Primary Photochemistry of Photosynthesis

A perspective in honor of Vlad Shuvalov

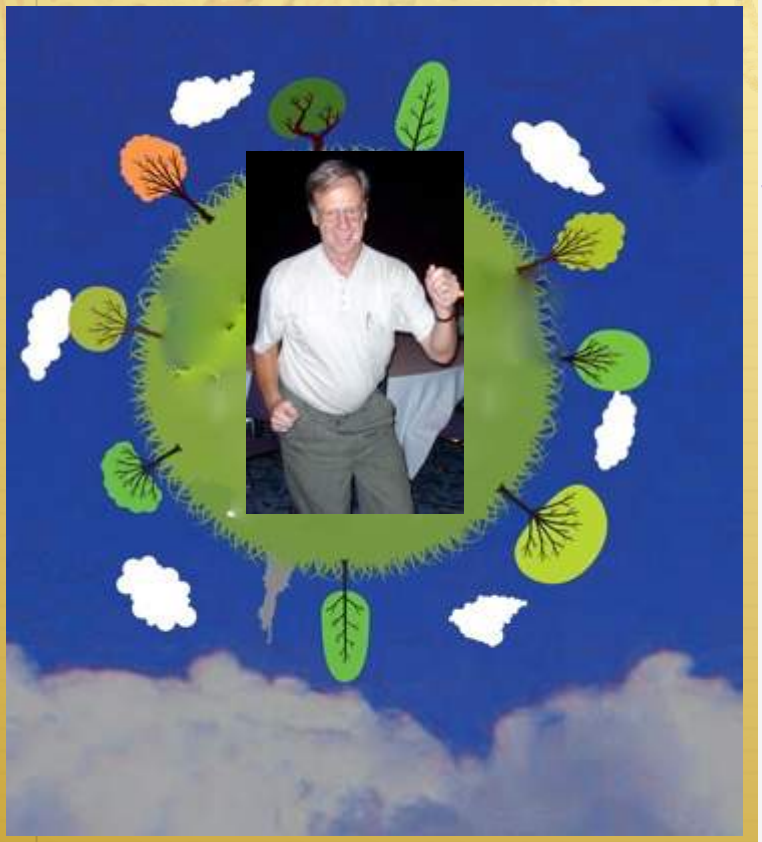
by

Govindjee

University of Illinois at Urbana, Illinois, USA

E-mail: gov@illinois.edu

URL: http://www.life.illinois.edu/govindjee



Владимир А. Шувалов мужчина на ходу ...

Мы чтим его сегодня, а не потому, что он 70, а потому, что он знает, что такое жизнь.

И, как растения, водоросли и фотосинтезирующие бактерии преобразовать все обильные солнечную энергию в энергию, что полномочия его танцевать.

щ

Что еще мы хотим!

Продолжайте, Владимир, и научить нас о жизни.

И, как вы сделали все это возможным.

(Говинджи, 2014)

GCP

Vladimir A. Shuvalov is a man on the go…

We honor him today not because he is 70, but because he knows what life is all about

And how Plants , Algae and Photosynthetic Bacteria do their basic thing,

i.e., convert the all-abundant solar energy into energy that powers him to dance..

What more do we want..

Keep going, Vlad and teach us your tricks of life and how you made it all happen

Well, well.. From being a 6-year old handsome happy eager boy (1949) to a charming young man of 20, still quite happy (1963) at Moscow State University

Faculty of Biology and Soil Science,MSU

From Russia to USA: Now in his 30s.. really grinning

After his PhD in 1969 on "Studying persistence of chlorophyll in photosynthetic electron transfer"; and while he was a researcher at the Academy of Science of the USSR (1969—1979), he went to the Charles F. Kettering Lab in Yellow Springs, Ohio, to work with Bacon Ke (1978-1979) and then with Bill Parson (1980-1981), at the University of Washington, Seattle

1991: USSR State Prize Winner
1997: Russian Academy of Sciences

ПОИСК

Еженедельная всесоюзная газета

1991

КУЗНЕЦЫ ДЕФИЦИТА

КАКОЙ БЫТЬ НАУКЕ?

РАВНЫЕ БОГАМ

Publication in Russian newspaper Poisk (1991)

РОССИЙСКАЯ АКАДЕМИЯ НАУК

ДЕЙСТВИТЕЛЬНЫЙ ЧЛЕН РОССИЙСКОЙ АКАДЕМИИ НАУК (академик)

Владимир Анатольевич ШУВАЛОВ

Личная подпись

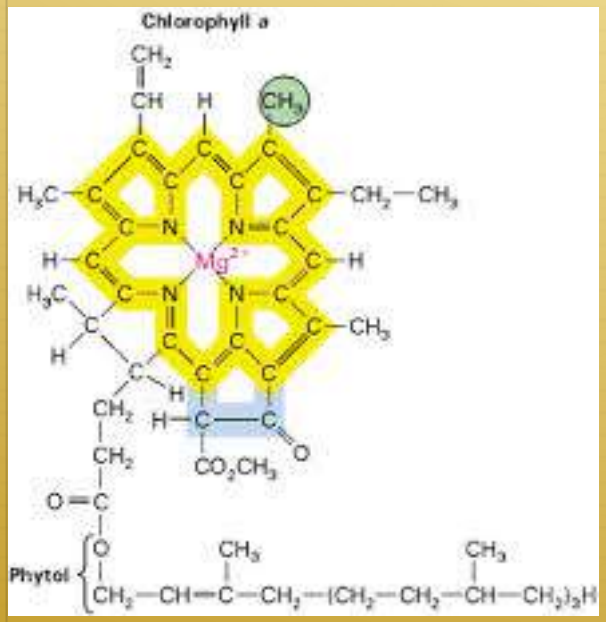
Избран 29 мая 1997 г.

№ 947

1997

OK Vlad, it was 2011:You have really won Slava agrees

Well, Vlad, your PhD was on Chlorophyll, which is the Green King that reigns our field



1. Richard Wilstätter 1872-1942; Prize in 1915; studied at Univ. of Munich)
2. Hans Fischer (1881-1945; Prize in 1930; studied at Univ. of Marburg)
3. Richard Burns Woodward (1917-1979; Prize in 1965; studied at MIT)

A Glimpse of Some of the Discoveries of Vladimir Anatoly Shuvalov

- In bRC, BPheo is an electron acceptor that precedes Q_A (Shuvalov& Klimov, 1976; cf. Dutton; and Parson, 1975)
- In BRC, BChl is an electron acceptor before BPheo (Shuvalov, Klevanik et al., 1978)
- In PSII RC, a Chl is an alternate e-acceptor to Pheo : $P^+ Chl_{D1}^-$ (Shelaev et al., 2008, 2011)
- In PSI RC, a Chl (Ao) is actually reduced within 100fs (Shelaev et al.,2010; cf. Fenton et al., 1978; Wasielewski et al., 1987))
- In bRC, $P_A^+ P_B^-$ is formed in fs (120-180 fs) within P870*

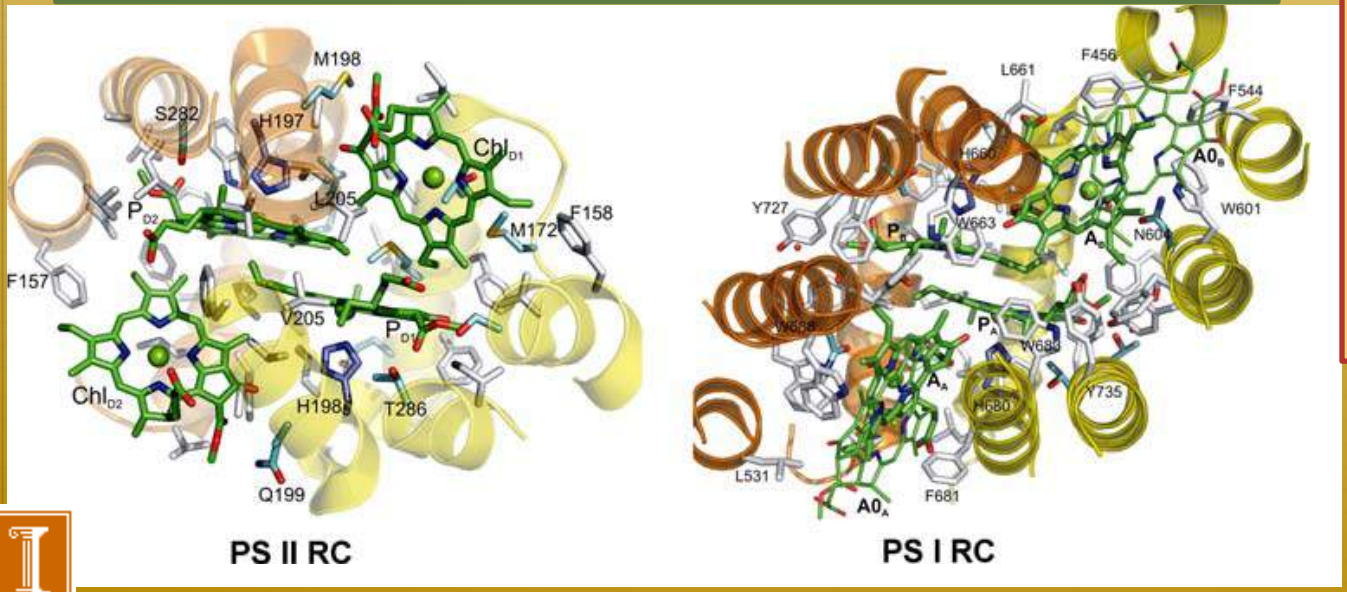
D-P-A of PSII and of PSI: Vlad really focused on all the A's; P's were done; did not want to touch D's: Chls and Pheos
Background on Chl a: Why Chl a does different things? Short answer: Redox potential; amino acid environment

Photosynth Res (2009) 99:85–98
DOI 10.1007/s11120-008-9395-x

REVIEW

A viewpoint: Why chlorophyll *a*?

Lars Olof Björn · George C. Papageorgiou · Robert E. Blankenship · Govindjee



PSII: P_{D1}; P_{D2}: His 198, His 197

PSI: A_o: Met 688; Tyr 696

Giacomo Luigi Ciamician (1912) "The Photochemistry of the Future", Science 36 (926) 385-394.

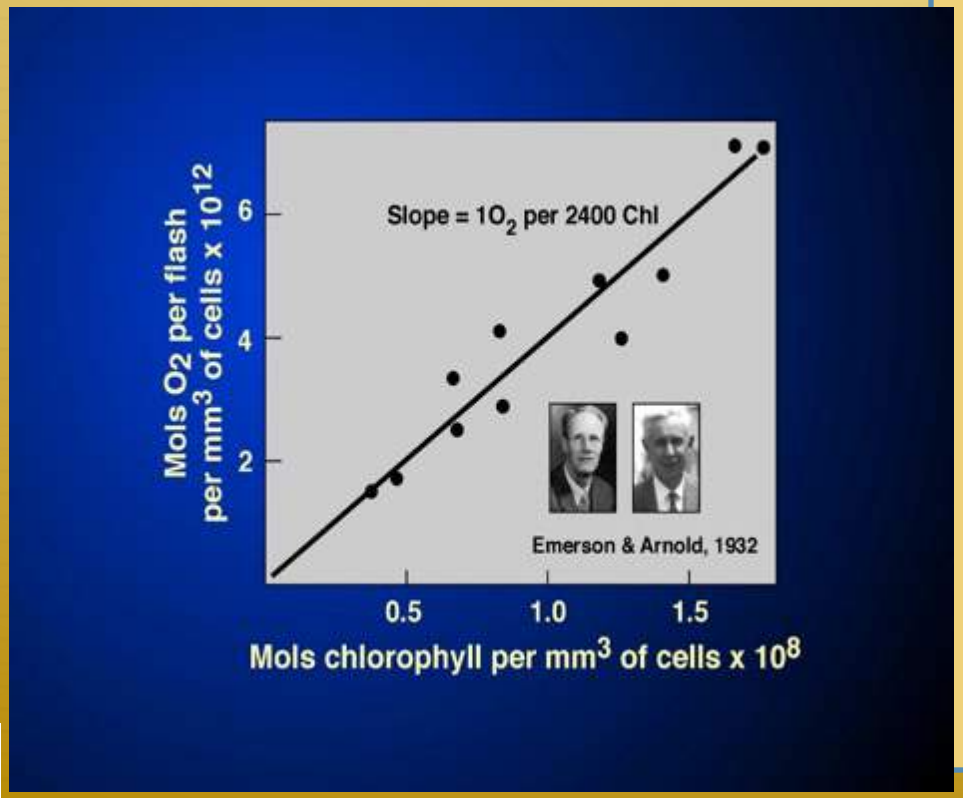
"For our purposes the fundamental problem from the technical point of view is how to fix the solar energy through suitable photochemical reactions. To do this it would be sufficient to be able to imitate the assimilating processes of plants."

To imitate it, we must understand it, and Vlad Shuvalov has provided much understanding to us ..

A bit of history before Vlad Shuvalov began his exciting experiments with top-of-the line instruments built and assembled by him and his brilliant analysis of the new data on the "Primary Photochemistry of Photosynthesis"… He will talk about them himself right after my talk

1932

The discovery of "Photosynthetic Unit" (2400 Chlorophylls per Oxygen)

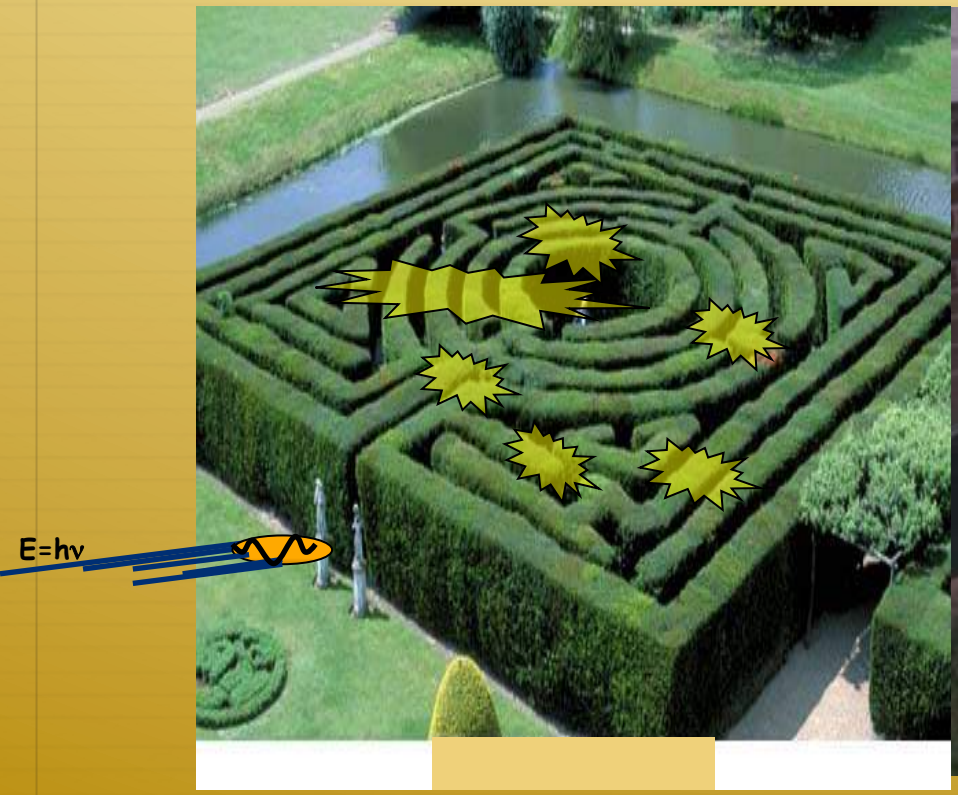


- We need only suppose that for every 2480 molecules of chlorophyll there is present in the cell one unit capable of reducing one molecule of carbon dioxide each time it is suitably activated by light"

1936

Hans Gaffron (1902-1979)

The "Concept of Excitation Energy Transfer" and a "photoenzyme"



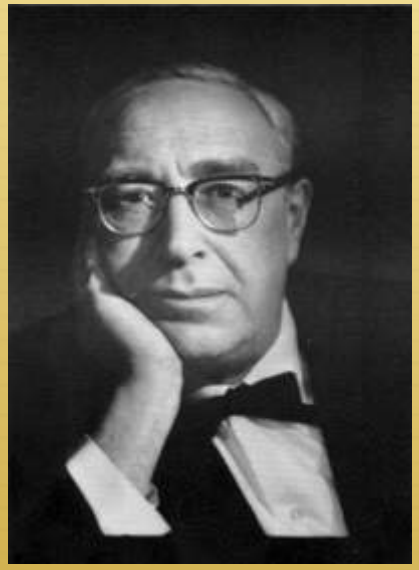
Provided by Late Bob Clegg

Hans Gaffron

Photo by Govindjee

Rabinowitch and Weiss (1936, 1937)

$$Chl + Fe^{+3} \rightarrow Chl_{ox} + Fe^{+2} \rightarrow Chl$$



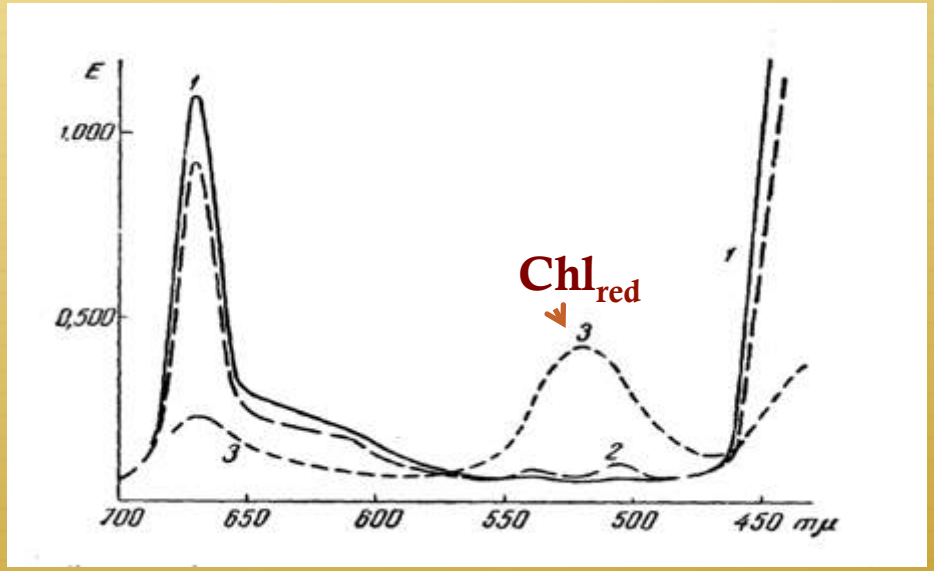
- "**Reversible Oxidation and Reduction of Chlorophyll**" by E.Rabinowitch and J. Weiss, Nature 138: 1098-1099 (1936)

- They observed reversible oxidation (and reduction) of ethyl chlorophyllide by ferric and ferrous chloride, where the oxidation was stimulated by light.

1948

$h\nu \rightarrow$ Chl + ascorbic acid $\rightarrow$ Chl_{red} $\rightarrow$ Chl

Krasnovsky



Reversible photochemical reduction of chlorophyll (Krasnovsky reaction) [from: A.A. Krasnovsky (1948) SSSR 60: 421-424]

1947-1948
Theodor Förster (of the Förster theory of Energy Transfer) with Robert (Bob) Knox

Theory: Energy transfer depends upon 3 major parameters:

- 1) $1/r^6$, where r is the distance between donor and acceptor molecules
- 2) Kappa squared, where Kappa is orientation factor
- 3) Overlap integral of emission spectrum of donor and absorption spectrum of acceptor molecule

1952

Energy transfer, the trap (P) and oxidation of Chl:

PhD thesis of L.N.M. Duysens

In Duysens' 1952 thesis "On excitation energy transfer" the important reaction center concept of P870 (in vivo) for oxidation of just a few molecules of BChl (Chl) was born---and so was the

Concept of two types of Chl a's –precursor to the PSII and PSI Chl a's

The Z-Scheme

Govindjee et al. (2005)

Bessel Kok discovered P700 in 1956-1957; in 1959, he showed the two-light effect on it– and much more.. Later, the Kok-Joliot Oxygen Clock

Jack Myers (1987) Bessel Kok (1918-1979) Biograph Mem of the Natl Acad of Sci, Washington, DC, pp. 125-147

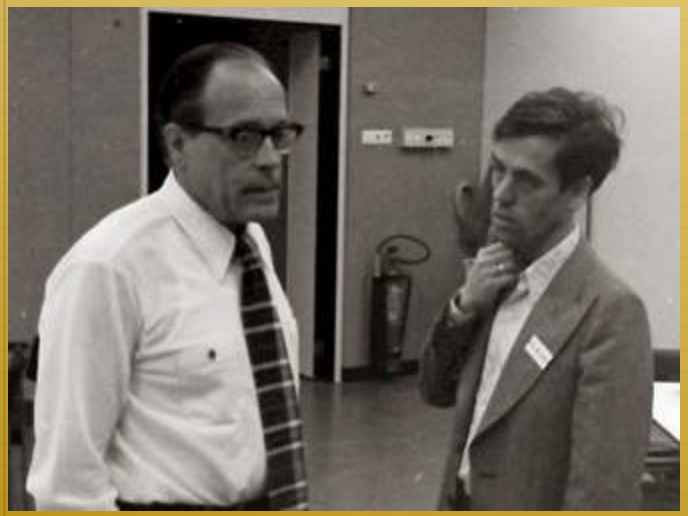


Photo by Tiny Pulles

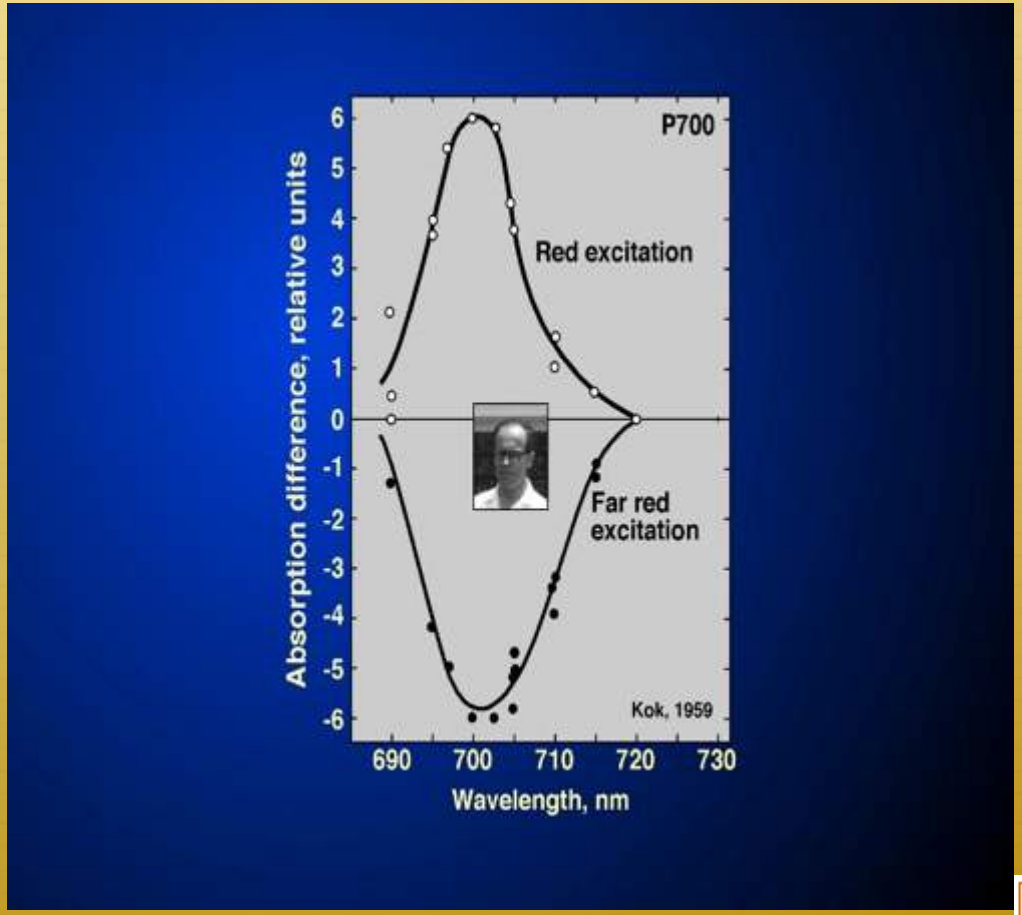


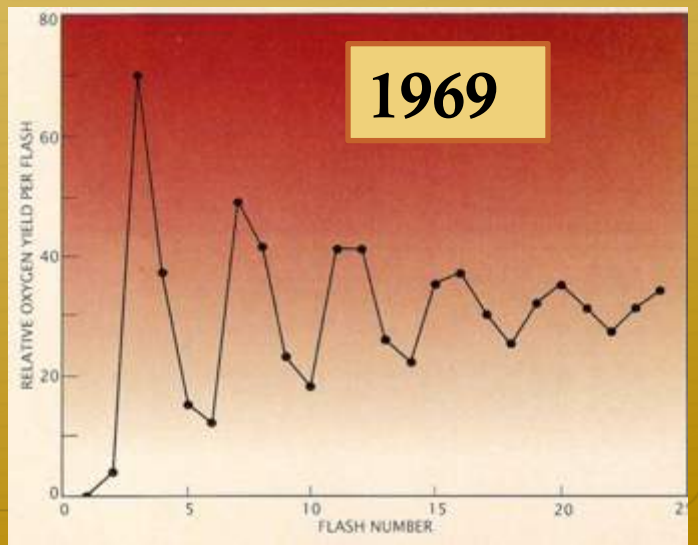
Photo: Courtesy of Tiny Pulles

Pierre Joliot

- Discoverer of the Oxygen Clock in Photosynthesis

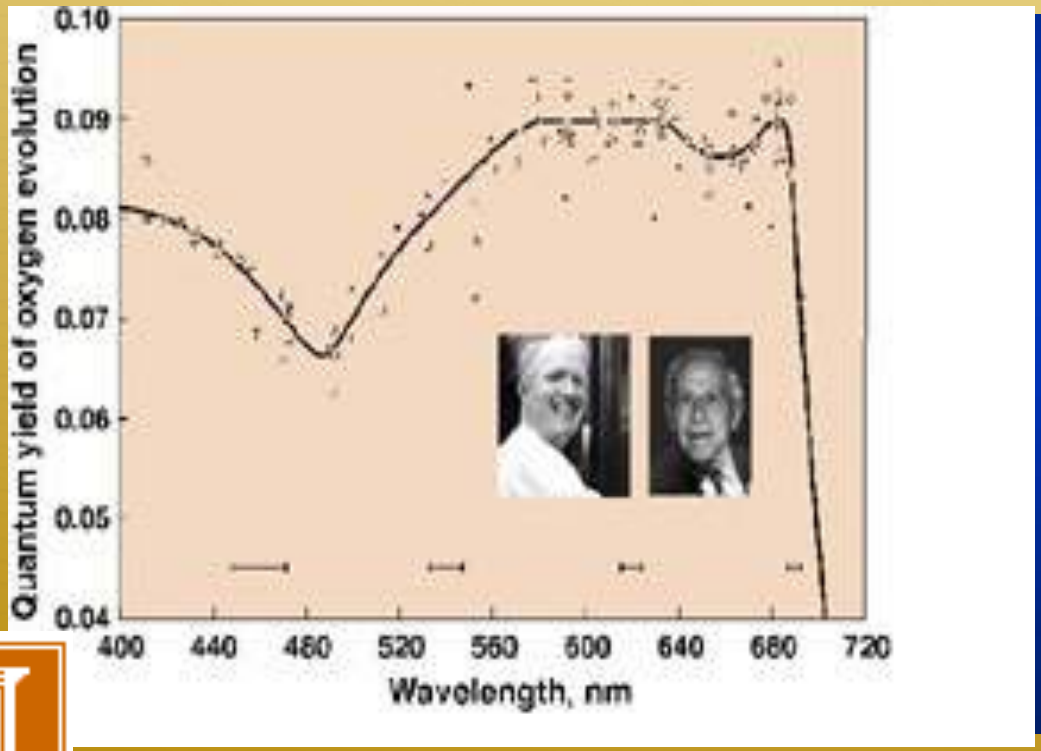
P. Joliot (2003) Period-four oscillations of the flash-induced oxygen formation in Photosynthesis. *Photosynthesis Research* 76: 65–72

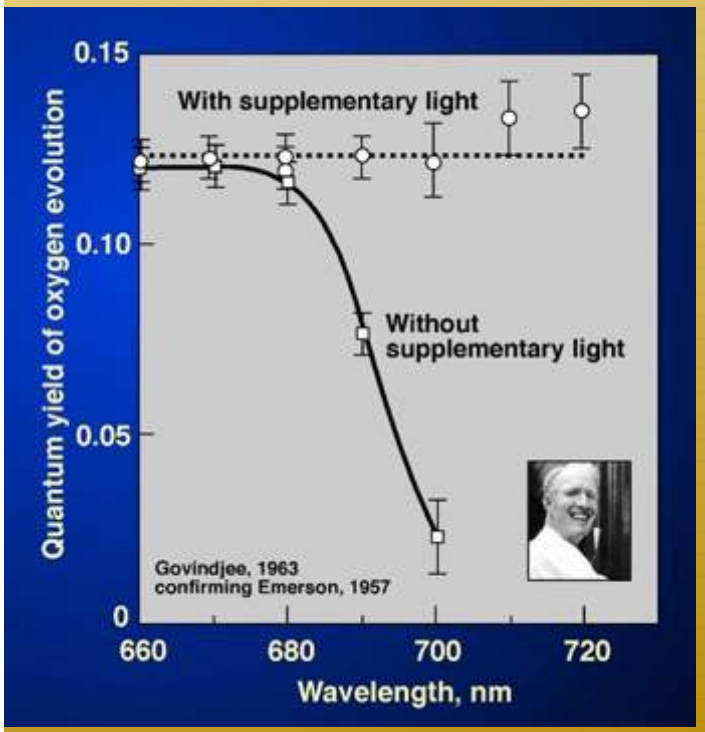
Source of figure:
Govindjee and W.J. Coleman (1990)
How Plants Make Oxygen.
Scientific American 262: 50-58



1943; 1957

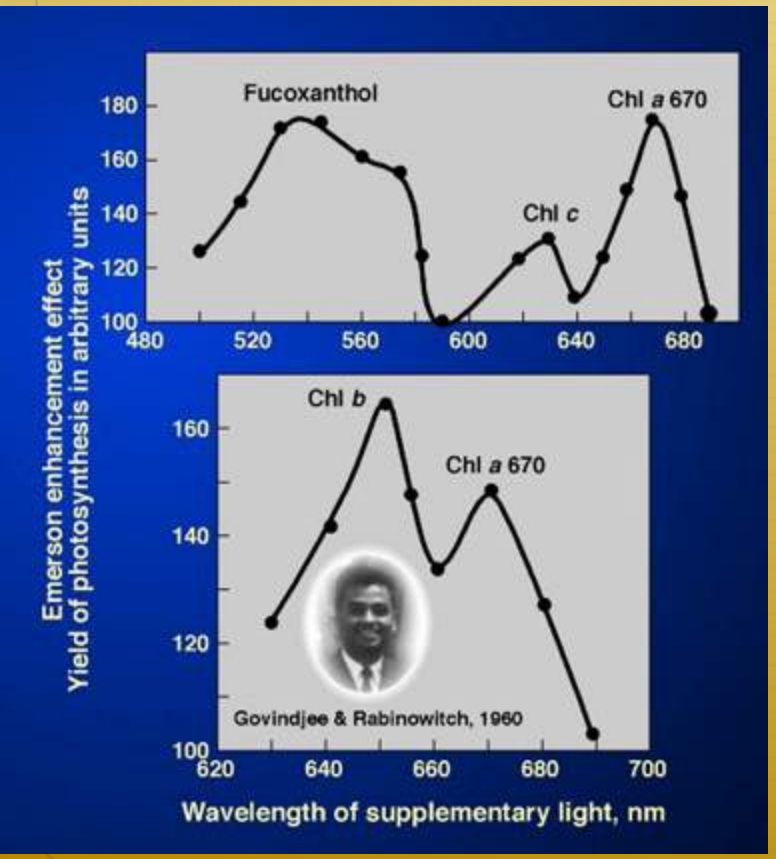
The Red Drop; and the Emerson Enhancement Effect: Two Light Reaction and Two Pigment System Concept

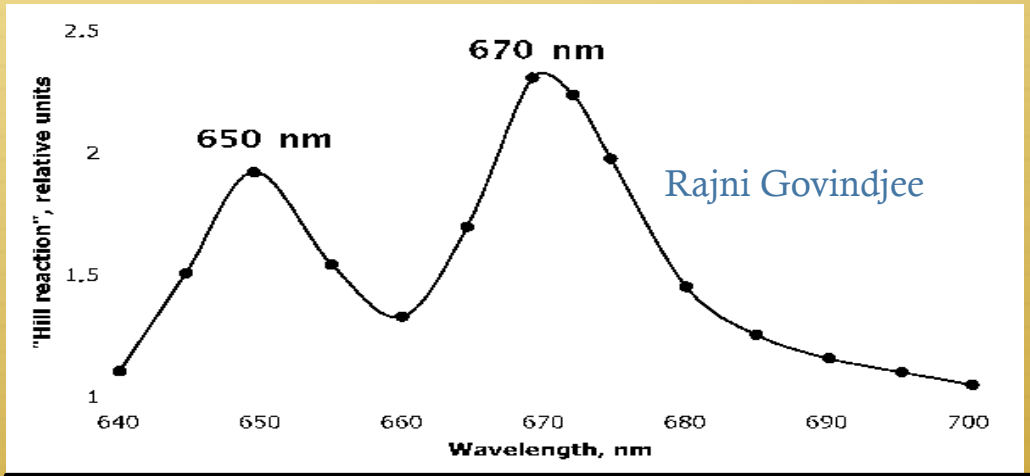




1960

Govindjee and Rajni look back at their experiments done 54 years ago..

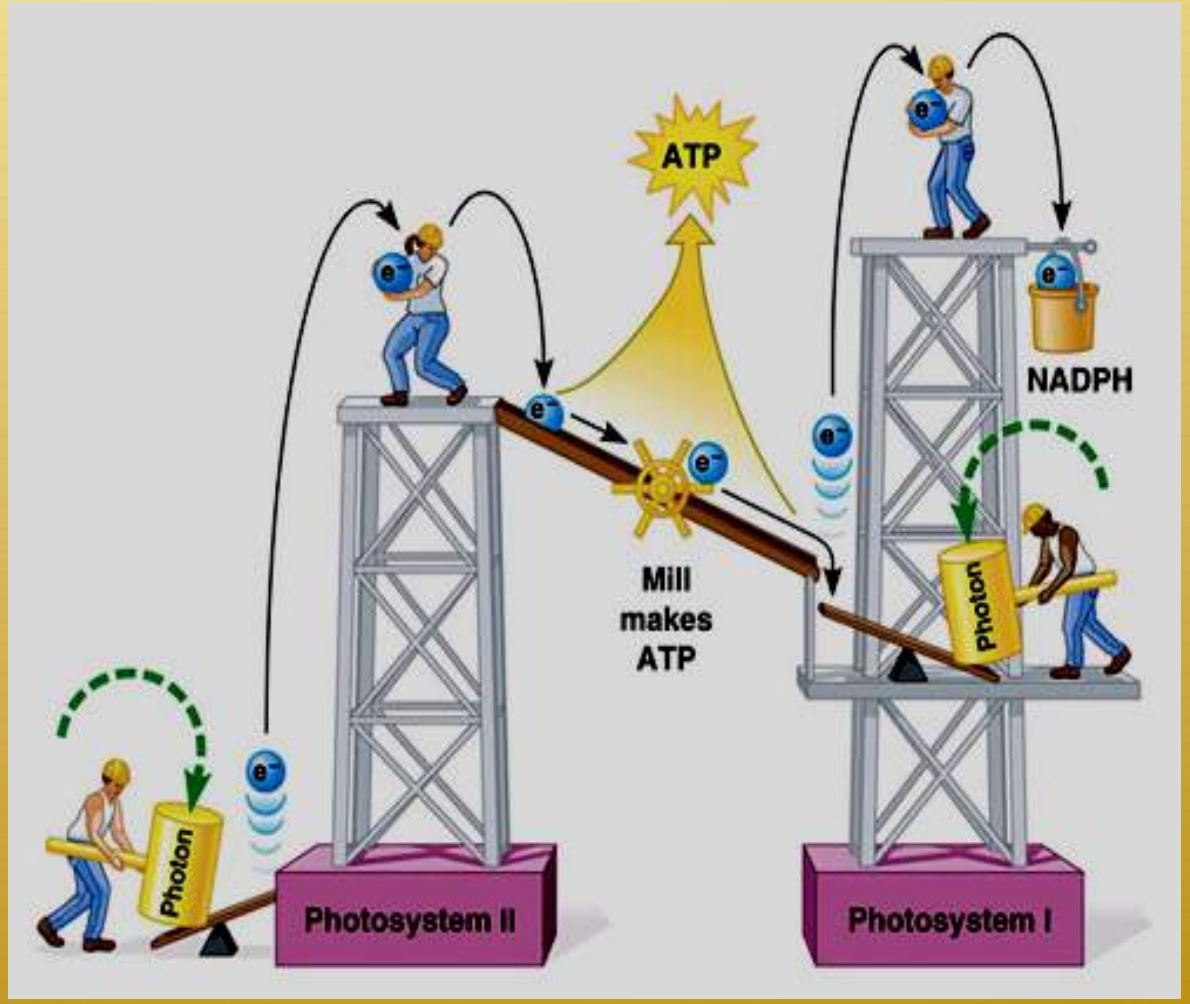




A short wavelength absorbing form of chlorophyll a (Chl a 670) is present in the system that has chlorophyll *b*.
And the effect is not on respiration as Larry Blinks had said!

In 1960-- "the Z" Scheme was invented by Robin Hill and Fay Bendall

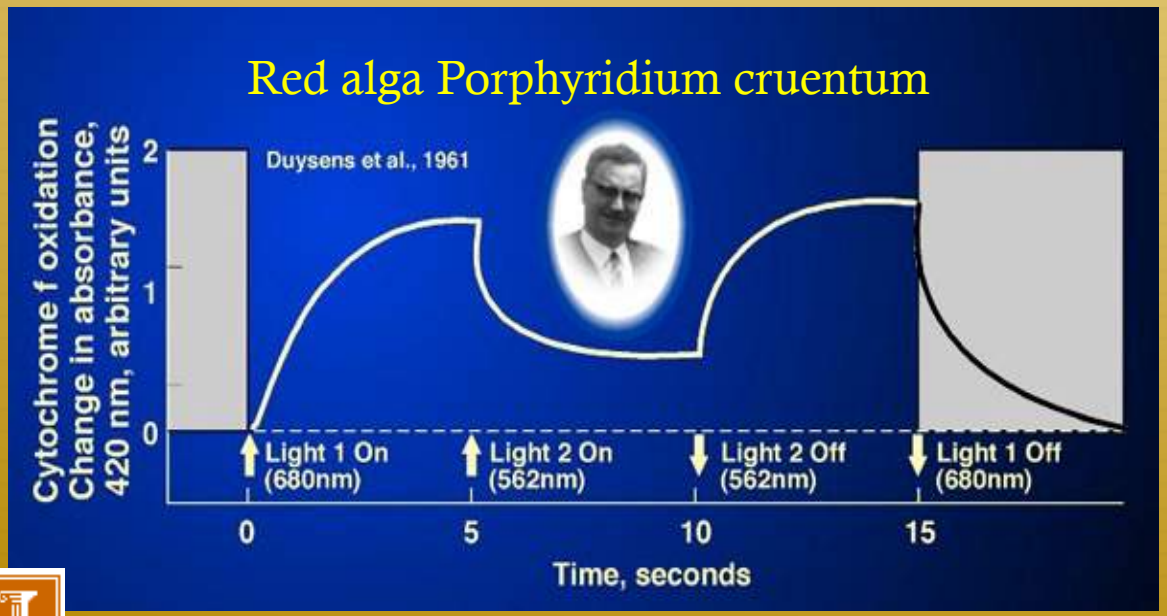
R.C. Prince (1992) "Robert Hill, FRS; his published work". Photosynth Res 34: 329-332

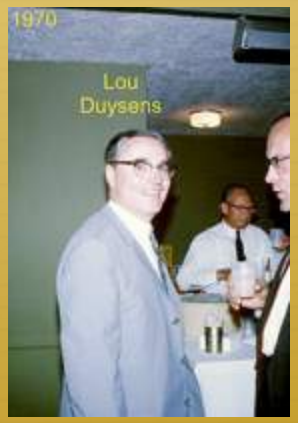


Louis N. M. Duysens et al. (1961) and Duysens and Amesz (1962) were responsible for the names of the photosystems we use today

Light 1 (red light) oxidizes cytochrome f (called Light Reaction 1 and its Photosystem, PS 1) ; whereas, Light 2 (green light) reduces it (called Light Reaction 2, and its photosystem, PS 2).

This push-pull antagonistic effect on a redox intermediate is the crux of the Z-Scheme.





1977: Discovery of pheophytin as PSII acceptor

V.V. Klimov, A.V. Klevanik, V.A. Shuvalov and A.A. Krasnovsky (1977) Reduction of pheophytin in the primary light reaction of Photosystem II. FEBS Lett 82: 183-186 ; they discovered that membrane fragments enriched in PSII showed photoreduction of pheophytin coupled to photooxidation of Chl.

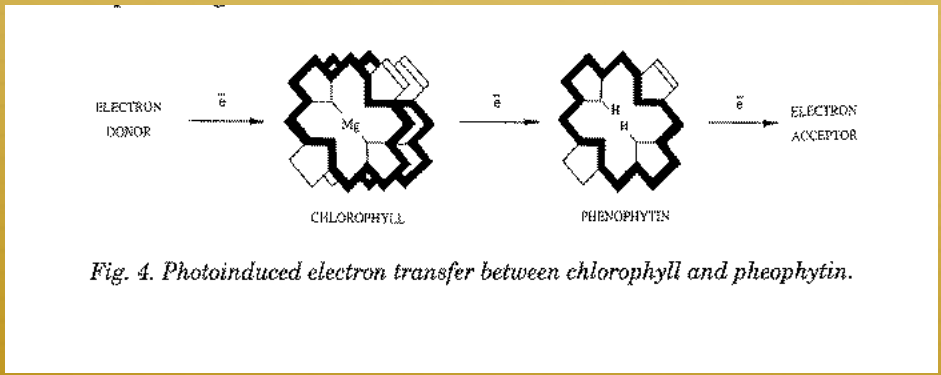
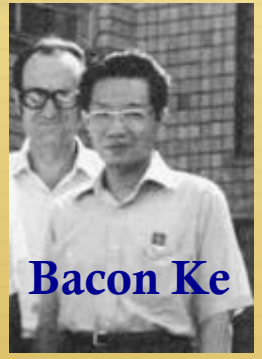


Fig. 4. Photoinduced electron transfer between chlorophyll and pheophytin.

1979: Kinetic and Spectral Properties of A_1 in Photosystem I



Bacon Ke

Volume 100, number 1 FEBS LETTERS April 1979

KINETIC AND SPECTRAL PROPERTIES OF THE INTERMEDIARY ELECTRON ACCEPTOR A_1 IN PHOTOSYSTEM I

Subnanosecond spectroscopy

V. A. SHUVALOV+, Bacon KE* and Ed DOLAN
Charles F. Kettering Research Laboratory, Yellow Springs, OH 4538

Received 26 January 1979

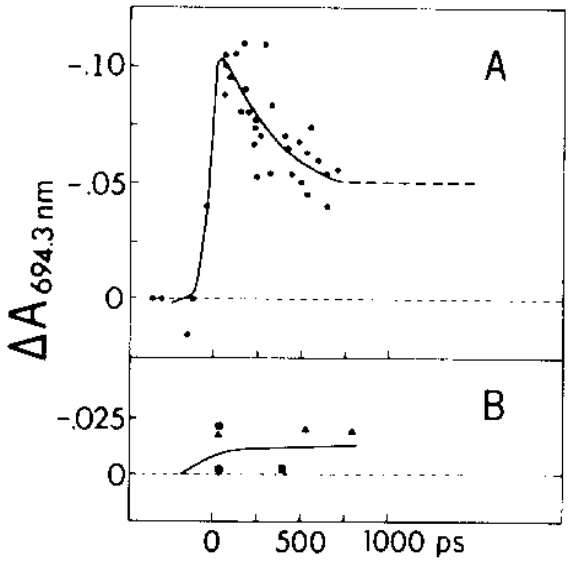


Fig.2. Kinetics of $\Delta A_{694.3}$ in TSF
694.3 nm pulses (50–60 ps dur
of 1 mJ/cm²) at 20°C. Each poi
average of 10–20 measurement

PSI prep (Chl/P700=26), TSF1(Triton)

prep. Wavelength,694 nm; 1mJ; 50-60 ps pulse

Result: Decrease in absorption at ~700 nm :A1 was reduced in <60ps; next step 200ps

1989

Primary Photochemistry: Conversion of light energy into chemical energy occurs in picoseconds: Our very first measurements(Proc Natl Acad Sci, 86: 524-528)

$P680^+$ (oxidized form of reaction center chlorophyll) is formed within 3 picoseconds and excited state of chlorophyll disappears simultaneously with a half-time of 3 picoseconds (Wasielewski et al., 1989)

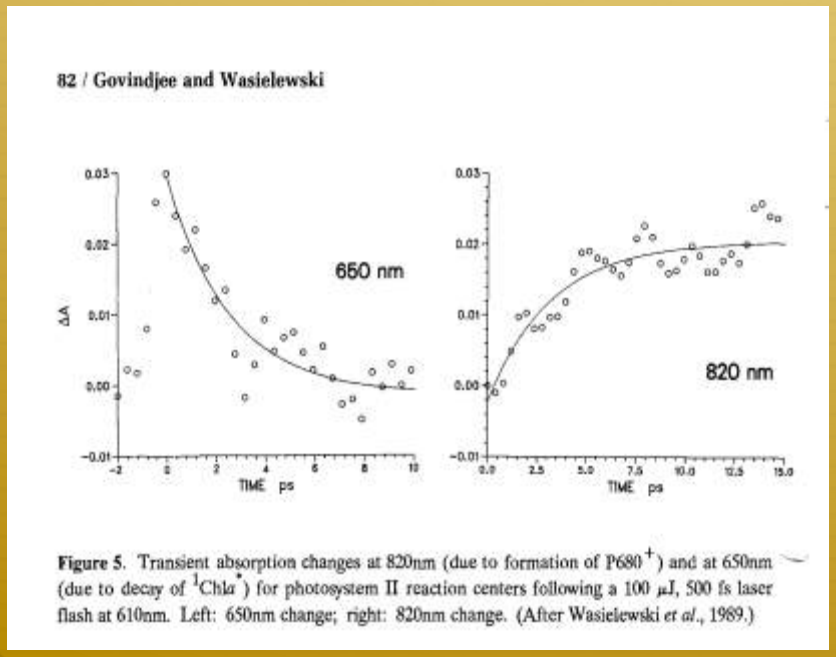


Figure 5. Transient absorption changes at 820nm (due to formation of $P680^+$) and at 650nm (due to decay of $^1Chla^*$) for photosystem II reaction centers following a 100 μJ, 500 fs laser flash at 610nm. Left: 650nm change; right: 820nm change. (After Wasielewski *et al.*, 1989.)

Mike Wasielewski's 60th birthday

Photosynth Res (2008) 98:95–103
DOI 10.1007/s11120-008-9371-5

REGULAR PAPER

Primary light-energy conversion in tetrameric chlorophyll structure of photosystem II and bacterial reaction centers: II. Femto- and picosecond charge separation in PSII D1/D2/Cyt b559 complex

I. V. Shelaev · F. E. Gostev · V. A. Nadtochenko · A. Ya. Shkuropatov · A. A. Zabelin · M. D. Mamedov · A. Yu. Semenov · O. M. Sarkisov · V. A. Shuvalov

Biochimica et Biophysica Acta 1797 (2010) 1410–1420

Contents lists available at ScienceDirect

Biochimica et Biophysica Acta

journal homepage: www.elsevier.com/locate/bbabio

Femtosecond primary charge separation in *Synechocystis* sp. PCC 6803 photosystem I

Ivan V. Shelaev [a,c], Fedor E. Gostev [a], Mahir D. Mamedov [b], Oleg M. Sarkisov [a], Victor A. Nadtochenko [a,c,*], Vladimir A. Shuvalov [b,*], Alexey Yu. Semenov [b,*]

[a] N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

Shelaev et al. (2008,2010)

PSII (2008)
20 fs flashes
In 0.9 ps
$P680^+$ Chl^-_{D1}
is formed, and in 14 ps,
$P680^+$ $Pheo^-_{D1}$
is formed

PSI (2010)
20 fs flashes
< 100fs
$P700^+$ Ao^-
is formed; in 5 ps, Chl^* transfers its energy to P700, and in 25 ps, $P700^+$ Ao A_1^- is formed

2011
77K : 0.9 ps for charge separation in PSII
[Shelaev et al.: The title tells the story]

Journal of Photochemistry and Photobiology B: Biology 104 (2011) 44–50

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

P_{680} ($P_{D1}P_{D2}$) and Chl_{D1} as alternative electron donors in photosystem II core complexes and isolated reaction centers

I.V. Shelaev [a], F.E. Gostev [a], M.I. Vishnev [b], A.Ya. Shkuropatov [b], V.V. Ptushenko [c], M.D. Mamedov [c], O.M. Sarkisov [a], V.A. Nadtochenko [a], A.Yu. Semenov [c], V.A. Shuvalov [b,*]

[a] N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russia

A Global Scale Challenge for Science

"…if our black and nervous civilization, based on coal and oil, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness."

"…to fix the solar energy through suitable photochemical reactions with new compounds that master the photochemical processes that hitherto have been the guarded secret of the plants"

1912
Ciamician, *Science*

100 years later: Najafpour, M. M.; Shen, J-R.; Barber, J.; Moore, G. F.; Govindjee Running on Sun. *Chemistry World* **2012,** November, 43.

The Sun, the tree, the flower and the birds by my granddaughter Sunita Christiansen; she is now an undergraduate student at Cornell University

The End

Thank you Vlad for all your discoveries and contributions
And for teaching us how to live and dance!

Thank you Suleyman for being a wonderful friend and for inviting me here even though I am retired and do really nothing except e-mail

הַלְלוּיָהּ
halləlûyāh
ἀλληλούϊα