Solar Light Harvesting by Energy Transfer: Learning from Nature

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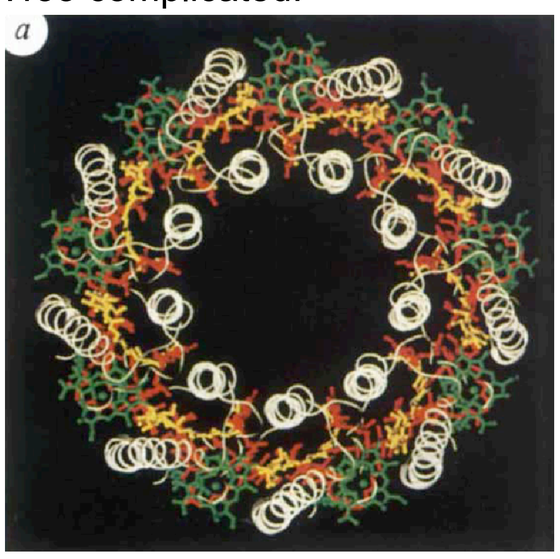
Introduction

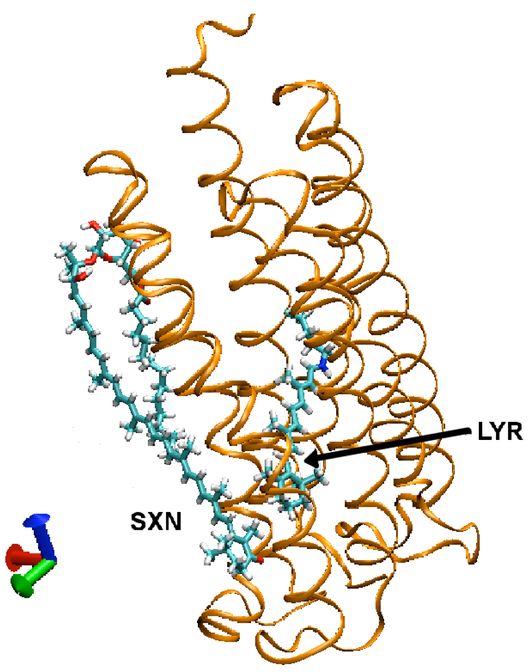
- Solar light harvesting is key to solving tomorrow's energy problems
- Excitation energy transfer underlies most light harvesting applications

Project goal: Understand how nature optimizes excitation energy transfer rate

Light-harvesting antenna complex LH2[1] :Too complicated!



Xanthorhodopsin in bacterium S. ruber:



- UC Irvine is the world's leading university in xanthorhodopsin research
- Spectroscopically well-characterized[2-4]
- X-ray structure has been determined[5]
- Single antenna (salinixanthin(SXN)) and single reaction center (retinal(LYR))
- Amenable to electronic structure methods and x-ray diffraction

Methods

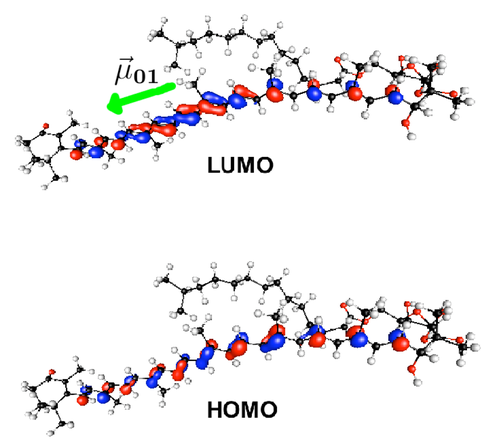
Multi-pronged approach:

1. State-of-the-art quantum mechanical computations of the chromophores using TURBOMOLE
2. Molecular dynamics simulations of 20ns of movement of the entire protein
3. Comparison to and validation of x-ray structures
4. Absorption, fluorescence steady state, and femtosecond spectroscopy

Results

Salinixanthin:

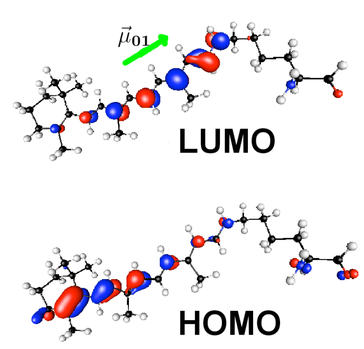
Relevant excitation: First π→π* transition



- Validation on beta-carotene: Must blue shift computed salinixanthin spectra 50nm.
- Oscillator strengths: 2-3 times larger than experiment (within experimental uncertainty).

Retinal:

Relevant excitation: First π→π* transition



Vertical excitation wavelengths of salinixanthin (shifted as indicated by beta-carotene computations) and retinal (nm)

	LYR	SXN
Best TDDFT	494	490
Best RI-CC2	565[a]	526
Exp.	565	521

[a]Gas phase

Effect of the environment on energy (shift in nm relative to gas phase):

	P	PC	PCL
SXN	+4	+4	+4
LYR	−62	−62	−89

Interactions included: P=protein, C=other chromophore,L=lipid

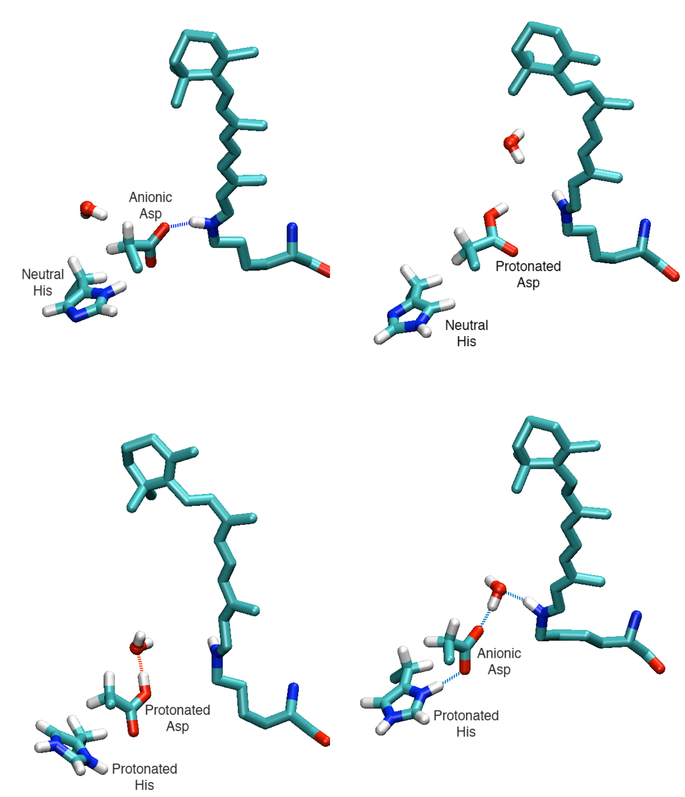
Effect of the environment on oscillator strength(f):

	gas	P	PC	PCL
SXN	4.81	4.84	4.47	4.48
LYR	1.29	1.35	1.68	1.75

Effect of structural change:

	f(gas)	f(prot)	$\Delta\lambda$
SXN	4.50	4.81	+91
LYR	2.03	1.29	+44

Protonation states:



- Results of 16ns of molecular dynamics.
- Only His protonated/Asp anionic in close agreement with x-ray

Conclusions and Outlook

- Nature uses protein environment to fine-tune chromophore properties
- Importance of interactions: Steric(chromophore structure) > electrostatics with protein > other
- Protonation state: $HisH^+Asp^-$
- After calibration of energy levels, our method will allow us to model the rate of excitation energy transfer
- Future work: Excited state deactivation vs. energy transfer

References

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