continuum Model (PCM) for solvents
4. Results: method test, solvent effects, new spectral assignment
5. Conclusions

Short Notation:
Pheo : Pheophorbide *a*
Chlo : Chlorophyllide *a*
CT : Charge-Transfer state

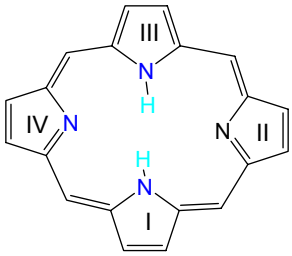
eV as energy unit:
1 eV = 1000 meV = 8065.5 cm^{-1} = 627.5 kcal/mol

Z.-W. Qu, H. Zhu, V. May, R. Schinke, *J. Phys. Chem. B*, 2009, 113(14), 4817-4825.

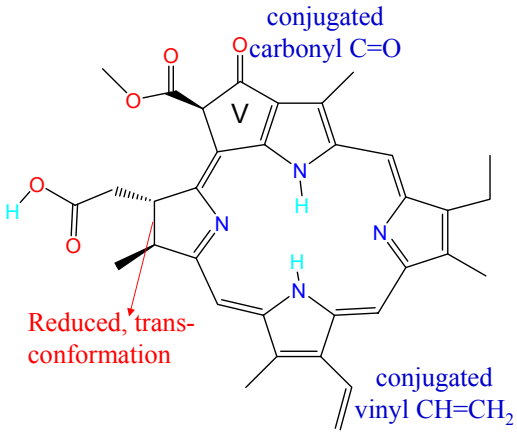
1. Introduction: chemical structures of Pheo and Chlo



pyrrole ring



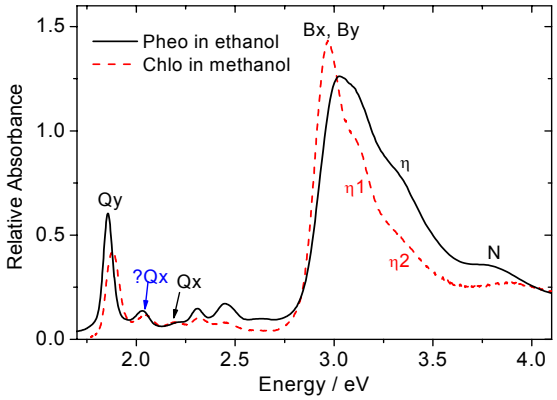
porphyrin ring

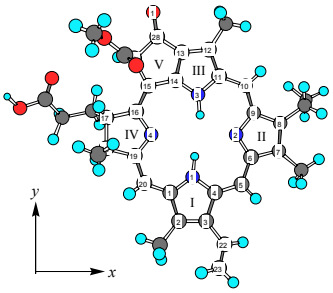


pheophorbide *a*

- Pheo and Chlo: conjugated tetrapyrrole with reduced ring IV
- Pheo: -two central protons Chlo: -one central Mg instead
  -80 atoms -79 atoms
- Important pigments for photosynthesis

Experimental absorption spectra of Pheo and Chlo in solvents





Remaining Problems unsolved in literature:

- Effects of Solvation and central Mg-coordination?
- Qx band origin : third or second peak? Magnetic circular dichroism spectra
  (J. Am. Chem. Soc. 1970, 92, 779. Biochimica Biophys. Acta 1999, 1410, 19.)
- Photostability: Dark states between B and Q bands as internal conversion path?
- Nature of higher η and N bands: Valence or CT excitation ?

2. Basic principles of Density Functional Theory (DFT)

- Born-Oppenheimer approximation:

  Seperation of *fast* electronic and *slow* nuclear motion

- Hohenberg-Kohn theorems (for *N*-electron ground state for given *static* V_{ext})

$$\Psi(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N) \Leftrightarrow \rho(\mathbf{r}) \rightarrow E_0[\rho(\mathbf{r})]$$

N-electron wavefunction Electron density Electronic energy

$$E_0[\rho(\mathbf{r})] = \langle \Psi[\rho(\mathbf{r})] \Big| -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|} \Big| \Psi[\rho(\mathbf{r})]\rangle$$

- Kohn-Sham DFT: T[ρ] + U[ρ] + molecule-specific $V_{ext}[\rho]$

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + V_{XC}[\rho(\mathbf{r})]\right]\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \qquad V_{XC}[\rho(\mathbf{r})] = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\Big|_{n=\rho}$$

Single-electron KS-orbital

Probelm: The exact, universal E_{XC} functionals are unknown!

Exchange-correlation functionals E_{XC}

$$E_{HF} = V + \langle h\rho\rangle + \frac{1}{2}\langle \rho J(\rho)\rangle - \frac{1}{2}\langle \rho K(\rho)\rangle$$

$$E_{DFT} = V + \langle h\rho\rangle + \frac{1}{2}\langle \rho J(\rho)\rangle + E_X[\rho] + E_C[\rho]$$

Total *n-n* 1e *e-e* E_{XC} : exchange-correlation functional

(a) *Local* Density Approximation (LDA): good for solids

$$E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r})\varepsilon_{XC}(\rho(\mathbf{r}))d^3r$$

⇐ homogenous electron gas

exchange-correlation energy density

(b) Generalized Gradient Approximations (GGA): BP86, ...

$$E_{XC}^{GGA}[\rho] = \int \rho(\mathbf{r})\varepsilon_{XC}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}))d^3r$$

good structure & energy for solids and molecules

(c) Hybrid functionals (mixing *nonlocal* HF-exchange): B3LYP, ...

$$E_{XC} = (1-A)\, E_X + A\, E_X^{HF} + E_c$$

A = 20%

Why DFT?

- Expanding molecular orbitals ϕ_i by a basis set: $\phi_i(\mathbf{r}) = \sum_j^M c_{ij}\psi_j(\mathbf{r})$
  (a) molecular : (LCAO) 6-31G(d,p)
  (b) periodic (crystal, surfaces): plane waves

Traditional DFT CPU time scales as M^3, with accuracy ~kcal/mol
Post-HF methods: MP2 $\propto M^5$, CISD and MRCI $\propto$ more than M^6

- Extended to time-dependent problems (TDDFT):
  (a) Runge–Gross theorem (1984): $V_{ext}(\mathbf{r},t) \Leftrightarrow \rho(\mathbf{r},t) = \sum_i^N |\phi_i(\mathbf{r},t)|^2$

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r},t) + \int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} d^3r' + V_{XC}[\rho(\mathbf{r},t)]\right]\phi_j(\mathbf{r},t) = i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t)$$

adiabatic aprroximation : $V_{XC}^{adiabatic}[\rho(\mathbf{r},t)] \approx V_{XC}^{gs}[\rho^t(\mathbf{r})]$ at fixed time

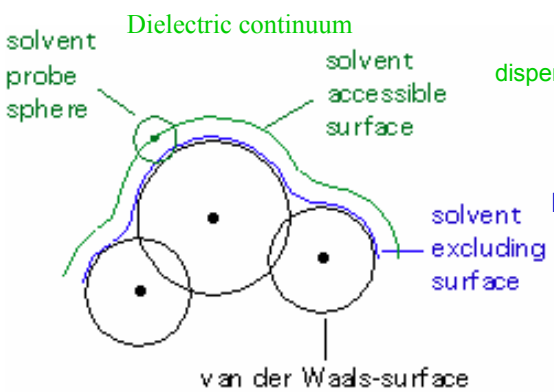
(b) Casida equation: linear response of ground state electron density $\rho(\mathbf{r},t)$

$$\delta\rho(\mathbf{r},t) \Rightarrow \bar{\alpha}(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2}$$

f_I : oscillator strengths
ω_I : excitation energies

Mean polarizibility *J. Chem. Phys.* 1996, 104(13), 5134.

3. Polarizable continuum model for solvents



dispersion-repulsion contribution G_{dr}

Electrostatic contribution G_{es}

$$G_{es} = \frac{1}{2}E_{\text{int}} = \frac{1}{2}\sum_i V_i q_i$$

Cavitation free energy G_{cav}

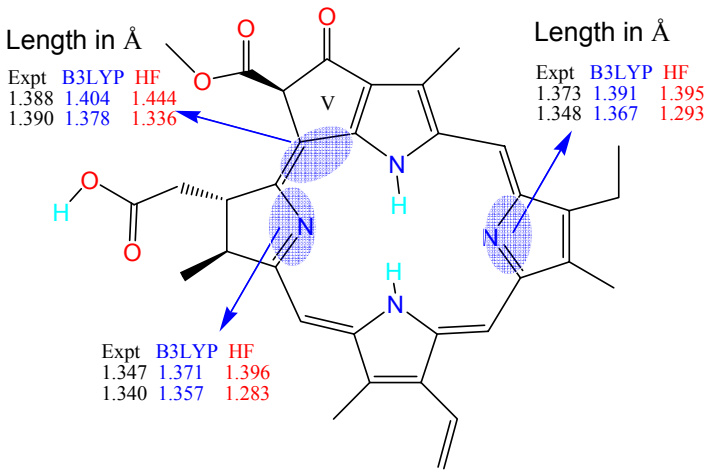
Solute molecule as overlapping spheres

$$V(\vec{r}) = \sum_i \frac{q_i}{|\vec{r} - \vec{r}_i|} \qquad H_{eff}|\Psi\rangle = (H_0 + V)|\Psi\rangle = E|\Psi\rangle$$

- Total solvation free energy is the sum over three terms:

$$G_{sol} = G_{dr} + G_{es} + G_{cav}$$

4. Results: B3LYP and HF optimized geometries

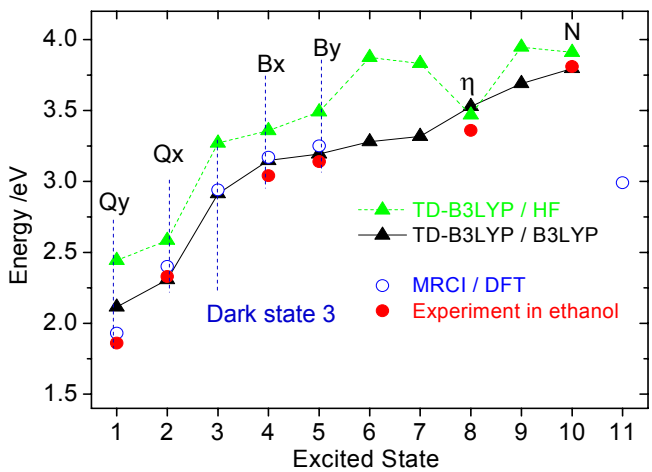


• Geometry optimization: B3LYP/6-31G(d,p) versus HF/6-31G(d,p)

B3LYP: delocalized (conjugated) π-system, agree with X-ray crystal structure.

HF : localized double bond, larger single-double bond variation

Effects of geometries on excitation energies of Pheo



• Excitation energies: Single-point TD-B3LYP/6-31+G(d,p) calculations

• HF geometry leads to too high excitation energies

• TD-B3LYP/B3LYP calculations reproduce well experimental data

• Dark state 3 between Q and B bands

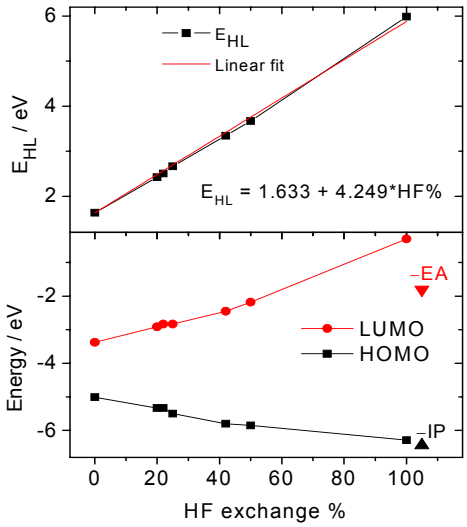
MRCI/DFT data: A.B.J. Parusel, S. Grimme, J. Phys. Chem B 2000, 104, 5395.

Effects of HF-exchange on HOMO-LUMO gap

- Based on B3LYP geometry
- Different DFT functionals:

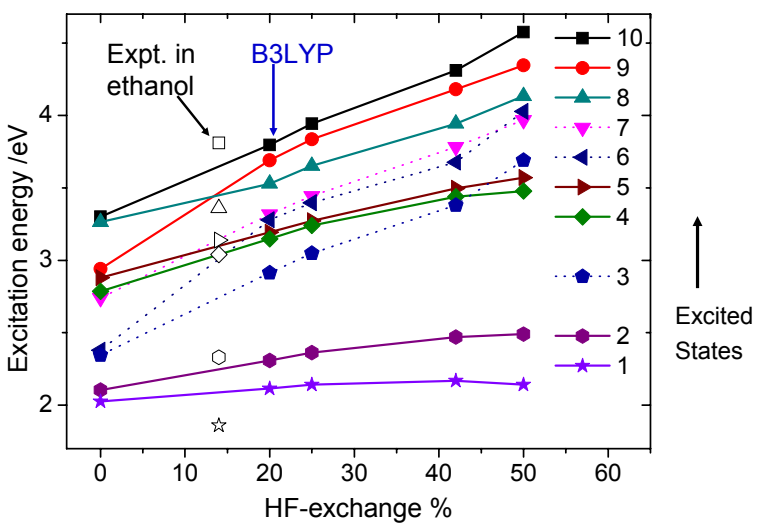
$$(1\text{-}A)\ E_X + A\ E_X^{HF} + E_c$$

Functionals	HF-exchange %
BP86	0
B3LYP	20
B98	22
PBE0	25
BMK	42
BHandH	50
HF	100



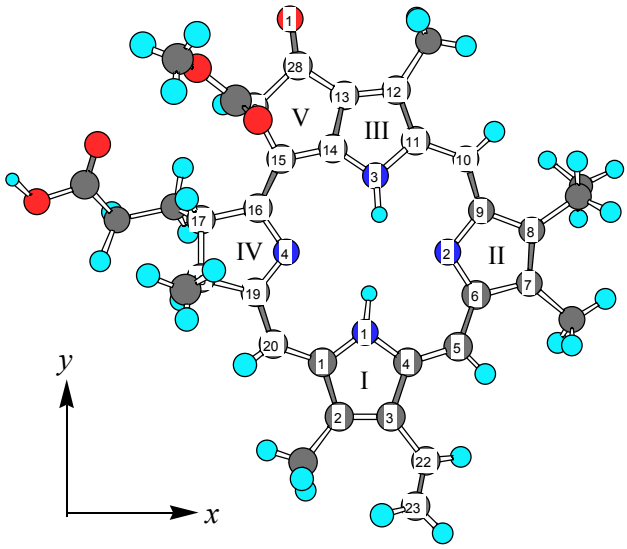
- HOMO-LUMO gap increases linearly with HF exchange percentage
- Koopmans' theorem: HF HOMO level as good estimation for ionization potential

Effects of HF exchange on excitation energies



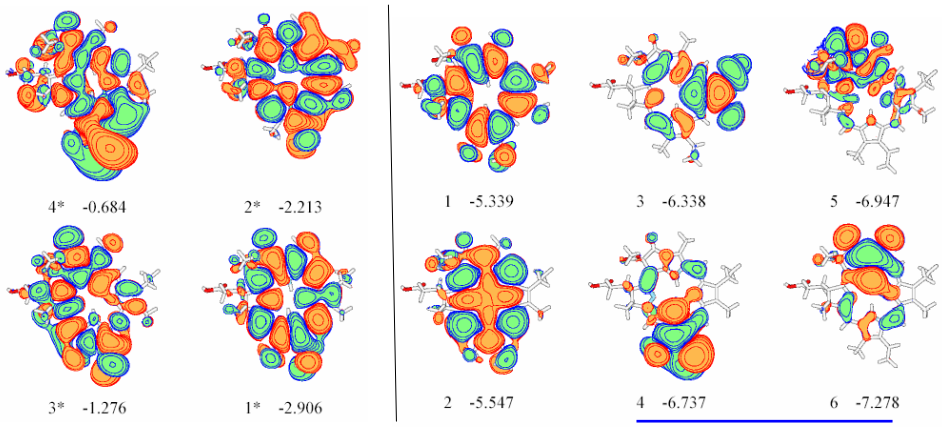
- Excitation energies increase almost linearly with HF-exchange percentage.
- Energies of dark states (Osc. < 0.1) 3, 6, 7 increase rapidly: partial CT?
- B3LYP: the best within the chosen DFT functionals

Ring structures of Pheo and Chlo



- Here, I just remind you where are the rings I, II, III, IV and V.

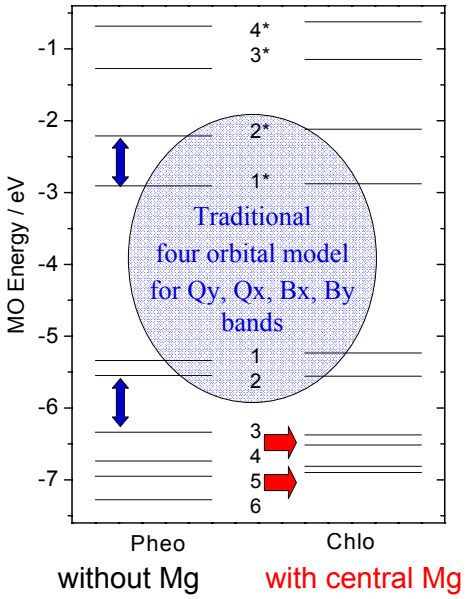
Important Frontier Molecular Orbitals



Unoccupied Occupied localized

- Delocalized π orbitals: LUMOs 1* up to 4*, and HOMOs 1 and 2
- Localized HOMOs: 3 (ring II), 4 (ring I), 5 (ring V lone pair), 6 (ring III, V)
- Chlo: with quite similar molecular orbitals (not shown)

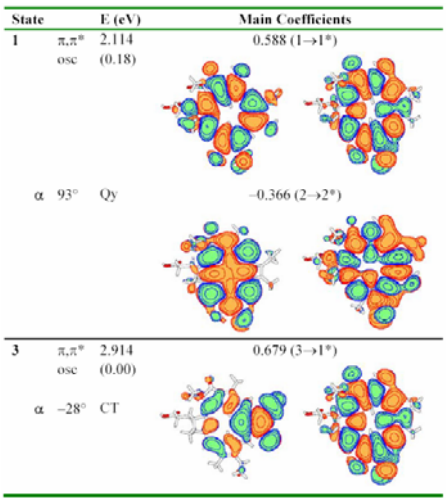
Effects of Mg-coordination on molecular orbital levels



- LUMO levels and HOMOs 1,2: hardly affected
- Traditional four orbital model for the four Q and B bands:
  LUMOs 1* and 2*
  HOMOs 1 and 2
- Comparable 1*-2* and 2-3 gaps (about 0.8 eV): → dark state 3
  invalid Four-orbital model
- Chlo : smaller 3-4 and 5-6 gaps
  → higher density of states
  for higher excitations

Nature of excited states

Assignment: Excitation energy, Oscillator strength, Main transition configurations



		Pheo		Chl		
N	**State**	**E (eV)**	**α**	**E (eV)**	**α**	**Comments**
1	π,π*	2.114 (0.18)	93	2.106 (0.24)	87	Qy
2	π,π*	2.308 (0.03)	10	2.286 (0.03)	-12	Qx
3	π,π*	2.914 (0.00)	-28	2.949 (0.02)	87	CT
4	π,π*	3.147 (0.50)	60	3.284 (0.71)	74	By
5	π,π*	3.193 (0.79)	-30	3.124 (0.41)	13	Bx
6	n,π*	3.280 (0.02)	8	3.192 (0.04)	-4	CT: carbonyl
7	π,π*	3.318 (0.00)	56	**3.112 (0.14)**	-9	CT: vinyl
11	π,π*			3.480 (0.14)	-19	η, CT: C=O
8	π,π*	3.529 (0.35)	99	3.682 (0.01)	-60	η, Pheo
9	π,π*	3.690 (0.11)	46	3.697 (0.09)	-30	CT
12	π,π*			3.831 (0.16)	58	N for Chl
10	π,π*	3.796 (0.43)	-65	3.891 (0.31)	76	N

- Singlet π,π* excited states except for the carbonyl (n,π*) CT state 6
- Dark state (Osc. ≤ 0.1) 3 below B band: invalid four-orbital model (3→1*)
- Higher density of state for Chlo: additional states 11, 12

Solvent induced spectral shifts for Pheo

	State	Energy /eV		Shift /meV				
N	Nature	Ethanol	experiment	chloroform	ethanol	methanol	water	water[b]
1	Q_y	2.087 (0.28)	1.86 (0.28)	–25	–27	–25	–25	–27
2	Q_x	2.290 (0.06)	2.33 (0.04)	–10	–18	–18	–20	–39
3	**CT**	**2.891 (0.00)**	**--**	**–26**	**–23**	**–20**	**–15**	**–39**
5	**B_x**	**3.075 (0.79)**	**3.04 (0.95)**	**–103**	**–118**	**–113**	**–117**	**–136**
4	B_y	3.115 (0.93)	3.14 (0.90)	–34	–32	–27	–29	–36
7	CT	3.205 (0.04)	--	–72	–113	–113	–115	–136
8	η	3.489 (0.19)	3.36	–40	–39	–36	–33	–51
6	**CT**	**3.497 (0.05)**	**--**	**126**	**216**	**220**	**224**	**735**
9	η	3.609 (0.19)	--	–56	–81	–80	–81	–117
10	N	3.720 (0.46)	3.81	–58	–76	–75	–79	–129

PCM model for solvents [b]Additional H-bonding to ring V carbonyl

- Dark state 3 between B and Q bands.
- Most states are red-shifted (**minus signed**).
- The *Bx* band is red-shifted more than the Q bands (1 and 2).
- (n,π*) CT state 6: blue-shifted, enhanced by hydrogen bonding

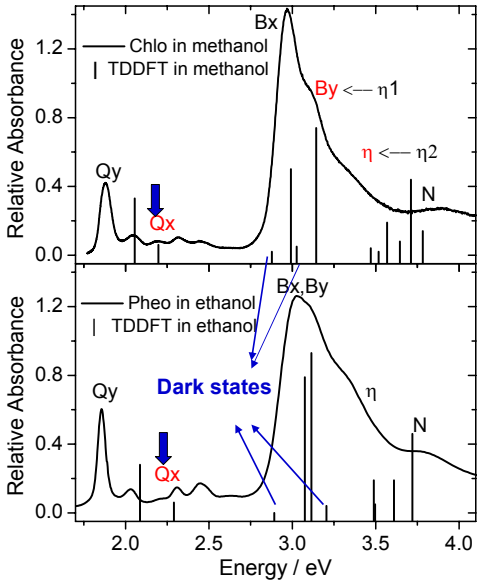
Solvent induced spectral shifts for Chlo

	State	Energy /eV		Shift /meV				
N	Nature	MeOH[b]	experiment	MeOH	MeOH[a]	MeOH[b]	water	water[b]
1	Q_y	2.050 (0.35)	1.88 (0.23)	–47	–51	–56	–50	–60
2	Q_x	2.167 (0.08)	2.21 (0.03)	–52	–88	–118	–97	–118
3	**CT**	**2.854 (0.01)**	**--**	**–72**	**–72**	**–95**	**–72**	**–88**
5	**B_x**	**2.973 (0.44)**	**2.97 (1.36)**	**–109**	**–133**	**–150**	**–130**	**–153**
7	**CT**	**3.005 (0.04)**	**--**	**–60**	**–85**	**–107**	**–72**	**–108**
4	**B_y**	**3.128 (0.74)**	**3.13 (0.85)**	**–102**	**–141**	**–156**	**–144**	**–168**
6	**CT**	**3.483 (0.01)**	**--**	**325**	**326**	**291**	**279**	**339**
9	η	3.528 (0.30)	3.37	–100	–128	–169	–118	–210
10	N	3.630 (0.32)	3.84	–129	–185	–266	–179	–265
12	N	3.692 (0.28)	--	–35	–48	–139	–37	–142
8	CT	3.796 (0.15)	--	–23	–37	114	–25	103
11	**CT**	**3.896 (0.07)**	**--**	–30	–10	**415**	–9	**435**

PCM for solvents [a]Solvent-Mg coordination. [b]H-bonding to ring V carbonyl.

- Again, mostly red-shifted (minus signed), B > Q, blue-shifted (n,π*) state 6
- Dark states 3 and 7 near or below B bands.
- Carbonyl (π,π*) partial CT state 11 is blue-shifted by H-bonding.

Electronic Spectra of Chlo and Pheo: new assignment



For Chlo

- *By* instead of old η1 assignment
  η instead of old η2
  larger *Bx-By* gap than Pheo

For both Chlo and Pheo:

- Third vibronic peak: *Qx* band origin
  Vibrational effects for MCD spectra
- Dark states near or below B:
  internal conversion paths
  for photostability
- η and N band: Valence (π,π*) excitation with *partial* CT Nature.
  CT excitations are weak!

5. Conclusions

- TDDFT: HF-exchange percentage is crucial for correct excitation energies
- Solvation: red-shifted bright π,π* excitations;
  blue-shifted carbonyl CT excitations: enhanced by H-bonding
- Central Mg in Chlo: larger *Bx-By* gap → *By* instead of old η1 assignment
  higher density of states for higher η and N bands
- *Qx* band origin: the third vibronic peak
- Photostability: dark states 3 and 7 near or below *B*-bands
  → possible internal conversion paths after ultraviolet excitation.
- η and N bands: valence (π,π*) excitation with *partial* CT nature.

Acknowledgement

- Financial supports: DFG (MA 1356-10/1), SFB450
- Collaboration: Hui Zhu, Volkhard May, Reinhard Schinke

Thanks for your attention!

Born-Oppenheimer Approximation

- Separated electronic and nuclear problem (*adiabatic*)

(1) electronic Schrödinger equation ⇒ *electronic states for "fixed" nuclei*

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|}\right]\psi(\mathbf{r};\mathbf{R}) = E_{\text{el}}(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

Electron K.E. Electron-electron Electron-nucleus

$$V_{\text{eff}}(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}$$

Nucleus-nucleus interaction

I, J label atoms with positions $\mathbf{R}_I$, $\mathbf{R}_J$

i, j label electrons with positions $\mathbf{r}_i$, $\mathbf{r}_j$

(2) nuclear Schrödinger equation ⇒ *rotational and vibrational levels*

$$\left[-\frac{1}{2M}\nabla^2_{\mathbf{R}} + V_{\text{eff}}(\mathbf{R})\right]\chi(\mathbf{R}) = E\chi(\mathbf{R})$$

Hartree-Fock (HF) Approximation

- Pauli exclusion principle ⇒ Slater determinants as *N*-electron basis functions

N-electron basis function

$$\Phi = \frac{1}{\sqrt{N!}}\det\begin{vmatrix}\varphi_1(\mathbf{r}_1) & \varphi_1(\mathbf{r}_2)\cdots & \varphi_1(\mathbf{r}_N)\\ \vdots & \ddots & \vdots\\ \varphi_N(\mathbf{r}_1) & \varphi_N(\mathbf{r}_2)\cdots & \varphi_N(\mathbf{r}_N)\end{vmatrix}$$

1-electron basis functions: Molecular Orbital

Electronic wavefunction

$$|\psi\rangle = \sum_{\alpha=1,M} c_\alpha |\Phi_\alpha\rangle$$

- Single Slater determinant ⇒ HF equation for 1-electron MO orbitals φ_i

$$\left[-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} + \int\sum_j \frac{\varphi_j^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dr'\right]\varphi_i(\mathbf{r}) - \int\sum_j \frac{\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\varphi_j(\mathbf{r})dr' = \varepsilon_i\varphi_i(\mathbf{r})$$

Electron-nucleus e-e Coulomb potential "exchange" potential

- The HF equation needs to be solved iteratively (self-consistent field).
- Correlation between opposite-spin electrons is missing (1% of total E).
- HF method scales as N^3 to N^4, with accuracy < kcal/mol

TDDFT

(b) Casida equation: linear response of ground state electron density

$$\delta\rho(\mathbf{r},t) \Rightarrow \quad \bar{\alpha}(\omega) = \sum_I \frac{f_I}{\omega_I^2 - \omega^2}$$

f_I : oscillator strengths

ω_I : excitation energies

In practice, $\sum_{q'} \Omega_{qq'}(\omega_I^2) a_{q'} = \omega_I^2 a_q$

with $\Omega_{qq'} = \omega_q^2 \delta_{qq'} + 2\sqrt{\omega_q \omega_{q'}} \langle q | f_{HXC}(\omega) | q' \rangle$

Index q: singly occupied $\phi_i \rightarrow$ unoccupied ϕ_a transition

$$\langle q | f_{HXC} | q' \rangle = \iint \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{XC}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right] \phi_j(\mathbf{r}') \phi_b^*(\mathbf{r}') dr dr'$$

Hartree exchange-correlation kernel