

## Light and Life: Real Life Applications of Photochemistry

### What is LIGHT?



Particles!



Action at a distance,  
Particles!

Electromagnetic field,  
wave-like



Newton  
1643-1727



Faraday  
1791-1867



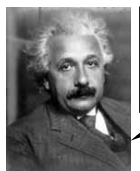
Maxwell  
(1831-1879)

Waves!  
Electro-  
magnetic



Max Planck (1918)

Waves!  
Absorption and  
emission  
are quantized



Albert Einstein (1921)

$E = h\nu$ ,  
Particles,  
Light is quantized,  
photons



Niels Bohr (1922)

$E_2 - E_1 = h\nu$   
Energy levels are  
quantized; Light is  
absorbed and  
emitted in quantas

### Wave and/or Particle

### Particles and Waves

- Some experiments are best explained by the particle model.
- Some are best explained by the wave model.
- We must accept both models and admit that the true nature of light is not describable in terms of any single classical model.
- The particle model and the wave model of light complement each other.

# A SURVEY OF PHYSICAL THEORY



Max Planck

“---- knowledge must precede application, and the more detailed our knowledge ----, the richer and more lasting will be the results which we can draw from that knowledge.”



Nobel Prize, 1918

## Light and Life



- ⇒ Photomedicine
- ⇒ Lithography
- ⇒ Industrial Synthesis of Chemicals
- ⇒ Photography, Xerography and Holography
- ⇒ Sunscreen, Photochromic Glass
- ⇒ Photostabilization
- ⇒ Photocuring
- ⇒ TiO<sub>2</sub>: Environmental Cleanup
- ⇒ Solar Energy Conversion

## Light: Prosperity through basic science



Candle lamp



Oil lamp



Filament lamp



Fluorescent lamp



Light emitting diodes



## The Nobel Prize in Physics 2014

"for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources."



Isamu Akasaki



Hiroshi Amano



Shuji Nakamura

## LASER (Light Amplification by the Stimulated Emission of Radiation) Invention and Innovation



1917: Albert Einstein derives the theoretical basis for the laser.



1960: The first working (ruby) laser.

Nicolay G. Basov



Charles H. Townes



Aleksandr M. Prokhorov

### The Nobel Prize in Physics 1964

"for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle."

## Nobels in Photochemistry

### Development of Flash Photolysis and Femtosecond Chemistry



Norrish



Porter



Zewail

The Nobel Prize in Chemistry 1967



The Nobel Prize in Chemistry 1999



## Lasers Applications



1965: The compact laser disc (CD) invented.



1974: A laser-driven barcode scanner used for the first time.

- Medical
- Metallurgical
- Electronic and computer
- Military
- Communications
- Microscopy
- Metrological
- Entertainment industry

The world market for laser technology is now over  
\$ 12 billion a year (2020)



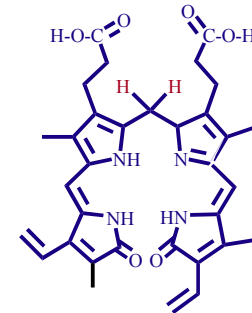
## Medicinal Applications of Photochemistry

## Photomedicine

- ❖ Phototherapy - Jaundice treatment
- ❖ PUVA therapy - Skin disorders, Blood cancer
- ❖ Photodynamic therapy - Cancer
- ❖ Lasik surgery - Vision correction

## Phototherapy for Neonatal Jaundice Treatment

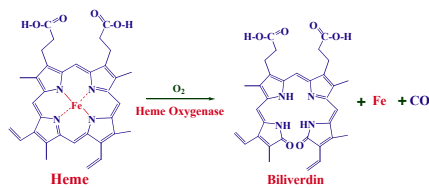
- ❖ Accumulation of the potentially toxic yellow lipophilic bilirubin in human serum leads to Jaundice.
- ❖ If the percentage of bilirubin increases to 15-25 mg/100 ml, it will lead to hyperbilirubinemia.
- ❖ Severe hyperbilirubinemia cases, sufficient pigment may partition into the brain to cause irreversible damage, even death.



Bilirubin

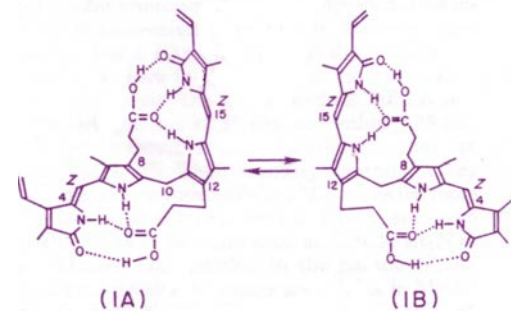
McDonagh et al., *Science*, 208, 1980, 145-151.

## Biosynthesis of bilirubin



Glucuronyl transferase activity in fetal and new born liver is very low.

## Why bilirubin is lipophilic (hydrophobic) ?



## Natural Cure for Jaundice



## Different ways to cure jaundice

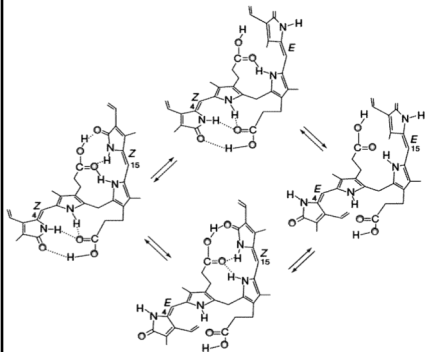
- ☐ Wait till liver matures soon enough to clear bilirubin unaided.
- ☐ Exchange transfusion: blood along with threatening pigment drained and replaced with clean blood.
- ☐ Phototherapy - irradiate the baby with light.

## Discovery of phototherapy

The discovery of phototherapy stems from the observations of Sister J. Ward, a nurse in U.K.

Evening walk with hyperbilirubinemia patients - lead to discovery of phototherapy by scientists.

## Phototherapy - Jaundice Treatment



**“light converts bilirubin to a less hydrogen bonded (more water soluble) isomer”**

## Skin Disorders



Psoriasis



Polymorphic light eruption



Vitiligo

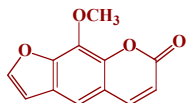


Acute dermatitis

### PUVA- therapy

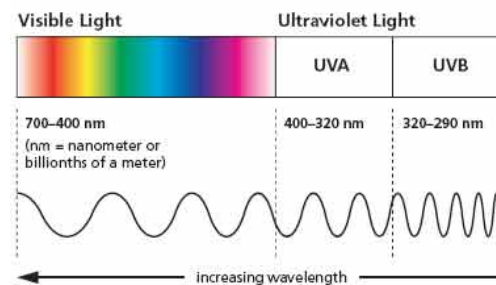
- ❑ Egyptians and Asian Indians practiced this therapy centuries ago.
- ❑ Boiled extracts of fruits of plants *Ammi majus* in Egypt and *Psoralea Corylifolia* L in India plus sunlight cured vitiligo.
- ❑ In 1988, PUVA was the first FDA (Food and Drug Administration) approved selective immunotherapy for skin disorders including cancer.

Psoralen + UVA = PUVA therapy



### What is UV-A light?

Visible Light/UV

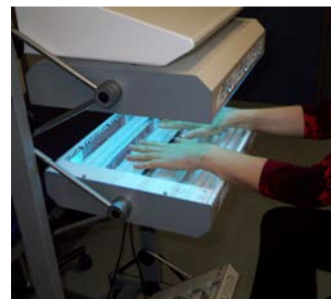
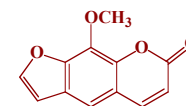


### How PUVA therapy is done ?

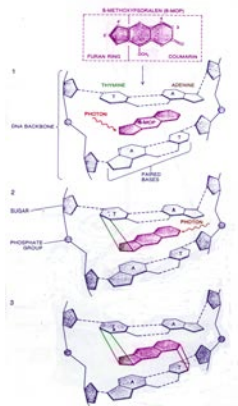
- ❑ Methoxsalen capsules are taken two hours before exposure to UVA.
- ❑ Bath PUVA: hands and/or feet are soaked in a dilute solution of methoxsalen for 30 minutes, then exposed to UVA.
- ❑ A few patients may be treated with topical tripsor PUVA - a lotion is applied on the affected areas 10 minutes before UVA exposure.

### PUVA therapy

Psoralen + Ultraviolet A = PUVA



### Photoadduct representation with DNA



- Intercalation
- Monofunctional adduct (3, 4 with pyrimidine base)
- Bifunctional crosslinked adduct(3, 4 and 4', 5' with pyrimidine bases)

### PUVA -therapy to treat cancer

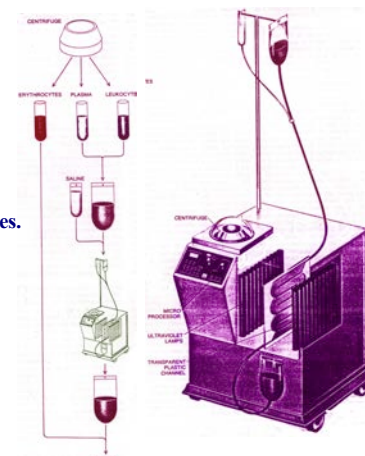
Centrifugation.

Separate white blood cells.

Drug in saline + Leukocytes.

Irradiate in the machine.

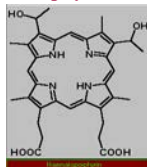
Collect white blood cells.



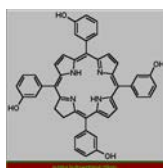
### Photodynamic therapy

- ❑ Photodynamic therapy first introduced in 1978.
- ❑ Currently several photodynamic drugs are available on the market.
- ❑ Approved for the treatment of esophageal and lung cancers.

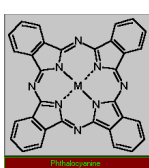
#### Porphyrins



#### Chlorins

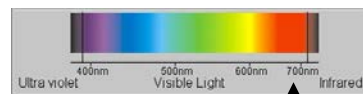
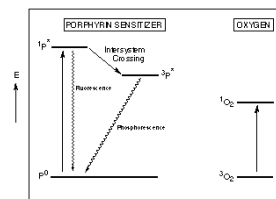


#### Phthalocyanines



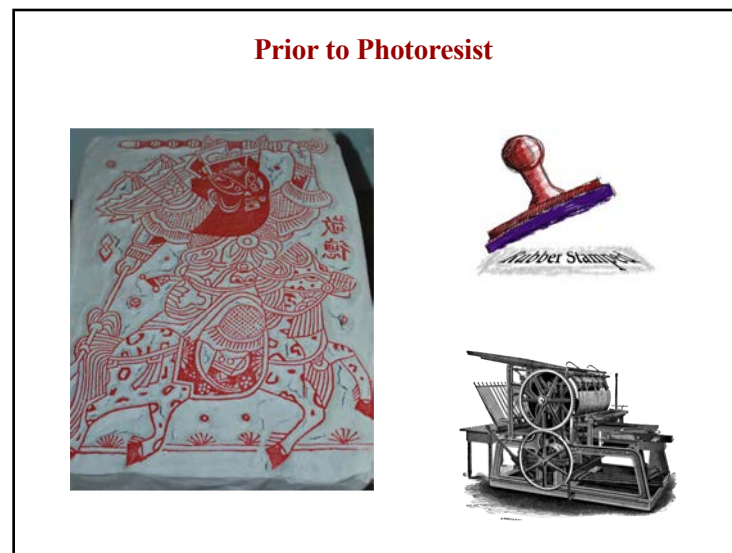
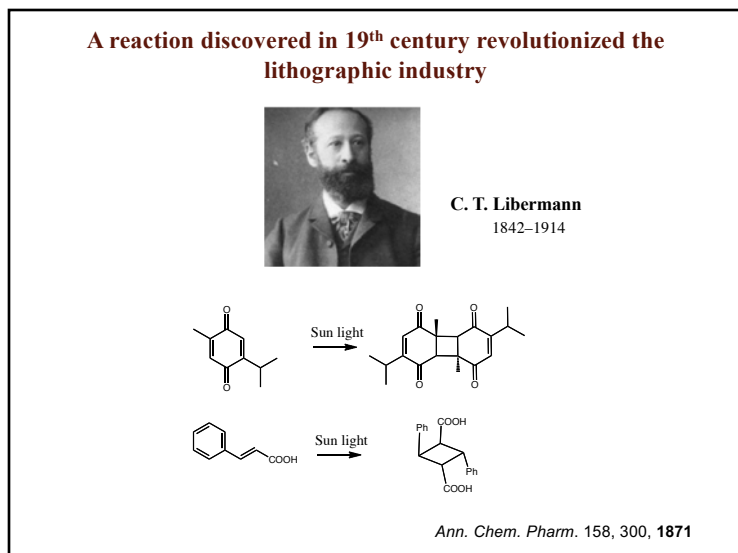
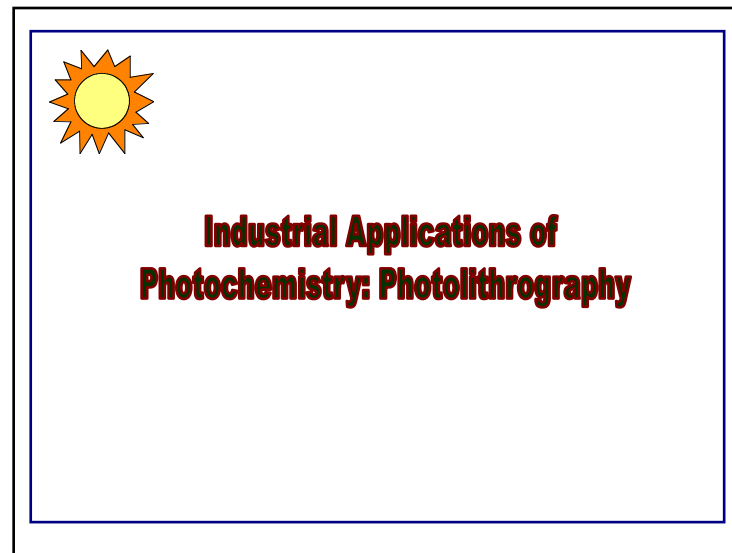
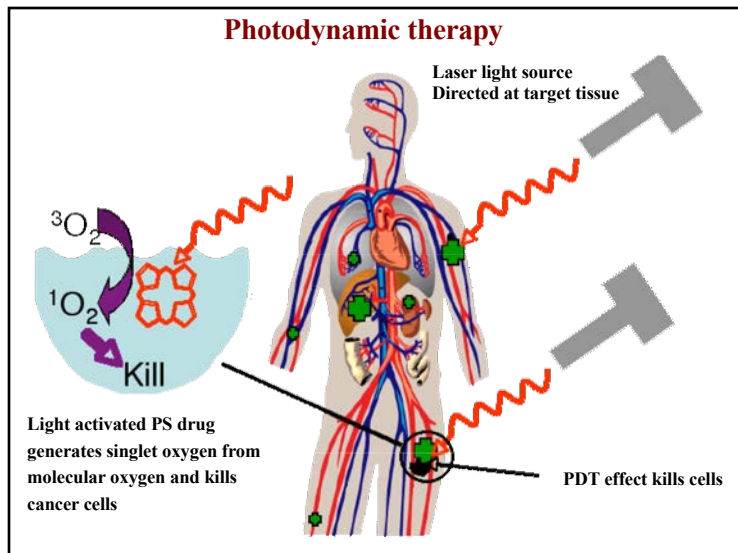
### How does photodynamic therapy work?

- ❑ PDT requires sensitizer, light and oxygen in the target tissue.
- ❑ Light generates reactive oxygen species.
- ❑ Reactive oxygen species can kill targeted cells either by necrotic mechanisms or by initiating the apoptotic cascade.



Ideal wavelength 650nm







## Photolithography: Invention 1949-50



**Louis Minsk** (Kodak)  
Polyvinylcinnamate-Based  
Photoresist

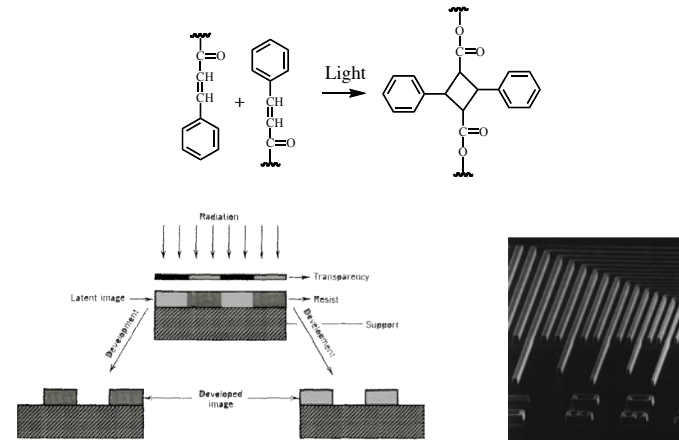


**Otto Suess** (Kalleys)  
Diazoquinone-Based  
Positive Photoresist



**Louis C. Plambeck** (DuPont)  
Acrylate-Based  
Photopolymer Imaging

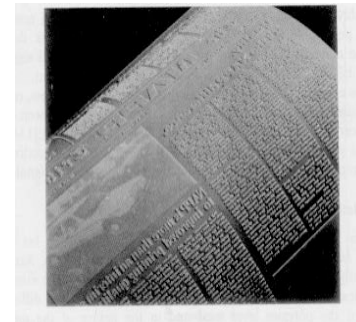
## Photoresist



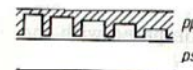
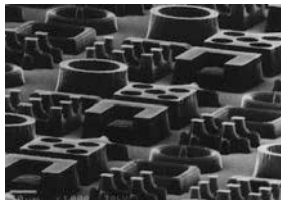
## Applications of the Principles of Photoresists and Lithography *The Workhorses of Electronics and Printing*

- Printing, Litho, Package, Billboards
- Color Printing
- Printed Circuit Boards (PC)
- Integrated Circuit Chips (IC)
- DNA and Biochips
- Micromachines

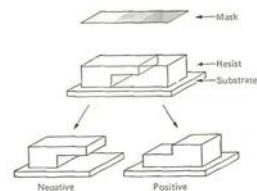
## Lithographic Printing Is the Backbone of Modern Printing Industry



### Gray Shading



a)



### Three Color Printing

- ❑ Color Printing Requires Color Separation
- ❑ Color Printing is Done Through Four Color Processing



Yellow



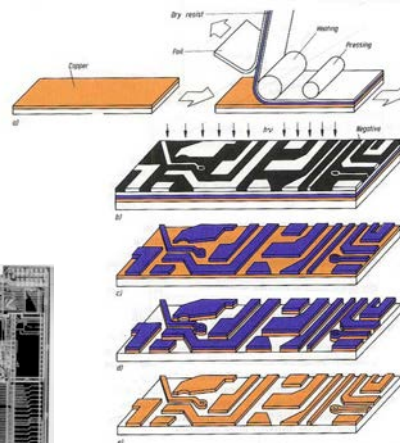
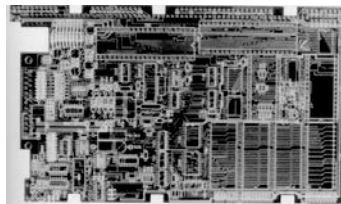
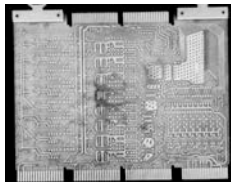
Magenta



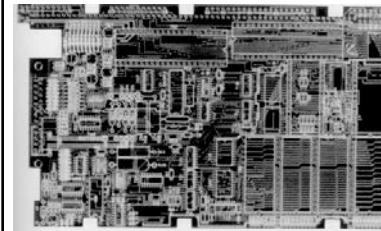
Cyan

Overlay of  
the three

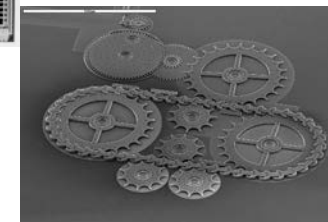
### Printed Circuit Board Making



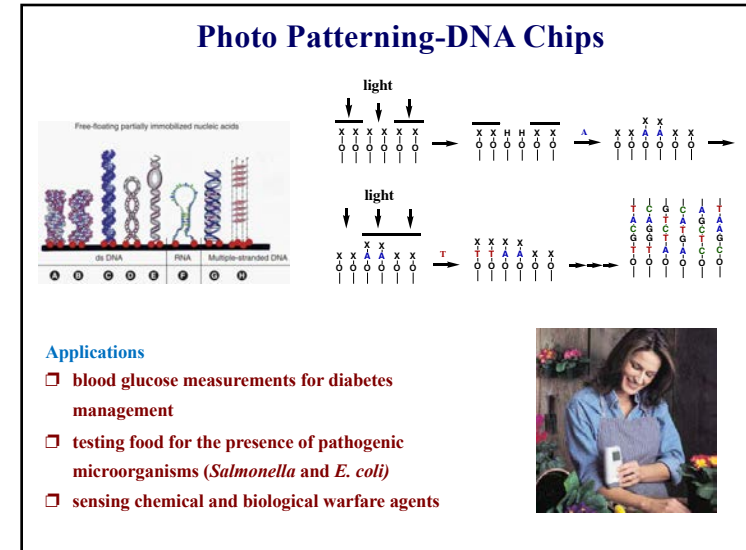
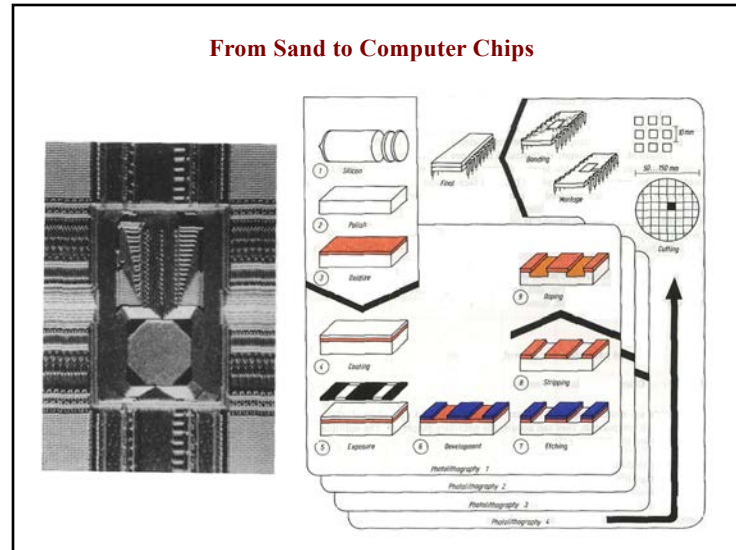
### Photolithography Applications in Electronic Industry






Printed Circuit Boards



Micro-Electro Mechanical Systems (MEMS)



### Lithography to Lasik Surgery






**R. Srinivasan**

**S. Blum**

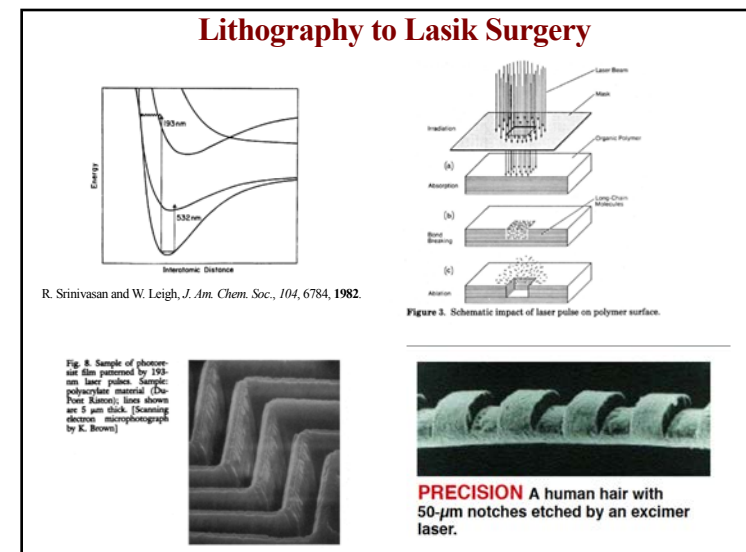
**J. Wyne**

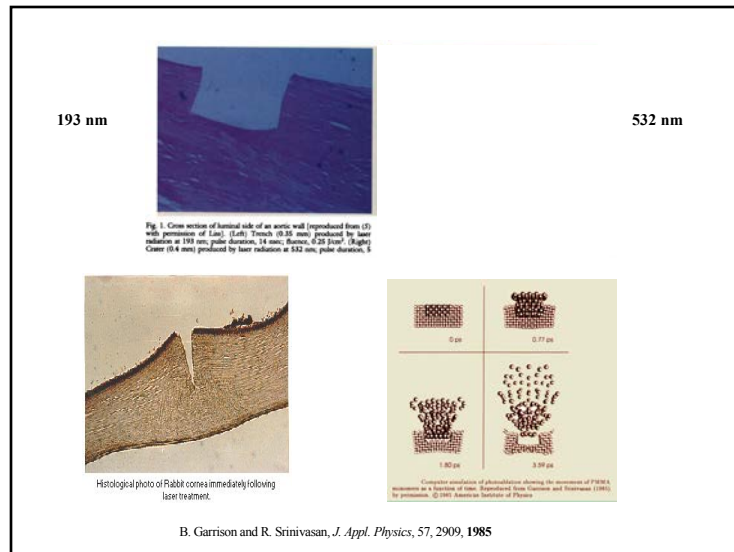
**1981: Discovery of laser ablation technique.**  
**1995: US FDA approval of human Lasik surgery.**  
**2002: Inducted into US Inventors Hall of Fame.**



**National Medal of Technology and Innovation (2011)**

For the pioneering discovery of excimer laser ablative photodecomposition of human and animal tissue, laying the foundation for PRK and LASIK, laser refractive surgical techniques that have revolutionized vision enhancement.





## Photoablation with Excimer Lasers

Defined areas of a cornea can be removed by ablating the tissue to a predetermined length.

Far-UV laser irradiation produces a trench with sharp and cleanly defined boundaries by light microscopy. There are no changes in the adjacent tissues due to thermal effects.

Significantly, laser ablation can be used to remove a shaped area of cornea to any depth.

S. Trokel, R. Srinivasan and B. Braren, *American J. Ophthalmology*, 96, 710, (1983)



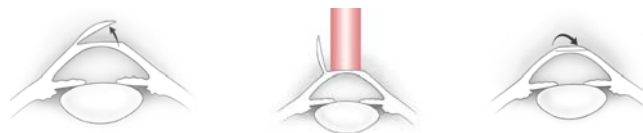
1987: Lasik surgery

R. Srinivasan, *Science* 234, 565, 1986

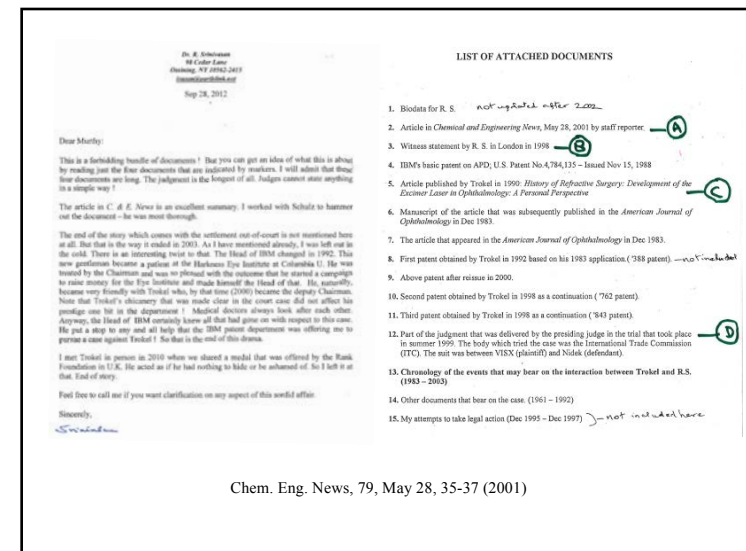
S. Trokel, *Refractive and Cosmetic Surgery*, 6, 357, 1990

## How is LASIK done?

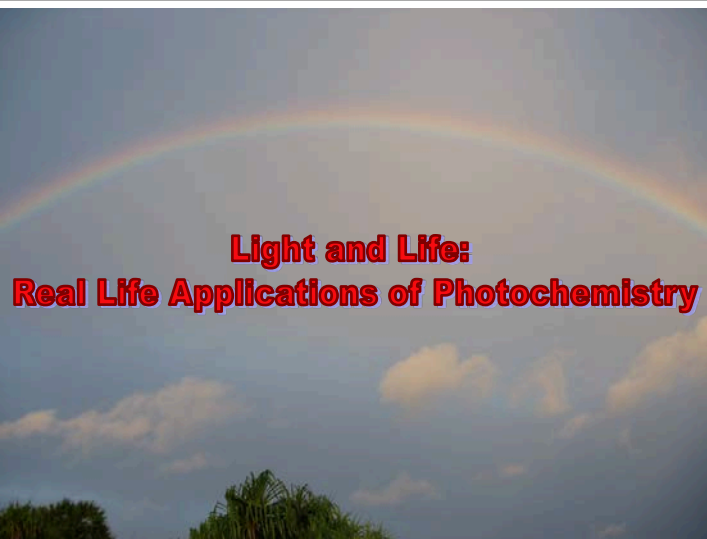
- ❑ First step is the lifting of corneal flap and then ablation
- ❑ Treatment is given beneath the flap



- ❑ Brief recovery time
- ❑ Very low infection risk and low enhancement rate
- ❑ Very low risk of scarring and minimal discomfort



Chem. Eng. News, 79, May 28, 35-37 (2001)

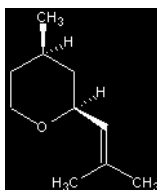


## Light and Life: Real Life Applications of Photochemistry



## Synthetic Applications of Photochemistry

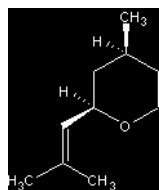
### Rose oxide



(4r,2s)-(-)-cis-roseoxide

floral green with clean sharp, light, rose green note, diffusive, strong (Matsuda); also has been described as powerful fruity.

Odor Threshold = 0.5 ppb

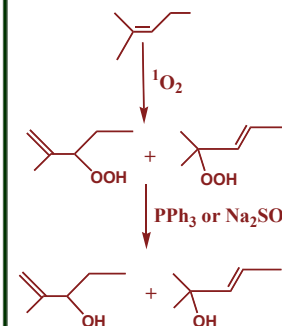
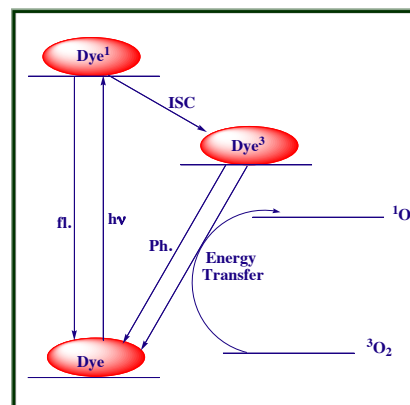


(4s,2r)-(+)-cis-roseoxide

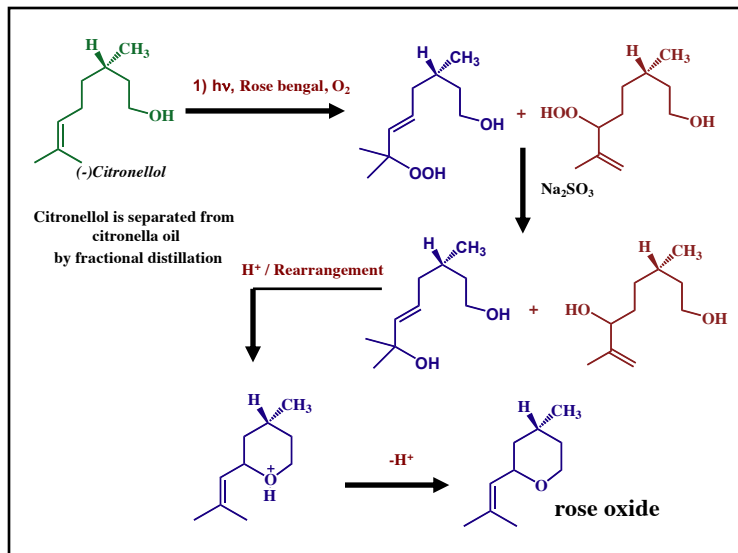
herbal, green floral, hay green, earthy, heavy (Matsuda); also has been described as sweet, floral

Odor Threshold = 50 ppb

### Schenk 'ene' - Reaction



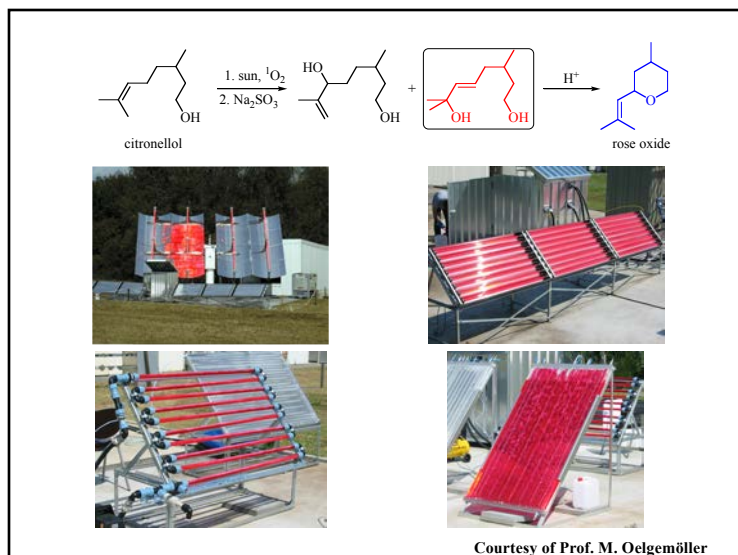




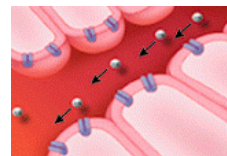
Photograph of the cylindrical immersion type reactors used by Dragoco for the production of (-)-rose oxide

The reactor is about 3 m tall, and is equipped with a 5 k W light source.

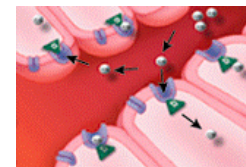
Scanned from *Photochemical technology*, Braun, A. M., Maurette, M.- T., Oliveros, E.



Vitamin D is absolutely necessary for the efficient absorption of calcium and phosphate from our diet



Without vitamin D, the calcium passes through the digestive system unused.

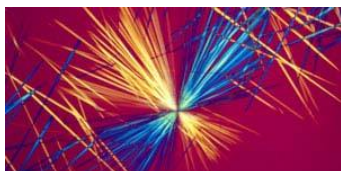


Vitamin D is essential for the body's absorption of calcium.



Child with rickets

At the present time almost all milk sold commercially in the United States has 400 IU of chemically synthesized vitamin D<sub>3</sub> added per quart.



vitamin D<sub>2</sub> (ergocalciferol: plant origin)  
vitamin D<sub>3</sub> (cholecalciferol: animal origin).

Vitamin D crystals

Commercially synthesized by Roche-Vitamins

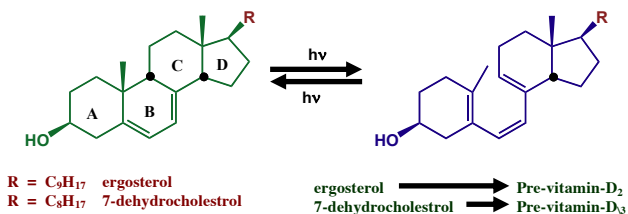
Commercial production of vitamin D<sub>3</sub>:

a) 7-dehydrocholesterol

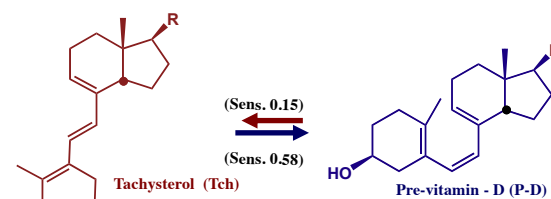
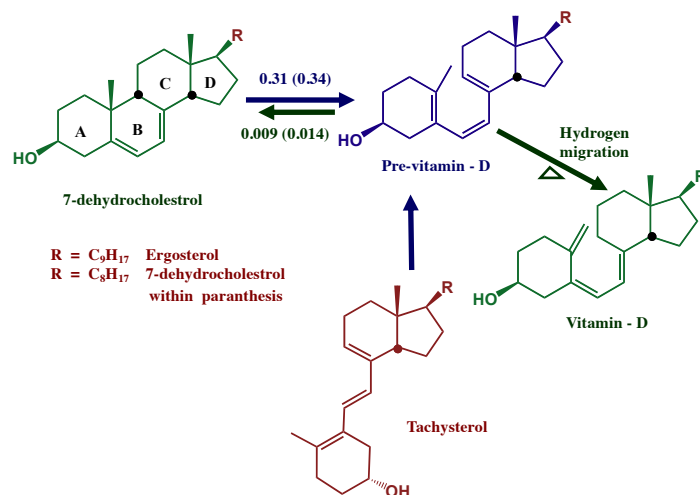
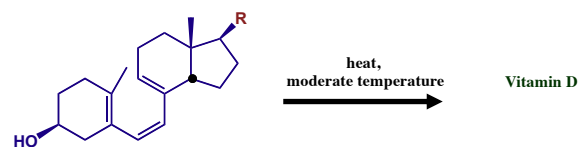
Extracted from **animal skins** (cow, pig or sheep) followed by an extensive purification.

b) cholesterol.

Extracted from the lanolin of **sheep wool** and can be converted to 7-dehydrocholesterol.



The ring opening takes place from the first excited singlet state



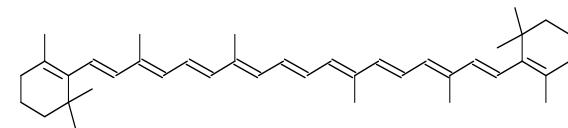
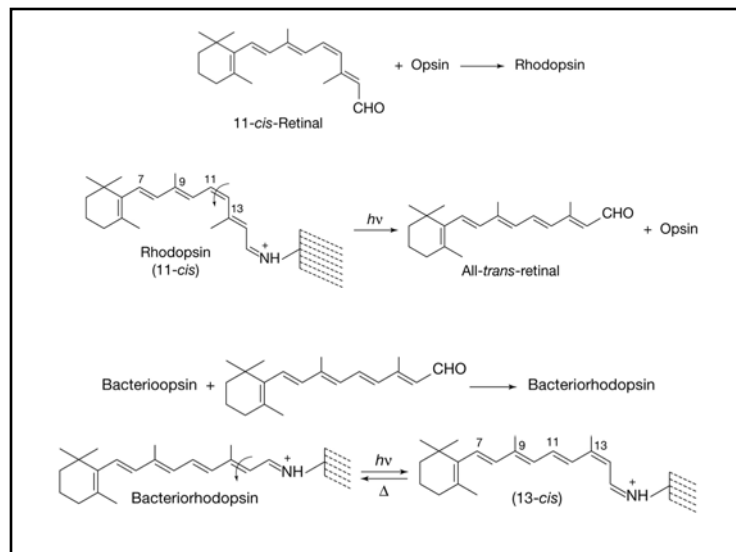
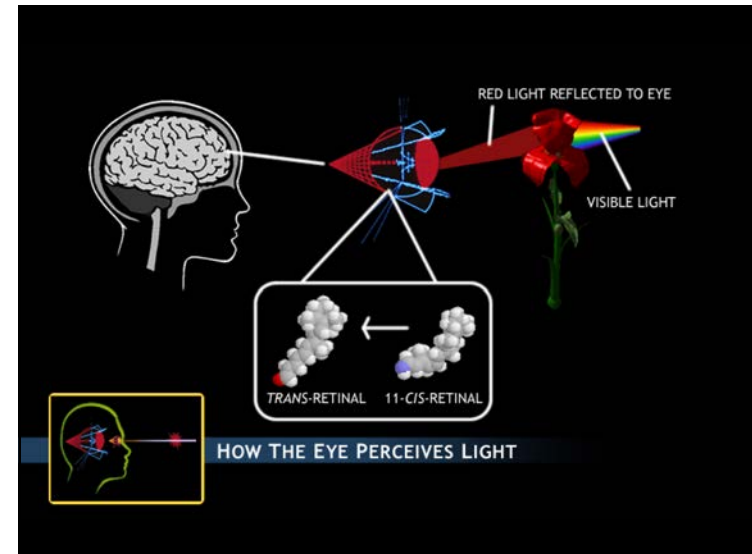
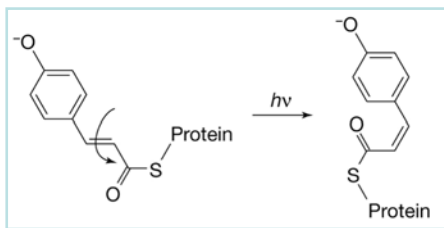
Sensitizer	$E_T$ KJ Mol <sup>-1</sup>	(P-D/Tch)
Benzophenone	286.3	2.6
Anthraquinone	260.8	2.1
2-Naphthylphenylketone	247.8	1.5
Benzil	225.0	1.8
9-Fluorenone	222.8	4.4
Benzanthrone	196.5	5.6
7,12-Dimethylbenzanhracene	185.2	16.3

Initial ratio (P-D/Tch)= 0.5; solvent=ethyl ether.





### Role of Photoactive Yellow Protein (PYP) in plant growth



11 double bonds

$\lambda_{\text{max}}$  460 nm ( $\epsilon$  139,000)

### The Nobel Prize in Physiology or Medicine 1967



Ragnar Granit

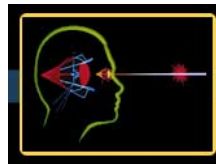


Haldan Keffer Hartline

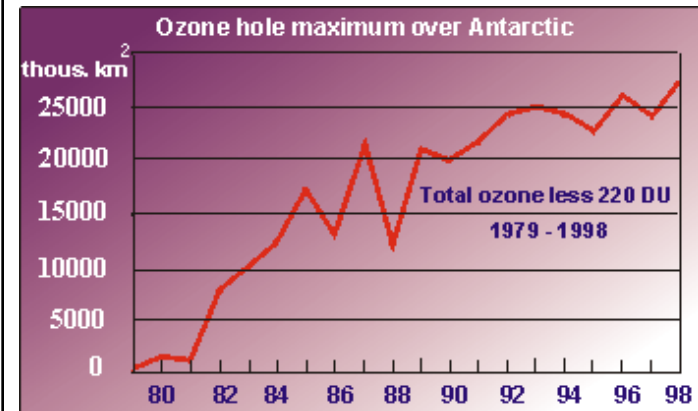


George Wald

"for their discoveries concerning the primary physiological and chemical visual processes in the eye"



### Ozone hole measurements over the Antarctic region 1980-98



### What is Ozone? Ozone Layer?

- **Ozone (O<sub>3</sub>)** is a highly-reactive form of oxygen.
- Unlike oxygen (O<sub>2</sub>), ozone has a strong scent and is blue in color.
- **Ozone** exists within both the tropospheric and stratospheric zones of the Earth's atmosphere
- **In the troposphere**, ground level ozone is a major air pollutant and primary constituent of photochemical smog
- **In the stratosphere**, the ozone layer is an essential protector of life on earth as it absorbs harmful UV radiation before it reaches the earth.

### Impacts

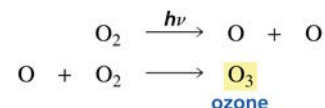
- Ozone layer absorbs most of the harmful UV-B radiation; more UV-B means:
  - more melanoma and non-melanoma skin cancers
  - more eye cataracts
  - weakened immune systems
  - reduced plant yields
  - damage to ocean eco-systems
  - more damage to plastics

## Ozone Depleting Substances

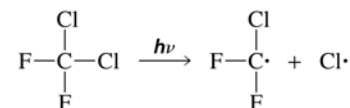
- Chlorofluorocarbons (CFC's)
  - contains: Cl, F, C
  - long-lived, non-toxic, non-corrosive, and non-flammable
  - in 1960's used in refrigerators, air conditioners, spray cans, solvents, foams
  - phase out by 1996 in developed countries

## Ozone hole

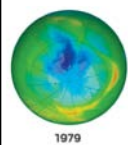
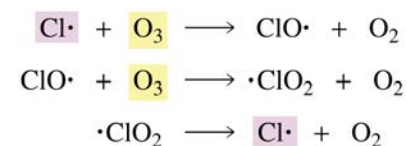
Generation of Ozone



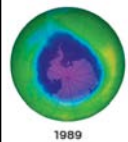
Culprit



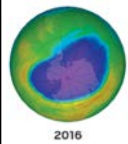
Destruction of Ozone



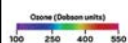
1979



1989



2016



## The Nobel Prize in Chemistry 1995



Paul J. Crutzen



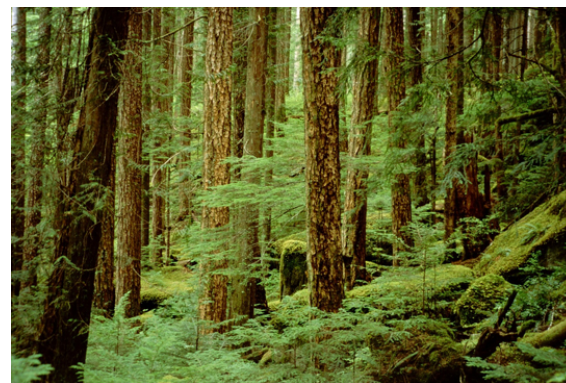
Mario J. Molina



F. Sherwood Rowland

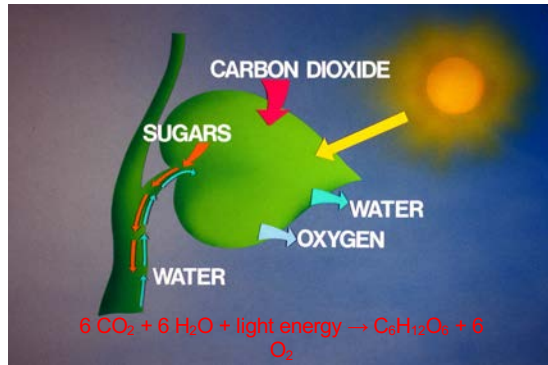
"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"

## Survival Strategy: Photosynthesis

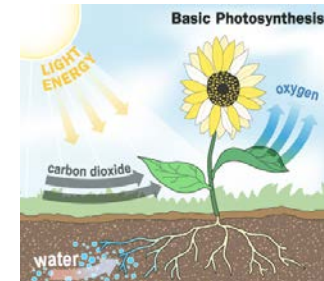


Plants that commonly grow in the shade benefit from having a variety of light-absorbing pigments. Each pigment can absorb different wavelengths of light, which allows the plant to absorb any light that passes through the taller trees.

## Light Energy Harvested by Plants



Joseph Priestley  
1733–1804



Joseph Priestley published in 1774: "Green plants absorb carbon dioxide from the atmosphere and give off oxygen".

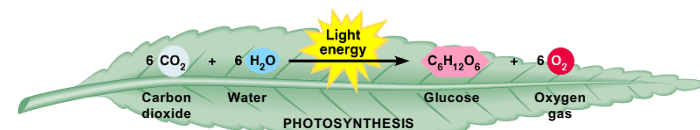
## Light Energy Harvested by Plants



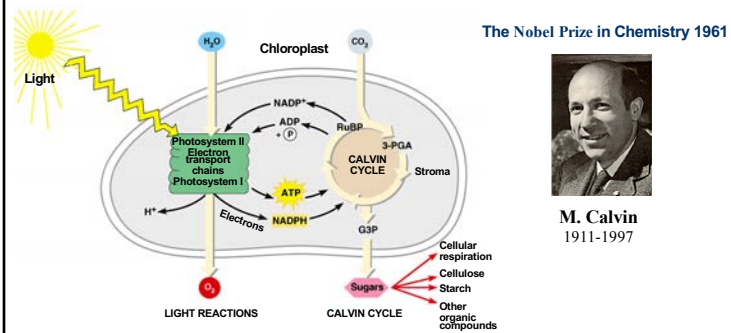
Ingenhousz, along with Benjamin Franklin and a few other traveling companions paid a visit to scientist Joseph Priestly, who had recently discovered that plant leaves absorb and emit gases. That exchange led Ingenhousz to eventually discover the chemistry that forms the foundation of nearly every food chain on Earth: photosynthesis.

## AN OVERVIEW OF PHOTOSYNTHESIS

- Photosynthesis is the process by which plants use light energy to make sugar and oxygen gas from carbon dioxide and water

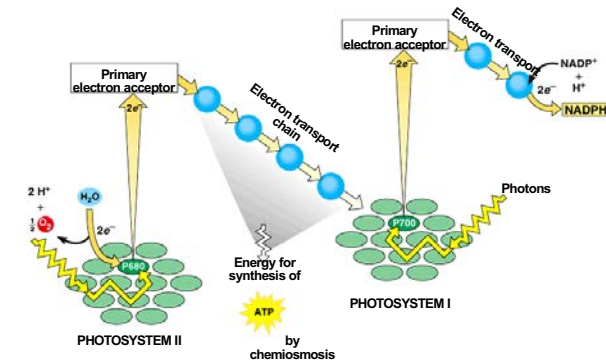


## Photosynthesis uses light energy to make food molecules

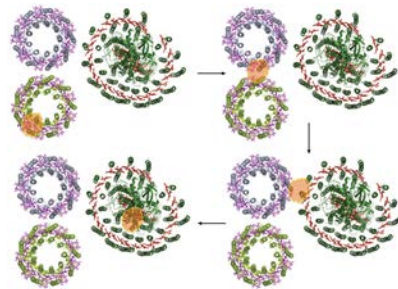


## Noncyclic Photophosphorylation

- Photosystem II regains electrons by splitting water, leaving  $O_2$  gas as a by-product



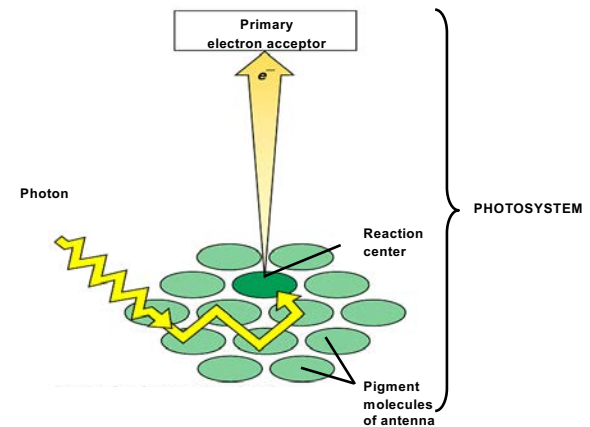
## Energy and Electron Transfer



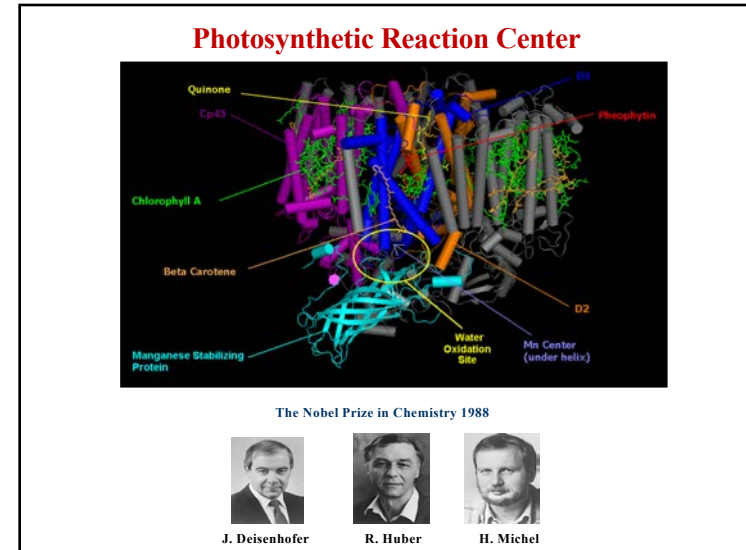
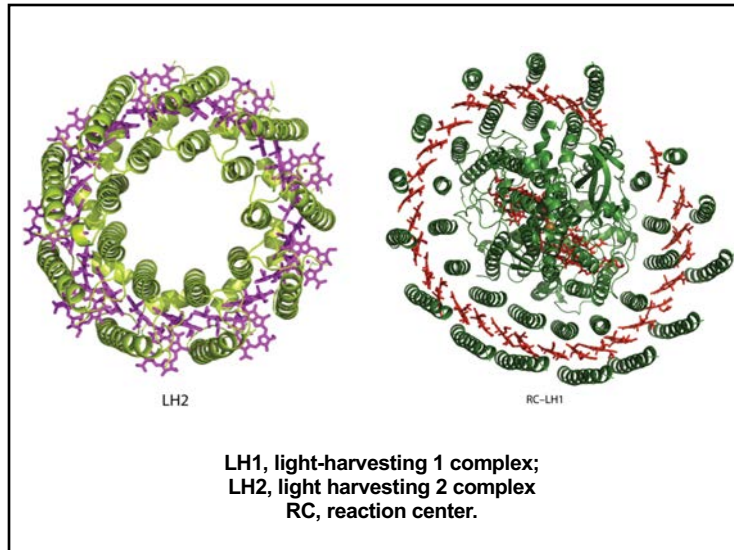

Nelson N, Junge W. 2015.  
Annu. Rev. Biochem. 84:659-83

Excitation transfer from light-harvesting 2 complex to the reaction center of photosynthetic bacteria. It is primarily the intercomplex, and not the intracomplex exciton transfer, that is critical for overall efficiency.

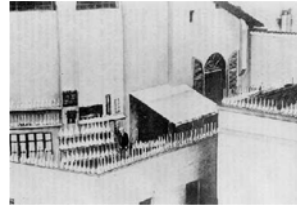
## Energy and Electron Transfer





Giacomo Ciamician  
1857-1922



*"On the arid lands there will spring up industrial colonies without smoke and without smokestacks, forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."*

(Giacomo Ciamician *Science* 1912, 36, 385.)

