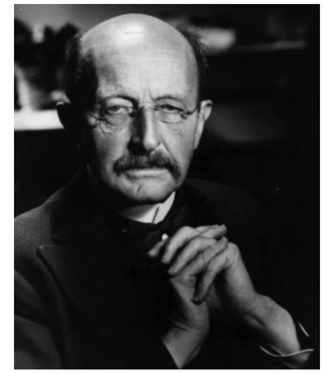
Personalities in Photochemistry

It is the people who make the science

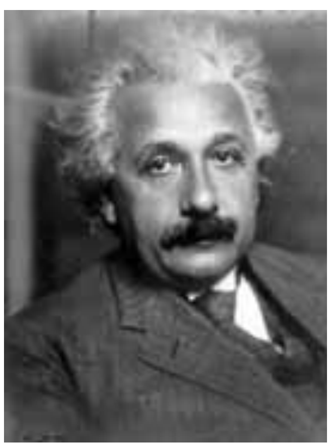
Concept of Photon

Newton
(1643-1727)

Maxwell
(1831-1879)



Max Planck (1918)



Albert Einstein (1921)

Niels Bohr (1922)

De Broglie (1929)

The Basic Laws of Photochemistry

Grotthuss-Draper law

The First Law of Photochemistry: <u>light must be absorbed for photochemistry to occur</u>.

Grotthus

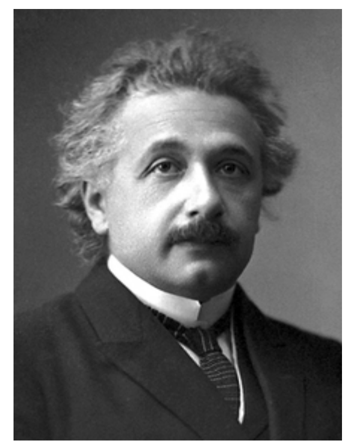
John William Draper (1811-1882)

Drapper

Stark-Einstein law

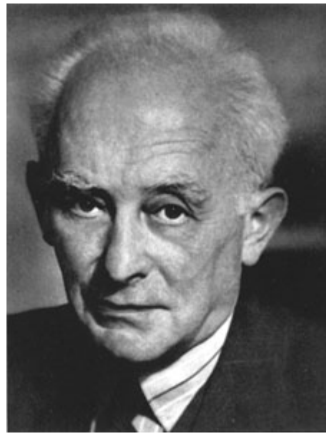
The Second Law of Photochemistry: for <u>each photon</u> of light absorbed by a chemical system, <u>only one molecule</u> is activated for a photochemical reaction.

Stark

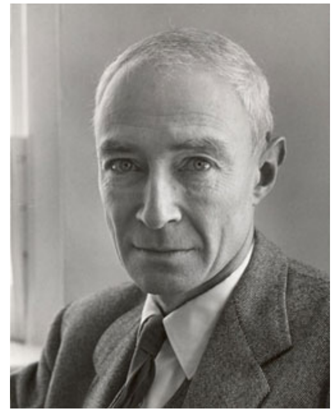


Einstein

Born – Oppenheimer Approximation



Born



Oppenheimer

- Electronic motion faster than nuclear vibration.
- Weak magnetic-electronic interactions separate spin motion from electronic and nuclear motion.

$$\Psi \quad - \quad \Psi_o \quad \chi \quad S$$

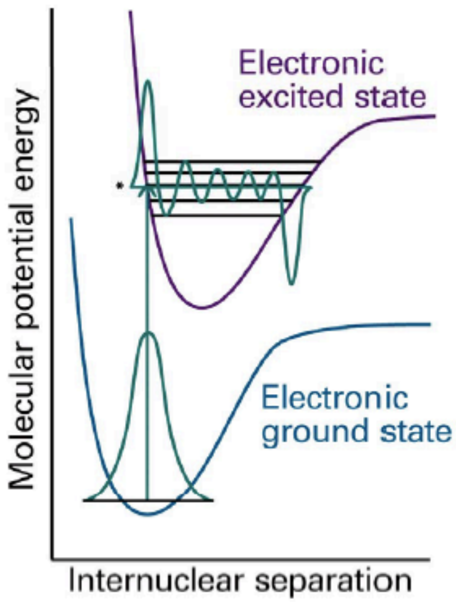
Electronic Nuclear Spin

Zeroth-order Approximation

Vibrational Part Limits the Electronic Transition

5.8 The Franck-Condon Principle

Assumption: electronic transitions take place on such a short timescale that the nuclei remain frozen (R unchanged) during the transition.



We talk of "vertical transitions" between potential energy curves.

There is no selection rule governing the allowed vibrational changes accompanying an electronic transition.

Instead, the probability of undertaking a $v'' \rightarrow v'$ transition is governed by Franck-Condon factors (the overlap of the two vibrational wavefunctions).

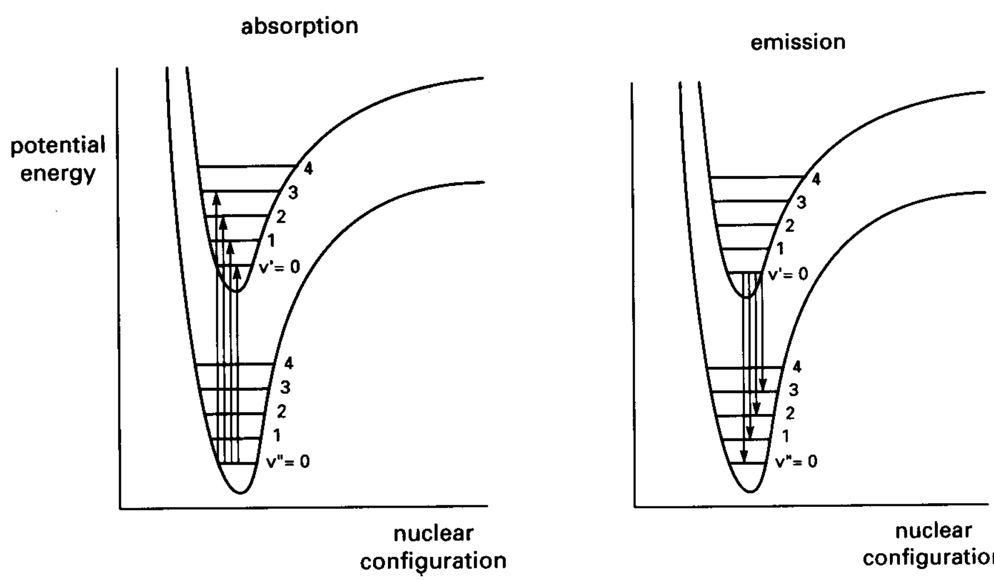
Franck

Condon

Stokes shift

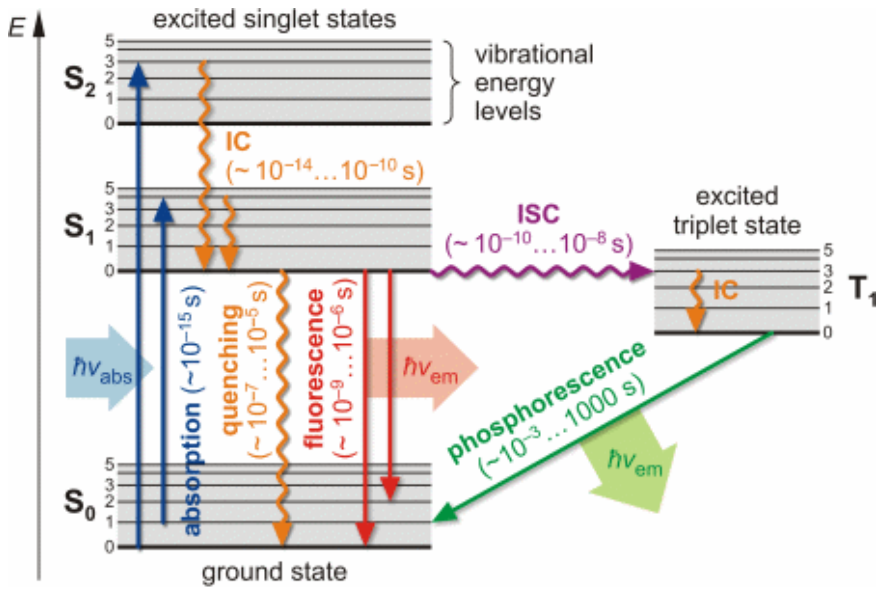
G.G. Stokes (1819-1903)

Owing to a decrease in bonding of the molecule in its excited state compared to that of the ground state, the energy difference between S_0 and S_1 is lowered prior to fluorescence emission (in about 0.1 to 100 ps). This is called Stokes' shift.



Vavilov's rule

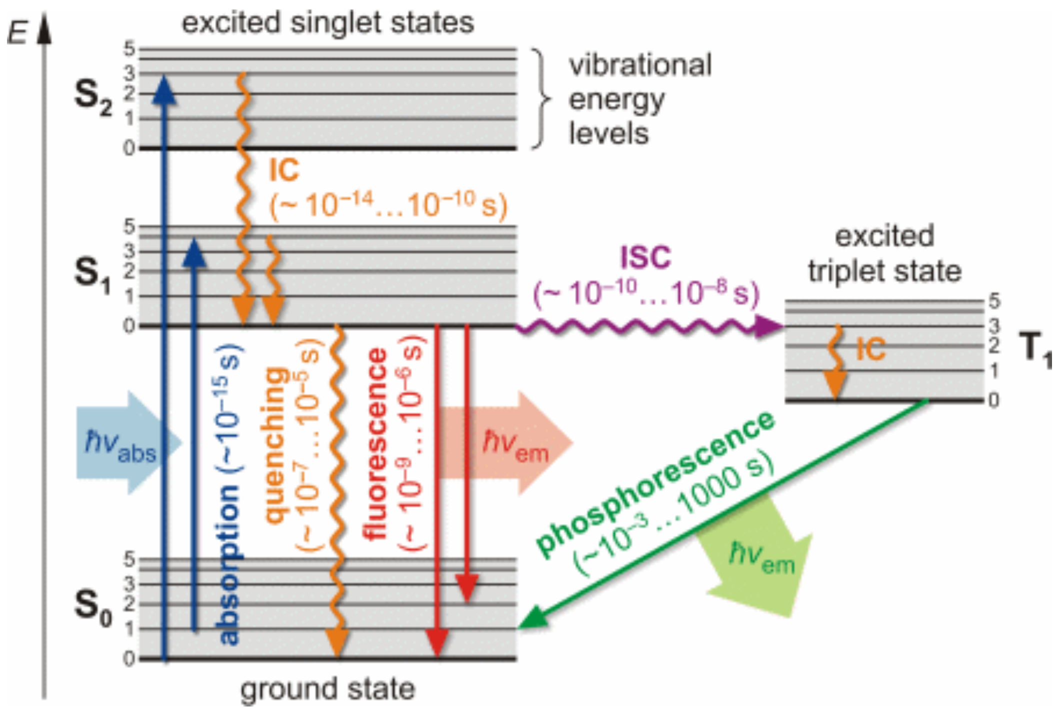
The quantum yield of fluorescence and the quantum yield of phosphorescence are independent of initial excitation energy.

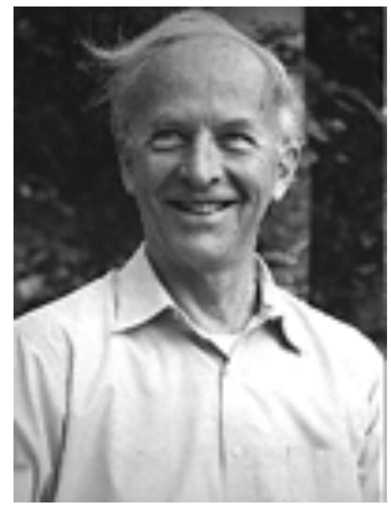


S. Vavilov

Kasha's rule

Fluorescence occurs only from S_1 to S_0; phosphorescence occurs only from T_1 to S_0; S_n and T_n emissions are extremely rare.





Kasha

Ermolaev's rule

For large aromatic molecules the sum of the quantum yields of fluorescence and ISC is one i.e., rate of internal conversion is very slow with respect to the other two.

Table 4.2 *Quantum yields for fluorescence* ($S_1 \rightarrow S_0 + h\nu$) *and intersystem crossing* ($S_1 \rightsquigarrow T_1$) *for some aromatic hydrocarbons in ethanol solution* (*Data from Birks, J. B.* (*ed.*) (*1975*). Organic molecular photophysics, *Vol. 2, Tables 2.6 and 3.4. Wiley, London*)

Compound	ϕ_f	ϕ_{ISC}	$\phi_f + \phi_{ISC}$
Benzene	0.04	0.15	0.19
Naphthalene	0.80	0.21	1.01
Fluorene	0.32	0.68	1.00
Anthracene	0.72	0.32	1.02
Tetracene	0.66	0.16	0.82
Phenanthrene	0.85	0.13	0.98
Pyrene	0.38	0.65	1.03
Chrysene	0.85	0.17	1.03

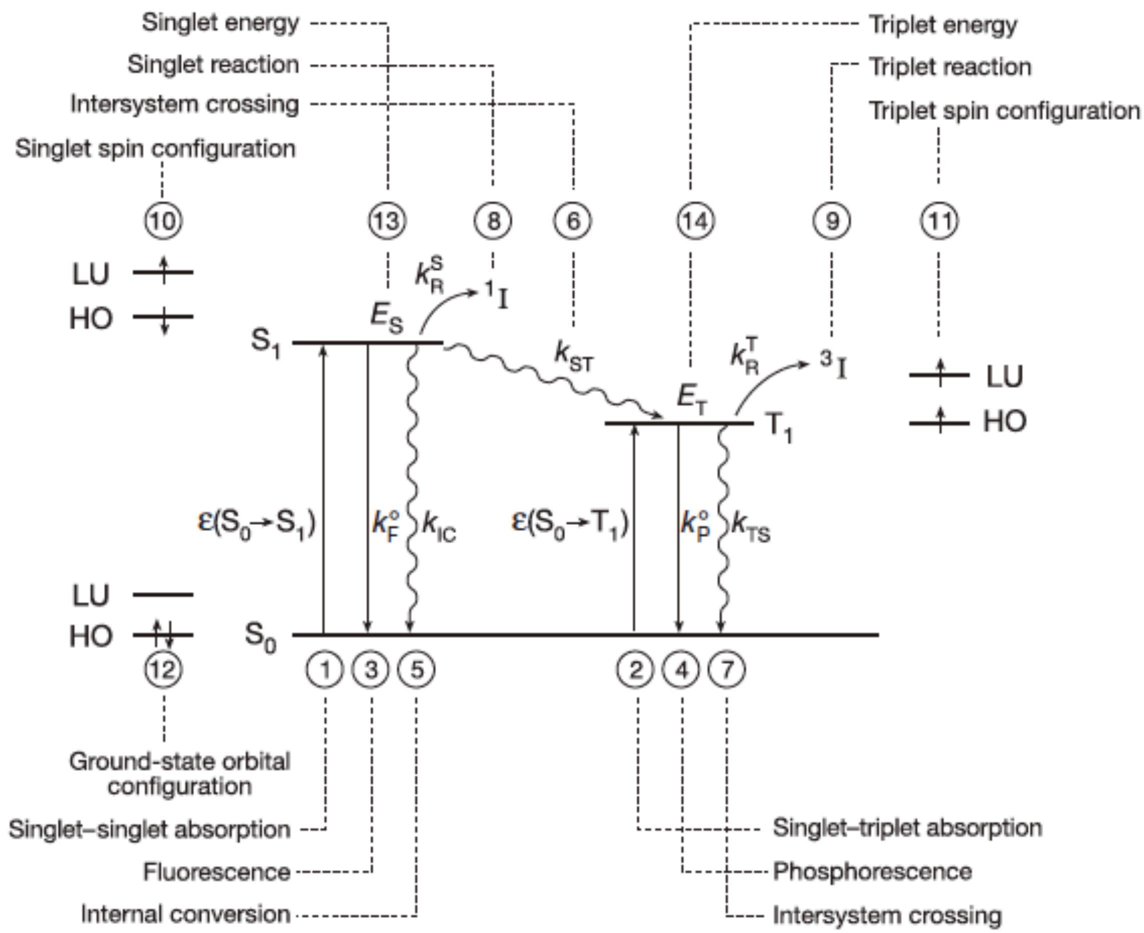
Valerii L. Ermolaev

El Sayed's Rule

El-Sayed

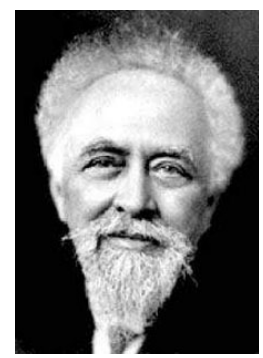
Intersystem crossing is likely to be very slow unless it involves a change of orbital configuration.

Jablonski Diagram



Alexander Jablonski
(1898-1980)

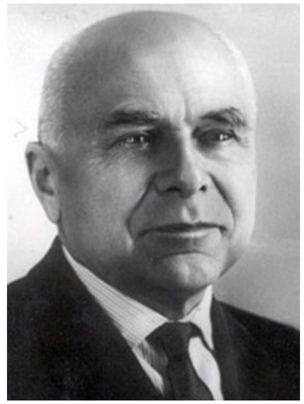
F. Perrin



J. Perrin

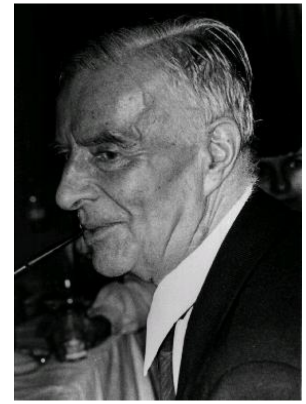
Triplet State (Phosphorescence)

S. Vavilov

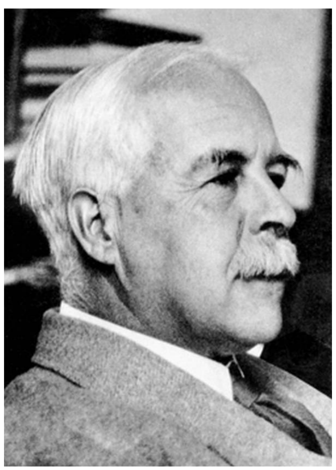


A. Terenin

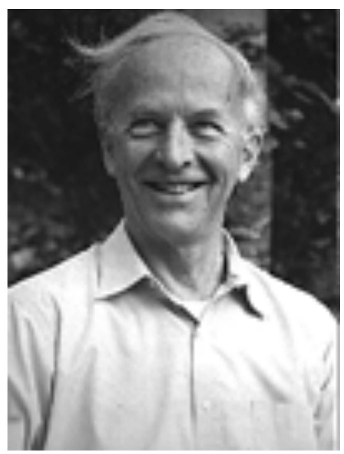
A. Perrin



A. Jablonski



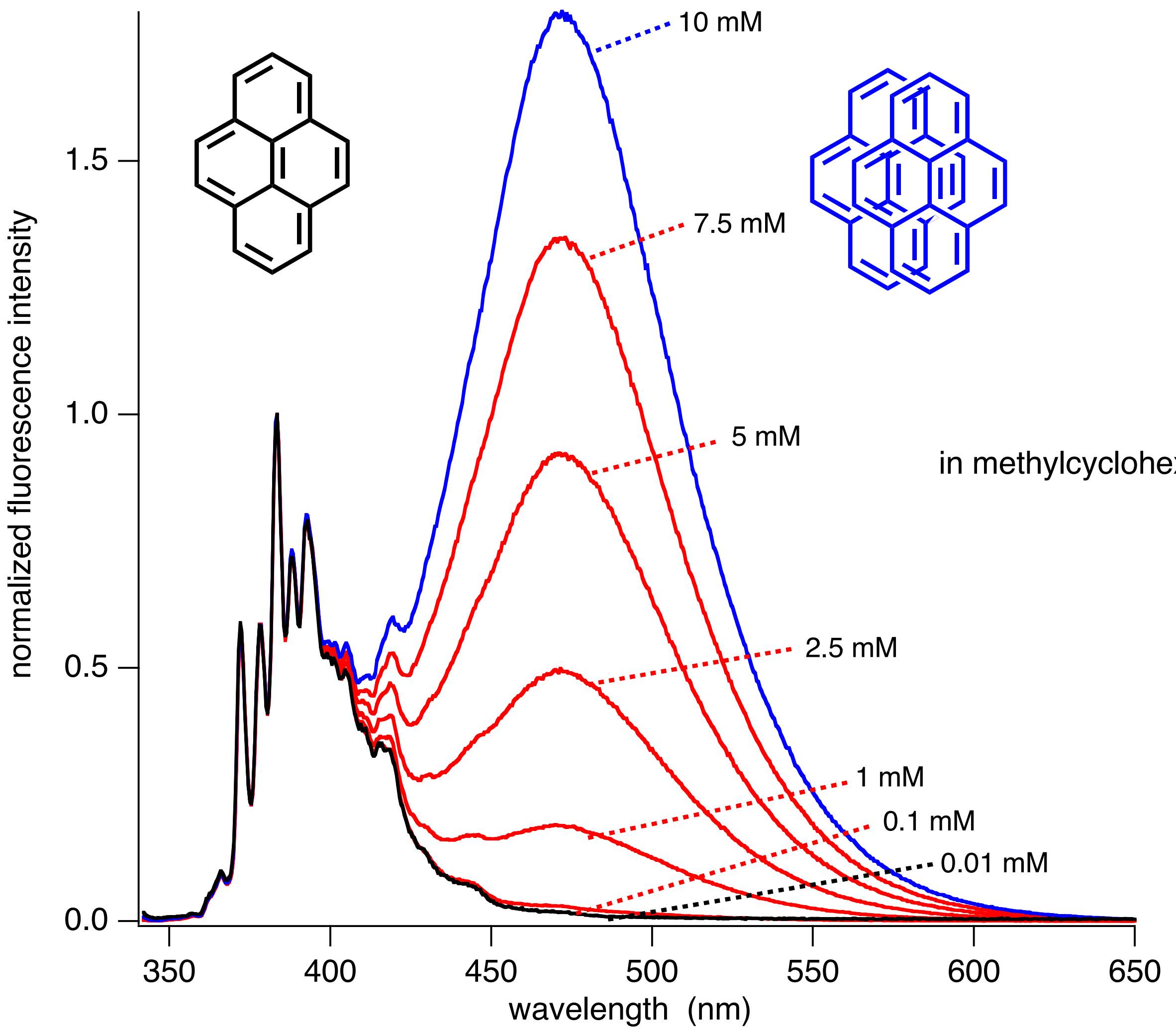
G. N. Lewis



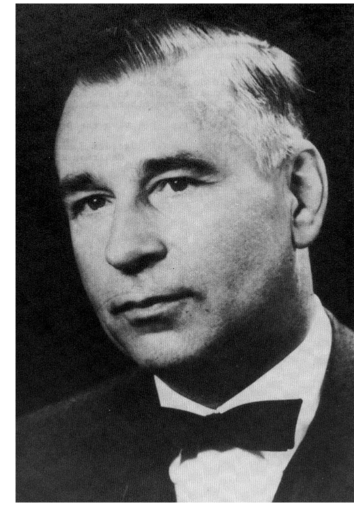
Kasha

Porter

Excimers



in methylcyclohexane solution



Th. Förster

A. Weller

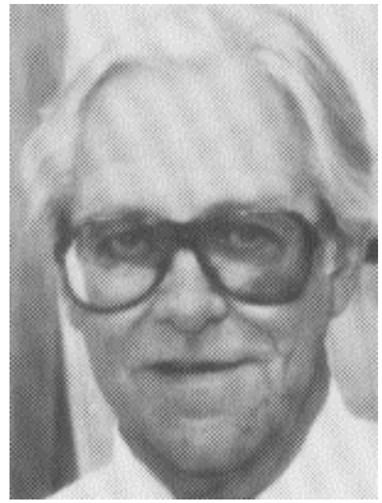
Energy transfer

Dexter Förster

Electron transfer

W. Libby

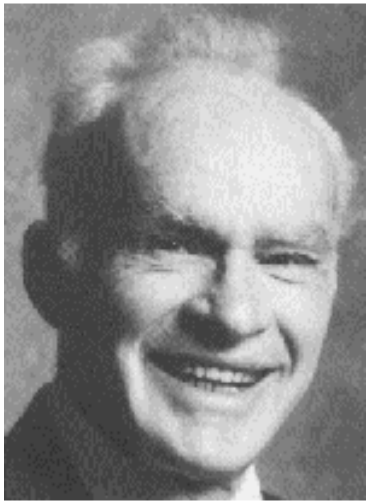
R. Marcus



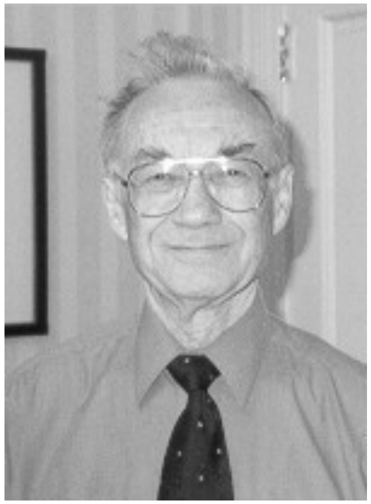
G. Closs

J. R. Miller

Organic Photochemistry



George S. Hammond



Howard E. Zimmerman

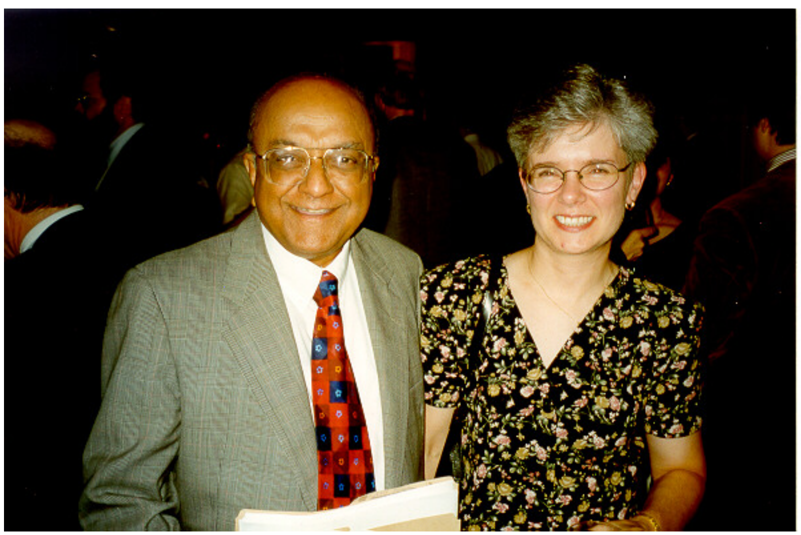
Egbert Havinga

G. O. Schenck

P. de Mayo

Nien-chu C. Yang

O. Chapman

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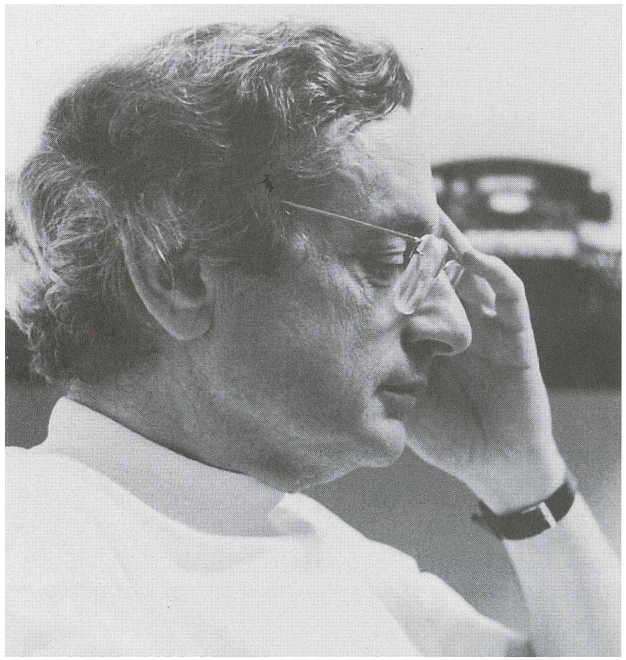
Supramolecular Photochemistry

G. M. J. Schmidt

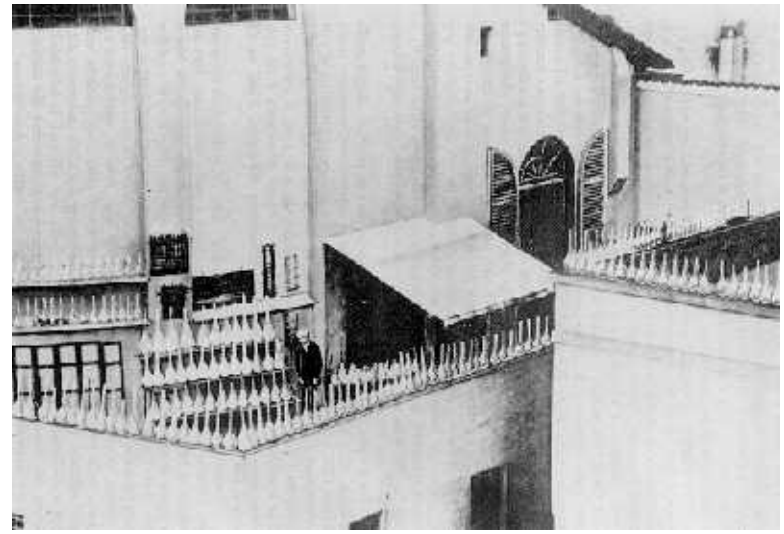


P. de Mayo

N. J. Turro

Giacomo Ciamician

1857-1922

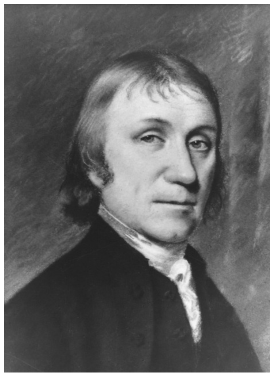


"On the arid lands there will spring up industrial colonies without smoke and without smokestacks, forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the 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."

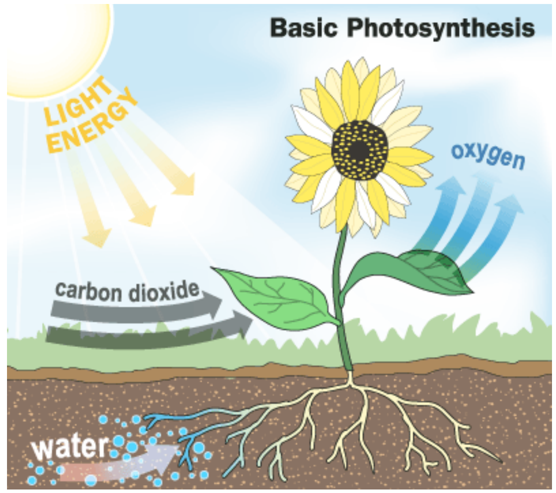
(Giacomo Ciamician *Science* **1912**, *36*, 385.)

Photosynthesis and Solar Energy

The Nobel Prize in Chemistry 1961



Joseph Priestley
1733–1804



M. Calvin
1911-1997

The Nobel Prize in Chemistry 1988

J. Deisenhofer

R. Huber

H. Michel

The Nobel Prize in Chemistry 1992

R. Marcus

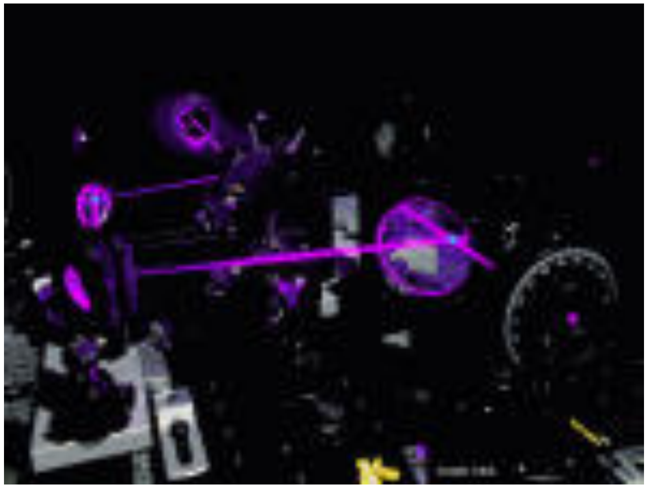
Nobels in Photochemistry

Development of Flash Photolysis and Femtosecond Chemistry

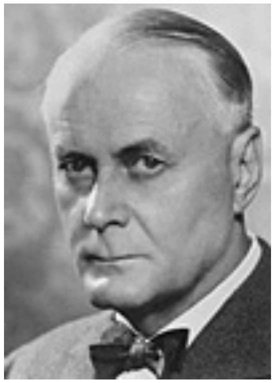

Norrish


Porter


Zewail

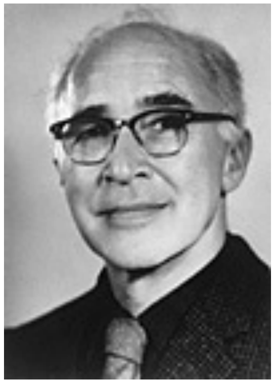


The Nobel Prize in Physiology or Medicine 1967



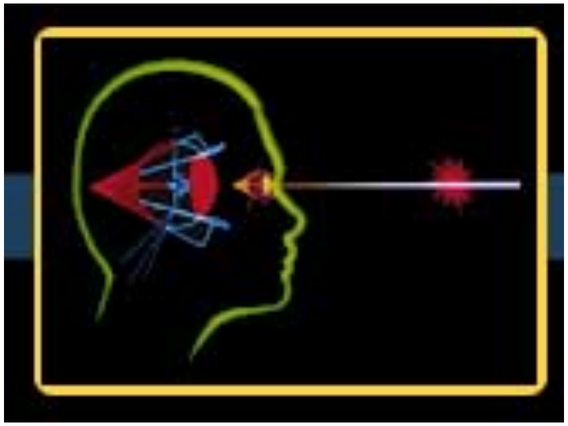
Ragnar Granit

Haldan Keffer Hartline

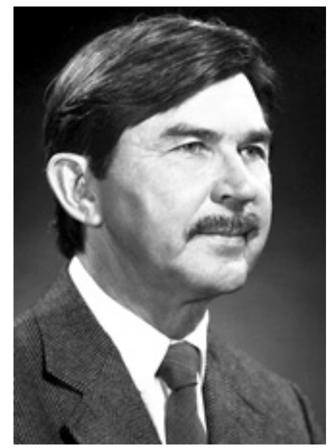


George Wald

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



The Nobel Prize in Chemistry 1992

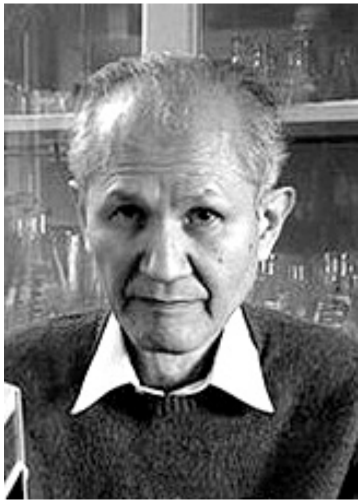


The Nobel Prize in Chemistry 1983 was awarded to Henry Taube "for his work on the mechanisms of electron transfer reactions, especially in metal complexes".

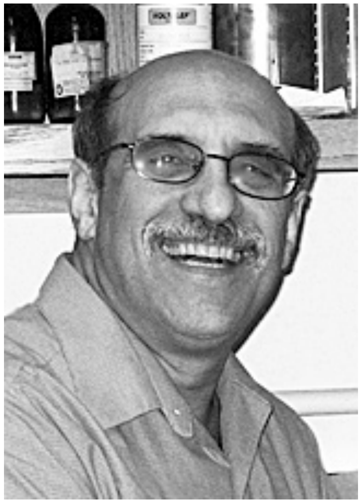
The Nobel Prize in Chemistry 1992 was awarded to Rudolph A. Marcus "for his contributions to the theory of electron transfer reactions in chemical systems".

The Nobel Prize in Chemistry 2008

"for the discovery and development of the green fluorescent protein, GFP"

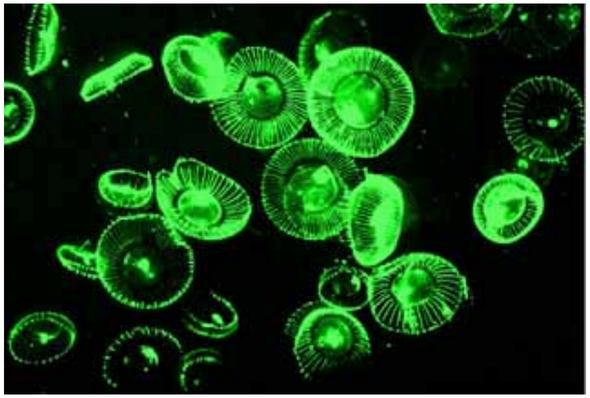


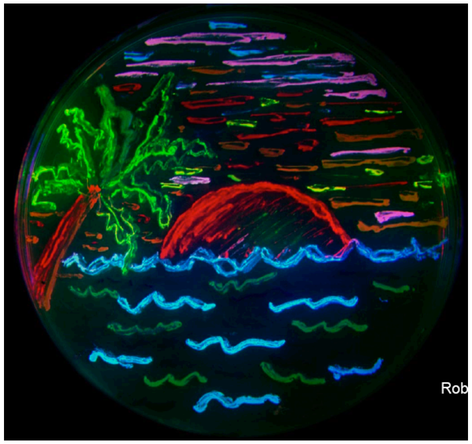
Osamu Shimomura



Martin Chalfie

Roger Y. Tsien





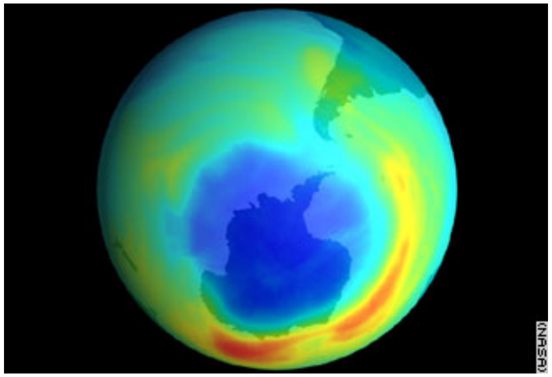
The Nobel Prize in Chemistry 1995

Paul J. Crutzen

Mario J. Molina

F. Sherwood Rowland

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



The Antarctic ozone hole is recorded at approximately 10.5 million square miles on September 19, 1998. This image shows when chlorine and bromine from human-produced compounds started to contribute to large annual losses of ozone.