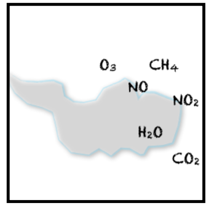
18 Oct. 2014

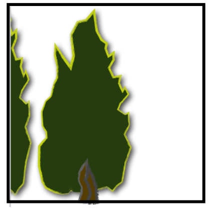
天体形成研究会@CCS
太陽系外惑星における光合成モデル:
光吸収とエネルギー移動計算

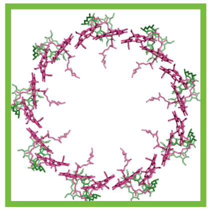
Yu Komatsu (D3)

outline

- introduction
  - exoplanets
  - photosynthetic biosignatures
- methods
  - quantum chemical calculation in antenna system
- results
  - comparison calculated values with experimental ones
  - evaluate absorption efficiencies in different stellar photoenvironments
- summary & future prospects

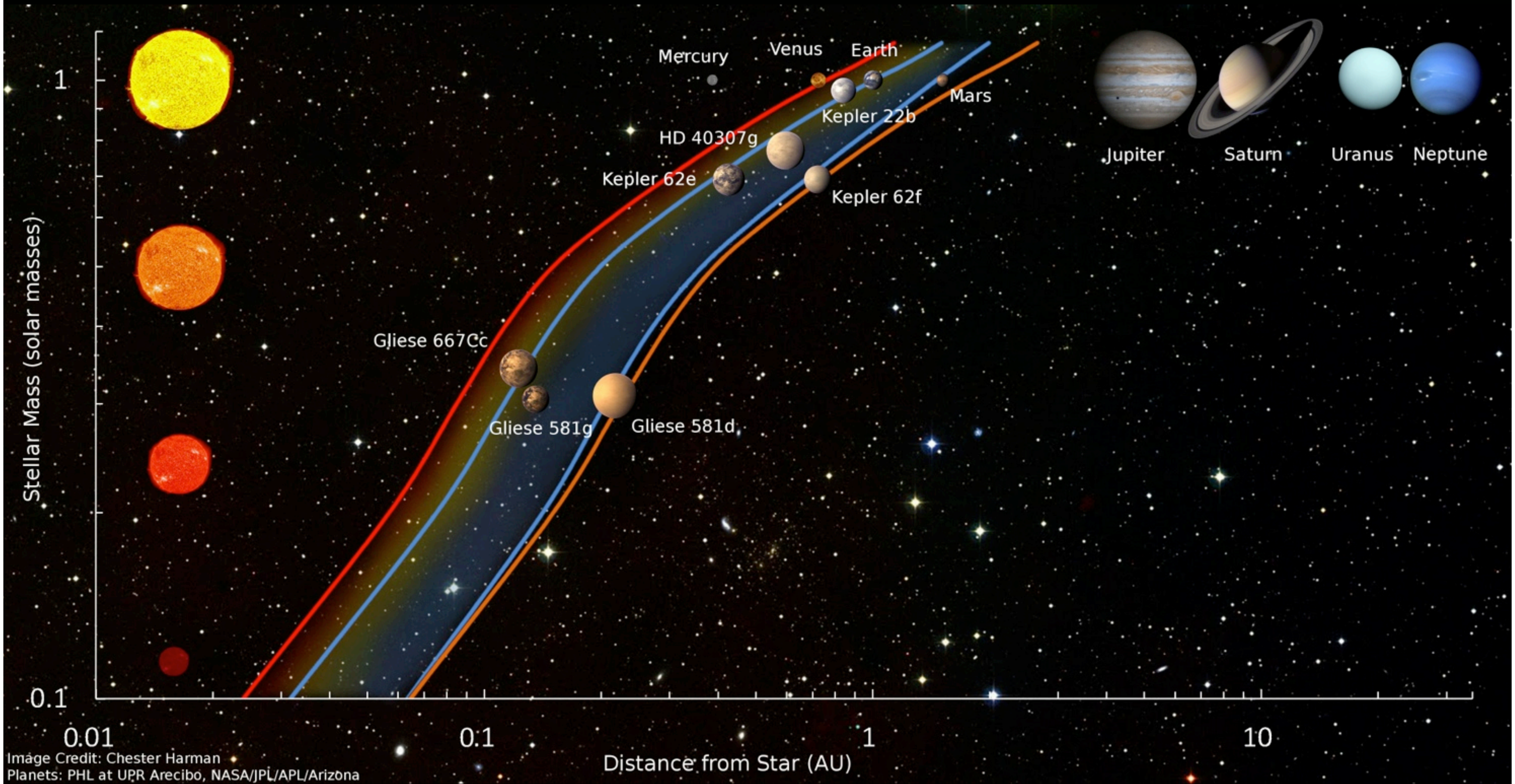




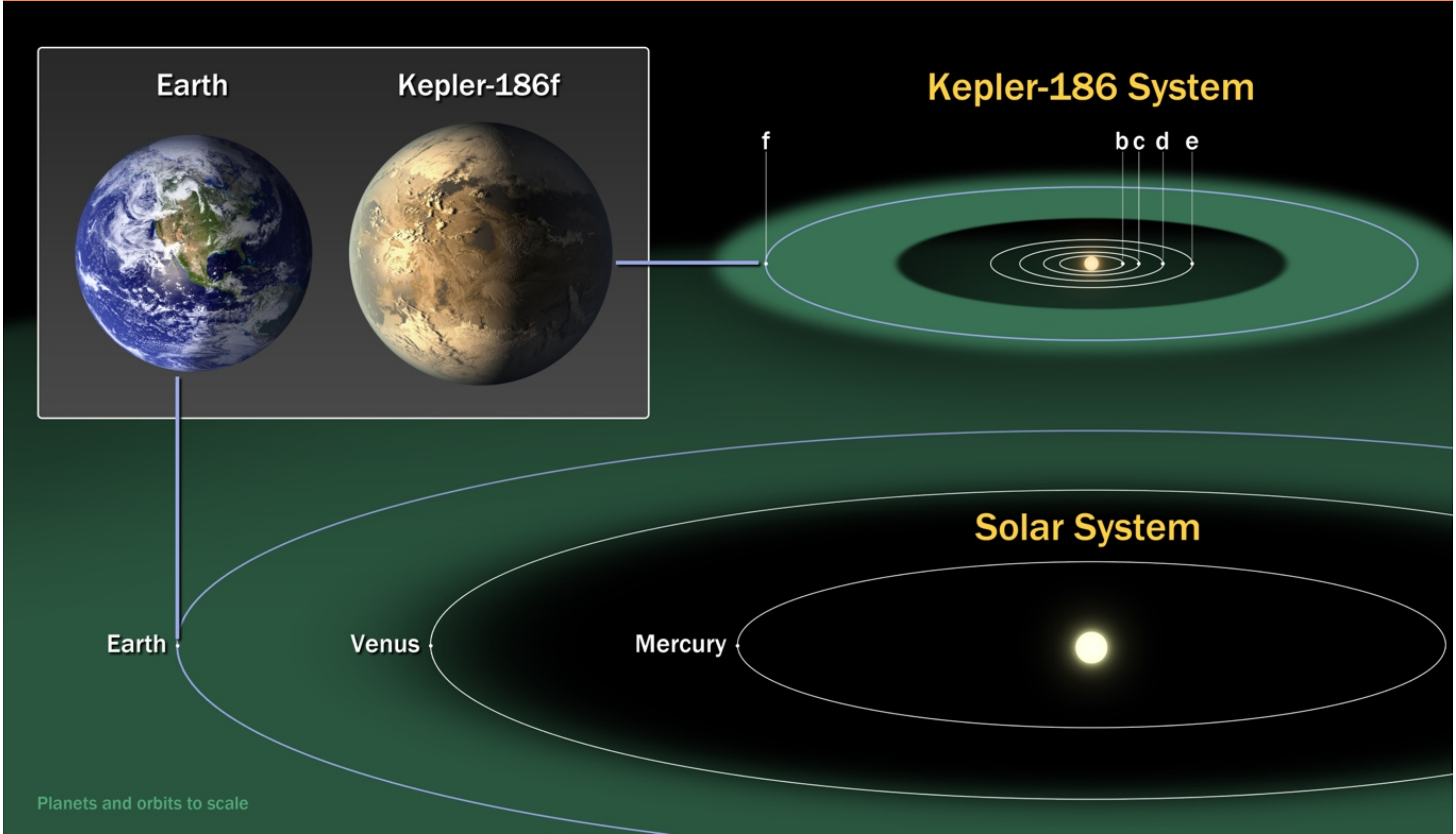


introduction

the (circumstellar) habitable zone



the first Earth-size planet in the habitable zone



Kepler-186f

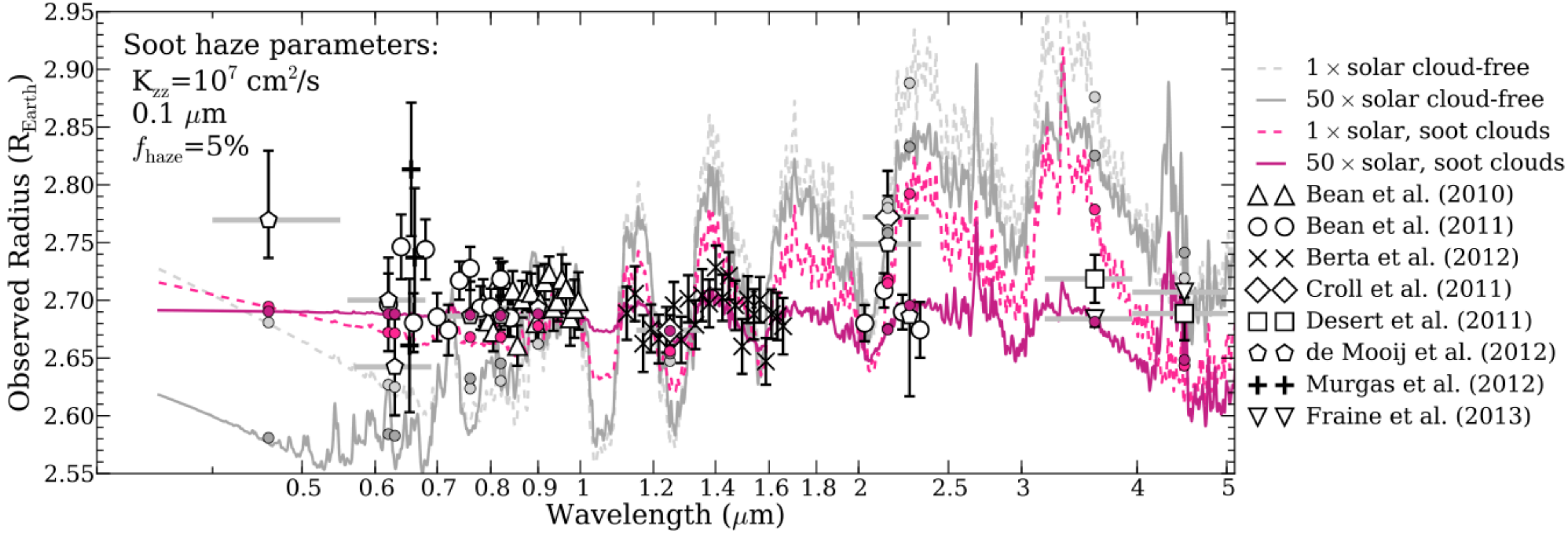
- 5 light yrs from Earth
- orbital period: 130 day
- orbiting M dwarf star

17 Apr. 2014

spectrum of exoplanet

transmission spectroscopy

GJ 1214b (Super-Earth)



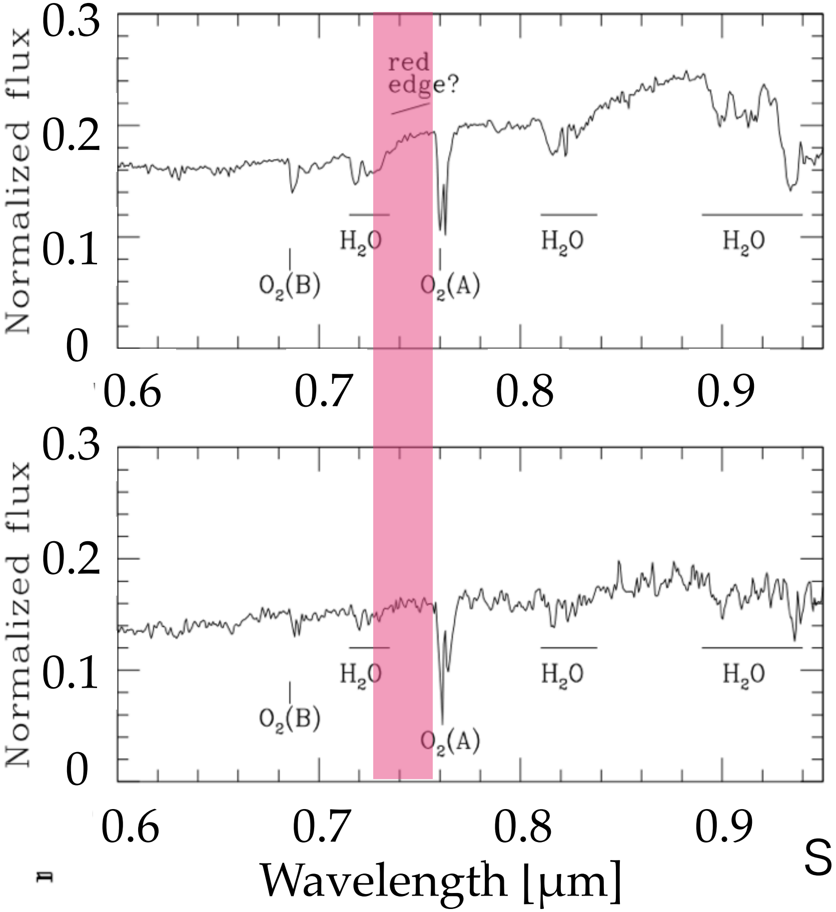
Morley et al. 2013

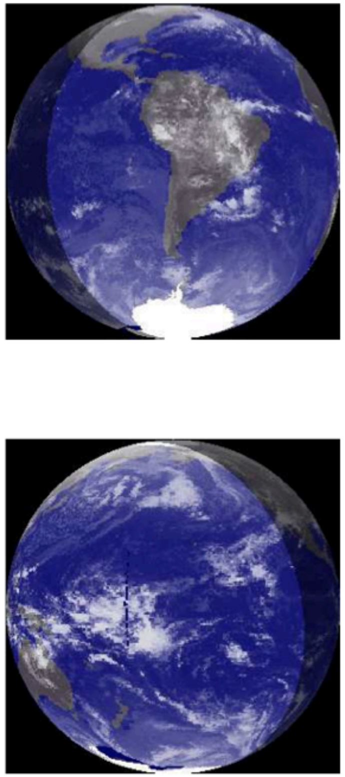
the vegetation red edge

biosignature

1. gas absorption: O_2, O_3, CH_4, ... Kiang et al. 2007
2. vegetation red edge in NIR region (700-750 nm)

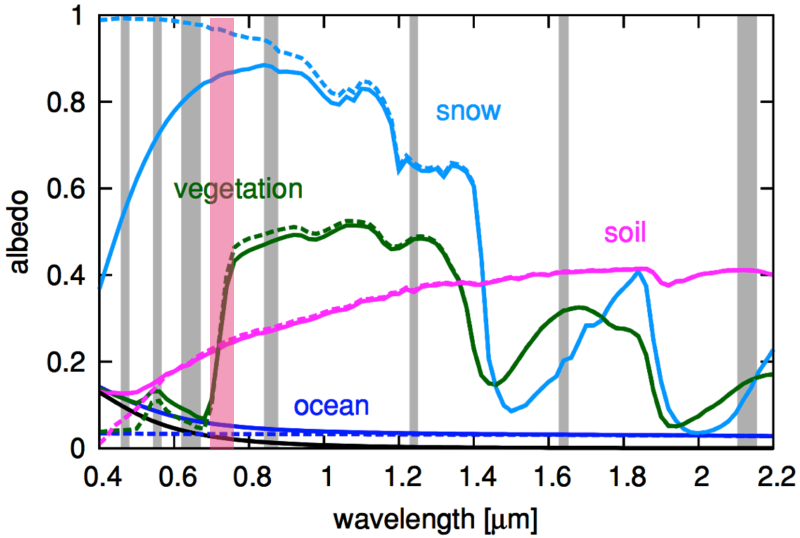
reflection spectra on Earth





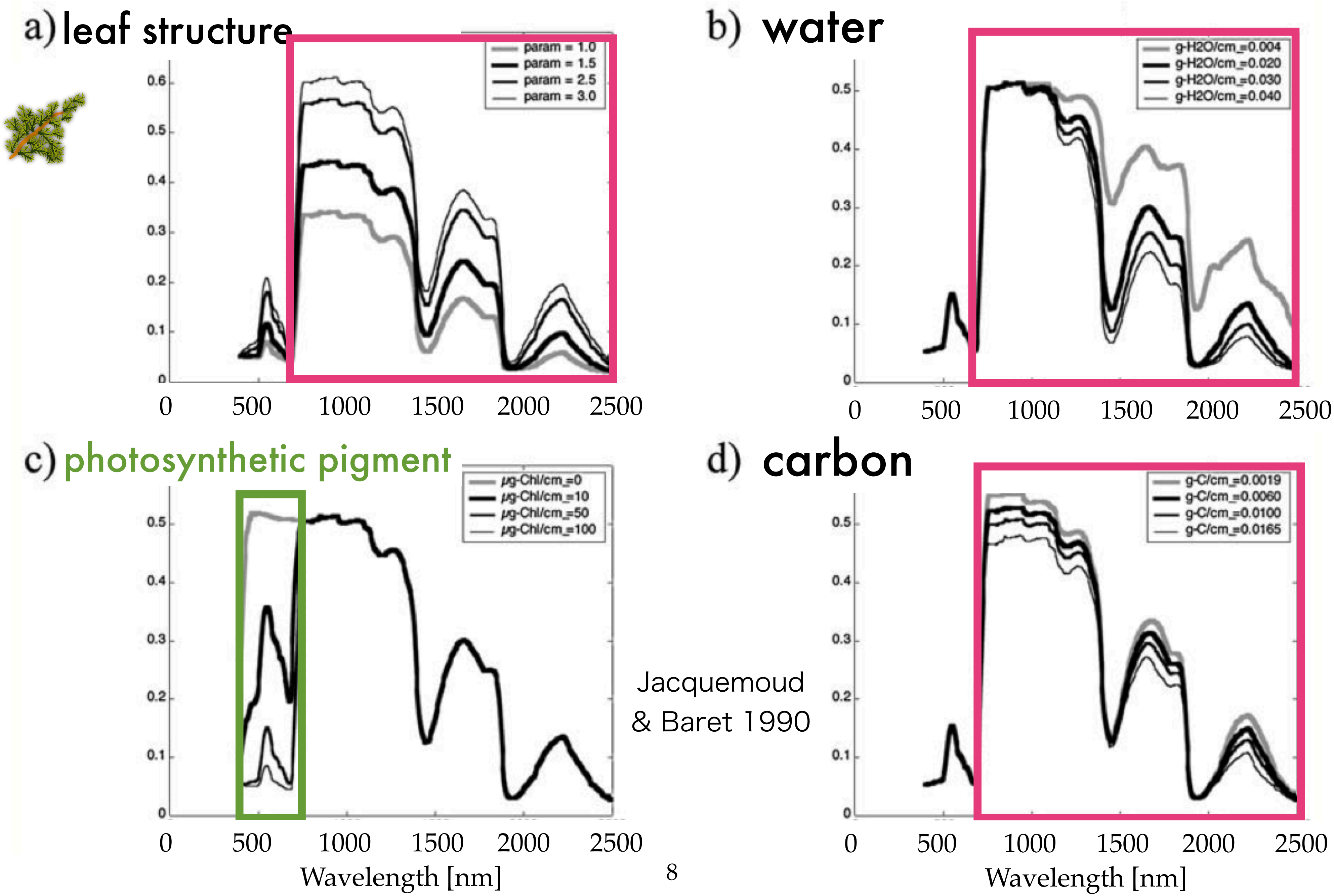
Seager et al. 2005

reflection spectra for several surface types



Fuji et al. 2010

origins of VRE

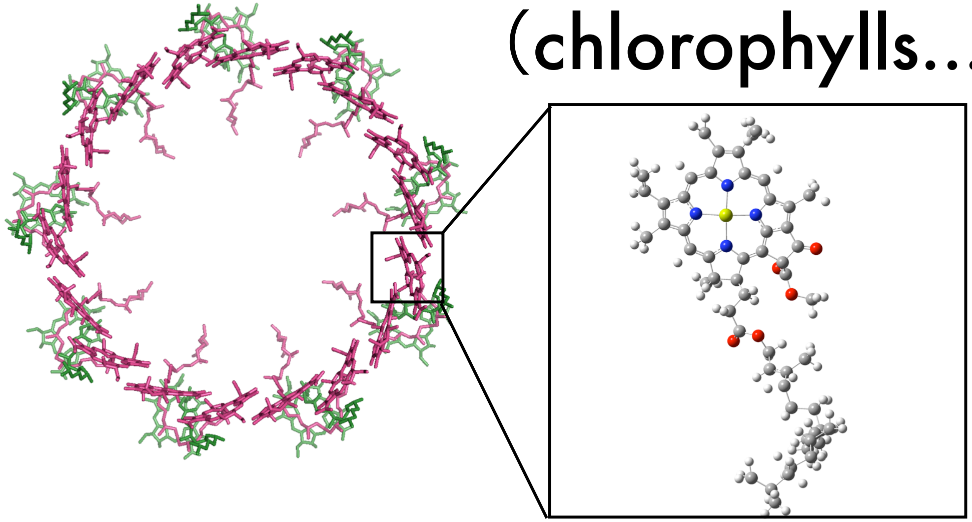


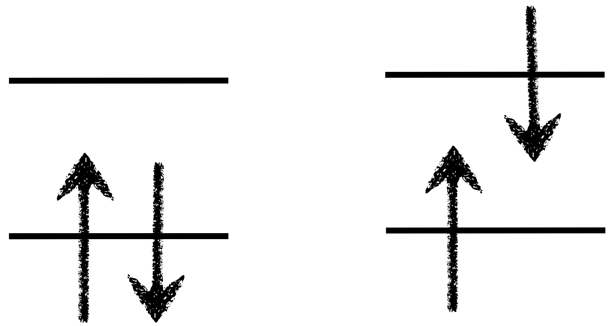
Jacquemoud & Baret 1990

light absorption in photosynthesis

antenna complex

photosynthetic pigment (chlorophylls...)





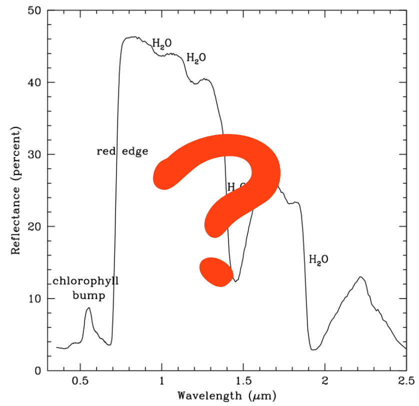
ground state　excited state

- ✓ antenna complex is composed of the pigments
- ✓ (1) light absorption→

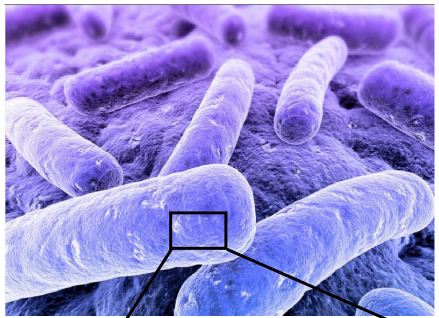
  (2) excitation energy transfer (EET) is accomplished by collective electronic excitation of photosynthetic pigments

purpose

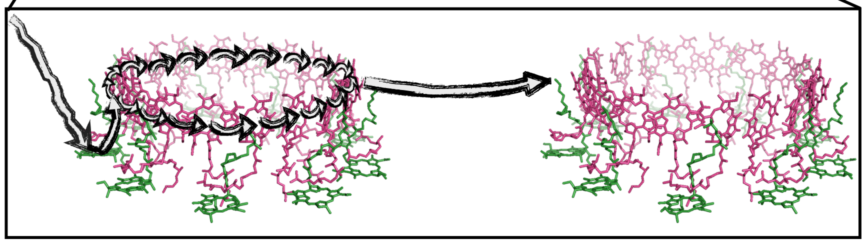
- Exovegetation should have evolved to utilize the spectra of their principal star to show different spectral feature.



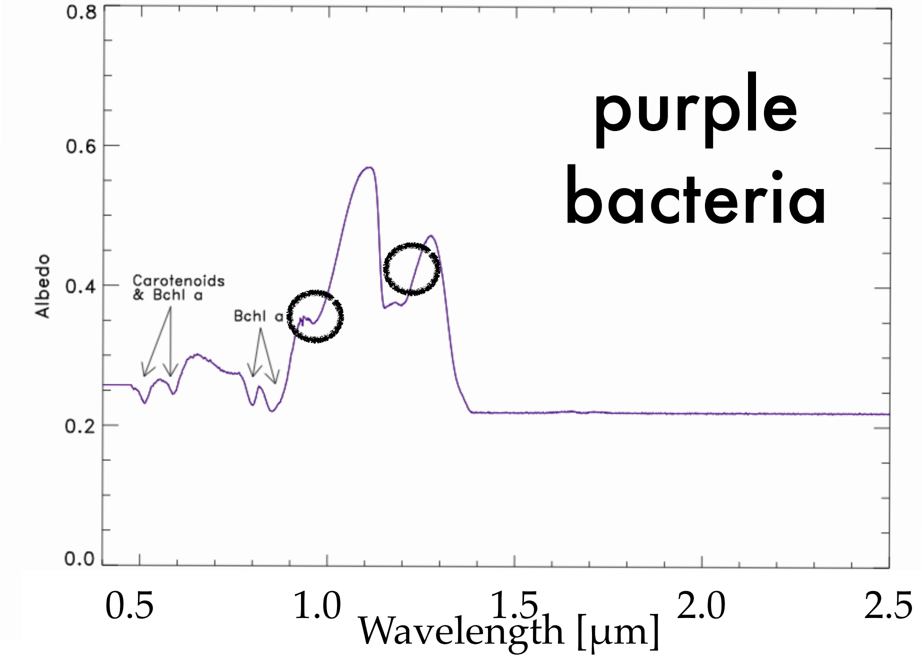
- We focus on purple bacteria, which absorb longer wavelength radiation than plants (M stars will be main targets) and its antenna structure is simple to be investigated easier.

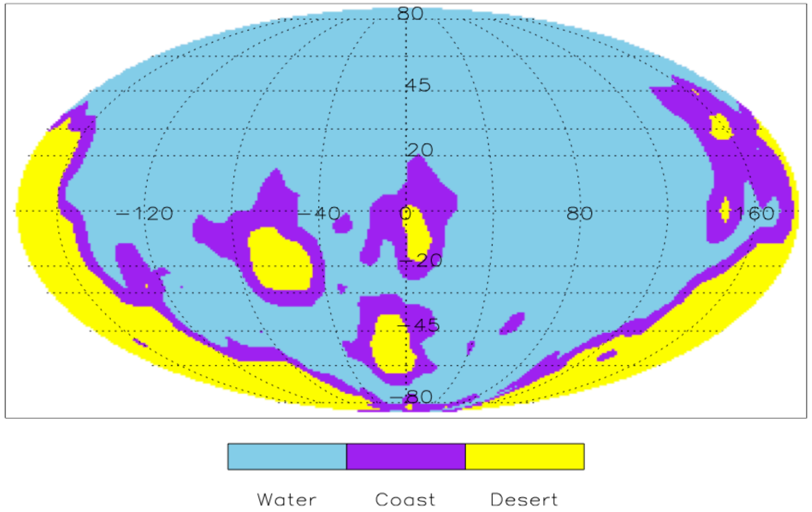


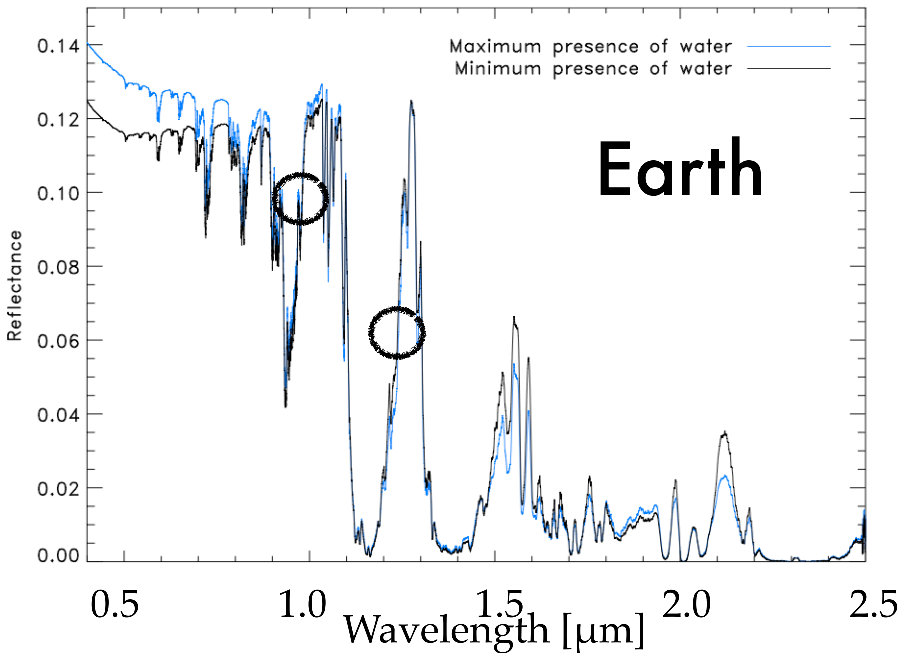
- We investigated how they absorb light efficiently depending on the stellar radiation using light absorption & EET model.



purple bacteria can be biosignature ?







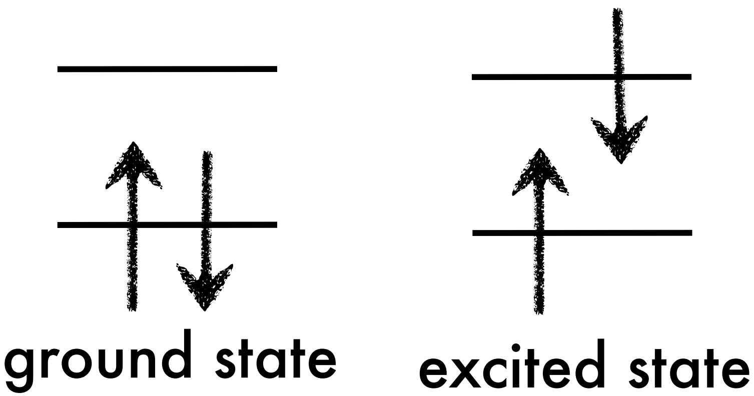
- continental distribution during the Late Cambrian (500 Myr ago)
- distributing in continents & oceans
- calculating detectible signal to reflection spectra in purple bacteria from outside the Earth

Sanromá et al. 2014

methods

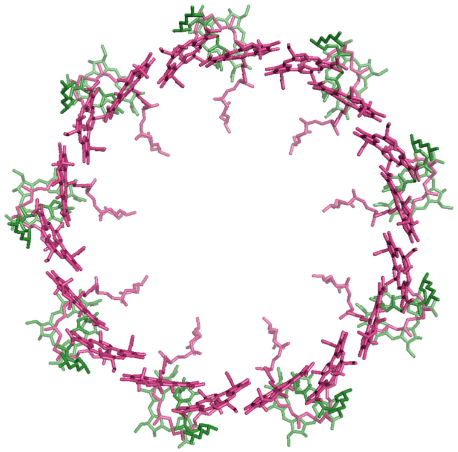
quantum chemical calculation

- a lot of spectra of earth-size exoplanets will be obtained
→next decade
- before the observation,
the computer simulation is the effective tool
to accumulate fundamental theory
- the properties of (1) light absorption & (2) EET in
photosynthesis need to be investigated
→quantum chemical calculation



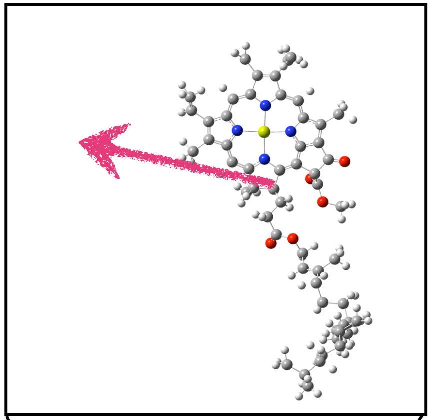
dipole-dipole interaction model

electronic excited states in antenna system can be calculated by TDDFT



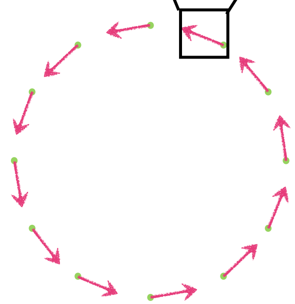
→huge computational cost!

1. TDDFT



electronic excited states in the pigments by solving wave function approximately

2. dipole-dipole interaction model



a dipole-dipole approximation is used for electronic interaction between pigment excitations

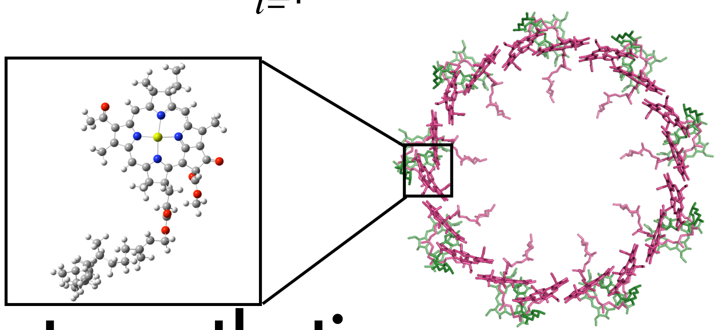
excited states of the pigments

TDDFT (time-dependent density functional theory)

time-dependent Kohn-Sham equation

$$\left[-\frac{1}{2}\Delta+\sum_{A=1}^{N_{atom}}\frac{Z_A}{|\mathbf{r}-\mathbf{R_A}|}+\int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\underbrace{\frac{\delta A_{XC}[\rho]}{\delta\rho(\mathbf{r}',t)}}_{\text{exchange-correlation term}}\right]\phi_i(\mathbf{r},t)=i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t)$$

$$\rho(\mathbf{r},t)=\sum_{i=1}^{N_{elec}}\left|\phi_i(\mathbf{r},t)\right|^2$$



photosynthetic pigments

→calculate electronic excited states of the pigments

1. light absorption model

$$H_{all} = H_0 + H_{\text{int}}$$

H_{all} : Hamiltonian in a system

H_0 : non-interaction term

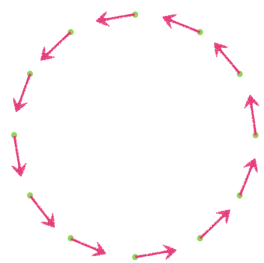
H_{int} : dipole-dipole interaction term

$$H_0 = \sum_{k=0}^{N} E_k a_k^+ a_k$$

$$\boxed{H_{\text{int}} = \sum_{k<l}^{N} \mu_k \mu_l \frac{\cos(\theta_{k_l} - \theta_{l_k}) - 3\cos\theta_{k_l}\cos\theta_{l_k}}{4\pi\varepsilon R_{kl}^3} a_k^+ a_l}$$

E_k: transition energy of the *k*th pigment

μ_k: transition dipole moment of the *k*th pigment

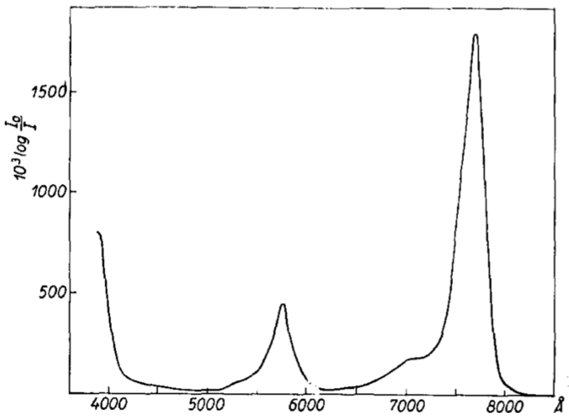


- solve eigenvalue problem & calculate eigenstates E_m' & μ_{mn}' in the system

oscillator strength to state *m*

$$\boxed{f_{m0} = \frac{2m}{3\hbar^2 e^2}\left(E_m' - E_0'\right)\left|\mu_{m0}'\right|^2}$$

➡investigate light absorption



2. EET (excitation energy transfer) model

<u>time evolution: Liouville equation</u>

$$\boxed{i\hbar\frac{\partial}{\partial t}\rho(t)=[H,\rho(t)]-\underline{i\Gamma\rho(t)}}$$

relaxation term

$$H=\sum_{m}^{N}E'_m b_m^+ b_m$$

$\rho(t)$: density at time *t*

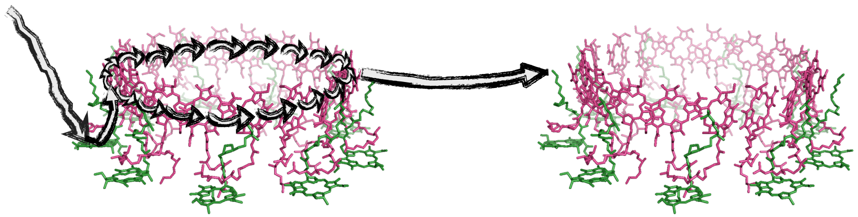
relaxation term

$$\begin{cases}\{-\Gamma\rho(t)\}_{mn}=-\Gamma_{mm}\rho_{mm}-\sum_{n\neq m}^{N}\gamma_{nm}\rho_{nn} \\ \{-\Gamma\rho(t)\}_{mm}=-\Gamma_{mn}\rho_{mn} \qquad m\neq n\end{cases}$$

$$\begin{cases}\Gamma_{mm}=\sum_{n\neq m}^{N}\gamma_{mn} \\ \Gamma_{mn}=\frac{1}{2}(\Gamma_{mm}+\Gamma_{nn})+\Gamma'_{mn}\end{cases}$$

$$\boxed{\gamma_{mn}=C(E'_n-E'_m) \qquad m<n}$$

relax to lower energy

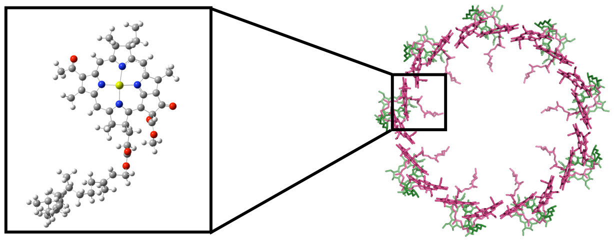



RoyalMileWhiskies.com
results
SPECIALIST WHISKY MERCHANTS

comparison with experiments (1. light absorption)

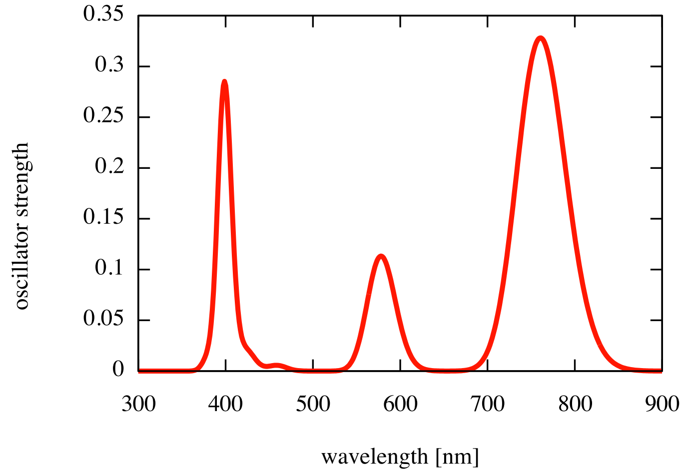
bacteriochlorophyll a

(TDDFT)

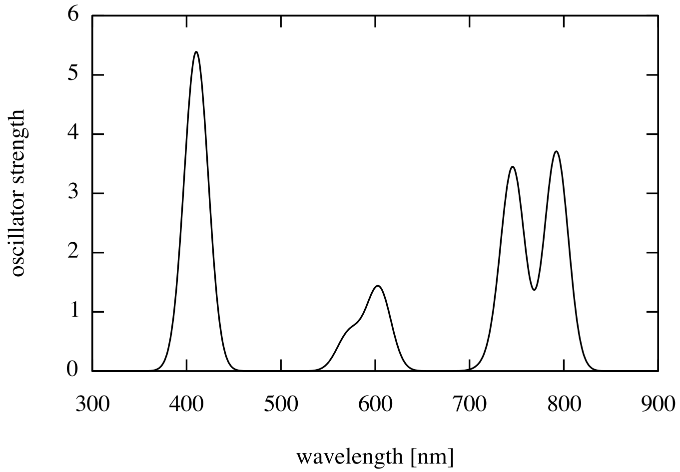


antenna complex

(light absorption model)



calculated



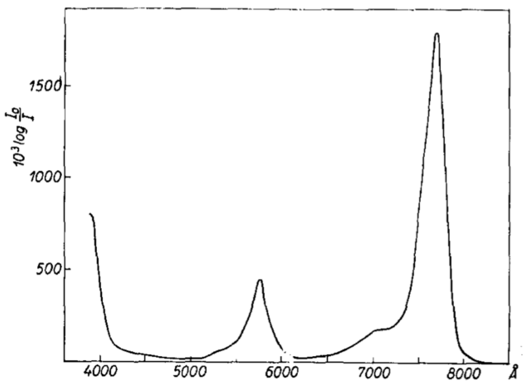
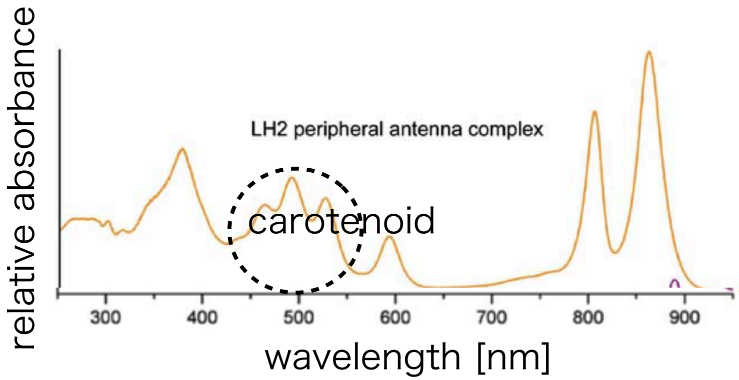


Fig. 1. Absorption spectrum of bacteriochlorophyll in a 1:1 mixture of ether and petrol ether.

Komen 1956

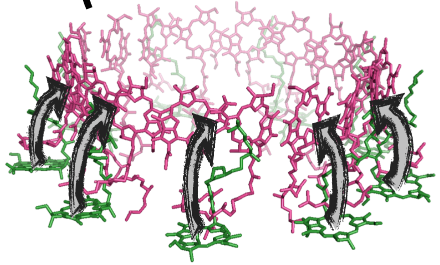
experimental



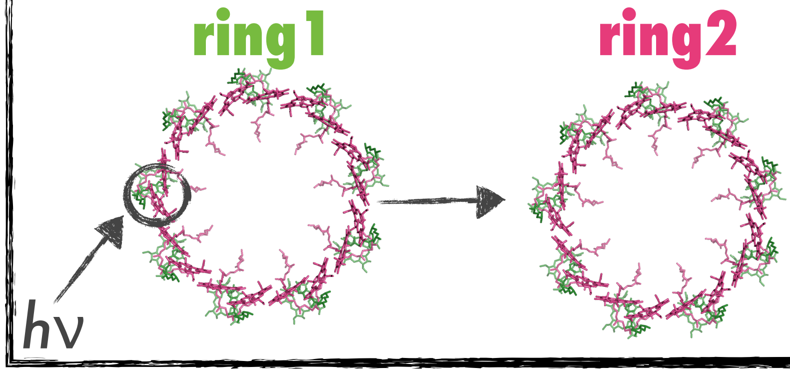
Cogdel et al. 2003

comparison with experiments (2. EET)

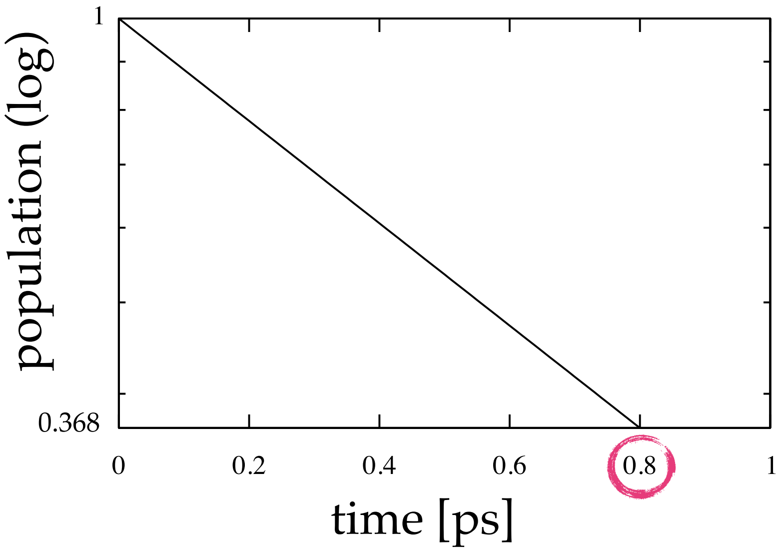
1. relaxation parameters are determined to the experimental transfer time (outer→inner ring): 0.8 ps

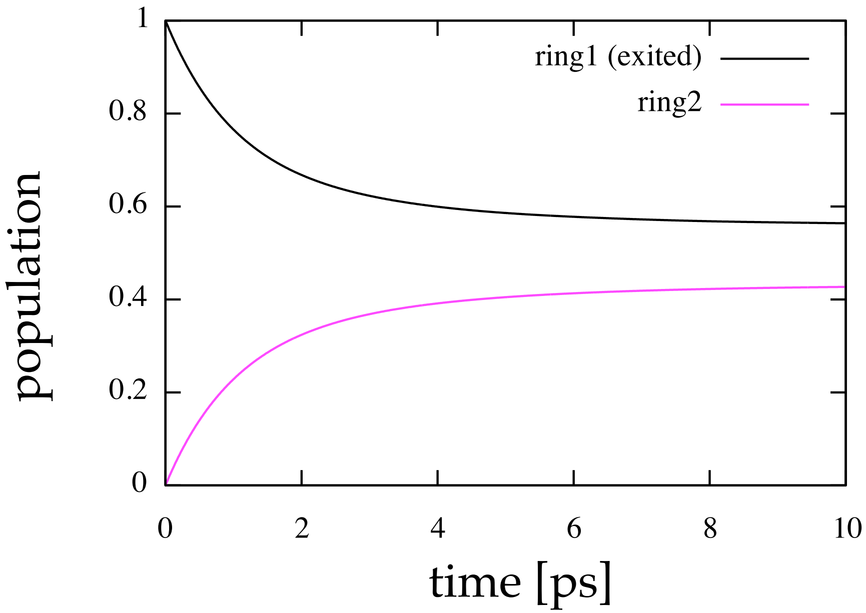


2. EET between 2 rings



population in the outer ring





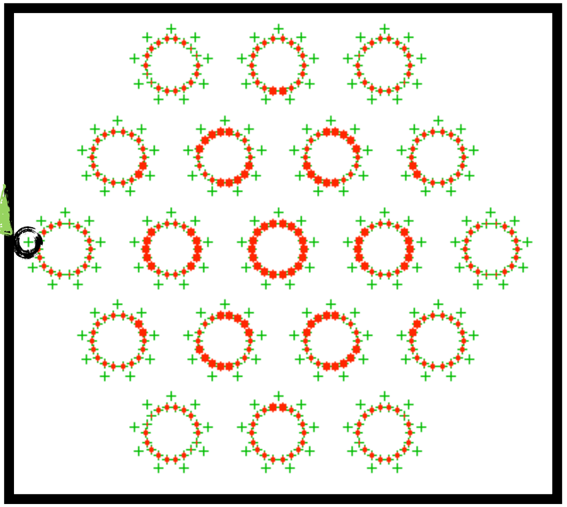
the transfer time to ring2: 1.33-1.34 ps

(experimental: 2-10 ps)

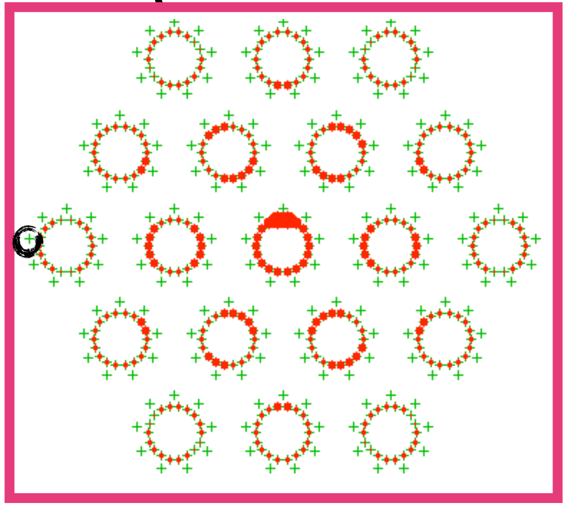
EET (larger system)

1. distribution at 10 ps after excited

initially excited pigment (0 ps)

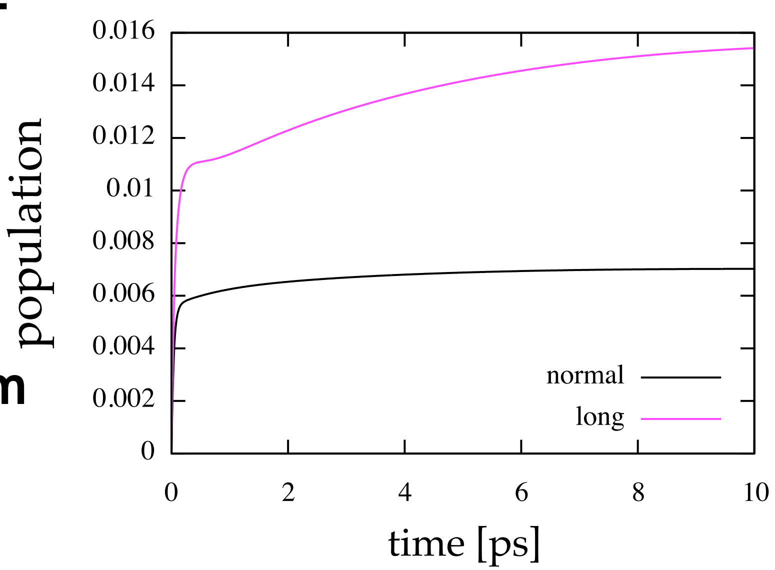


2. exchanging two original pigments in the center antenna to low energy pigments (850 nm→ 870 nm)



density of 2 central pigments

->quantum yield

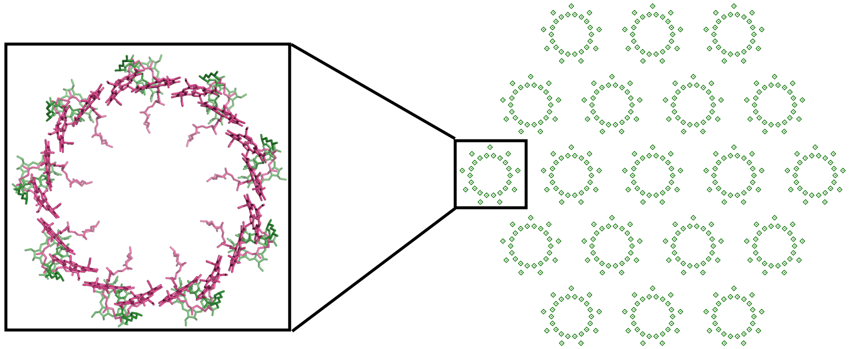


transfer velocity (initially excited pigment→central pigments)

1. 368.79 nm/ps
2. 727.27 nm/ps

→1.97 times

the correlation between the absorption & radiation



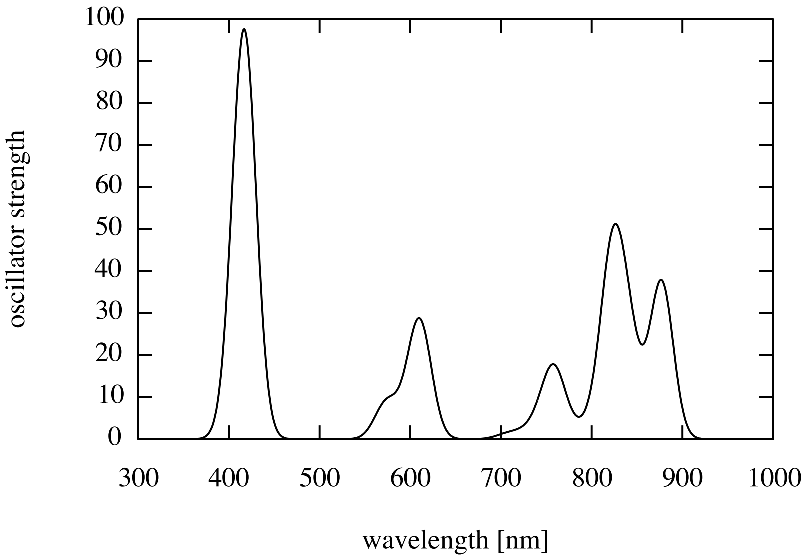
absorption efficiency：

$$\boxed{\chi(T) \equiv \frac{\int f(\lambda)u(\lambda,T)d\lambda}{\int u(\lambda,T)d\lambda}}$$

$f(\lambda)$：absorption strength (A)

$u(\lambda,T)$：photon flux density (B)

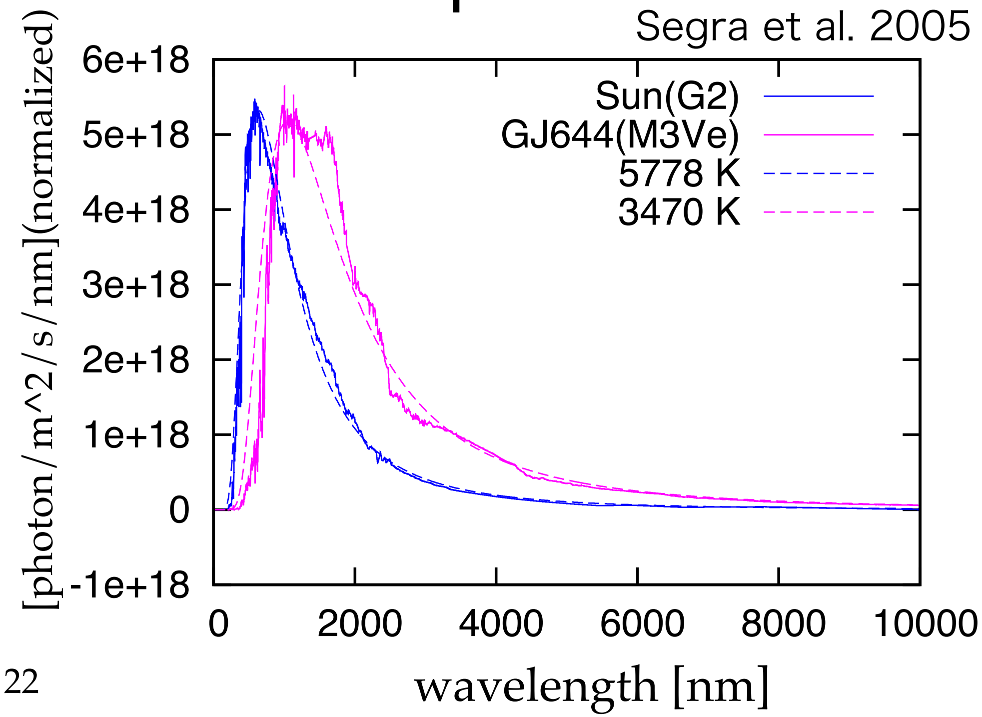
A. oscillator strength of antennas



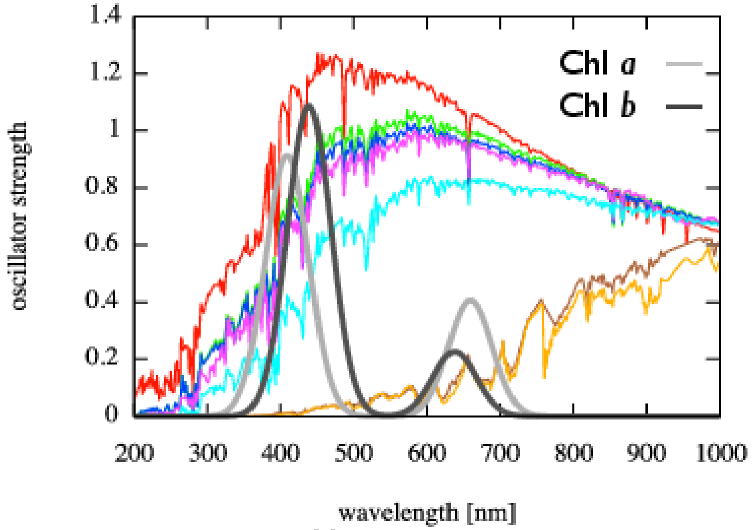
B. radiation spectra

Wehrli 1985

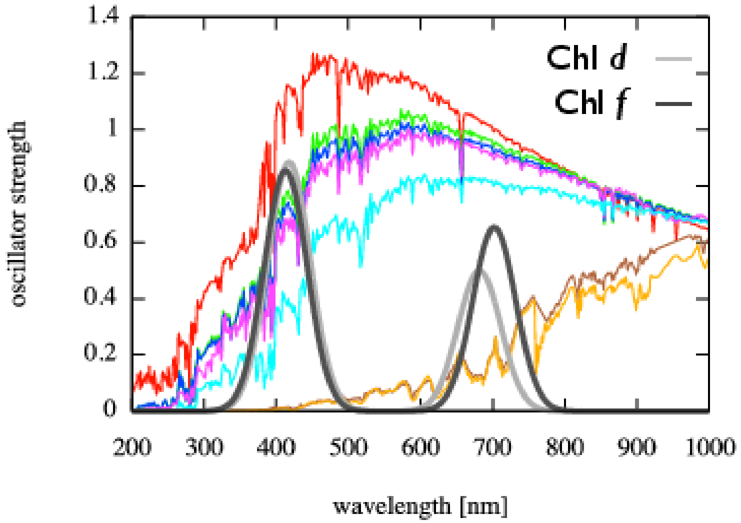
Segra et al. 2005



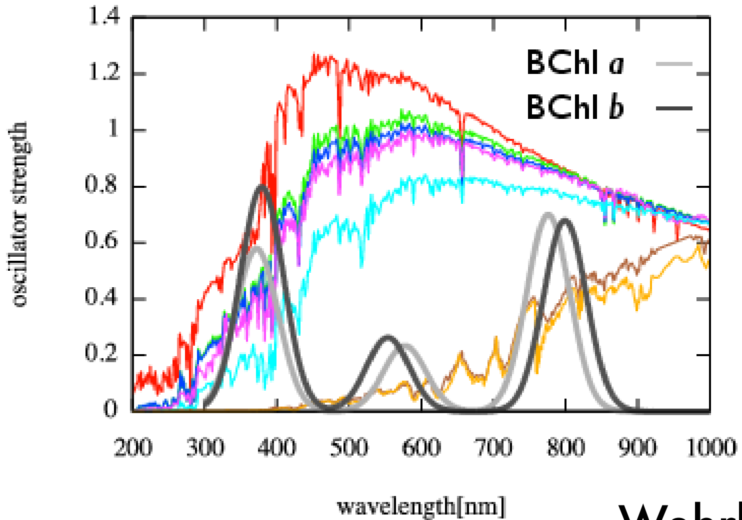
starting with sole pigment system (absorption)



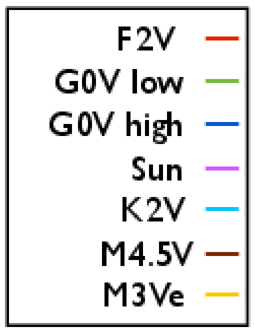
(i) Chl a & Chl b



(ii) Chl d & Chl f



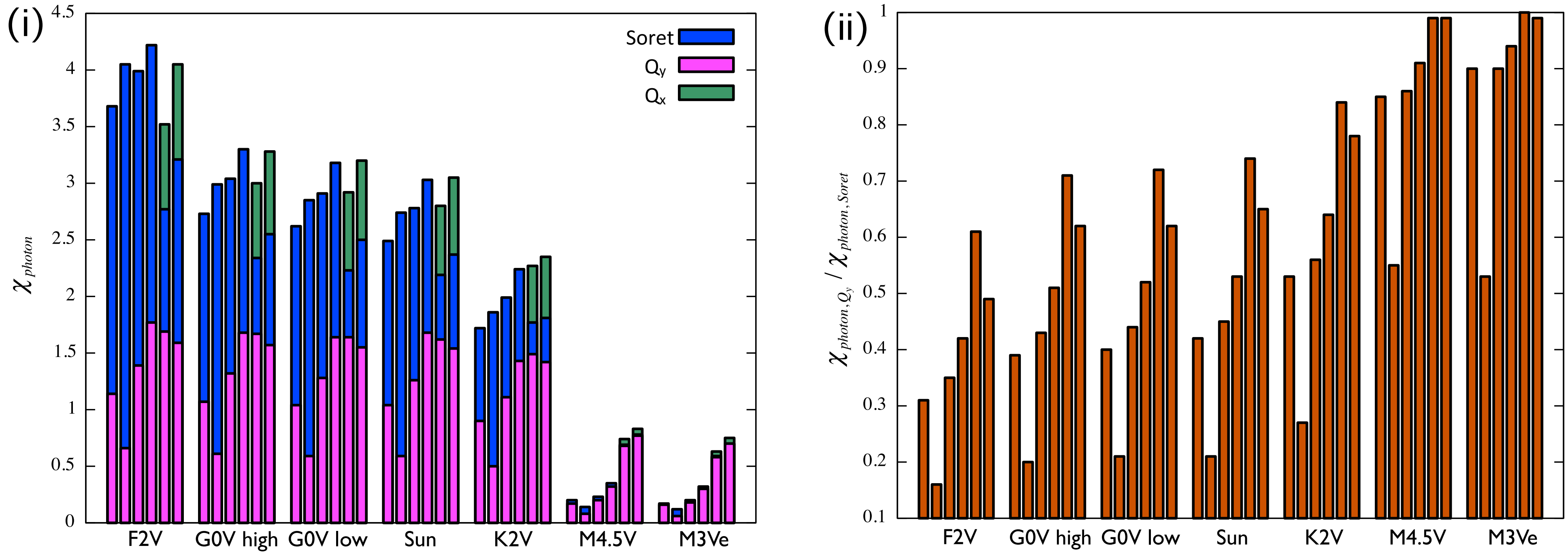
(iii) BChl a & BChl b



Wehrli 1985, Segra et al 2003, Segra et al 2005

- fluxes for each star were obtained as they would be received at the top of the atmosphere of a planet in the habitable zone (normalized fluxes are shown).

absorption efficiencies depending on the stellar radiation

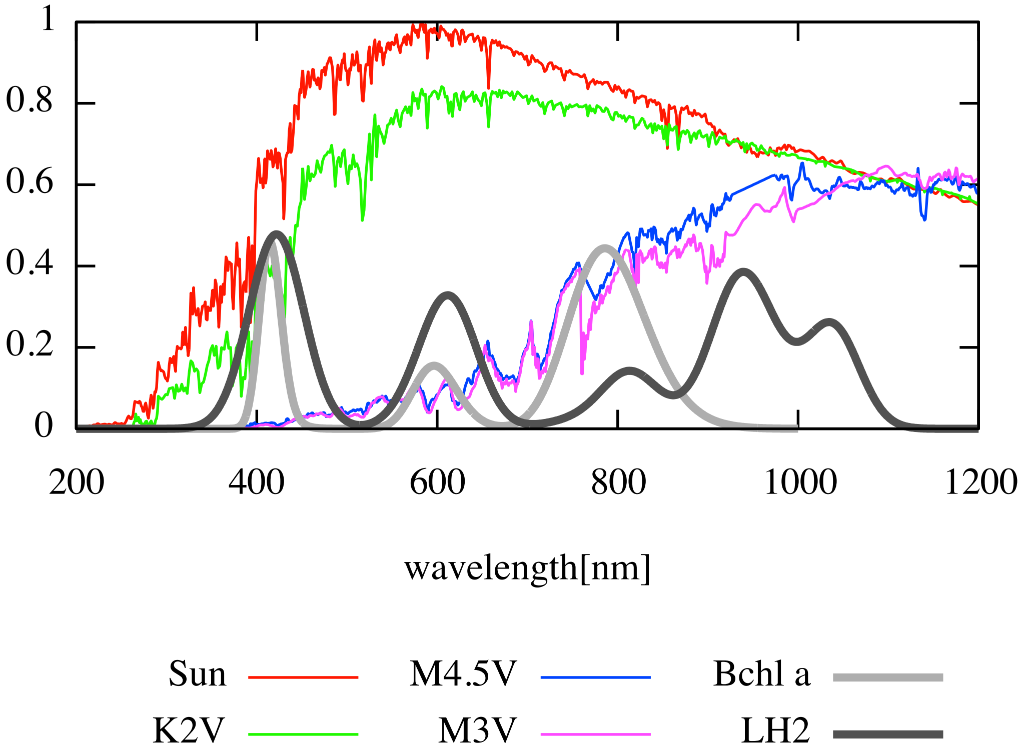


✱Chl a, Chl b, Chl d, Chl f, Bchl a, Bchl b from left to right for each stellar spectrum.

✱In cooler M stars, BChls > Chls, due to the Q_y band.

✱In high *T* stars, Chls > BChls, reflecting overlapping between Soret band & redward of 4000Å break.

comparison between pigment & antenna

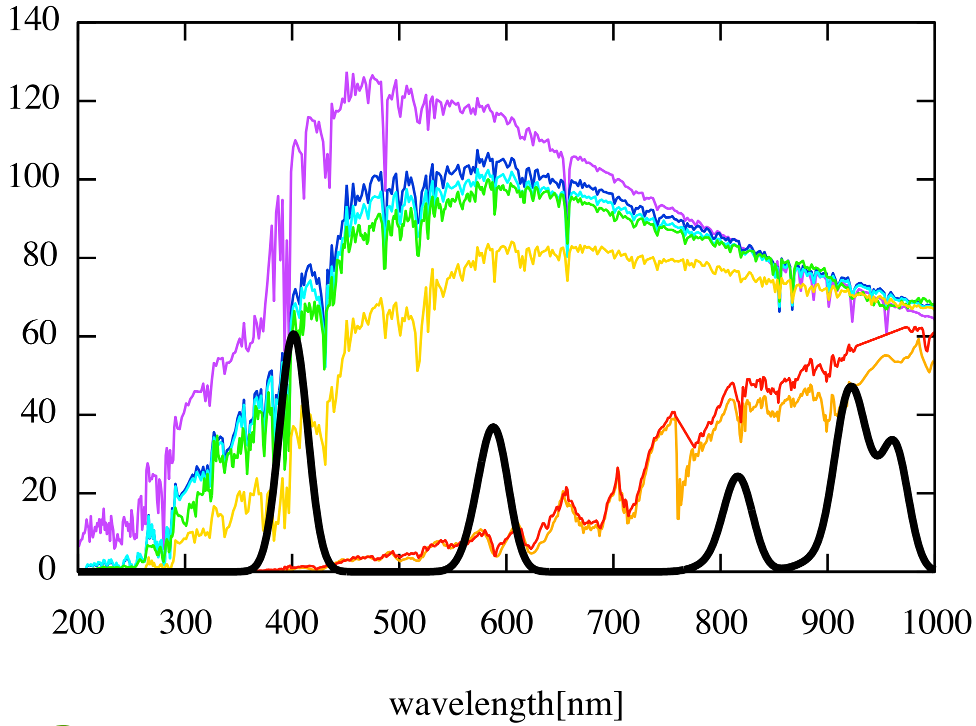


	Bchl a	LH2
Sun	0.0492566 (1)	16.3285 (1)
K2V HD22049	0.0420046 (0.853)	13.8673 (0.849)
M3Ve GJ644	0.0148644 (0.302)	6.0987 (0.374)
M4.5 AD Leo	0.0169216 (0.344)	6.78077 (0.415)

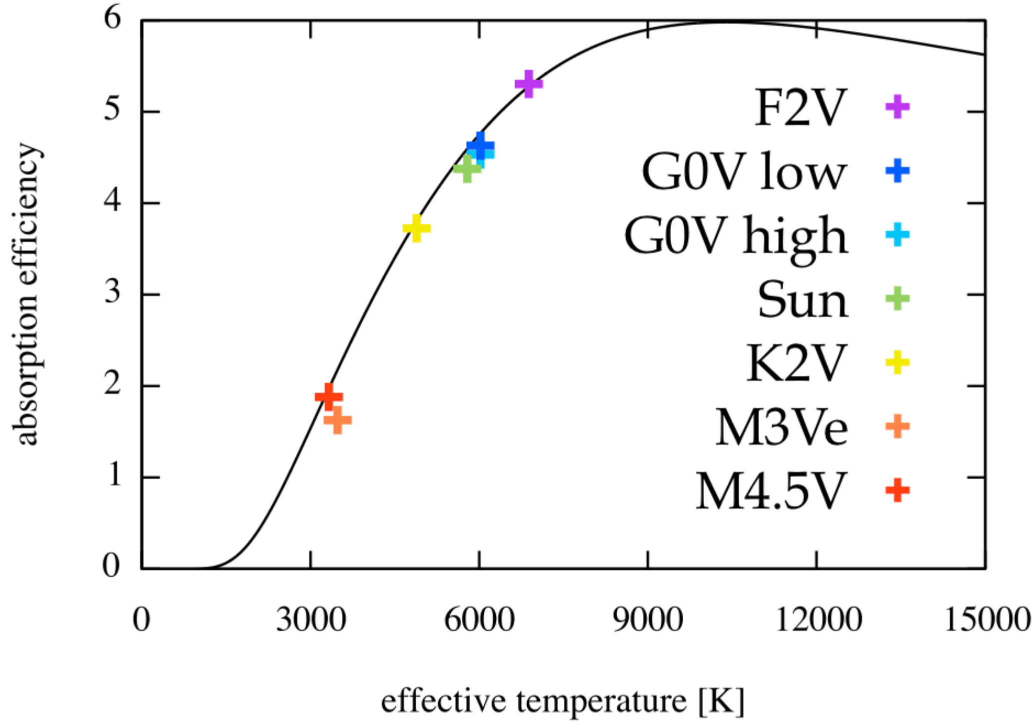
✱In our light absorption model, the absorption of 19 LH2 (antenna) system is more redshifted & the efficiency is higher compared to single pigment system (TDDFT calculation) especially in M star radiation.

absorption efficiencies of antenna system depending on stellar radiation

(a)



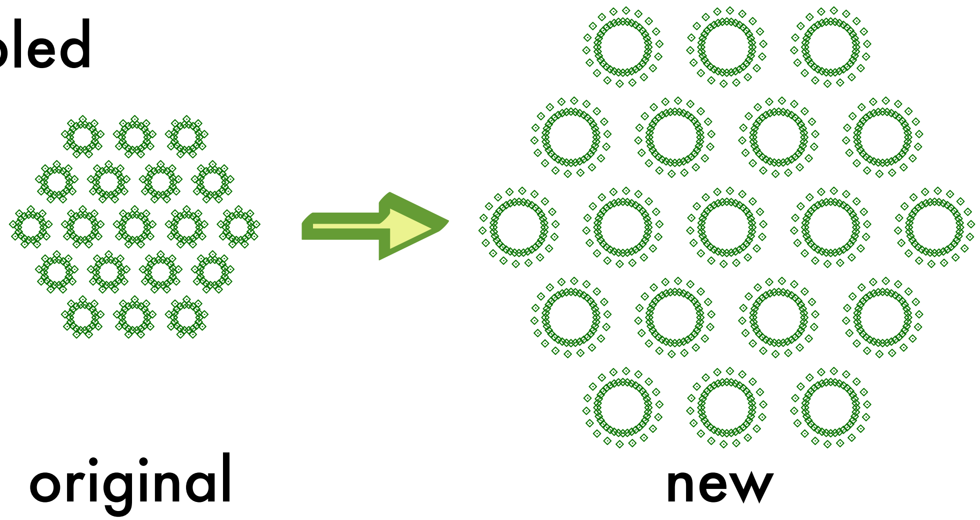
(b)

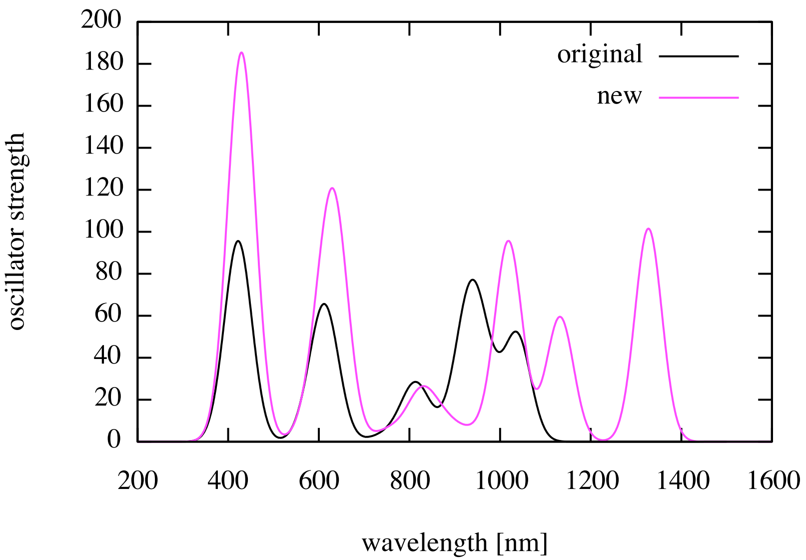


- Absorption efficiencies of antenna-aggregation system calculated using the seven stellar radiation (cross marks) & blackbody spectrum (black curve) (b)
- The efficiency is maximized at 9766 K, apart from the effective temperature of the Sun (5778 K)

changing conformation of antenna

radius of antennas, distance between antennas & number of pigments were doubled





	original	new
Sun	16.3285 (1)	28.4217 (1)
K2V HD22049	13.8673 (0.849)	23.9999 (0.844)
M3Ve GJ644	6.0987 (0.374)	11.5707 (0.407)
M4.5 AD Leo	6.78077 (0.415)	12.1337 (0.427)

➡but need constraint (quantum yield from EET simulation)

summary & future prospects

summary:

- We investigated how photosynthetic organisms absorb light efficiently depending on the stellar radiation.
  - We confirmed the validity of the model by calculating light absorption & EET properties.
  - single pigment (TDDFT): In cooler stars, BChls > Chls, due to the Q_y band. In hotter stars, Chls > BChls, reflecting overlapping between Soret band & redward of 4000Å break.
  - antenna-aggregation model (our model): We compared between black body & stellar radiation and the efficiency is maximized at 9766 K, apart from 5778 K.

future prospects:

- using more detailed spectra of planets (radiation transfer model)
- comparing with cyanobacteria (the first oxygen-generating photosynthetic microorganism) & plant

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Thank you for your attention !