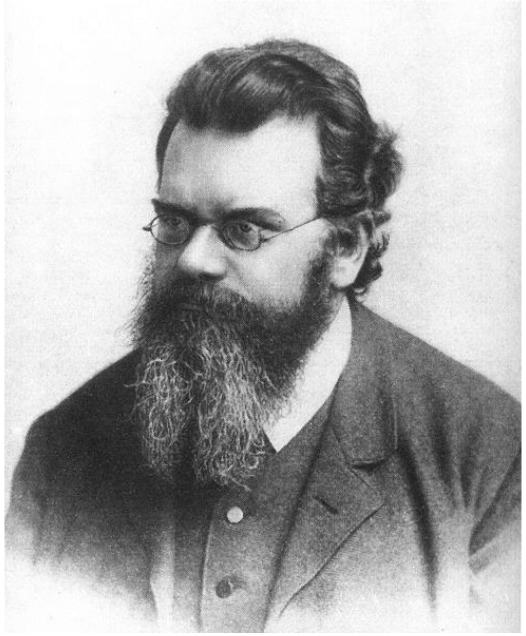
Kunstmatige fotosynthese en BioSolar Cells

Huub de Groot| Leiden Faculty of Science

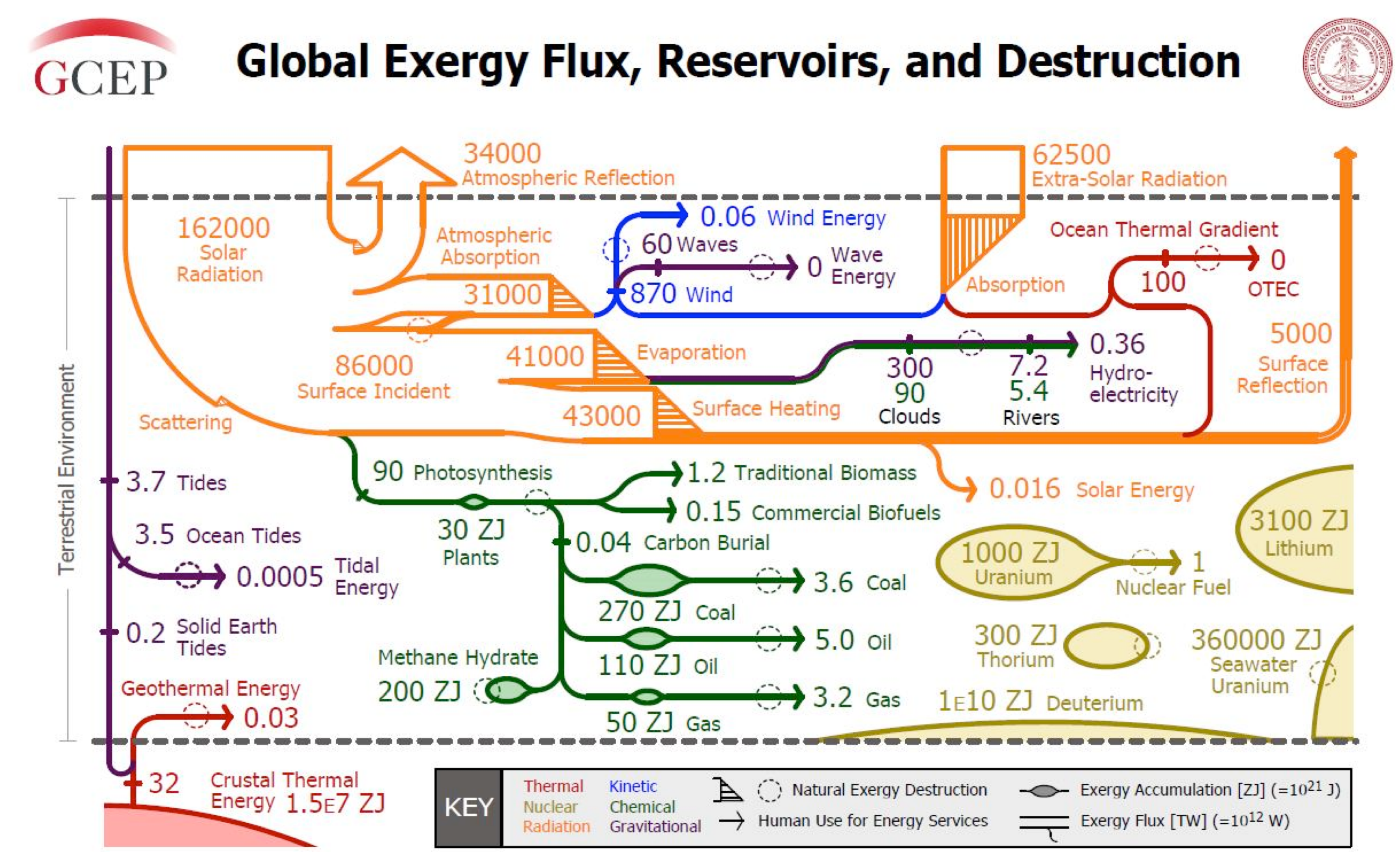
Universiteit Leiden
The Netherlands

Thermodynamics



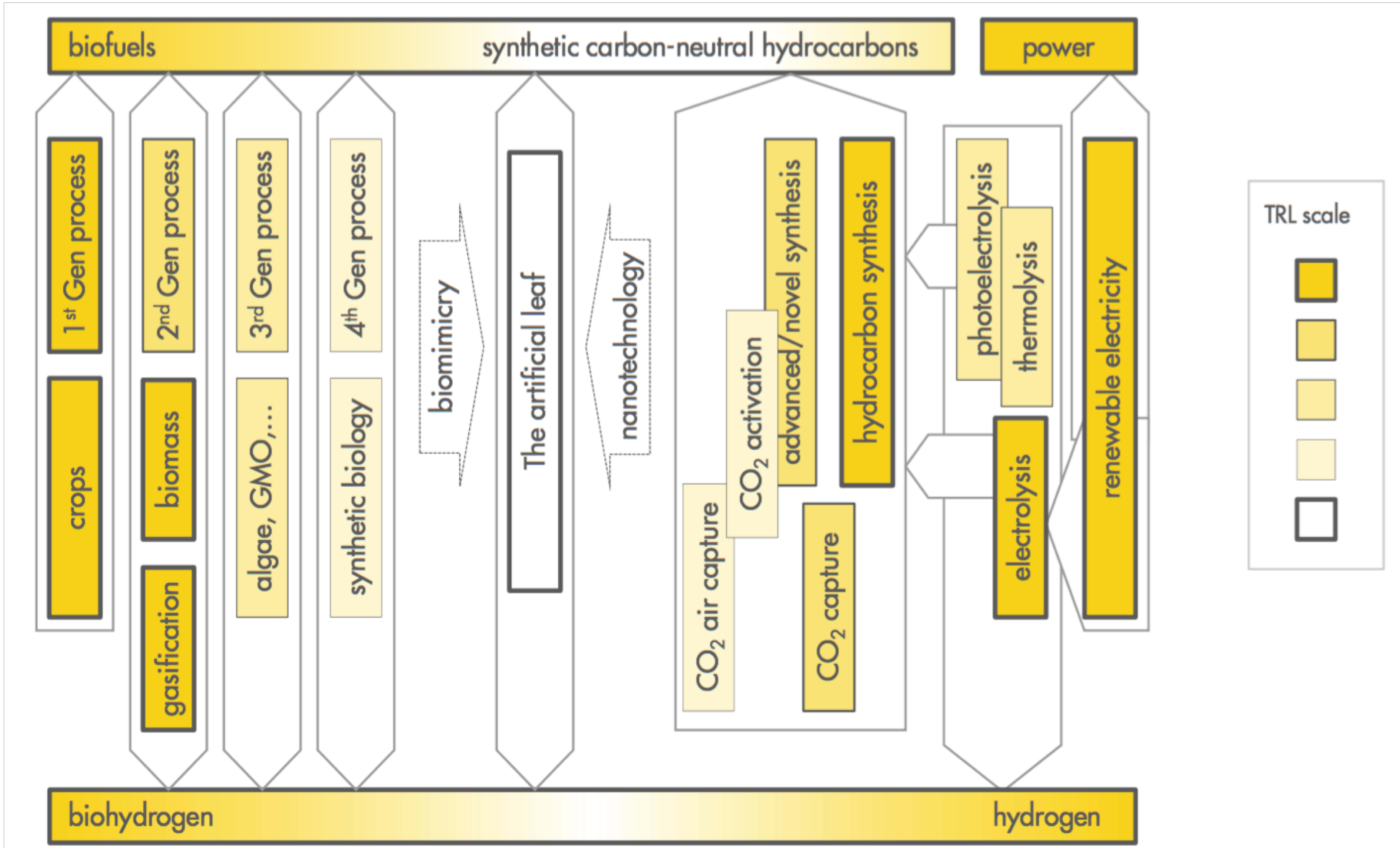
- 1st law
  - Energy cannot be destroyed or created
  - So why bother?
- 2nd law
  - With every conversion it will probably become less useful
  - Exergy is destroyed

Exergy



GCEP
Global Exergy Flux, Reservoirs, and Destruction
34000
Atmospheric Reflection
62500
Extra-Solar Radiation
162000
Solar
Radiation
Atmospheric
Absorption
31000
0.06 Wind Energy
60 Waves
0 Wave
Energy
870 Wind
Absorption
Ocean Thermal Gradient
100
0
OTEC
86000
Surface Incident
41000
Evaporation
43000
Surface Heating
300
90
Clouds
7.2
5.4
Rivers
0.36
Hydro-
electricity
5000
Surface
Reflection
Scattering
Terrestrial Environment
3.7 Tides
90 Photosynthesis
1.2 Traditional Biomass
0.15 Commercial Biofuels
0.016 Solar Energy
3.5 Ocean Tides
30 ZJ
Plants
0.04 Carbon Burial
0.0005 Tidal
Energy
1000 ZJ
Uranium
1
Nuclear Fuel
3100 ZJ
Lithium
3.6 Coal
270 ZJ Coal
0.2 Solid Earth
Tides
5.0 Oil
110 ZJ Oil
300 ZJ
Thorium
360000 ZJ
Seawater
Uranium
Methane Hydrate
200 ZJ
Geothermal Energy
0.03
3.2 Gas
50 ZJ Gas
1E10 ZJ Deuterium
32
Crustal Thermal
Energy 1.5E7 ZJ
KEY
Thermal
Nuclear
Radiation
Kinetic
Chemical
Gravitational
Natural Exergy Destruction
Human Use for Energy Services
Exergy Accumulation [ZJ] (=10^21 J)
Exergy Flux [TW] (=10^12 W)

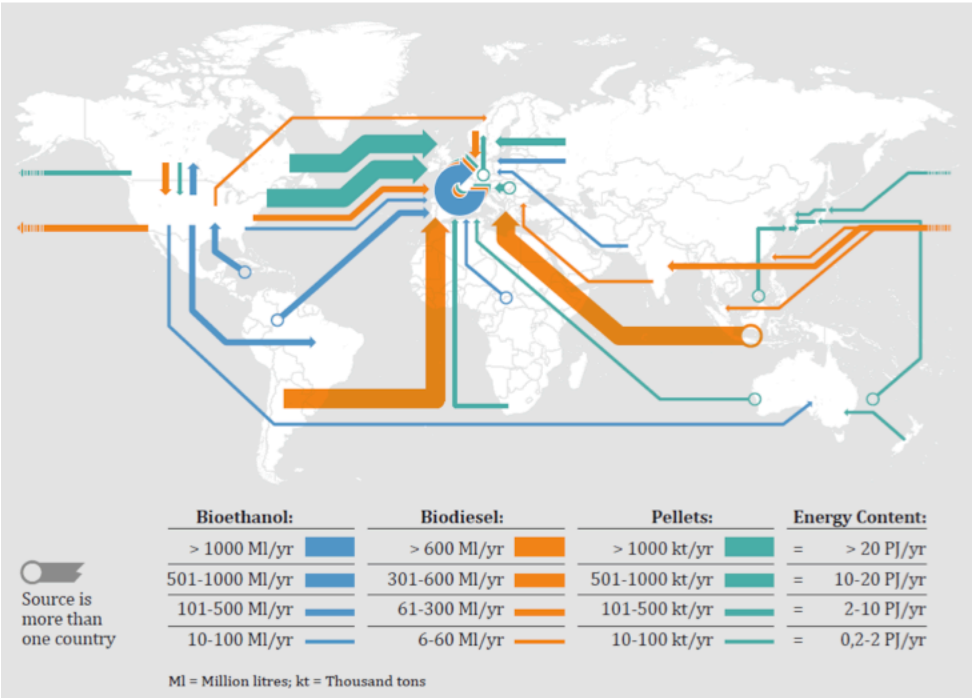
Technology conundrum



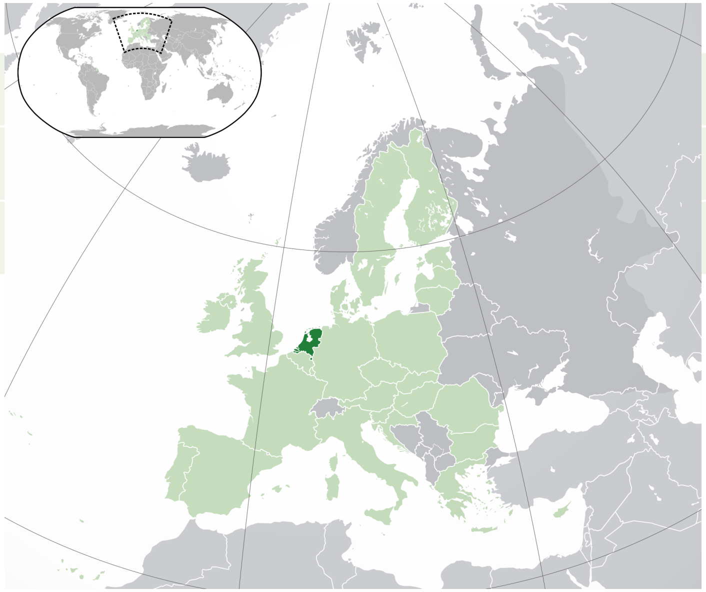
Source: Gert Jan Kramer, Shell, Leiden & Utrecht

Fuel Deliveries

Net streams of wood pellets,
biodiesel and bioethanol for Europe



Gasoline	5356
Diesel	8304
Jet-A1	4318



*In Millions of Liters per year, for The Netherlands

Source: Central Statistics Bureau

The world economy already runs on photosynthesis; it's all a matter of conversion

Photosynthesis:

- $H_2O + CO_2 \rightarrow$ Sugars + O_2
- Few conversion steps

Biomass:

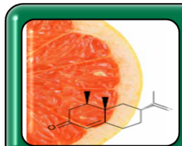
- Sugars → → → Complex molecules
- Many conversion steps

Fossil fuels:

- Biomass → → → Hydrocarbons
- Many conversion steps, millions of years

Refinery:

- Fossil fuels → → Simple molecules
- Few/many conversion steps



Product formation:

- Simple molecules → → → Complex molecules
- Few/many conversion steps

The world economy already runs on photosynthesis; it's all a matter of conversion

Photosynthesis:

- $H_2O + CO_2$ → Sugars + O_2
- Few conversion steps

Biomass:

- Sugars → → → Complex molecules
- Many conversion steps

Fossile fuels:

- Biomass → → → Hydrocarbons
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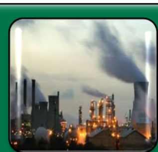
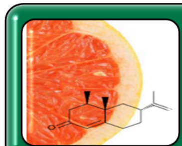


BioRefinery:

- Complex molecules → → Simple molecules
- Few/many conversion steps



Product formation:

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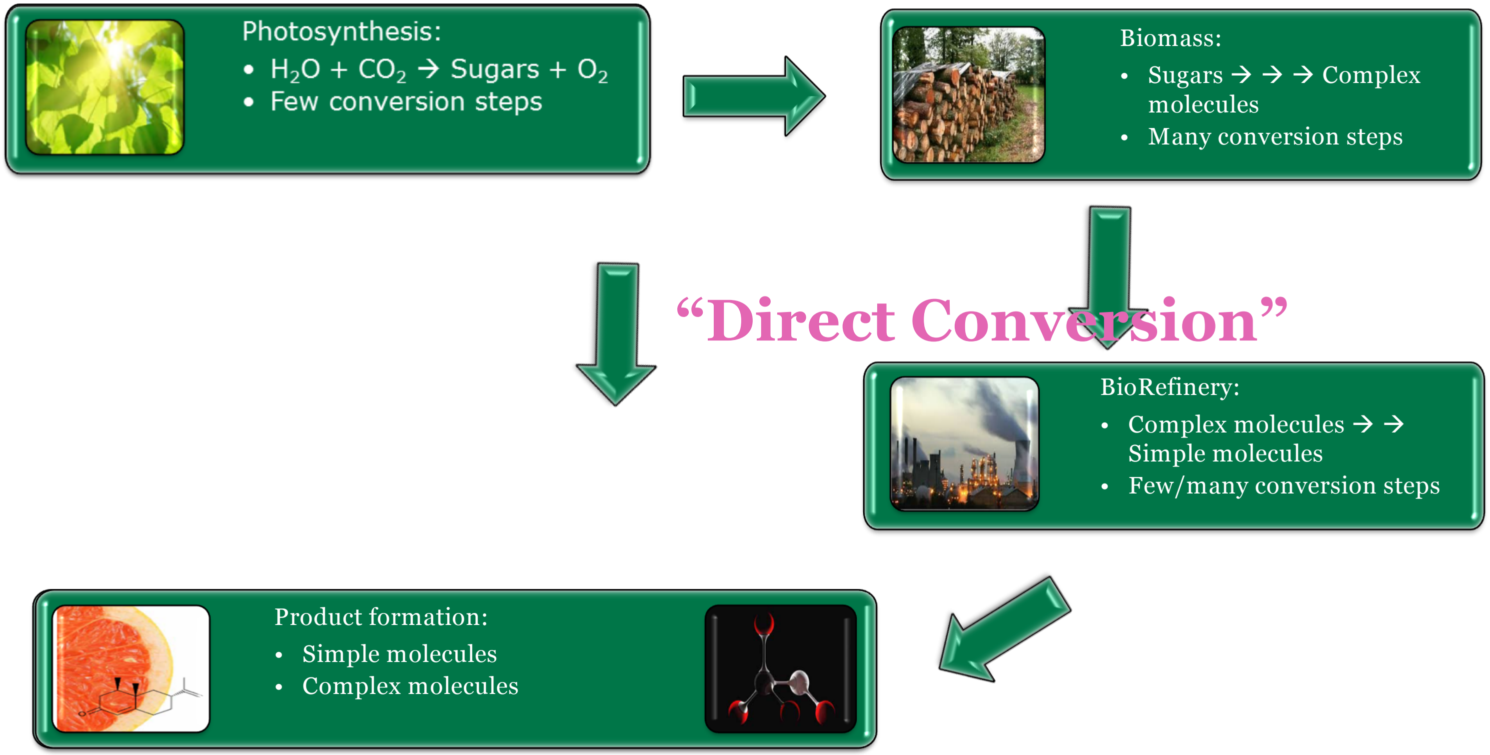
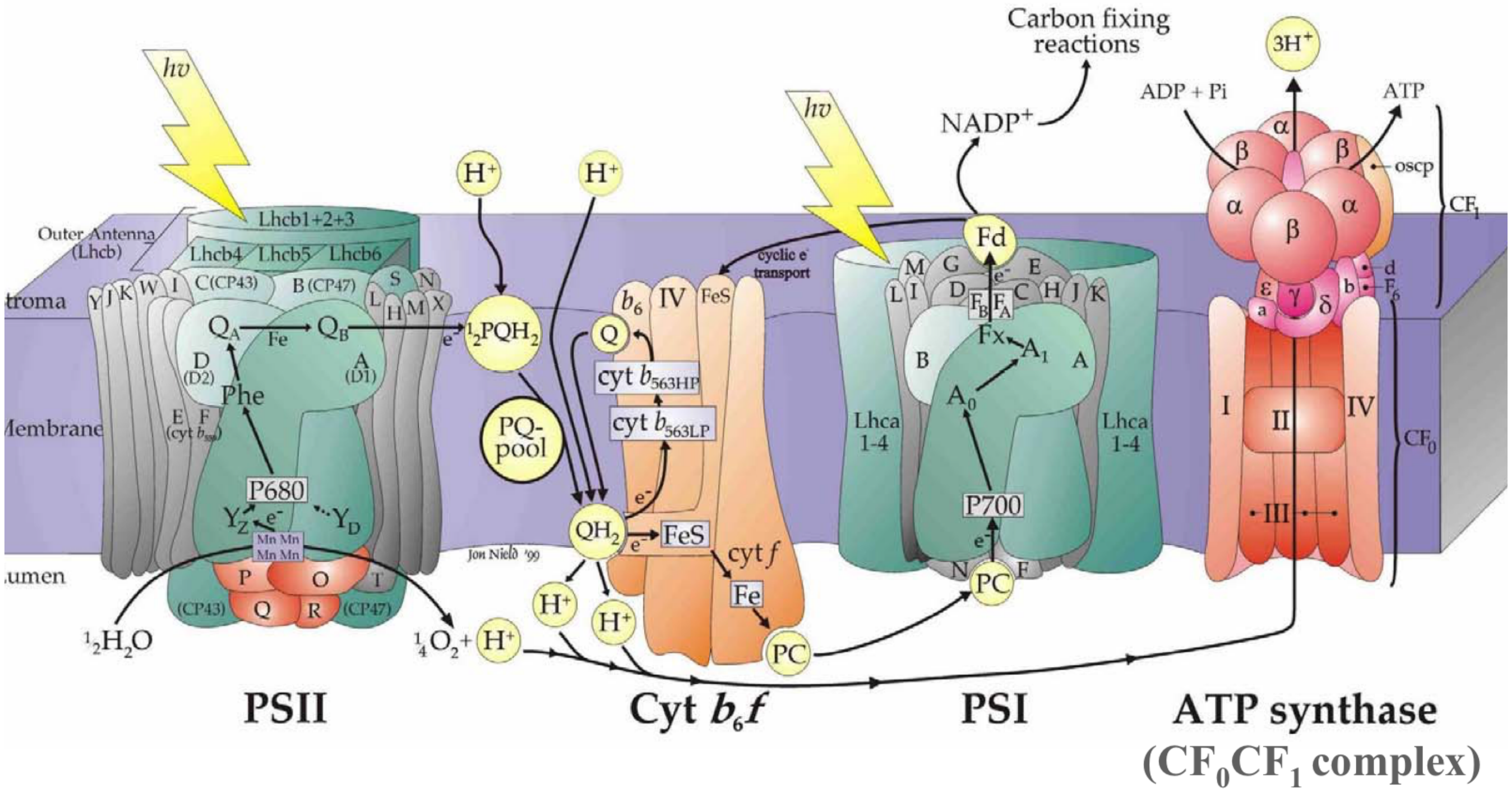
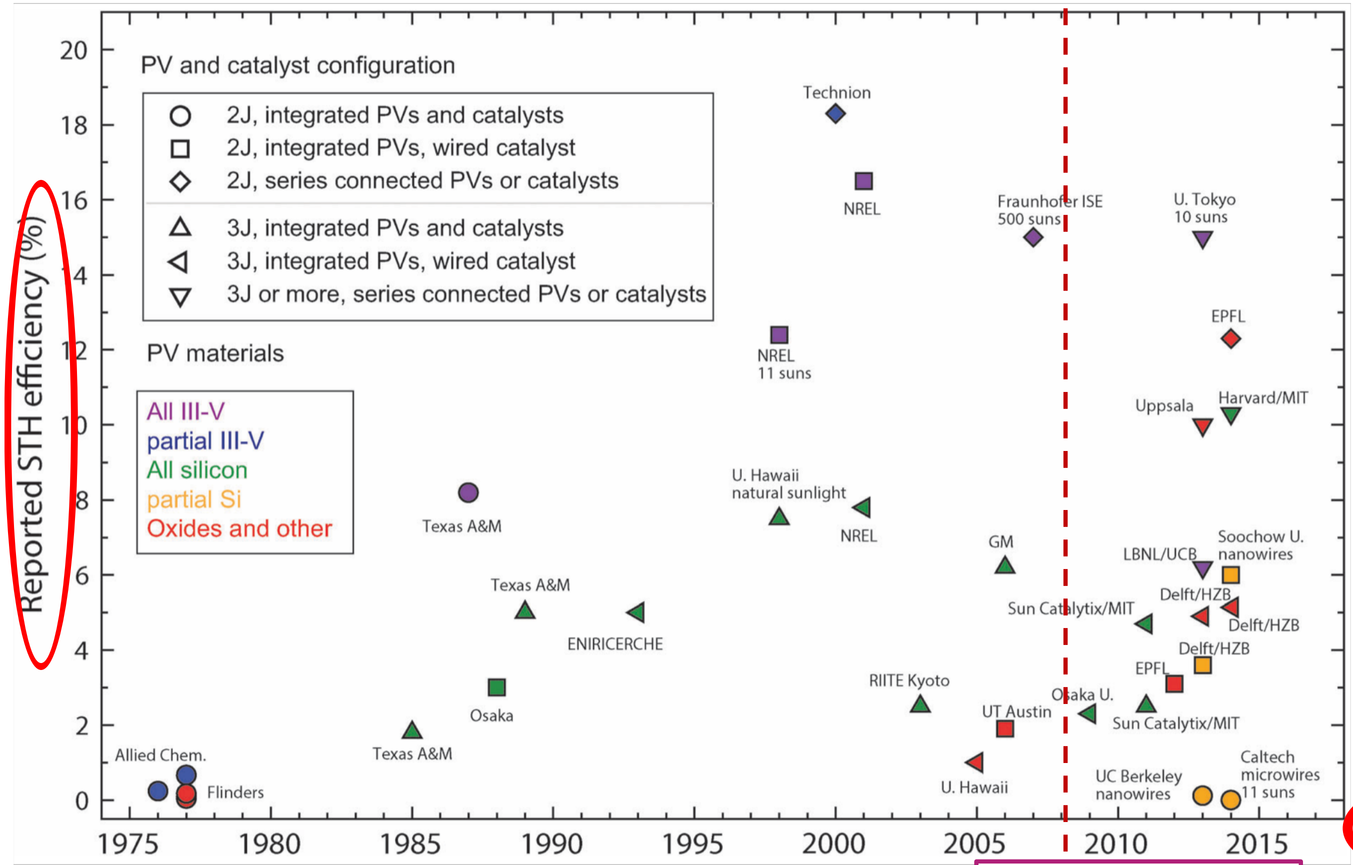
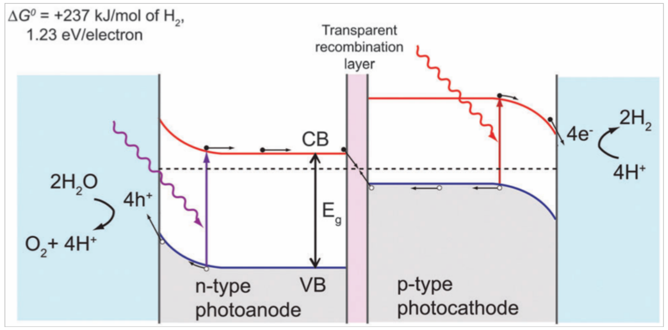


Direct conversion 8-12 photons per CO_2



AP is running around in circles…





Materials efficiency

16 years of uncorrelated electrons did not bring us much further

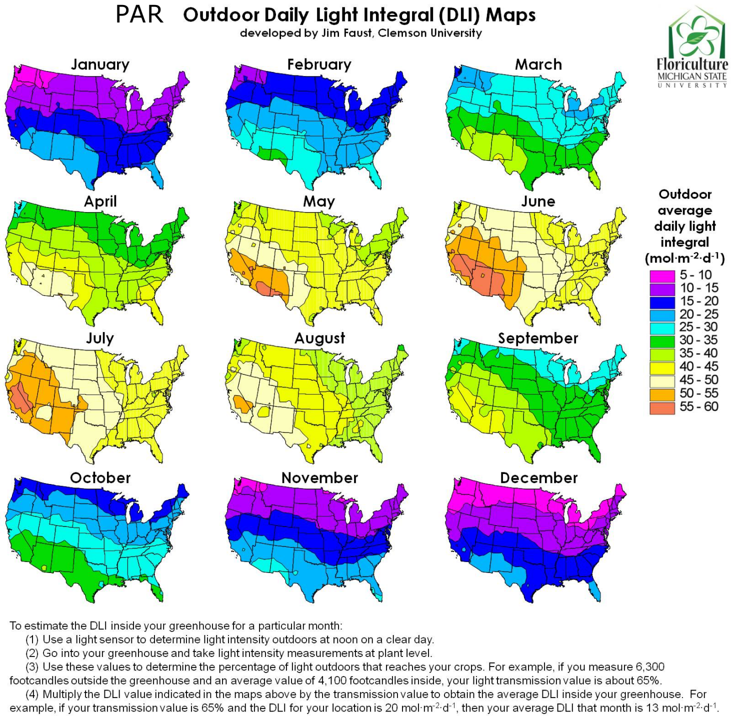
Energy efficiency

Quantum efficiency

ESF White paper

Ager, J. W., Shaner, M. R., Walczak, K. A., Sharp, I. D., & Ardo, S. (2015). Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. Energy & Environmental Science, 8(10), 2811–2824. http://doi.org/10.1039/C5EE00457H

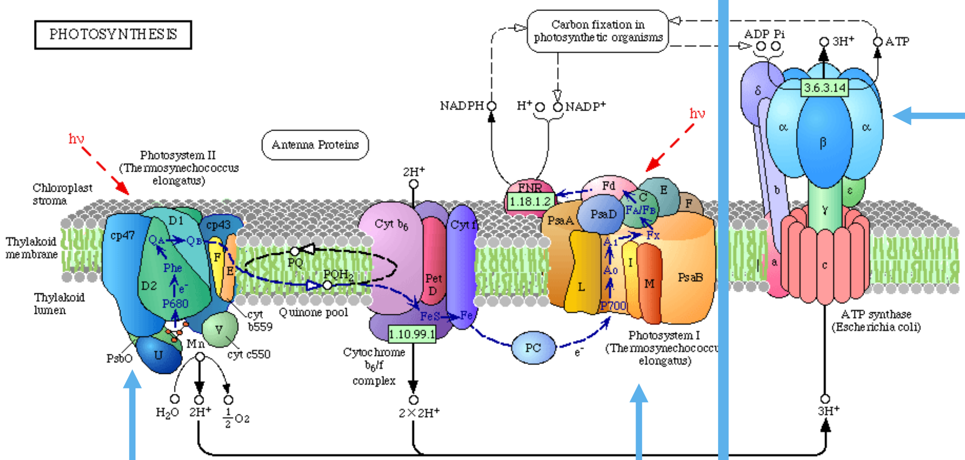
In photosynthesis every photon counts



- Add 18 mol photons/m^2.d with 700 nm LED at low light days
- Yield is 100 kg/m^2.y tomato at elevated CO_2 levels
- This is an ***absolute quantity***
- Relative percentages (STT, Solar to Tomato) are misleading

 http://www.lighting.philips.com/main/products/horticulture/press-releases/green-q

Photons to product, not energy



ATP

Maintenance, 2-4 photons

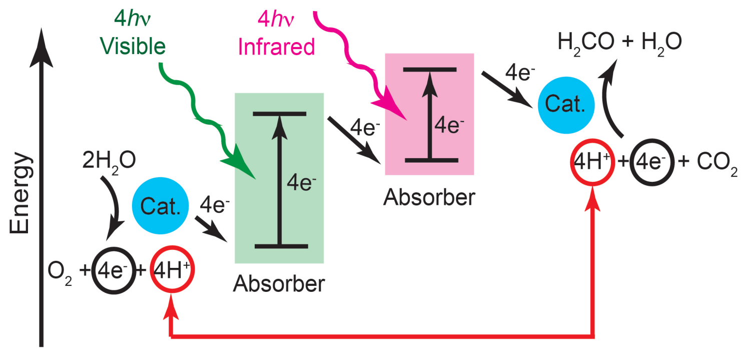
Reduce losses

$$2H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e^-$$

$$CO_2 + 4H^+ \xrightarrow{h\nu} (H_2CO) + H_2O$$

Production is close to the physical limit with 8 photons, however, only at low light intensity → 2 photons per electron

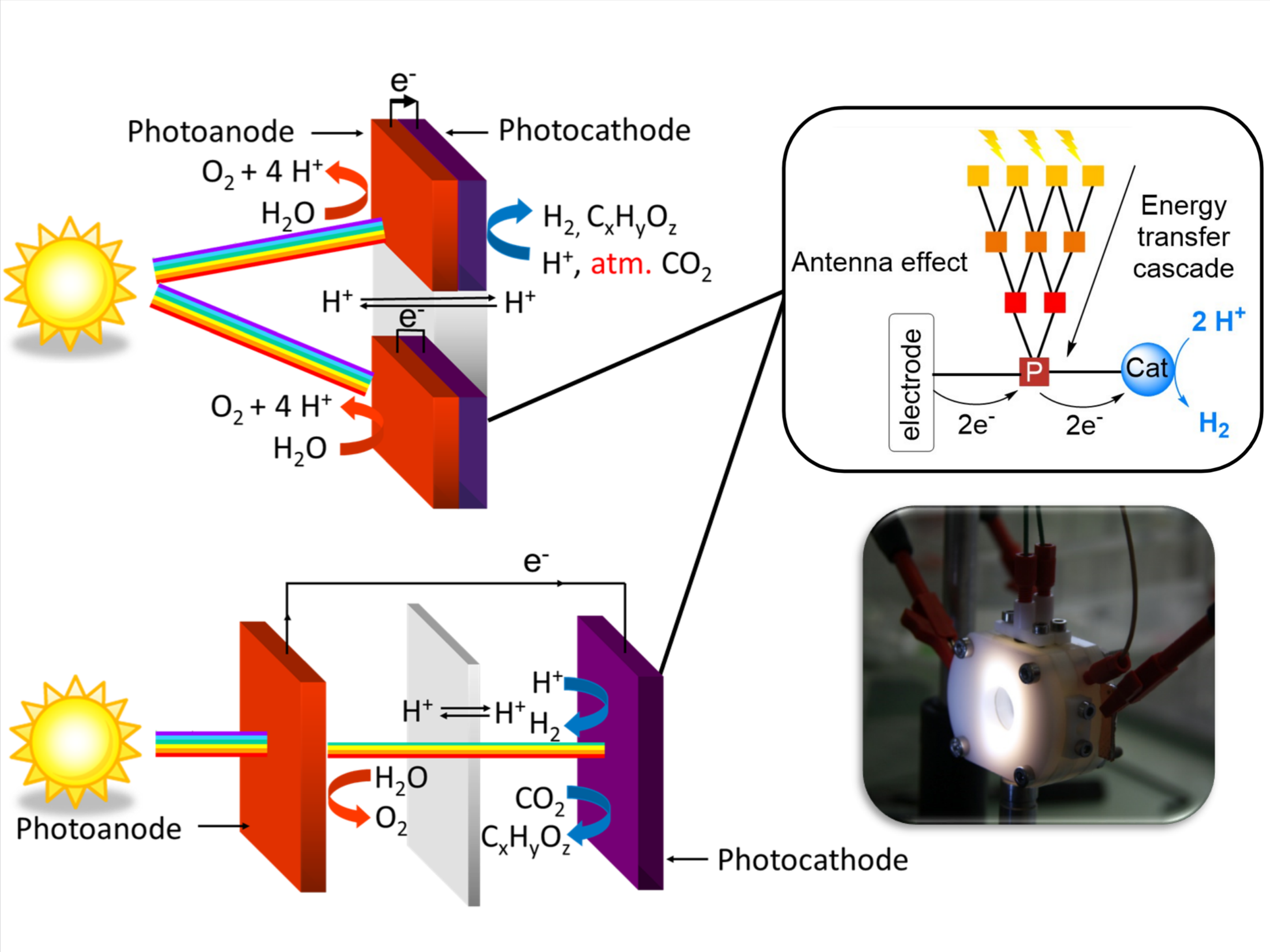
Cathode half-reactions



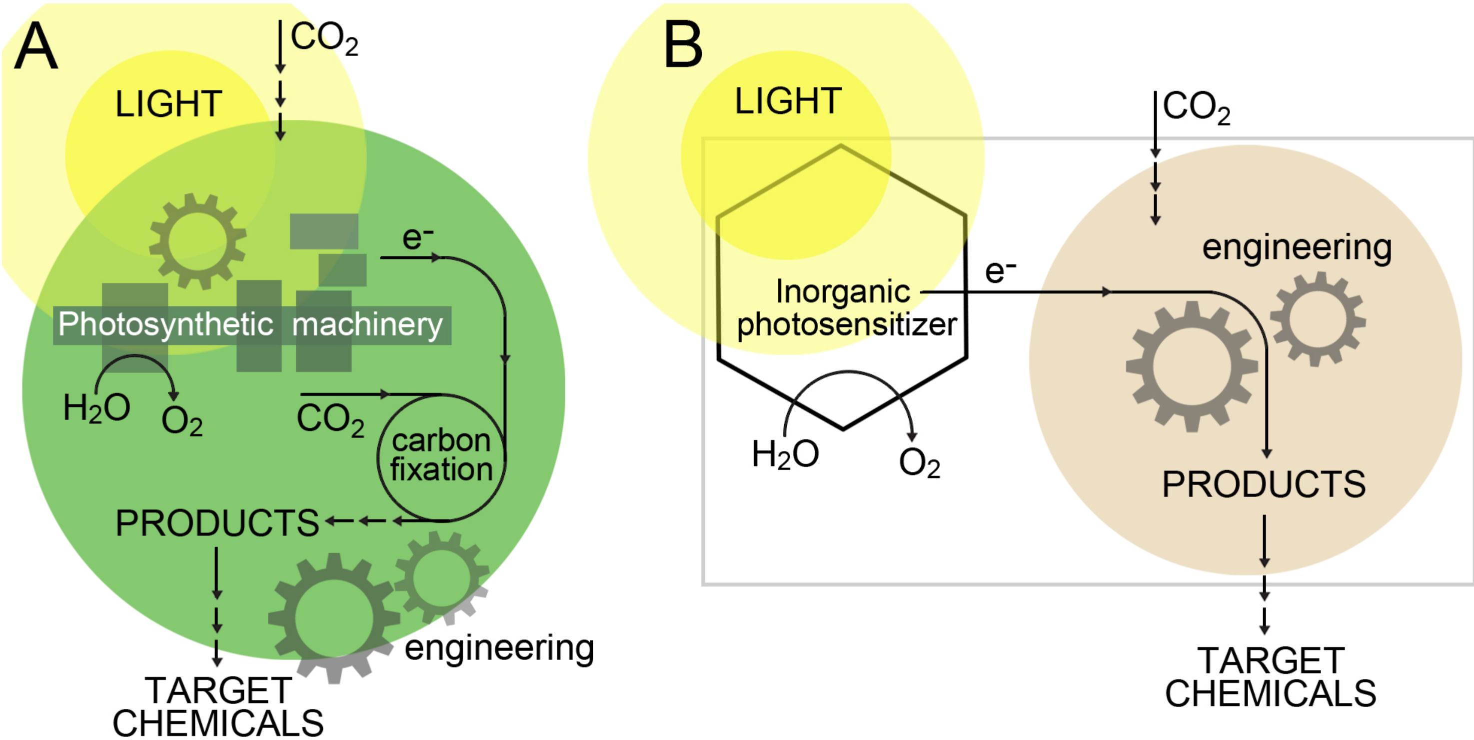
Reaction	Conversion rate AM1.5 [μmol cm^{-2}s^{-1}]	CO_2 conversion potential [tons ha^{-1} y^{-1}]	Fuel/chemical production potential [tons ha^{-1} y^{-1}]
$2H^+ + 2e^- \rightarrow H_2$	0.086	-	52 - 130
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	0.086	1120 - 2800	1182 - 2956
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	0.086	1120 - 2800	720 - 1799
$CO_2 + 4H^+ + 4e^- \rightarrow H_2CO + H_2O$	0.043	560 - 1400	386 - 964
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	0.029	378 - 945	274 - 686
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	0.022	280 - 700	103 - 257
$2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O$	0.014	378 - 945	197 - 494
$N_2 + 6\ H^+ + 6\ e^- \rightarrow 2\ NH_3$	0.029	-	308 - 772

http://edepot.wur.nl/341608

Direct Conversion



BioSolar Cells

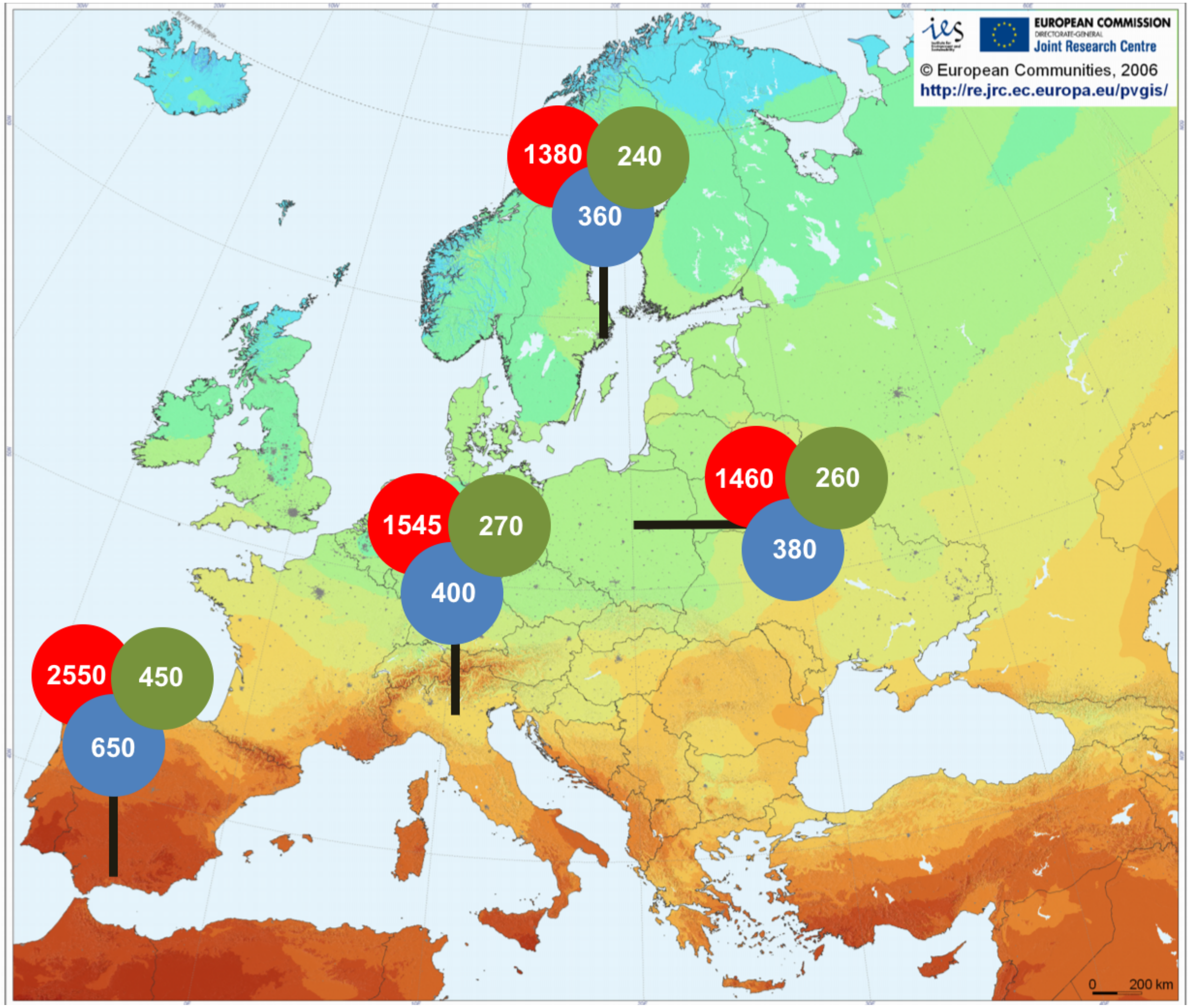


Conversion with unprecedented yield

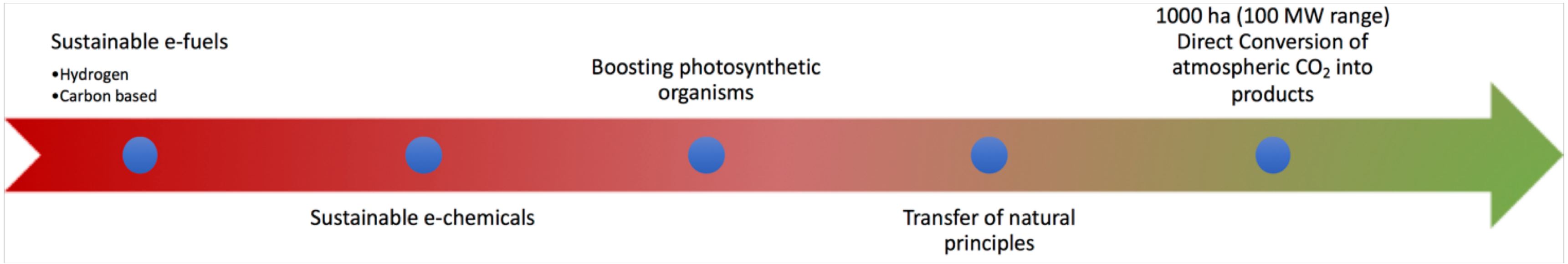
- CO2 (ton/ha.yr)
- Ethanol (ton/ha.yr)
- Ammonia (ton/ha.yr)

90% photon absorption,
80% chemical conversion,
70% overall yield

See: www.sunriseflagship.com

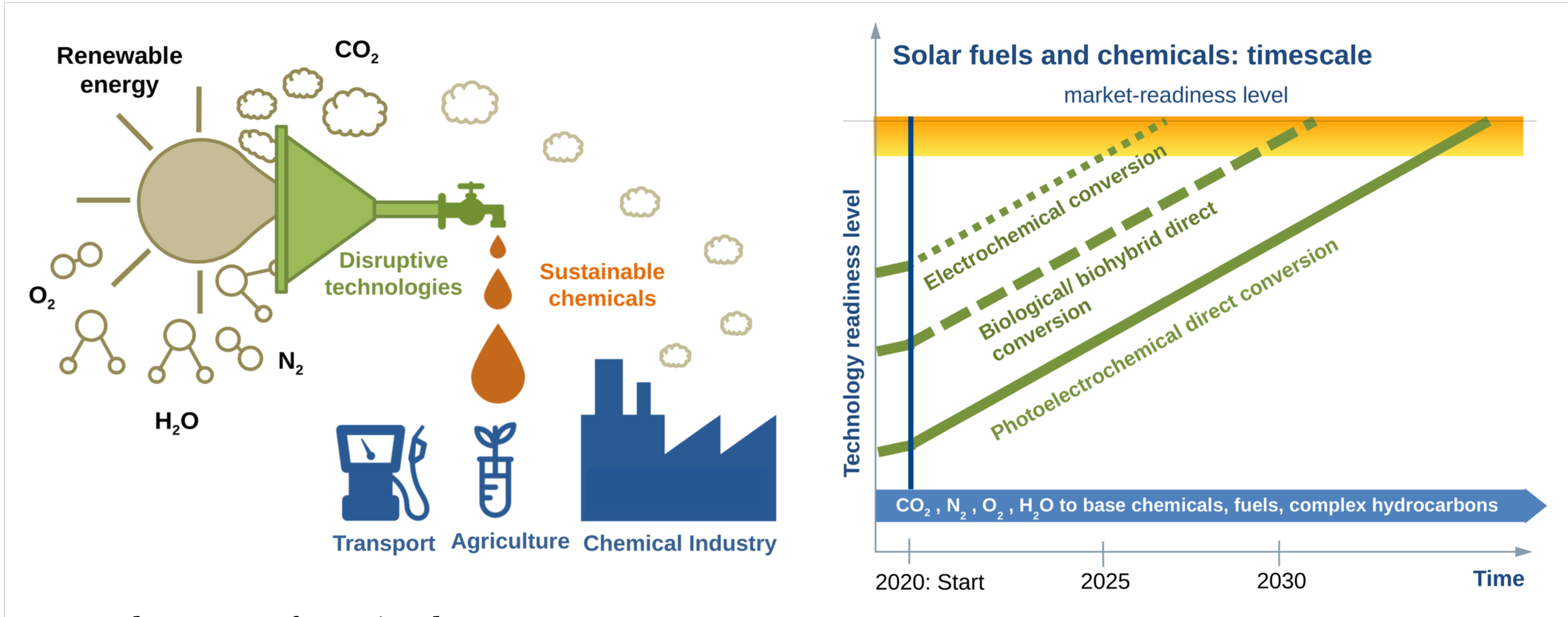


Artifical Photosynthesis Approaches



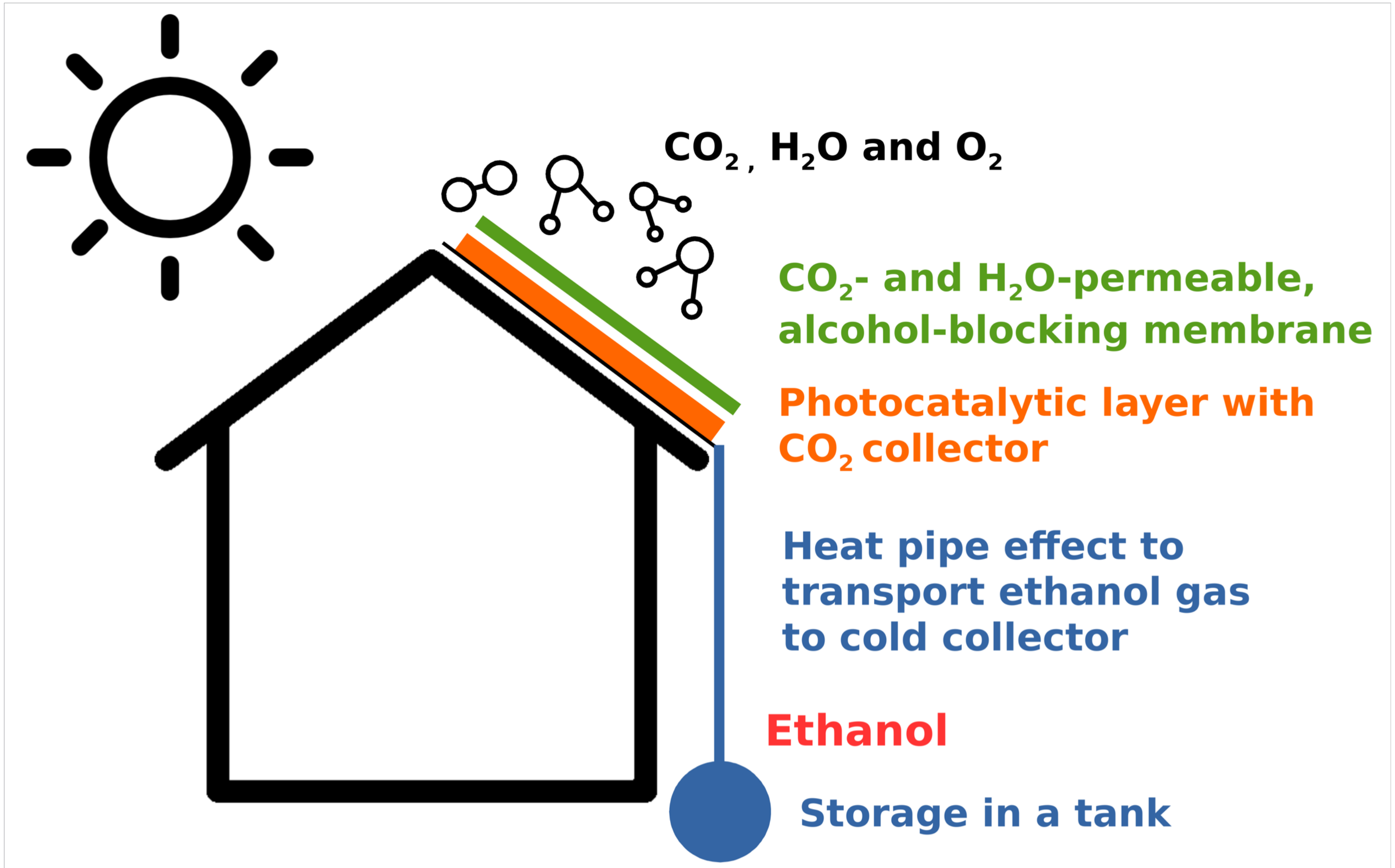
	Present TRL Level		
Approach	Mission A Fuels	Mission B Chemicals	Mission C Capture CO_2
1. Electrochemical conversion with renewable power **fuels and commodity chemicals from CO_2, H_2O, O_2, and N_2**	3-8	0-5	0-3
2. Integrated artificial systems **fuels and chemicals from CO_2, … N_2 and direct solar energy**	2-4	0-3	0-3
3. Direct conversion via biological and biohybrid systems **unconventional methodology for photochemical conversion of atmospheric CO_2 with high yield**	3-6	0-3	0-3

Carbon neutral industry



Solar energy for a circular economy

Atmospheric CO_2

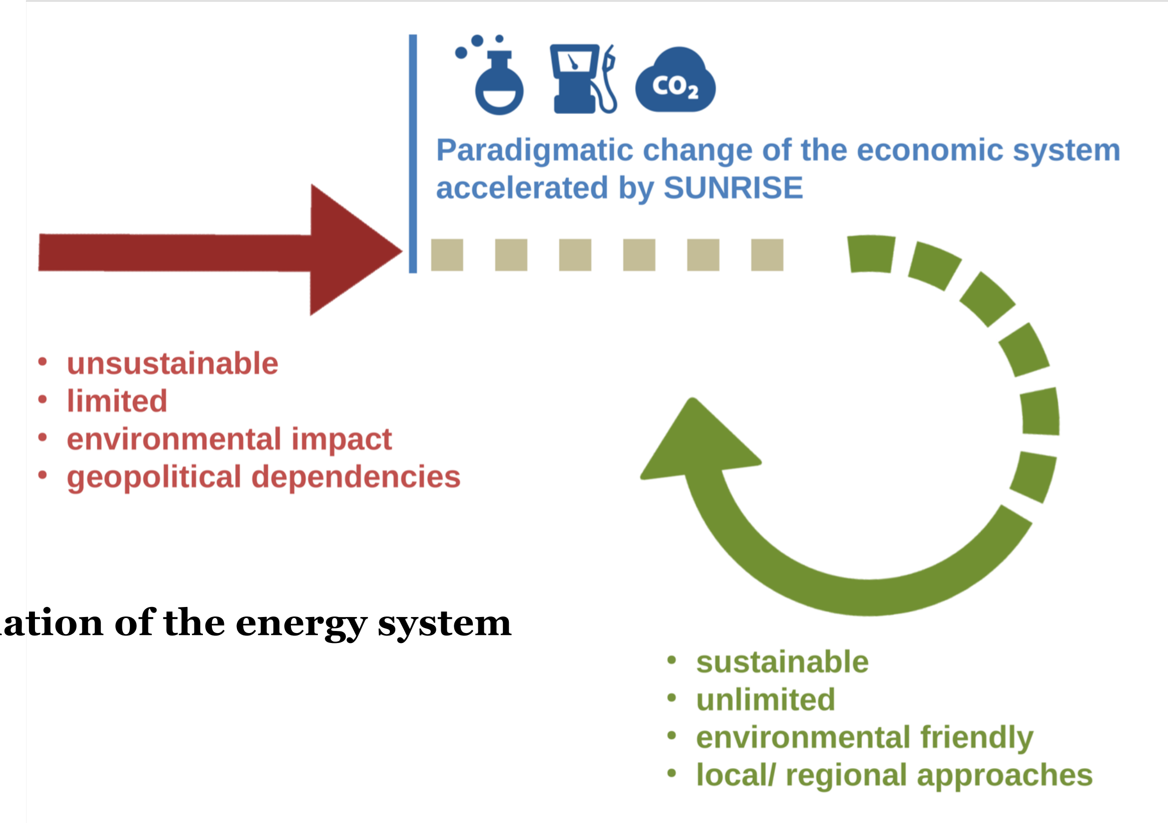


Seasonal energy storage

Europe beyond 2050:
700 million people - 2 TW SUNRISE Power

Efficiency of solar conversion	Surface per capita	Total area needed	
100 %	30 m^2	0.3 %	
10 %	300 m^2	3 %	**Artificial Photosynthesis**
1 %	3000 m^2	30 %	
0.1 %	30000 m^2	300 %	**Biomass**

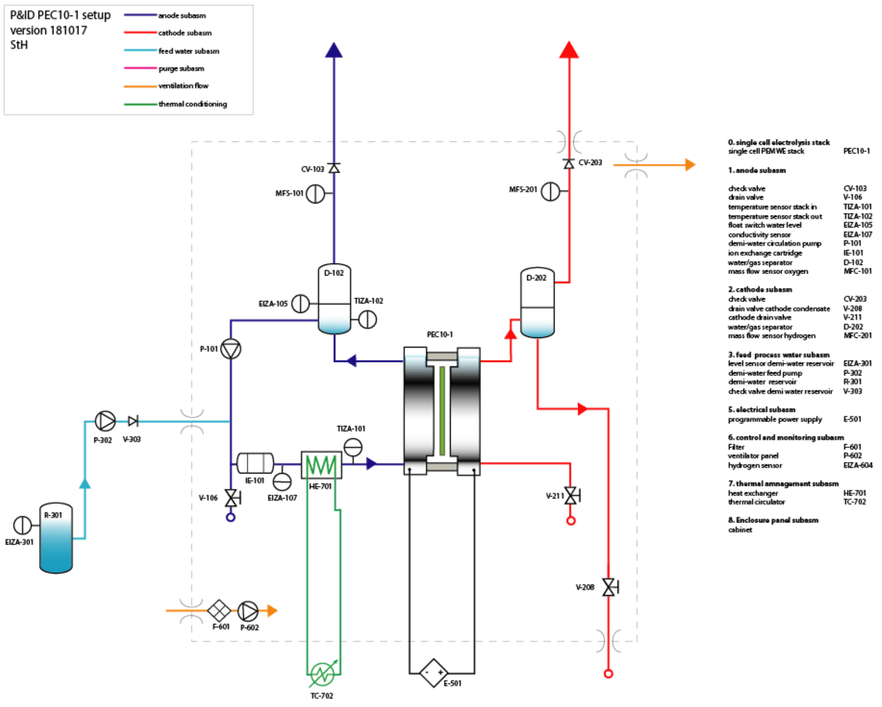
Zero waste society



Transformation of the energy system

Where are we now

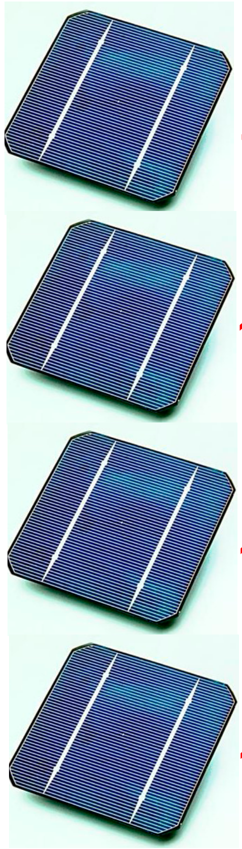
Lab technology platform



Pilot technology platform

Solar fuel: 3-4 fotonen per elektron

1.1 V band gap



~0.5 V

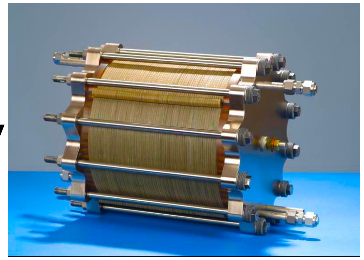
~0.5 V

~0.5 V

~0.5 V

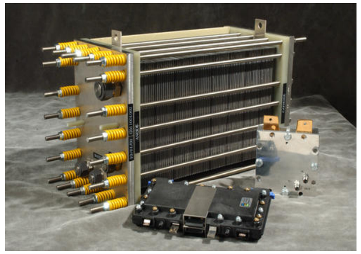
1.23 V ionisatie potentiaal

1.6-1.7 V



electrolyzer

H_2

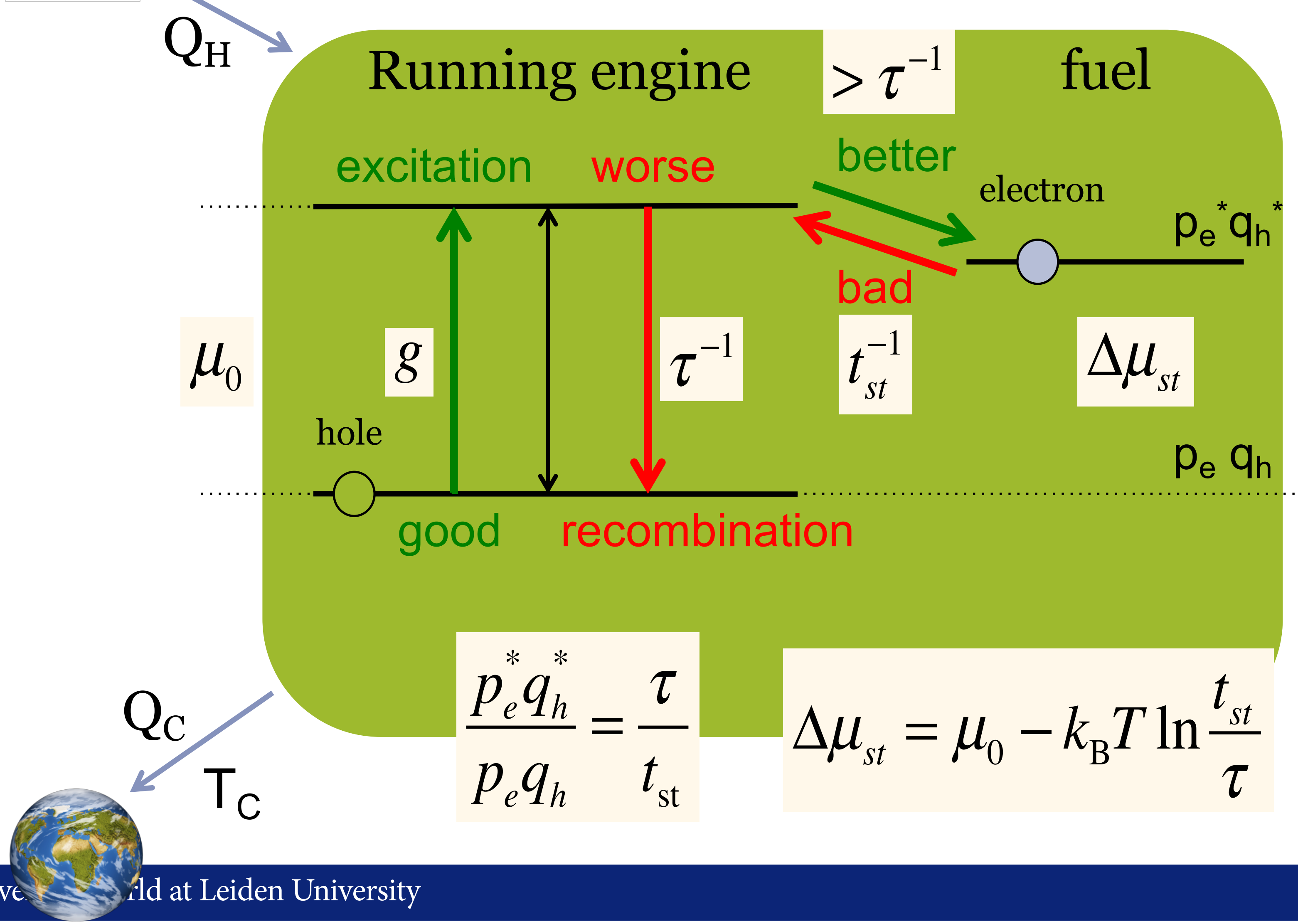


brandstofcel

0.9 V

$$\Delta\mu_{st}(t) = h\nu_0 - k_B T \ln(t/\tau)$$

Adiabatic: Detailed Balance



$$\frac{p_e^* q_h^*}{p_e q_h} = \frac{\tau}{t_{st}}$$

$$\Delta\mu_{st} = \mu_0 - k_B T \ln \frac{t_{st}}{\tau}$$

Overpotential budget

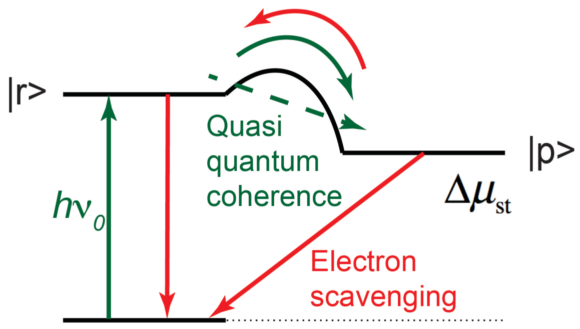
- Open voltage tandem 2.8V
- Thermoneutral potential 1.23+0.25=1.48
- Back reaction: 0.5V
- Overpotential: 0.4V (H_2O) +0.2V (H_2)
- Proton resistance: 0.2V
- Compression: 0.2V
- Triple play: use one potential loss (0.34 V) for
  - Thermoneutral (0.25 V),
  - Overpotential (0.4V)
  - back reaction (0.5V)

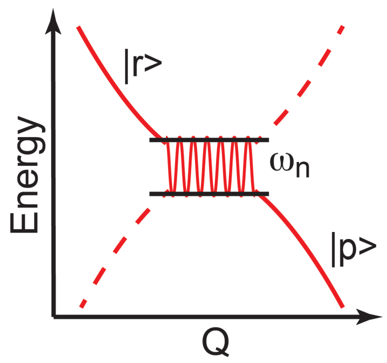
Non-adiabatic conversion for high yield

Time-dependent Schrödinger equation

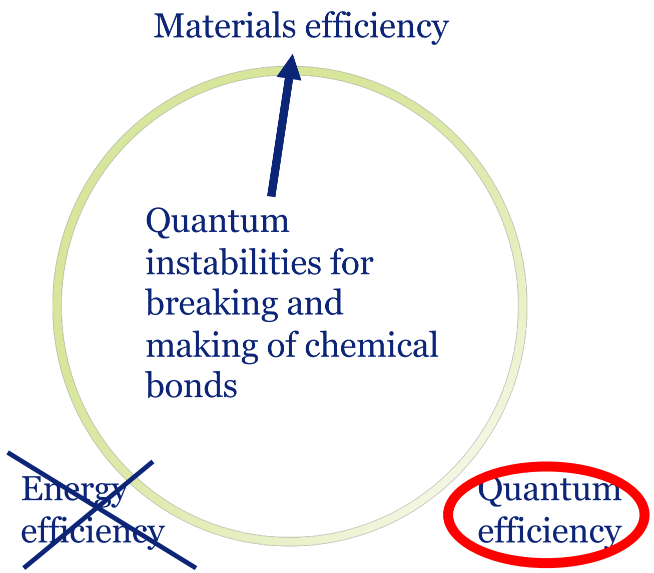
$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

- n adiabatic elements
- n^2-n nonadiabatic (off-diagonal) elements



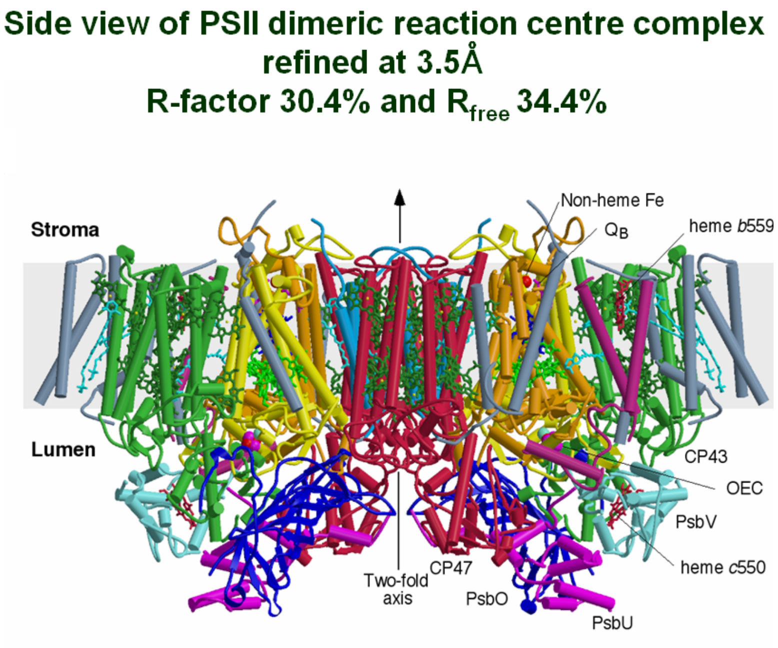


- Two photons per electron and 70% external chemical yield
- 90% absorption of photons
- 80% internal chemical yield



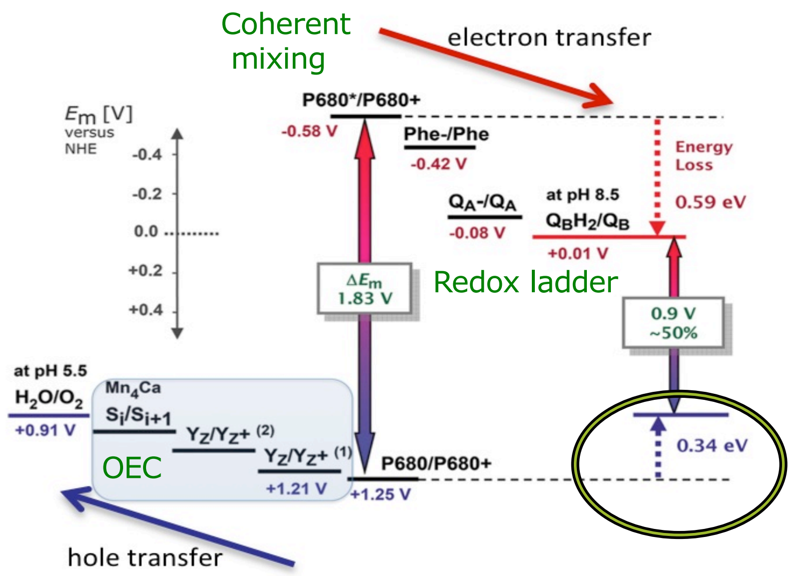
Photosystem II water oxidation

Responsive matrix



Barber et al.

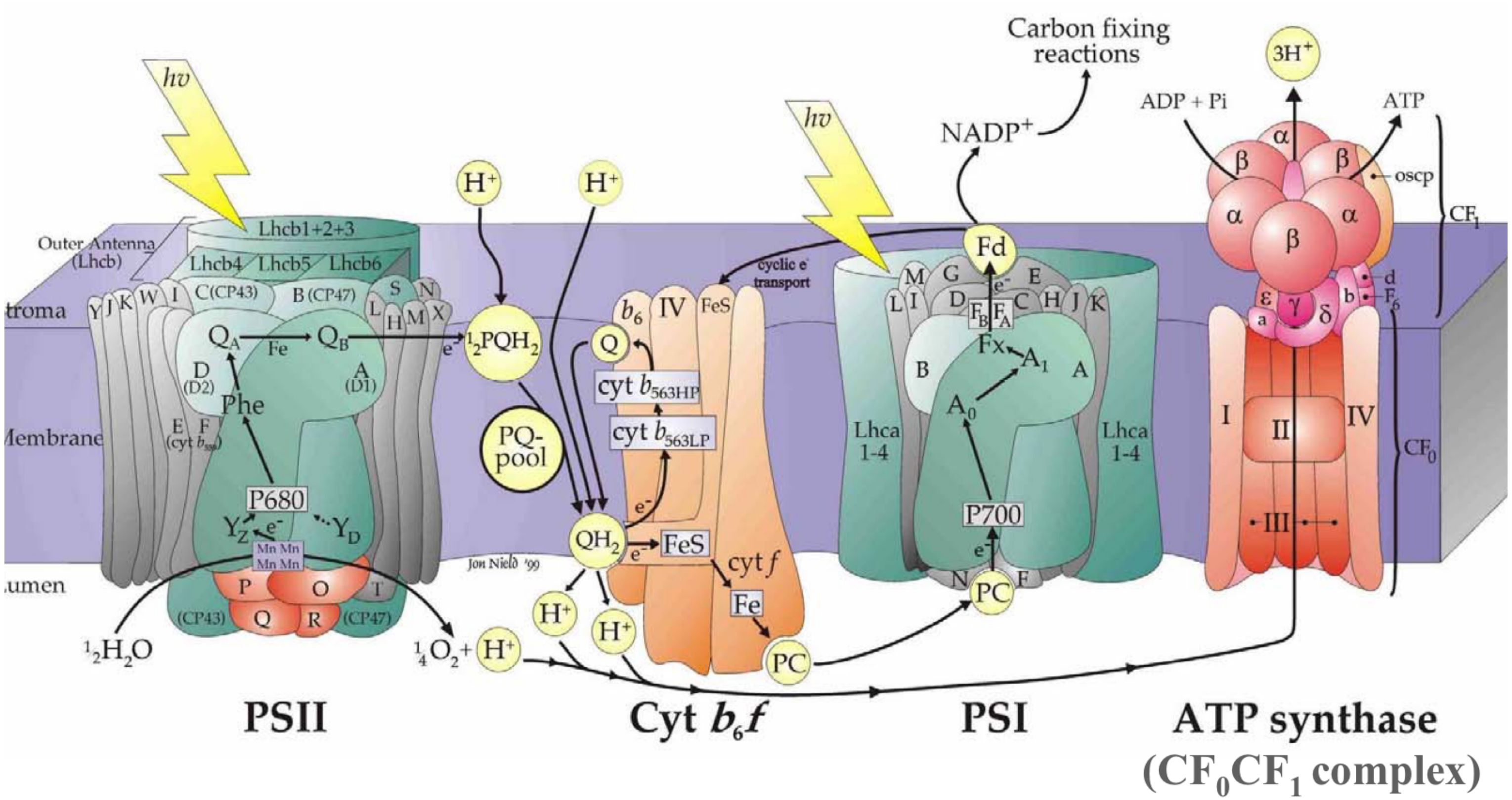
Photoanode (pH 5.5)



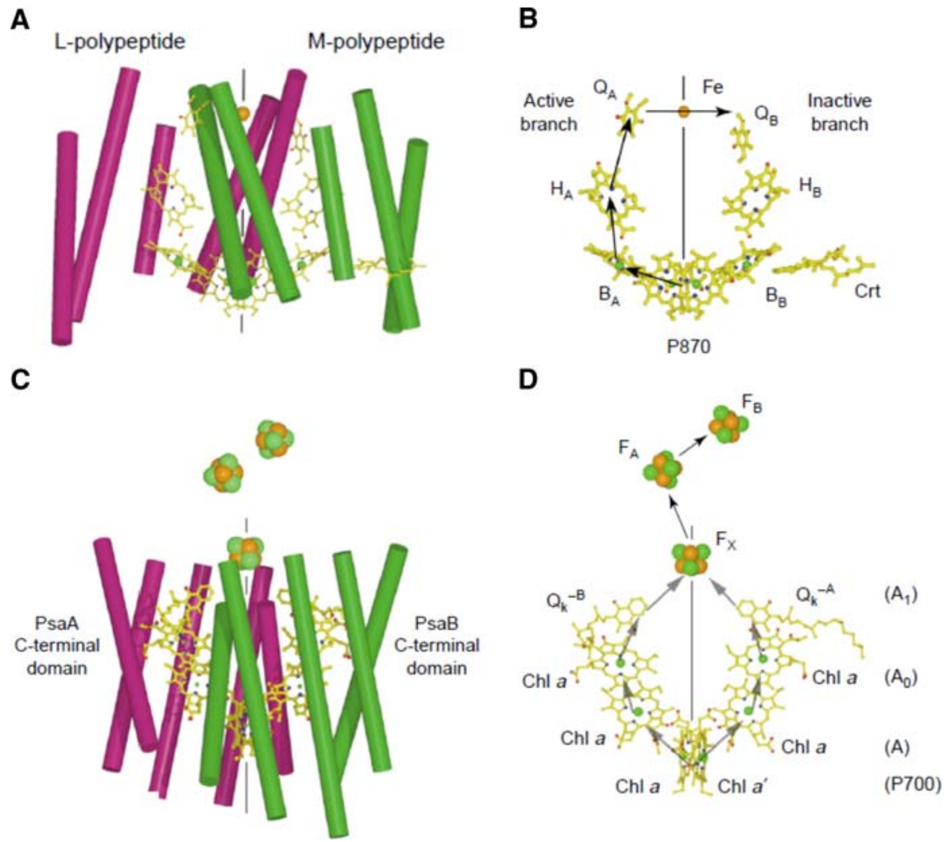
Overpotential

Dau et al.

Photosynthetic membrane

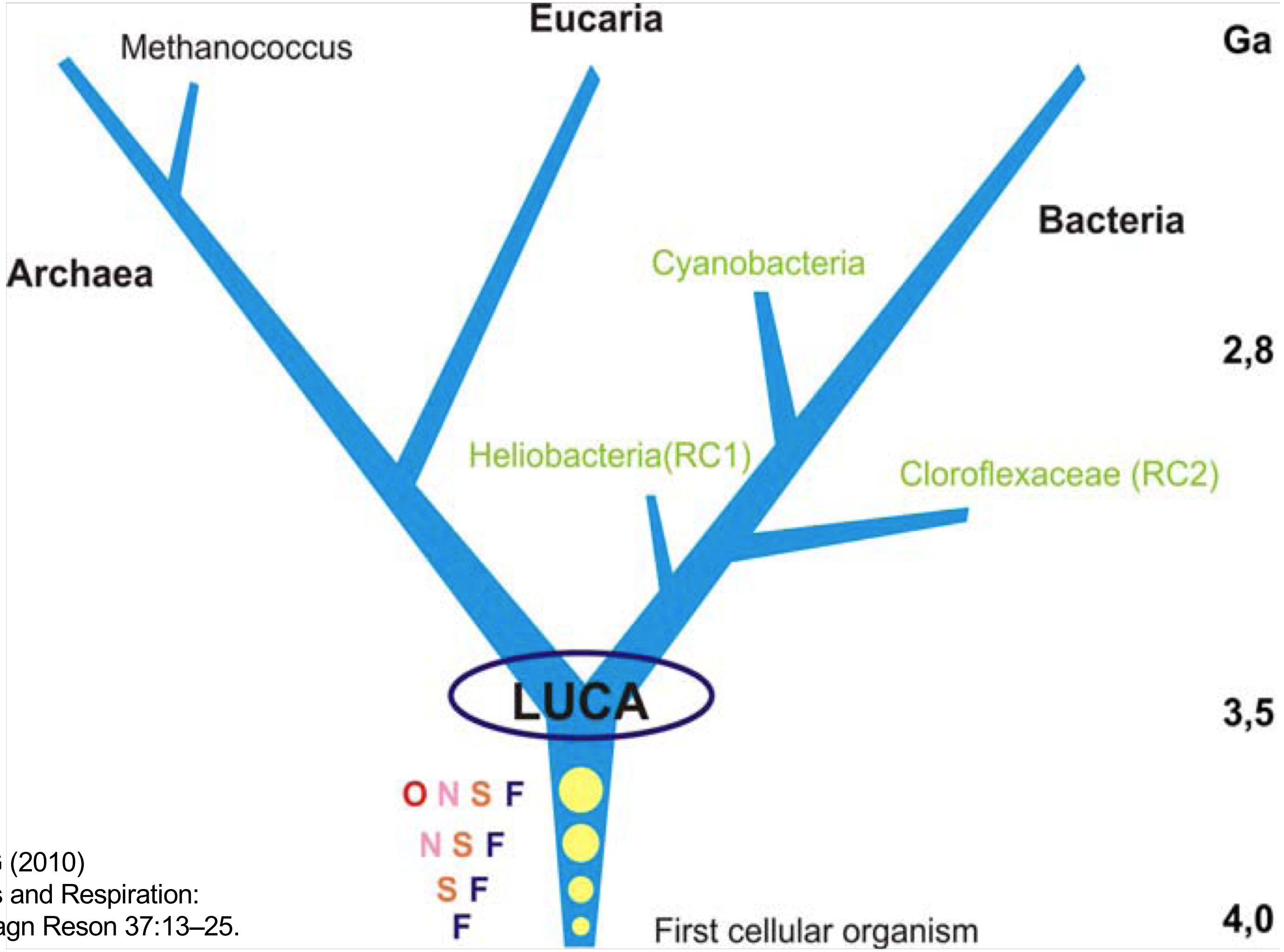


Photosynthesis: Complicated with little true complexity



Suggests commonality in enzyme mechanisms as well

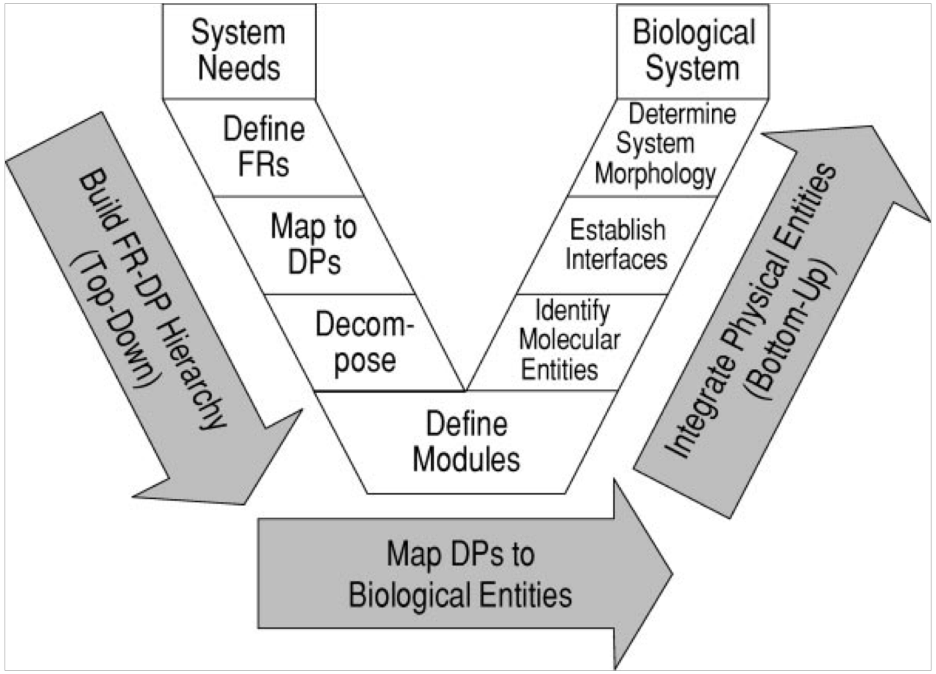
Evolution of Photosynthesis



Giacometti G, Giacometti G (2010)
Evolution of Photosynthesis and Respiration:
Which Came First? Appl Magn Reson 37:13–25.

Life Science Evolution: engineering complexity without redundancy

Function based framework



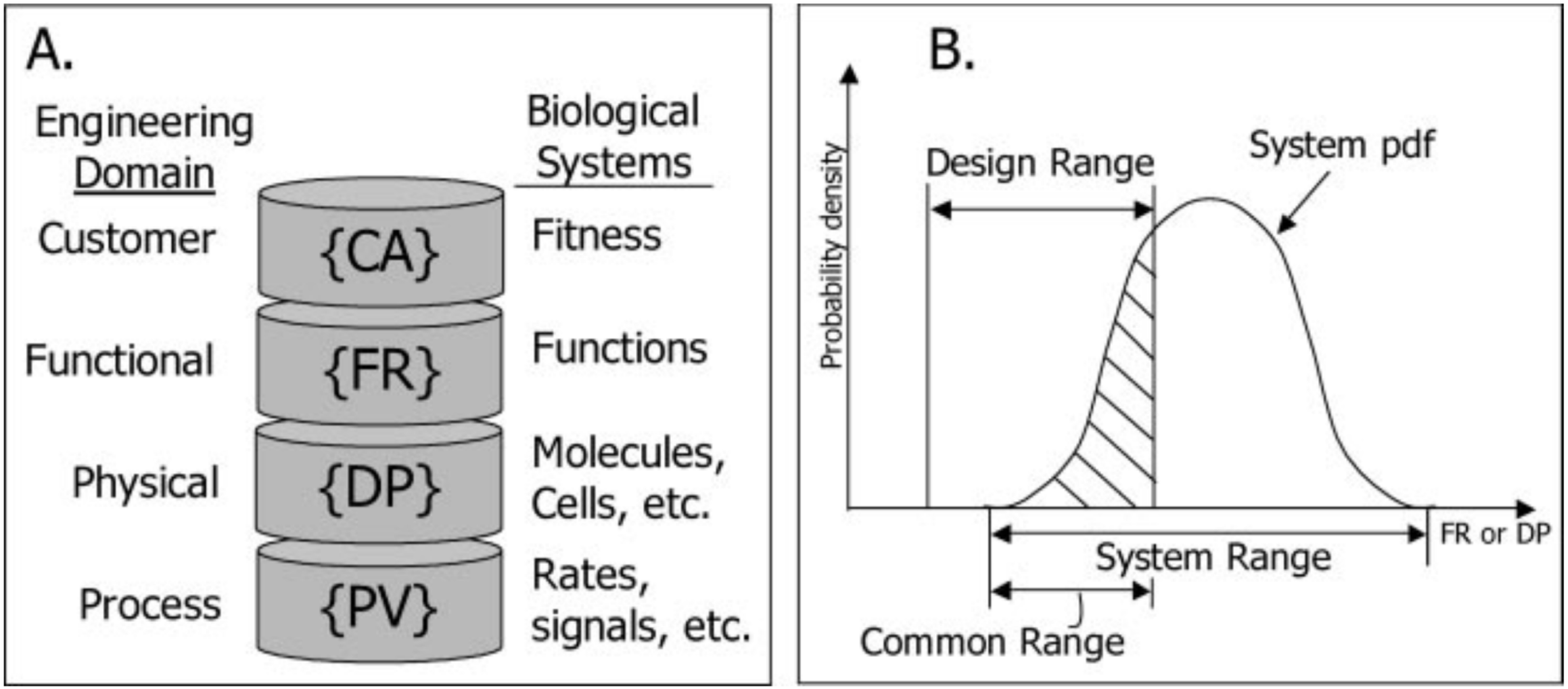
System robustness

- Independence Axiom
  - Maintain the independence of the functional requirements
- Information axiom
  - Minimize the information content of the design.

Allows for adaptation while withstanding environmental fluctuations

Thomas, J. D., Lee, T., & Suh, N. P. (2004). Annual Review of Biophysics and Biomolecular Structure, 33, 75–93.

Design domains and ranges



Responsive matrices

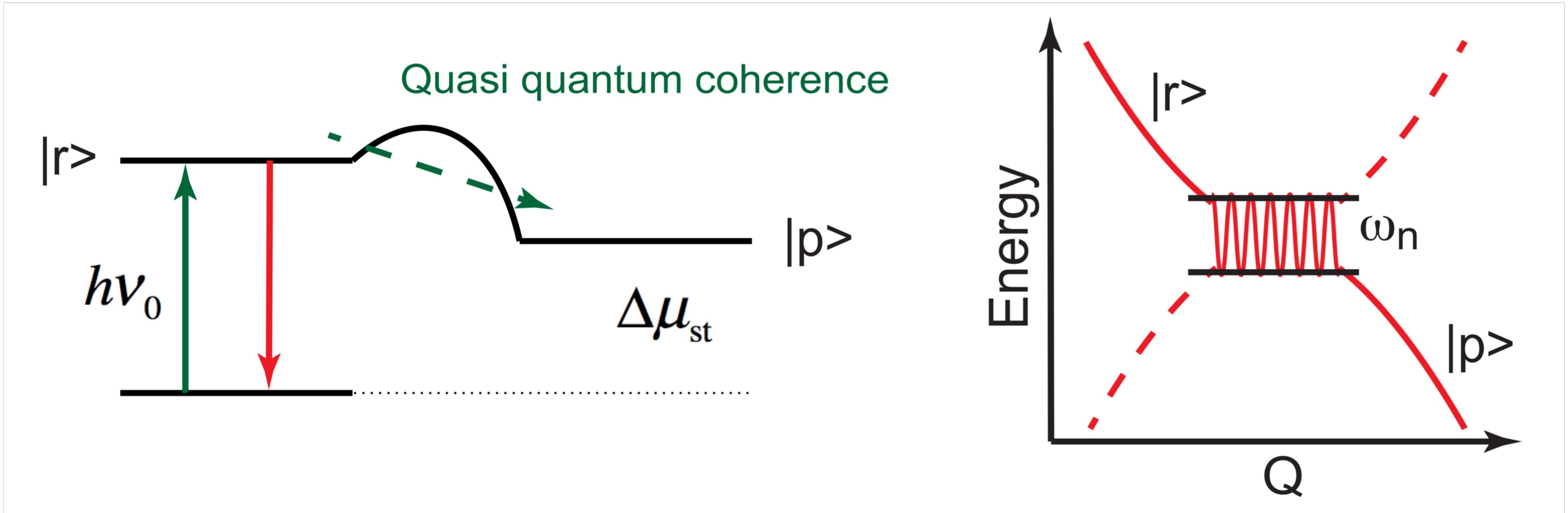
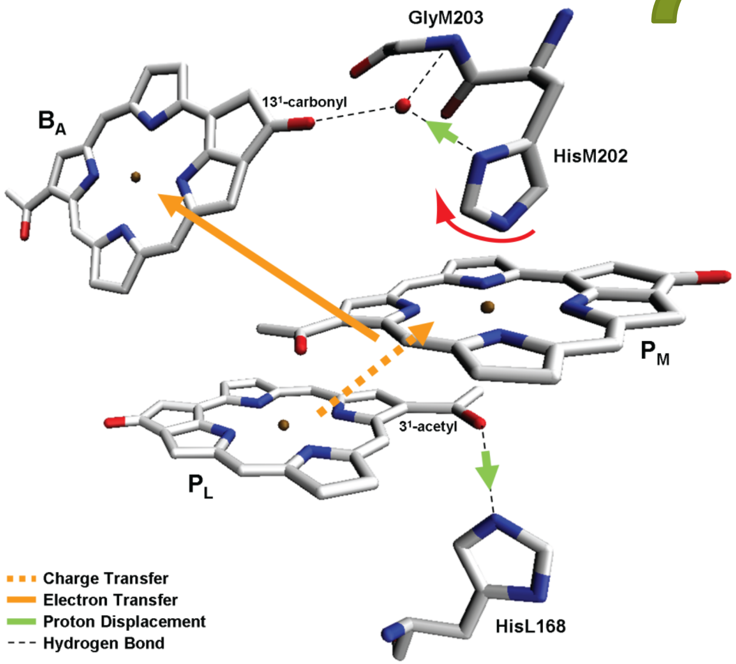
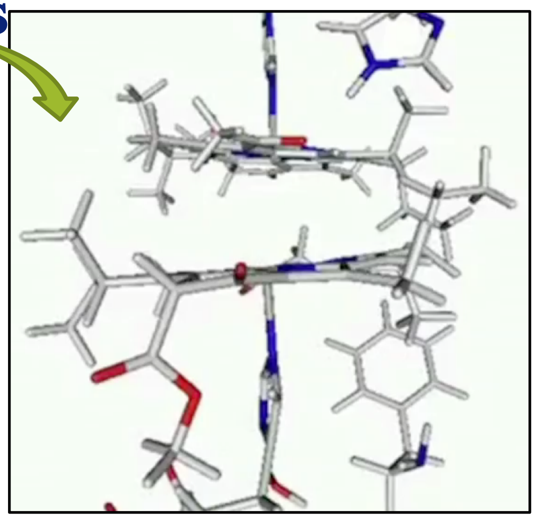
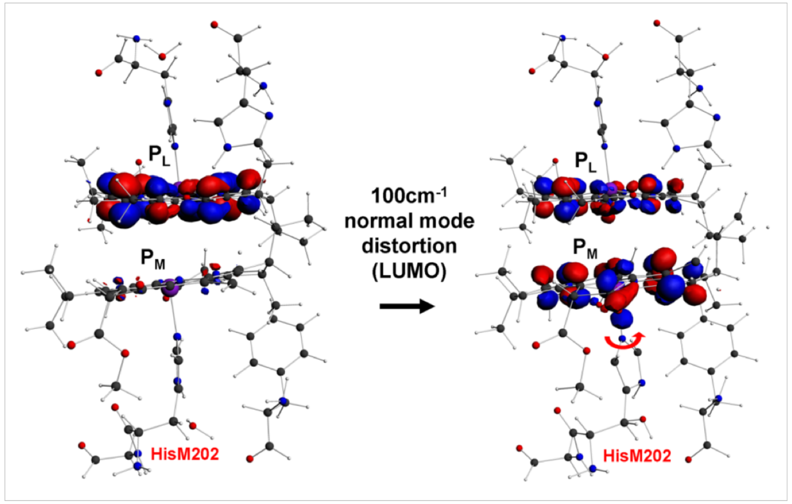


Photo-induced electron transfer and vibronic coupling in responsive matrices





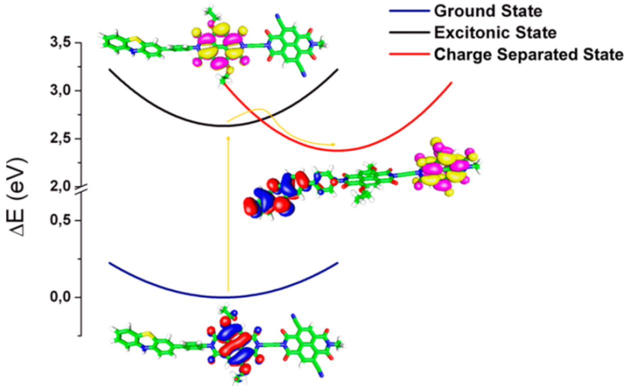


T. Eisenmayer, et al. (2013) J. Phys. Chem. B

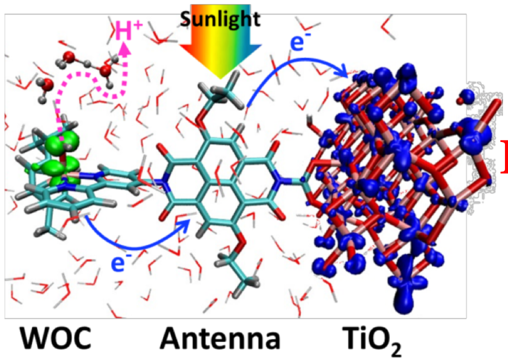
Highlights quantum chemical modelling (F. Buda)

•DFT, *ab initio* Molecular Dynamic simulations are used to elucidate structure and functional mechanisms:

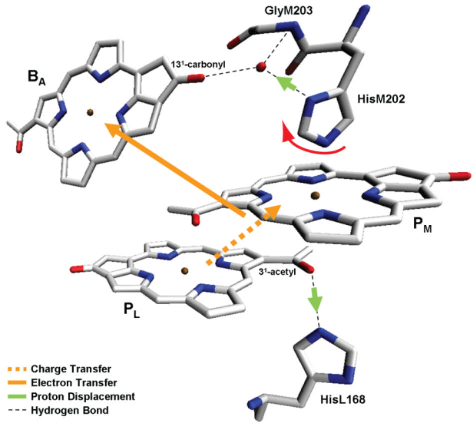
• *In silico* design of donor-antenna-acceptor complexes for photo-induced charge transfer



• Photo-catalytic water oxidation

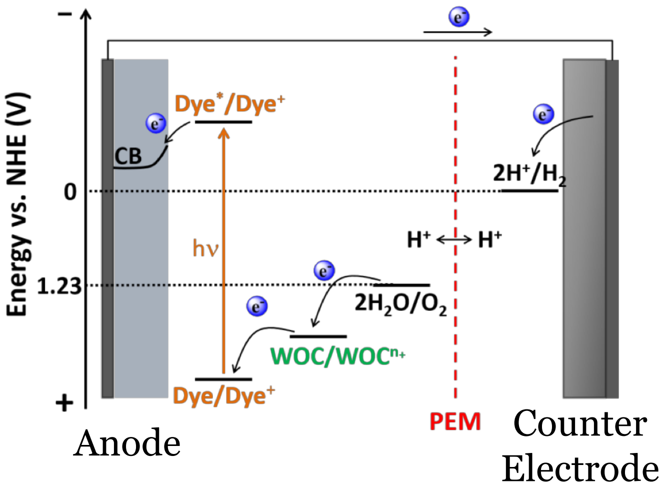


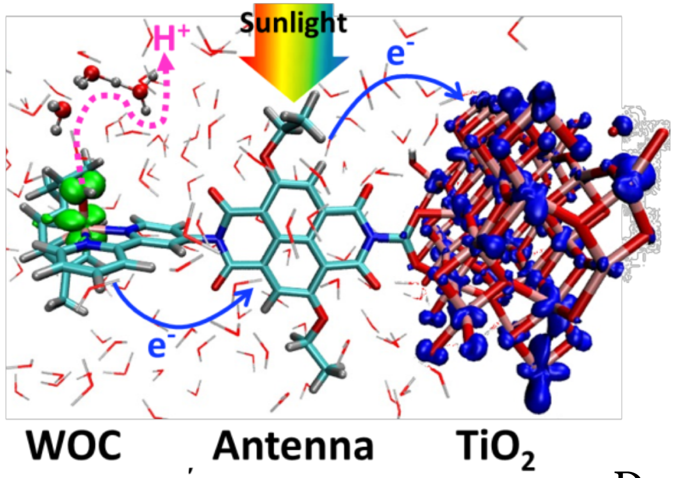
• Photo-induced charge transfer in Bacterial Reaction Center

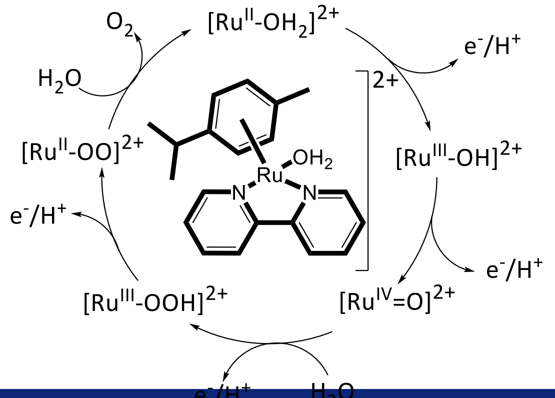


TOWARDS ARTIFICIAL PHOTOSYNTHETIS DEVICES

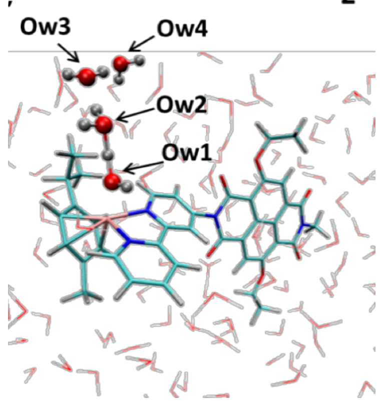
- Dye-sensitized Photoelectrochemical Solar Cell







Ru-WOC



Dynamic view of electron injection and PCET processes

J. de Ruiter et al. *ACS Catal.* 2016, 6, 7340; A. Monti et al. *JPCC* 2016, 120, 23074

Liouville-von Neumann equation of motion

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

$$\rho(t) = e^{-iHt}\rho(0)e^{iHt}$$

$$H = H_0 + H_1 = \hbar\omega_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - 2\hbar R_0 d_{12}^1 \omega_n \sin(\omega_n t) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (molecular\ frame)$$

$$H_{int} = R_z(-\omega_n t) H_1 R_z(\omega_n t) = -\hbar R_0 d_{12} \omega_n e^{i\omega_n t \boldsymbol{\sigma}_z} \left(e^{-i\omega_n t \boldsymbol{\sigma}_z} \boldsymbol{\sigma}_y e^{i\omega_n t \boldsymbol{\sigma}_z}\right) e^{-i\omega_n t \boldsymbol{\sigma}_z}$$
$$= -\hbar R_0 d_{12} \omega_n \boldsymbol{\sigma}_y \quad (interaction\ frame)$$

$$\rho(t) = \boldsymbol{\sigma}_z \cos(R_0 d_{12} \omega_n t) + \boldsymbol{\sigma}_x \sin(R_0 d_{12} \omega_n t)$$

Coherent transfer between states |r> and |p>

Time-independent Hamiltonian: $H_{int} = -\hbar R_0 d_{12} \omega_n \sigma_y$

Coupled differential equations:

$$i\frac{\partial \tilde{\chi}_1}{\partial t} = \frac{1}{2}\hbar R_0 d_{12} \omega_n \tilde{\chi}_2$$
$$i\frac{\partial \tilde{\chi}_2}{\partial t} = \frac{1}{2}\hbar R_0 d_{12} \omega_n \tilde{\chi}_1$$

Solution:

$$\tilde{\chi}_1(t) = \tilde{\chi}_1(0)\left(\cos\left(\frac{1}{2}R_0 d_{12}\omega_n t\right) + i\tilde{\chi}_2(0)\sin\left(\frac{1}{2}R_0 d_{12}\omega_n t\right)\right)$$
$$\tilde{\chi}_2(t) = \tilde{\chi}_2(0)\left(\cos\left(\frac{1}{2}R_0 d_{12}\omega_n t\right) + i\tilde{\chi}_1(0)\sin\left(\frac{1}{2}R_0 d_{12}\omega_n t\right)\right)$$

t=0, state |r>: $\tilde{\chi}_1(t) = 1\ ,\ \tilde{\chi}_2(0) = 0$

$t = \pi/(R_0 d_{12}\omega_n)$, state |p> $\tilde{\chi}_1(t) = 0\ ,\ \tilde{\chi}_2(0) = 1$

100% conversion through superposition wave function $\tilde{\Psi}(t) = \tilde{\chi}_1(t)|r\rangle + \tilde{\chi}_2(t)|p\rangle$