Einführung in die Photochemie und Umweltphotochemie

Gion Calzaferri, Barbara Sulzberger
und Antonio Currao

Dr. Johann Heinrich Schulze
geboren 1687, gestorben 1744

GESCHICHTE DER PHOTOGRAPHIE IN BILDERN
TAFEL 1

Dr. Johann Heinrich Schulze
(geboren 1687 in Colbitz im Magdeburgischen, gestorben 1744 in Halle a. S.)

Professor der griechischen und arabischen Sprache zu Altorf, später zu Halle a. S., entdeckte in Altorf im Jahre 1727 die Lichtempfindlichkeit der Silbersalze gelegentlich eines Versuches der Herstellung von Leuchtsteinen; er füllte Fläschen mit einem Brei von Kreide und gelöstem Silbernitrat und kopierte Schriftzüge durch aufgelegte Schablonen. In dieser unvollkommenen Form stellte er die ersten Photographien her und ist demzufolge als Entdecker des ältesten Verfahrens der Photographie zu bezeichnen

Verleger:
Nettel Camerawerk G. m. b. H. Sontheim a. Neckar
Neue Photographische Gesellschaft Aktiengesellschaft Berlin-Steglitz

SCHULZE, Johann Heinrich

b. 1684; d.1744

Schulze was a German Professor at the University of Altdorf, whose experiments paved the way towards photography. Though it was known that certain chemicals darken when exposed to the sun, it was not clear whether it was the action of light or heat which had this effect. In 1727 Schulze heated some silver nitrate in an oven, and discovering that it did not darken was able to eliminate heat as the darkening agent. Having noticed that a glass jar containing a particular chemical mixture changed colour on one side - that facing the window, he applied paper stencils to a bottle containing silver nitrate and chalk, discovering that where the substance was not exposed to light it remained white. He published details of his investigations, but these did not become popular until after he had died. He described his experiments thus:

I covered the glass with dark material, exposing a little part for the free entry of light. Thus I often wrote names and whole sentences on paper and carefully cut away the inked parts with a sharp knife. I struck the paper thus perforated on the glass wikth wax. It was not long before the sun's rays, where they hit the glass through the cut-out parts of the paper, wrote each word or sentence on the chalk precipitate so exactly and distinctly that many who were curious about the experiment but ignorant of its nature took occasion to attribute the thing to some sort of trick."

1. Womit beschäftigt sich die Photochemie
2. Photonen: Begriffe, Einheiten
3. Photochemische Primärprozesse und Quantenausbeuten
4. Elektronisch angeregte Zustände: Absorption und Emission von Licht
5. Photochemische Reaktionen in Lösungen
6. Umweltphotochemie
7. Photochemische Reaktionen an Phasengrenzflächen
8. Energieübertragung

1. Womit beschäftigt sich die Photochemie

1.1 Der Sehprozess

1.2 Photosynthese der grünen Pflanzen

1.3 Die Ozonschicht

1.4 Einige technische Anwendungen photochemischer Reaktionen

1.5 Nanomaschinen

In der Photochemie werden die chemischen Eigenschaften von Verbindungen, Materialien und Systemen jeglicher Art in elektronisch angeregten Zuständen untersucht.

Grothuss (1817) und Draper (1841):
Nur das von einem System absorbierte Licht kann eine chemische Reaktion auslösen
Erstes Photochemisches Gesetz

Stark (1908) und Einstein (1912-1913):
Pro Molekül, das einen photophysikalischen Primärprozess eingeht, wird ein Lichtquant absorbiert.
Zweites Photochemisches Gesetz

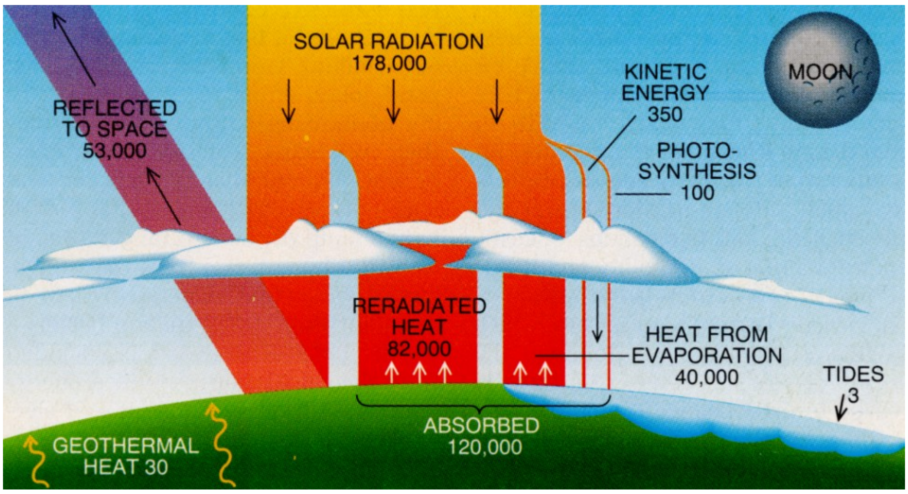
Wechselwirkung Licht mit Materie

Reflexion	Absorption	Streuung

Sichtbares und nahes UV Licht, das absorbiert worden ist,
wird in Form von Bewegungsenergie der Elektronen gespeichert

KINETISCHE ENERGIE DER ELEKTRONEN

In Wärme umwandeln	Als Lichtquanten aussenden	Elektron-Loch Paar erzeugen	Reagens für stoffliche Veränderungen
Ungeordnete Bewegung der Kerne	Lumineszenz	Photoströme	Photochemische Reaktion
Thermochemie		Optoelektronik	Photochemie

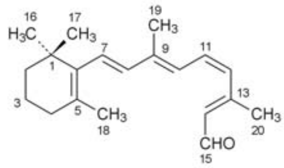


Die auf die Erde auftreffende Sonneneinstrahlung entspricht einer Leistung von 178‘000 TW. Davon werden 30 % sofort in den Weltraum reflektiert. Etwa 50 % werden absorbiert, 20 % erzeugen den Wind und treiben den Wasserkreislauf an. Ca. 1/1780igstel wird in der Photosynthese der grünen Pflanzen umgesetzt.
Aus Scientific American Sept. 1990, S. 24

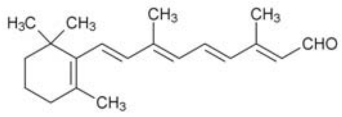
1.1 Der Sehprozess

Der Sehprozeß wird in der Netzhaut (Retina) durch eine photochememische cis-trans Isomerisierung (im Rhodopsin) initiiert.

Im Rhodopsin wandelt sich die Schiffsche Base des 11-cis Retinal in das all-trans Gegenstück um.



11-*cis*-Retinal



all-trans-Retinal, Retinal

Rhodopsin
= Opsin (Proteinanteil) + 11-cis-Retinal

hν ↓ ↑ Δ, in mehreren Schritten

Über mehrere Intermediate werden all-trans Retinal und Opsin freigesetzt.

Alle Stämme, die sehen können – Wirbeltiere, Gliedertiere, Weichtiere – verwenden 11-cis-Retinal als Sehchromophor.

Die Netzhaut enthält die Photorezeptoren: Stäbchen und Zapfen

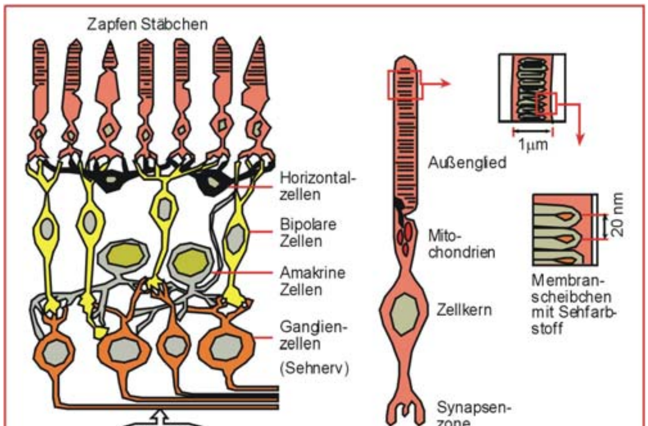


Bild aus Römp.

Transduktionsprozess
= Umwandlung von Lichtreizen zu elektrischen Signalen

wird über die Sehfarbstoffe, die in den Zapfen und Stäbchen vorhanden sind, vermittelt

Stäbchen:	schwarz-weiss Sehen
3 Sorten Zapfen:	Farberkennung (11-cis Retinal mit verschiedenen Protein-Anteilen)

Photorezeptoren - Photonen-Zähler - einzelne Lichtquanten

Transduktionsprozess in den Stäbchen

In scheibchenförmigen Einfaltungen der Zellmembran der Stäbchen befindet sich das **Rhodopsin** (besteht aus Opsin (Protein) und 11-cis-Retinal).

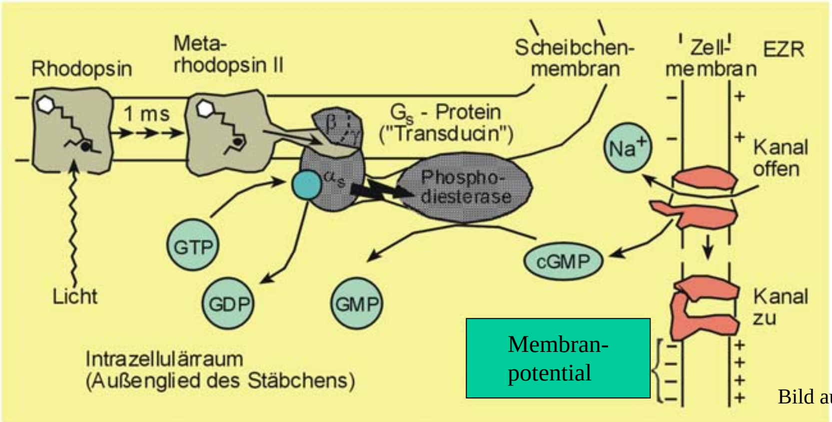
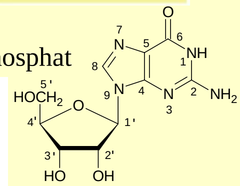


Bild aus Römp

cGMP entsteht durch Ausbildung einer Phosphodiester-Brücke zwischen der 3'- u. 5'-Hydroxy-Gruppe des Guanosins

GMP = Guanosinmonophosphat



Aktivierung eines Rhodopsin kann zur Hydrolyse von Bis zu 106 cGMP führen

1.2 Photosynthesis of green plants

Water

The antenna system

The Z-scheme

Photosynthesis of green plants

Molecular oxygen is a prerequisite of animal and therefore also human life on earth.

Only primitive organisms have survived over hundreds of millions of years without oxygen. Oxygen was even toxic for these early anaerobic creatures because it is able to oxidize other molecules.

Why and how did green plants start to produce oxygen in the photosynthesis process, despite of the fact that it is toxic?

From Bild der Wissenschaft, April 1990, p. 92.

The why has to do with the energy household of the plants.

Any life on earth is in the end powered by solar energy.

Cells can, however, not use or store this energy directly; they must first transform it into chemical energy.

Redox reactions, which means displacement of electrons, play an important role in this chemical energy transformation process.

Hence, cells need a source of electrons for living.
All green plants use the same source for electrons, namely

Water

as reducing agent!

Water

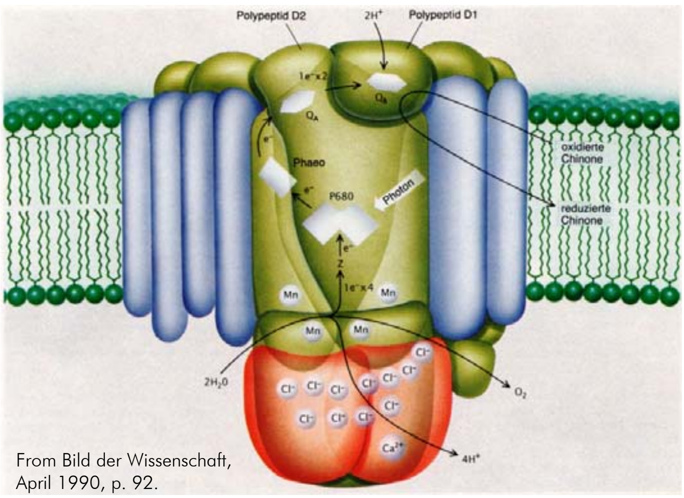
Some photosynthetically active cells have learned to withdraw electrons from water about three billion years ago.

They developed the ability, to decompose two molecules of water into four electrons, four protons and one molecule of oxygen.

The electrons and protons were used for the energy household of the cells.

The oxygen was a by-product, which, however, was essential to make highly organized living creatures possible.

The oxygen production in the cells is not yet fully understood. We know, however, that it takes exclusively place in the photosystem II.
The primary reactions take place inside of the thylakoid mebrane (T-M).
The essential function of the PS II is to separate + and – charges.
The electron transfer takes place in the RC: D1, D2, Cytochrome.
The RC is supplied with electronic excitation energy by means of the *antenna system.*

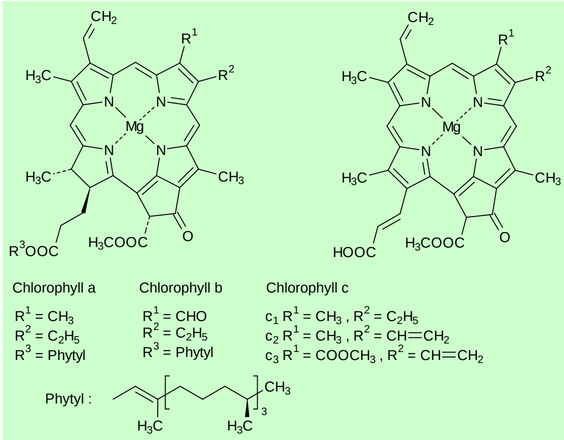


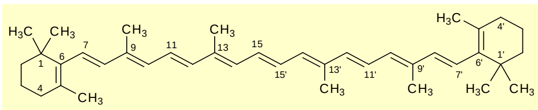
From Bild der Wissenschaft, April 1990, p. 92.

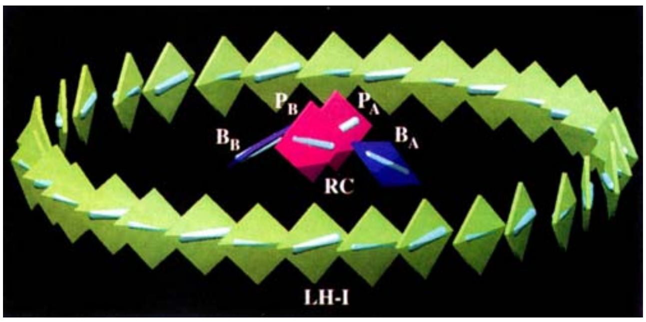
Photosystem II

The Antenna System

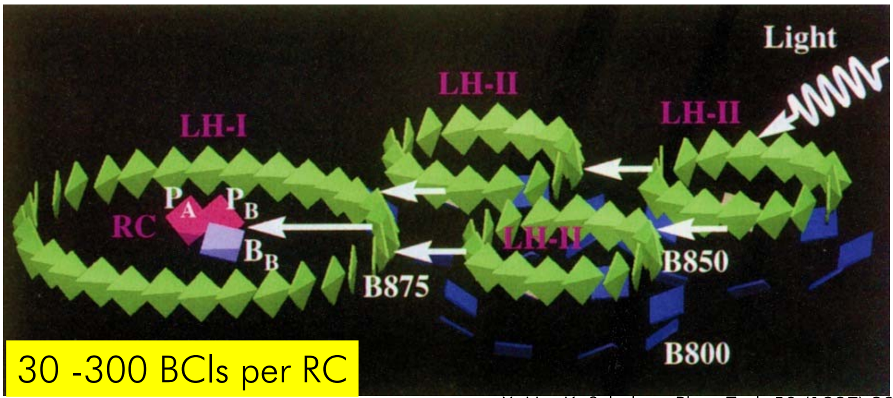
The antenna system is essentially composed of chlorophyll molecules, carotenoids, and of the proteins which build the framework.







X. Hu, K. Schulten, Phys. Tod. 50 (1997) 28

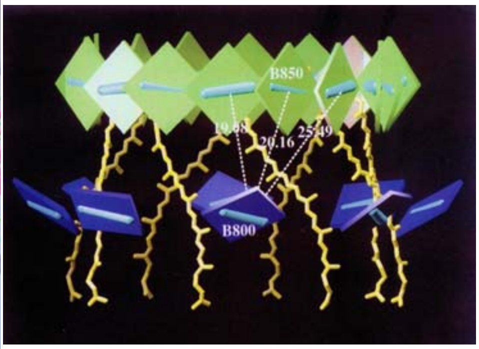


X. Hu, K. Schulten, Phys. Tod. 50 (1997) 28

RC = reaction centre
PA,PB = special pair

B800
B850
B875

These numbers are the absorption edges in nm.

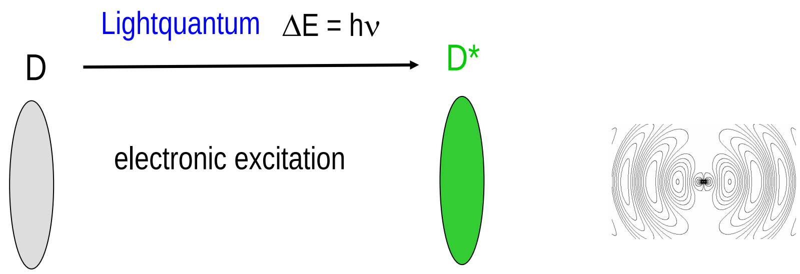


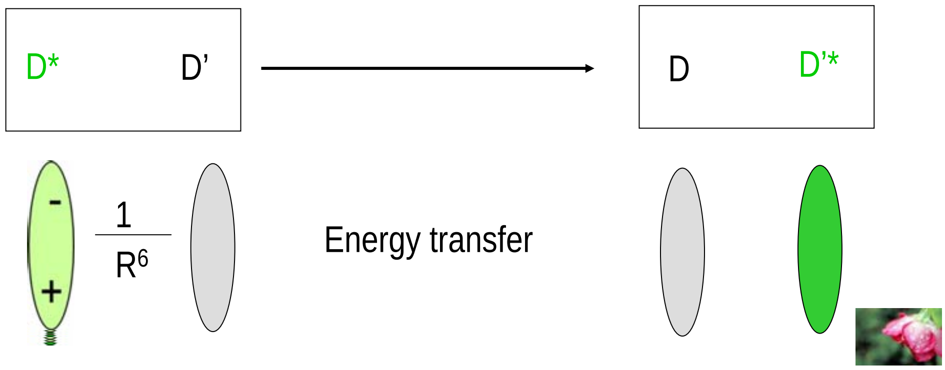
LH-II

Blue: a-helices formed by 56 amino acids

Purple: a-Helices formed by 45 amino acids

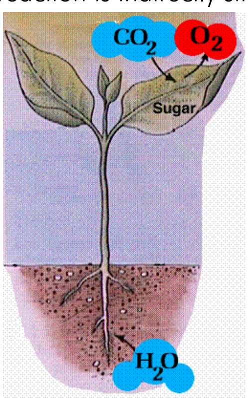
X. Hu, K. Schulten
Phys. Tod. 50 (1997) 28

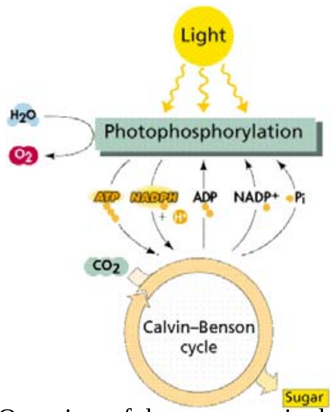




The Z-scheme

Photosynthesis is a two stage process. The first process requires the direct energy of light to make energy carrier molecules that are used in the second process. The dark reaction occurs when the products of the light reaction are used to form C-C covalent bonds of carbohydrates. It can usually occur in the dark, if the energy carriers from the light process are present. Recent evidence suggests that a major enzyme of the dark reaction is indirectly stimulated by light, thus this term is somewhat of a misnomer.





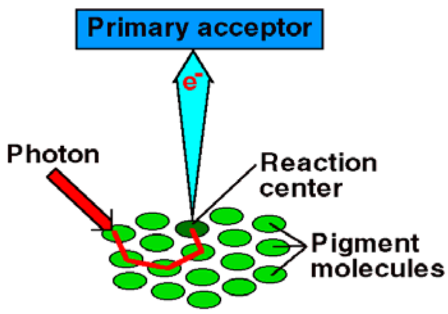
$$6H_2O + 6CO_2 \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2$$

Overview of the two steps in the photosynthesis process. Image from Purves et al., Life: The Science of Biology, 4th Edition, by Sinauer Associates.

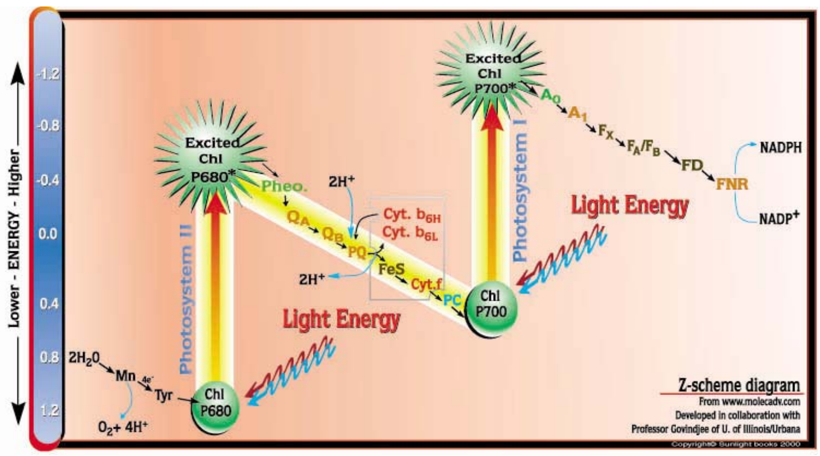
In the Light Reactions light strikes chlorophyll a in such a way as to excite electrons to a higher energy state. In a series of reactions the energy is converted (along an electron transport process) into ATP and NADPH. Water is split in the process, releasing O_2 as a by-product of the reaction. The ATP and NADPH are used to make C-C bonds in the Dark Reactions. In these Reactions, CO_2 is captured and modified by the addition of hydrogen to form carbohydrates ($[CH_2O]_n$). The incorporation of CO_2 into organic compounds is known as carbon fixation. The energy for this comes from the first phase of the photosynthetic process.

Photosystems are arrangements of chlorophyll and other pigments packed into thylakoids. Many prokaryotes have only one photosystem, Photosystem II (so numbered because, while it was most likely the first to evolve, it was the second one discovered).

Eukaryotes have Photosystem II plus Photosystem I. Photosystem I uses chlorophyll a, in the form referred to as P700. Photosystem II uses a form of chlorophyll a known as P680.



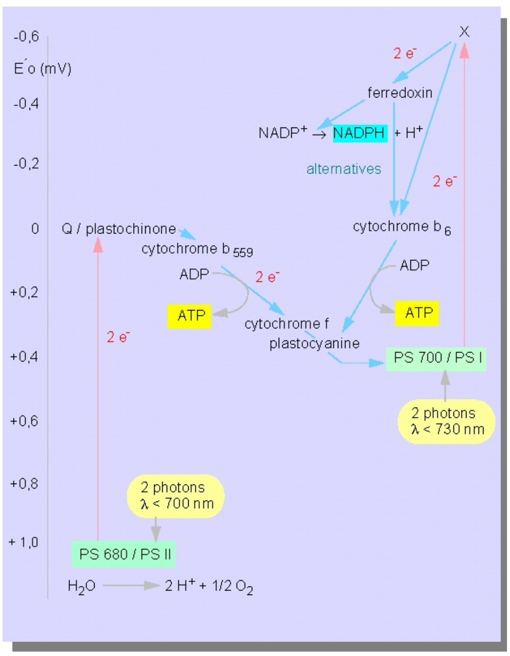
Action of a photosystem



Picture from Govindjee and Rajni Govindjee University of Illinois at Urbana-Champaign.

The Z-scheme is an energy diagram for electron transfer in the light reactions of plant photosynthesis. It applies equally well to photosynthesis by algae and cyanobacteria. It is called Z-Scheme because the diagram, when first drawn, was in the form of the letter "Z". The vertical energy scale shows each molecule's ability to transfer an electron to the next one from left to right. The ones at the top transfer electrons easily to the ones below them as it is a "downhill" reaction, energy-wise. However, for electron transfer from those at the bottom to those above them it is an "uphill" reaction and requires input of outside energy. The Z scheme shows the pathway of electron transfer from water to $NADP^+$.

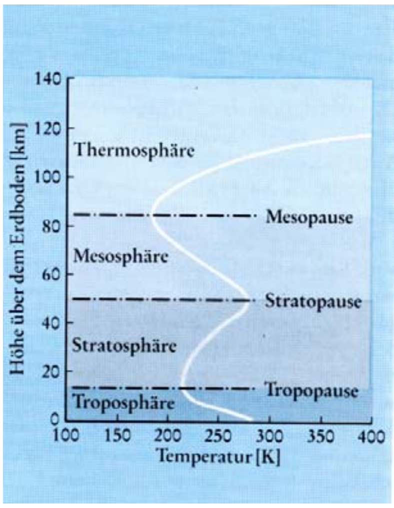
Mn is the manganese center, a complex containing 4 manganese atoms. Tyr is a special tyrosine molecule, which shuttles electrons to the "reaction center" of PSII. Chl P680 is the reaction center pair of chlorophyll *a* molecules of PSII. Excited Chl P680* has reached this state by absorbing a photon of light energy. Pheo is a pheophytin molecule, which is a chlorophyll with its central Mg^{2+} ion having been replaced by two H^+. It is the primary electron acceptor of PSII, whereas P680 is the primary electron donor. Q_A is a plastoquinone molecule, which is the primary stable electron acceptor of PSII, and it accepts and transfers one electron at a time. Q_B is a loosely bound plastoquinone molecule. It accepts 2 electrons and then takes on 2 protons, before it detaches and becomes mobile and called PQ. PQ is the detached plastoquinone. It is mobile within the hydrophobic core of the thylakoid membrane. FeS is the Rieske iron-sulfur protein. Cyt β_{6L} and Cyt β_{6H} are 2 cytochrome β_6 molecules (of lower and higher energy). PC is plastocyanin, a highly mobile copper protein. Chl P700 and excited Chl P700* are respectively the ground energy state and the excited energy state of the chlorophyll molecule of the "reaction center" of PSI. AO is a special chlorophyll *a* molecule that is the primary electron acceptor of PSI, whereas P700 is the primary electron donor of PSI. A_1 is a phylloquinone (vitamin K) molecule. F_X, F_A, and F_B are three separate immobile iron-sulfur protein centers. FD is ferredoxin, a somewhat mobile iron-sulfur protein. FNR is the enzyme ferredoxin-NADP oxidoreductase, which contains the active group, called FAD (flavin adenine dinucleotide). $NADP^+$ is the oxidized form of nicotinamide adenine dinucleotide phosphate. NADPH is its reduced form.

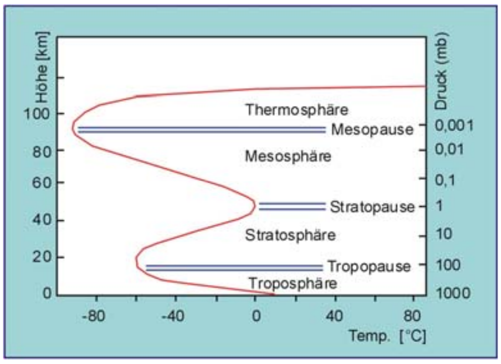


Another way to draw the Z-scheme.

1.3 Die Ozonschicht

Die Chemie der Atmosphäre, bei der vielfältige photochemische Reaktionen eine wichtige Rolle spielen, hat sich zu einem grossen, selbständigen Forschungszweig entwickelt.





Barometrische Höhenformel:

$p = p_0 exp[-Mgh/RT]$

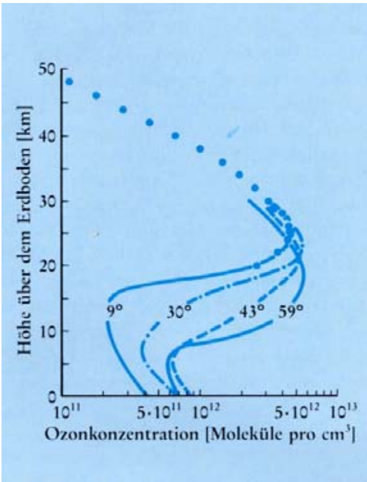
1.3.03

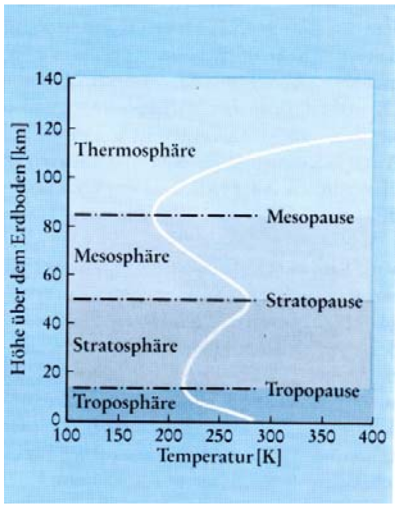
	Vol.-Konz	Verteilung	Hauptquelle	[10^6 Tonnen/a]
Methan CH_4	1,7 ppm steigend	gleichmäßig	Reisanbau, Haustiere Feuchtgebiete, Sümpfe Verbrennung von Biomasse weitere anthropogene Quellen	75 100 60 90 50
Wasserstoff H_2	0,6 ppm	gleichmäßig	Oxid. von Methan Oxid. von natürlichen Kohlen-wasserstoffen (HC) Verbrennung von Biomasse anthropogen	30 20 15 17
Kohlen-monoxid CO	0,1 ppm		anthropogen Verbrennung von Biomasse Oxid. von Methan Oxid. von natürlichen HC	640 1000 600 900
Ozon O_3	15–50 ppb	niedrig am Äquator, zu den Polen hin ansteigend	von der Stratosphäre Photochemie	600 1300
Distickstoff-monoxid N_2O	0,3 ppm, steigend	gleichmäßig	Emission vom Erdreich Emission von Ozeanen anthropogen	10 25 2

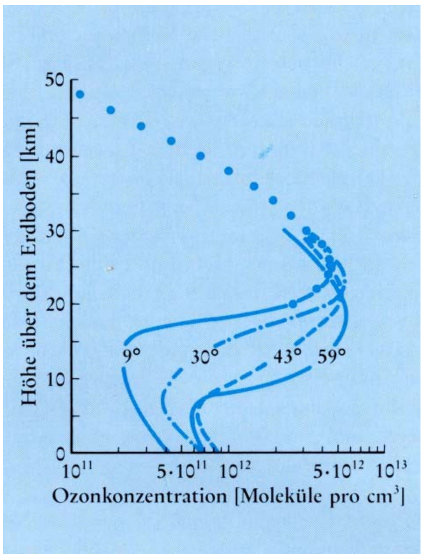
Stickoxide NO_2+NO	30 ppt 300 ppt 5 ppb 50 ppb	Meer Land, unbewohnt Land, ländlich Land, Stadt	anthropogen Verbrennung von Biomasse Blitzlampen Emission aus dem Erdreich	20 12 8 8
Ammoniak NH_3	100 ppt 5 ppb	Meer Land, ländlich	Haustiere Verbrennung von Biomasse Emission aus dem Erdreich	25 6 18
Carbonilsulfid COS	500 ppt	gleichmäßig	Emission vom Erdreich u. den Meeren	≤1
Schwefel-wasserstoff H_2S	5–90 ppt 25–150 ppt	Meer Land, ländlich im Stadtbereich höher	Emission vom Erdreich Emissionen von Meeren anthropogen	4 0,5 ?
Dimethyl sulfid CH_3SCH_3	5–70 ppt	Meer im Stadtbereich höher	Emission vom Erdreich Emissionen von Meeren	3 70
Schwefel-dioxid SO_2	29–90 ppt 200 ppt 4 ppb 30 ppb	Meer Land, unbewohnt Land, ländlich Land, Stadtbereich	anthropogen Vulkanismus Oxid. von Schwefelverb.	200 15 50

Isopren C_5H_8	0,6–2,5 ppb	Land, ländlich Oberflächenluft	Blattemission, Laubbäume	350
Terpen $C_{10}H_{16}$	0,03–2 ppb	Land, ländlich Oberflächenluft	Blattemission, Nadelbäume	480
Methyl chlorid CH_3Cl	0,6 ppb	gleichmäßig	Meeresemission Verbrennen von Biomasse	3,0 0,4
CCl_4	130 ppt ansteigend	gleichmäßig	mehrere anthropogene Quellen	
Tri Chloro Fluor methan $CFCl_3$	180 ppt ansteigend	gleichmäßig	anthropogen	0,06
Dichlorfluormethan CF_2Cl_2	290 ppt ansteigend	gleichmäßig	anthropogen	0,04

Als **Ozon-Schicht wird die Ozon-Anreicherung** in der Atmosphäre in der Höhe zwischen **10 und 35 km** bezeichnet
Etwa 90% des atmosphärischen Ozons befindet sich dort, einem maximalen mit Volumen-Anteil von 10^{-5} bzw. einer Teilchendichte von bis zu ~ $5 \cdot 10^{12}$ cm^{-3}.







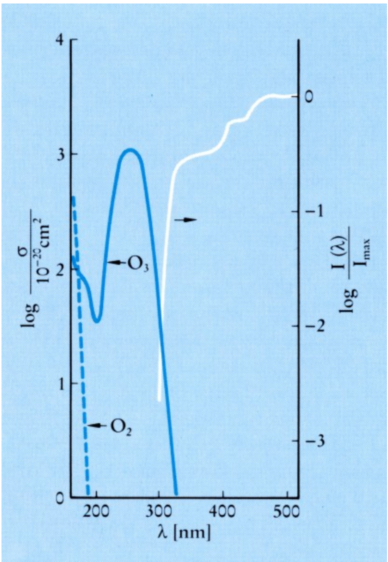
$$O_2 \xrightarrow{\lambda < 240\text{ nm}} 2\,O$$

$$O_2 + O + M \longrightarrow O_3 + M$$

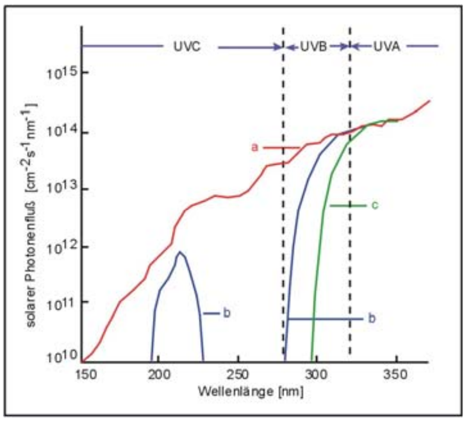
$$O_3 + h\nu \longrightarrow O_2 + O$$

$$O_3 + O \longrightarrow 2O_2$$

$$NO_2 \xrightarrow{\lambda < 400\text{ nm}} NO + O$$



$\ln(I_0(\lambda)/I(\lambda)) = \sigma(\lambda)N$



a) Ausserhalb der Atmosphäre

b) In 30 km Höhe

c) Auf Meereshöhe

1.4 Einige technische Anwendungen der Photochemie

Fotografische Verfahren
Fotolithografie
Fotopolimerisation
Fotobleichung
Fotochromie (z.B. Helligkeitsanpassung von Sonnenbrillen)
Leuchtstoffe (z.B. in Bildschirmen, in Neonröhren, etc.)
Laserfarbstoffe
Scintillatorfarbstoffe
Medizin (z.B. Fototherapie zur Tumorbekämpfung)
Chemilumineszent, Biolumineszenz (z.B. in der Analytik)
Wasseraufbereitung
Fotochemische Syntheseverfahren
Umwandlung und Speicherung von Sonnenenergie

1.5 Nanomaschinen