

ФОТОНИКА И БИОФОТОНИКА МОЛЕКУЛЯРНОГО КИСЛОРОДА

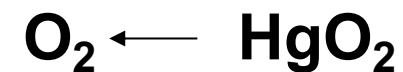
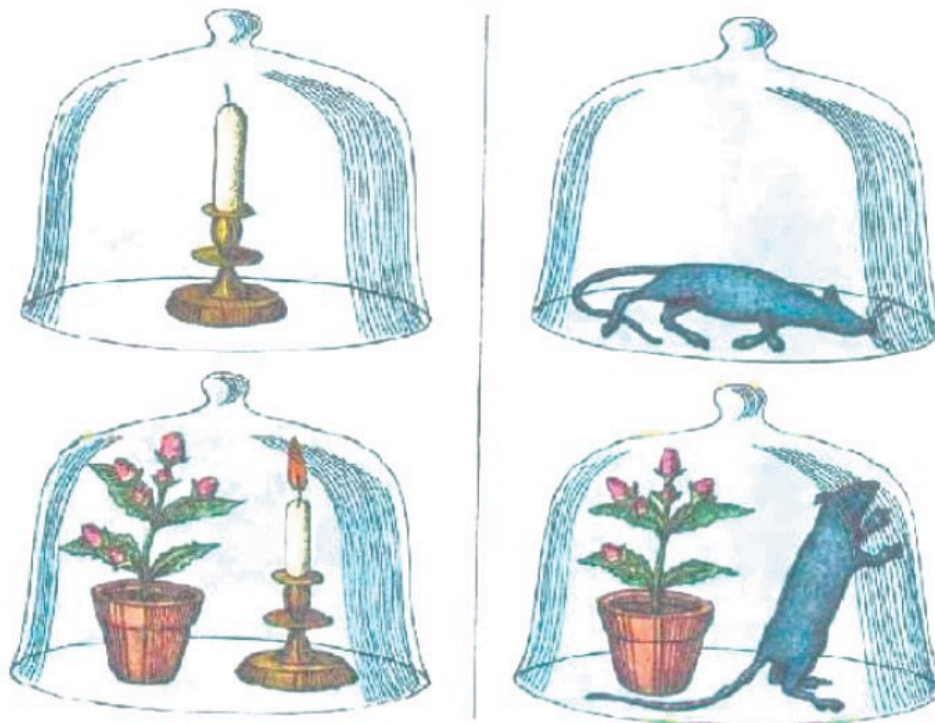
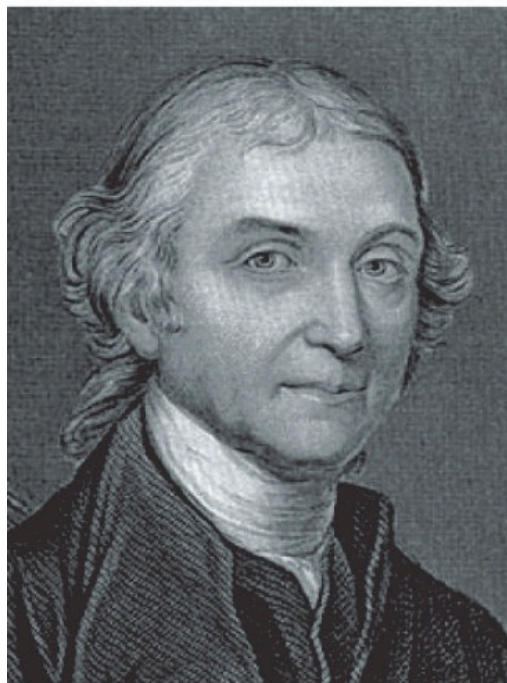
А.А. Красновский

ФИЦ биотехнологии РАН, Москва, Ленинский проспект, 33;

phoal@mail.ru

Жозеф Пристли, министр английского правительства, химик и философ обнаружил что растения очищают воздух, который испорчен горением свечи или дыханием мыши, однако он не заметил, что очищение воздуха происходит лишь при действии света на растения

Опыт Пристли



Priestley J. (1772) Observations on different kinds of air. Phil. Trans. R. Soc. London 62:147-264

Пристли был избран почетным членом Российской Академии Наук в 1781 г.

В 1779, Jan Ingen-Housz показал, что для исправления воздуха, испорченного горящей свечой или дыханием животных, растениям нужен солнечный свет

Jan Ingen-Housz (Dutch physician, physiologist and chemist)



1730 - 1799

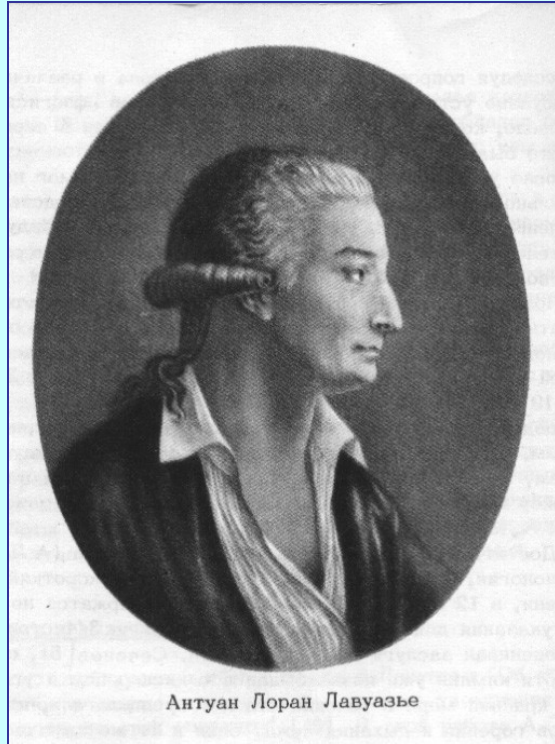
He also advanced two important ideas:

(1) Light is probably absorbed by green parts of plants (1779).

(2) Using Lavoisier judgment that fixed air is CO_2 , he proposed that fixed air is a source of carbon in plants (1796).

Ingen-Hous J. "Experiments upon Vegetables, discovering Their Great power of Purifying the common air in Sunshine and Injuring it in the Shade and at Night", Elmsly and Payne, London. 1779.

Антуан Лоран Лавуазье

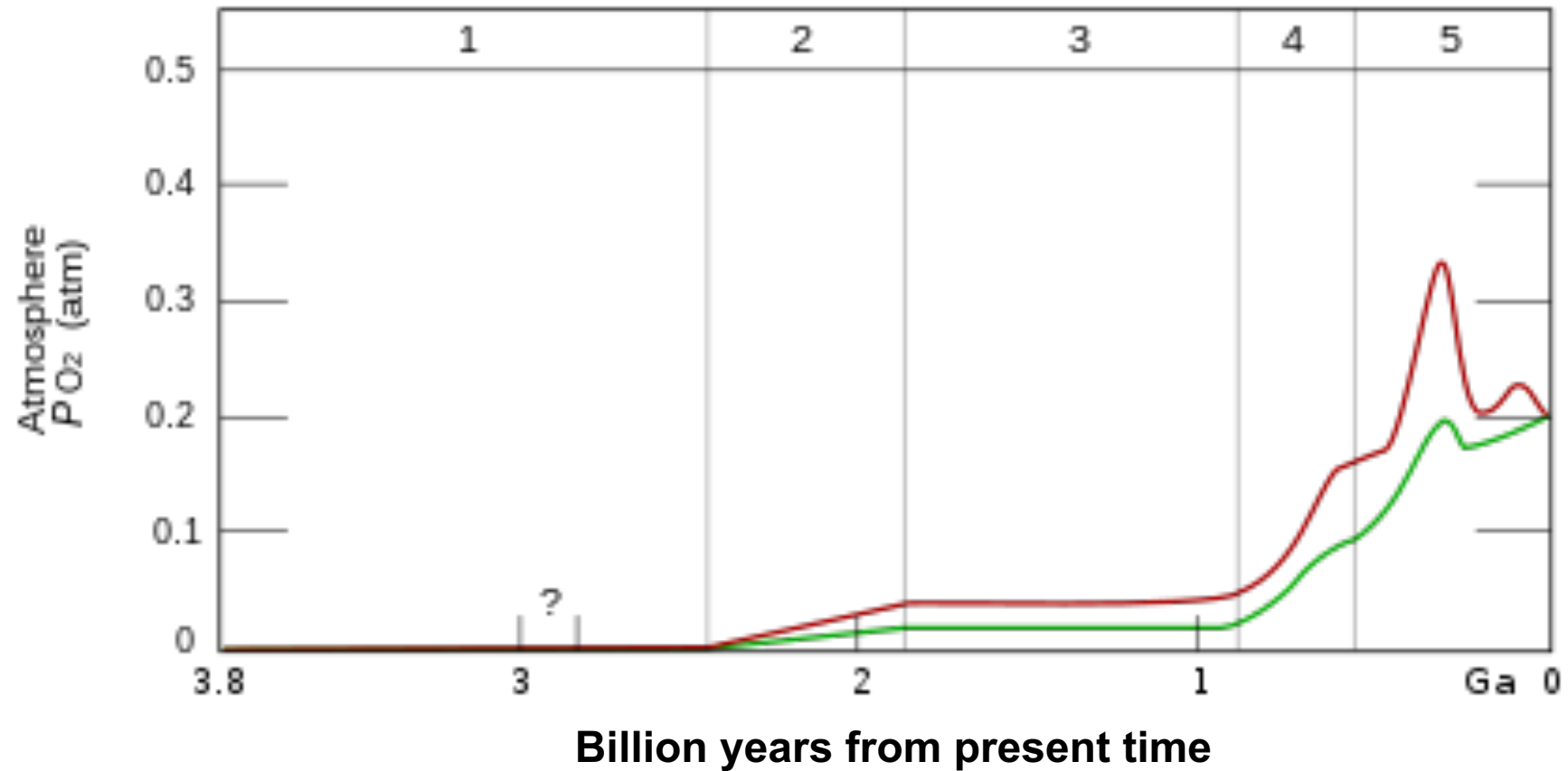


1743-1794

Показал, что все процессы горения и дыхания определяются кислородом воздуха. Термин **“oxygen”** был опубликован Лавуазье в 1785-1786 г. Смысл термина точно соответствует русскому переводу **‘кислород’**: рождающий кислоту. Ту часть воздуха, которая не участвует в дыхании, он назвал **азотом**. Газ, возникающий при горении и дыхании, он назвал **углекислым газом** и показал, что углекислый газ состоит из кислорода и углерода,

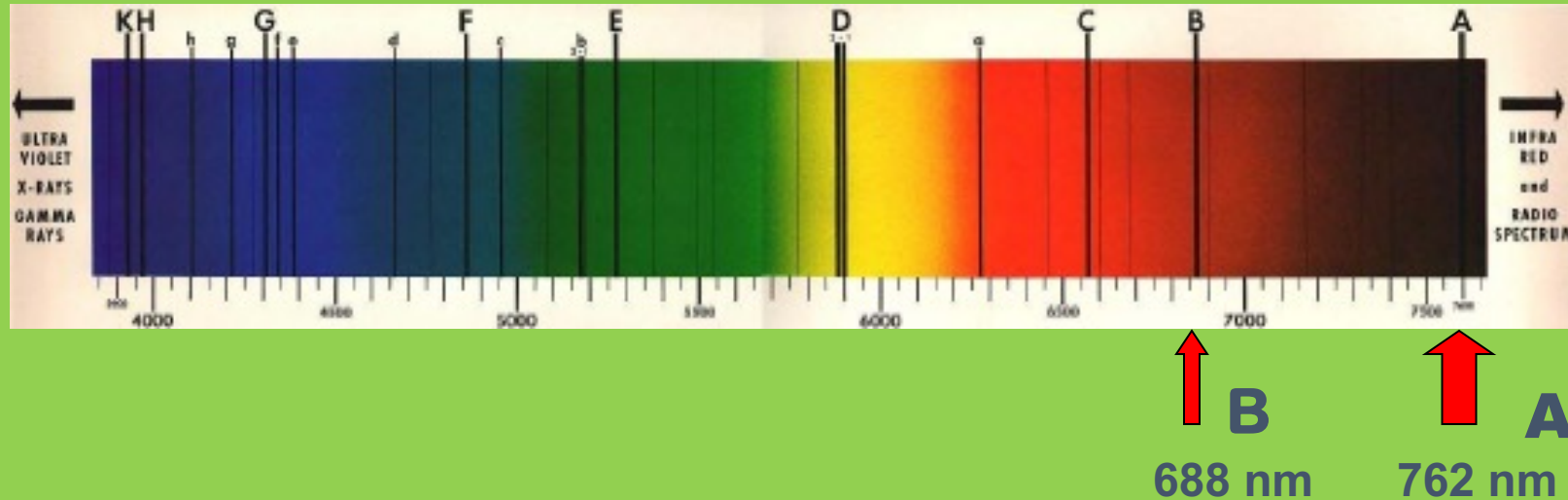
Lavoisier A.-L. Oeuvres de Lavoisier. Tome premier. Traité élémentaire de chimie. 1789.

Содержание кислорода в земной атмосфере в разные геологические эпохи



Absorption spectroscopy

Спектр солнечного излучения на поверхности Земли



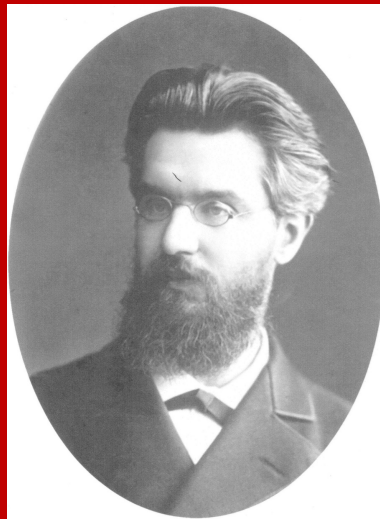
В 1801, Wollaston and в 1814, Fraunhofer обнаружили темные линии (Фраунгоферовы линии) в спектре солнечного излучения



William Hyde Wollaston, 1766-1828



Joseph von Fraunhofer, 1787-1826



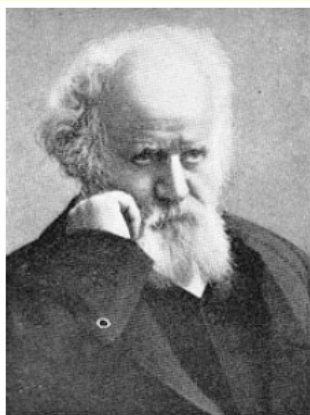
**Егоров
Николай Григорьевич
(1849-1919)**

***Журналъ Русскаго Физико-химическаго общества,
т. 17, 8А, с. 138, 1885***

“Н.Г. Егоров сообщает о результатах своих наблюдений над спектром поглощения атмосферного слоя толщиной в 3 км между Университетской астрофизической башней и Физическим кабинетом Медицинской академии в С. Петербурге. Этот слой оказался достаточным, чтобы дать в спектре электрического света волны группы А и В “.

In 1881-1885, Nikolai Egoroff (1849-1919) (Docent of the St. Petersburg University and Professor at the St. Petersburg Military Academy), using a strong projector and telescope found Fraunhofer's lines A and B (762 and 688 nm) in the absorption spectrum of the 3-10 km layer of air. Then, he observed these bands and also three additional bands at 626, 574 and 476 nm using a 60-m tube filled with oxygen pressured to 6 atm.

Egorov N.G. Compt. Rend. Acad. Sci, 101, 1143, 1885



P. Janssen
(1824-1907)



K. Olszewski
(1846-1915)

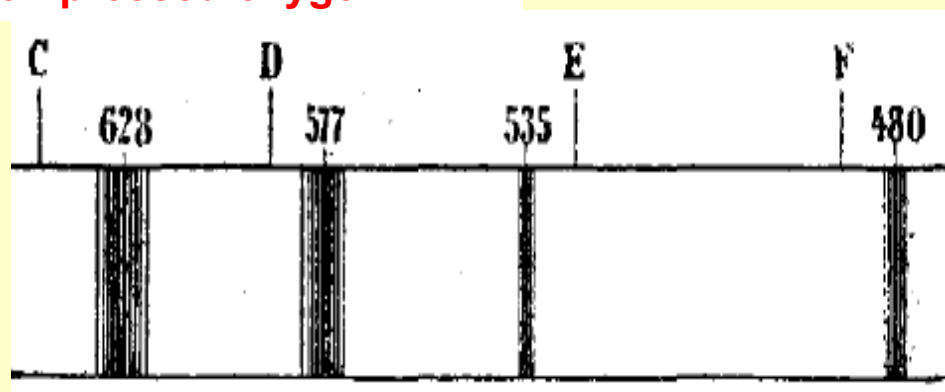


Sir J. Dewar
1842-1923

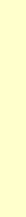
1889-1890

In 1885-1888 Janssen confirmed Egoroff's measurements with air and compressed oxygen

In 1887-1890 Olszewski found the same bands in liquid oxygen



Olszewski's spectrum of dimers (O₂)₂ in liquid oxygen



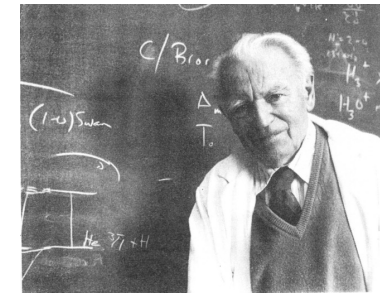
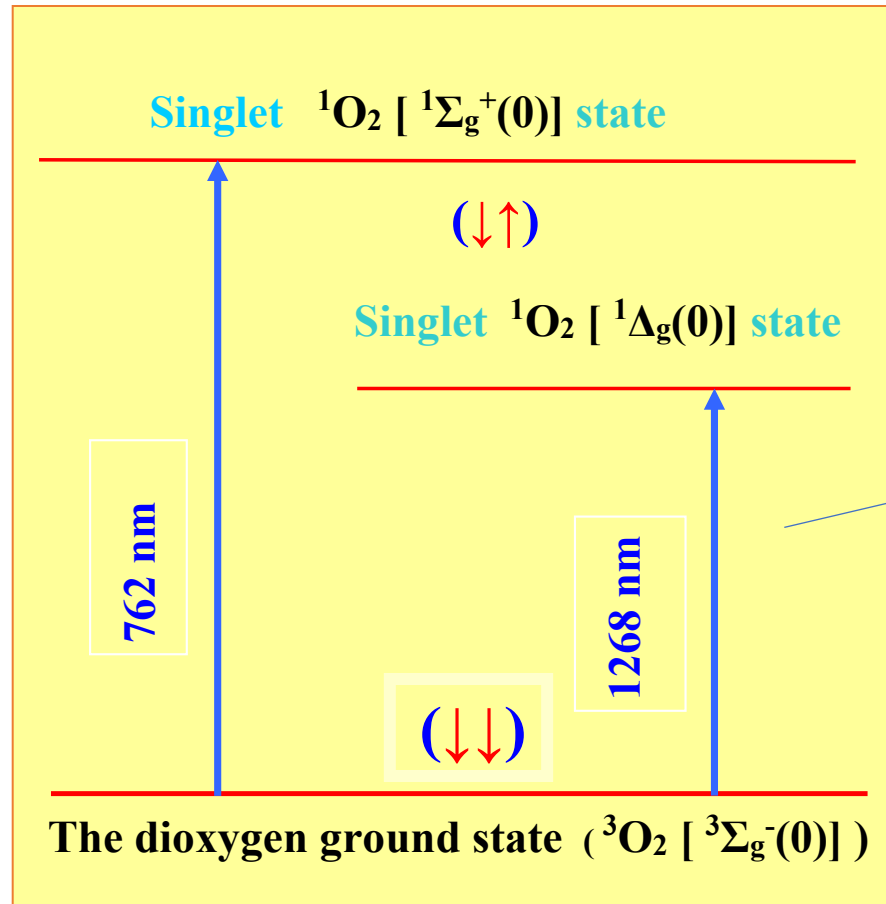
Harold Babcock
1882-1968

1927

In 1928, Mulliken applied to oxygen the molecular orbit theory and concluded that oxygen molecules have the triplet ground state and two excited singlet states of relatively low energy



Robert Sanderson Mulliken
1896-1986



Gerhard Herzberg
German and Canadian physicist
1904-1999

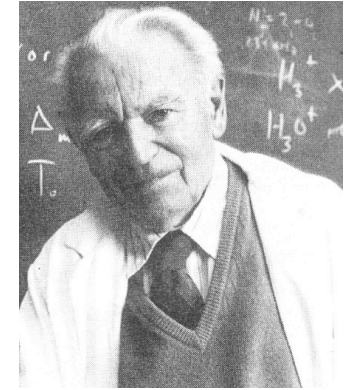
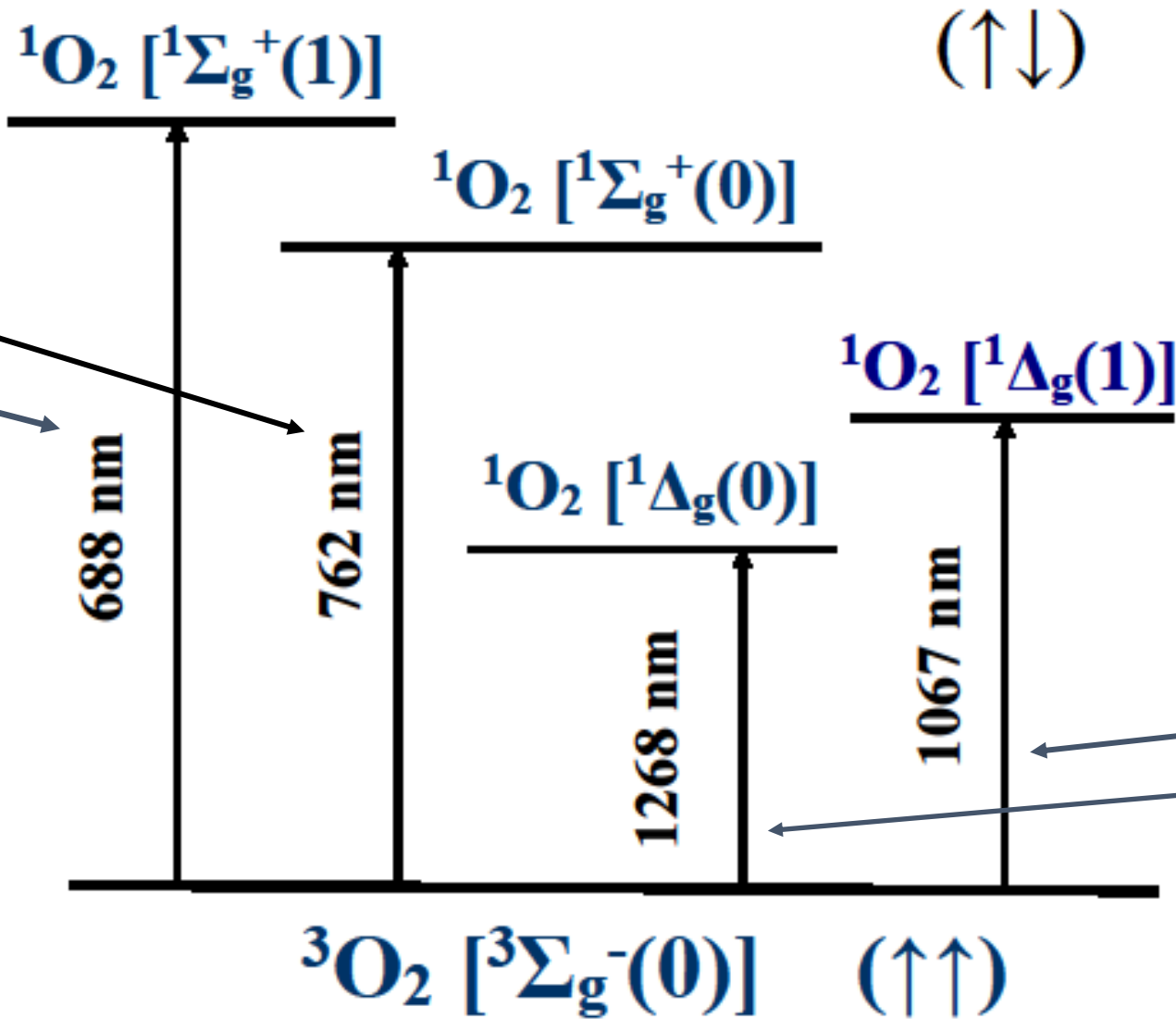
G. Herzberg. Photography of infrared solar spectrum to wavelength 12,900 A. Nature (London), 133, 759, 1934.

Mulliken. R.S. Nature, 122, № 3075, 505, 1928
Mulliken. R.S. Phys. Rev. 32, № 6, 880-887, 1928

Fraunhofer-Egoroff Lines`



Robert Sanderson Mulliken
1896-1986

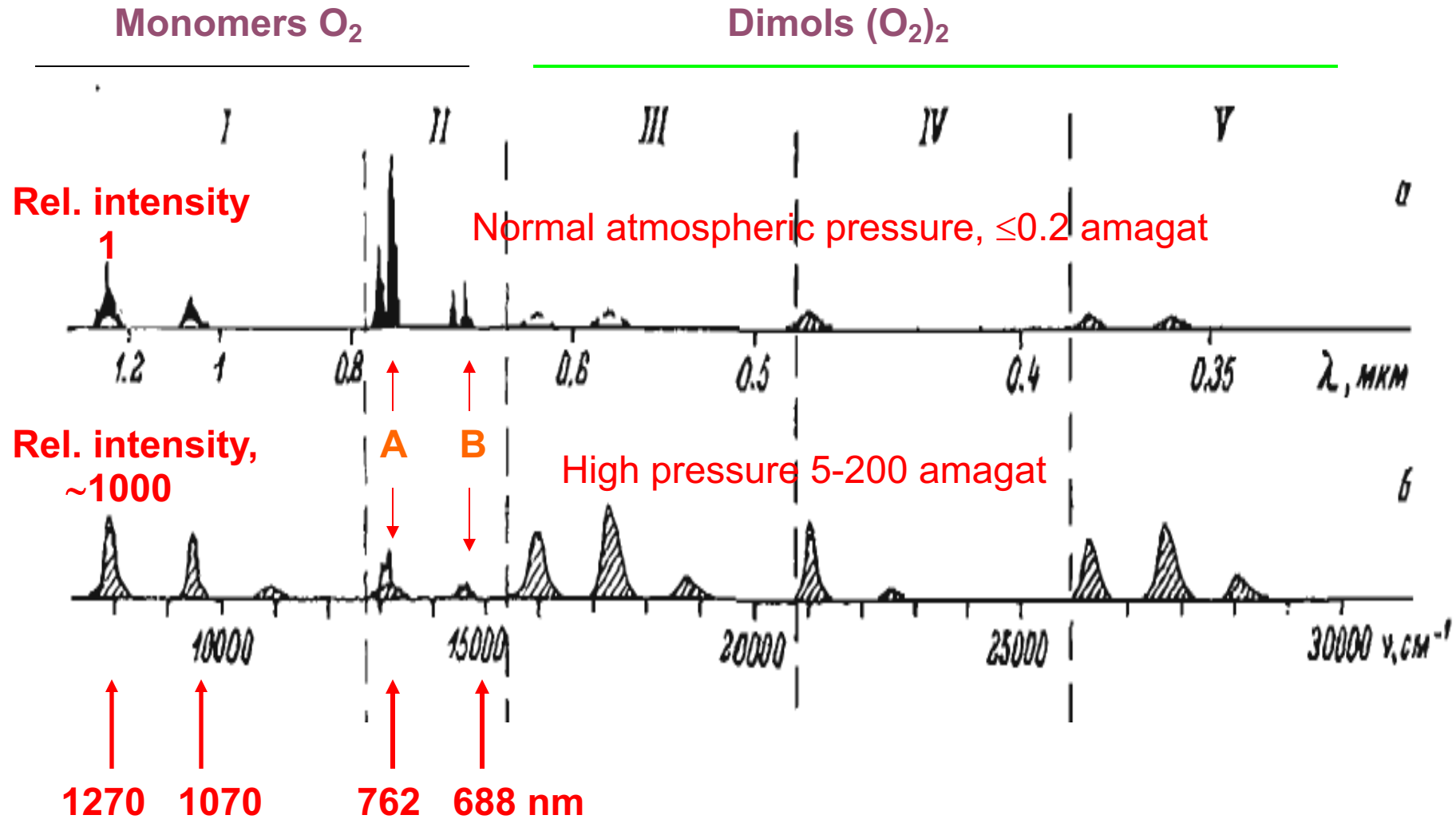


Gerhard Herzberg
1904-1999

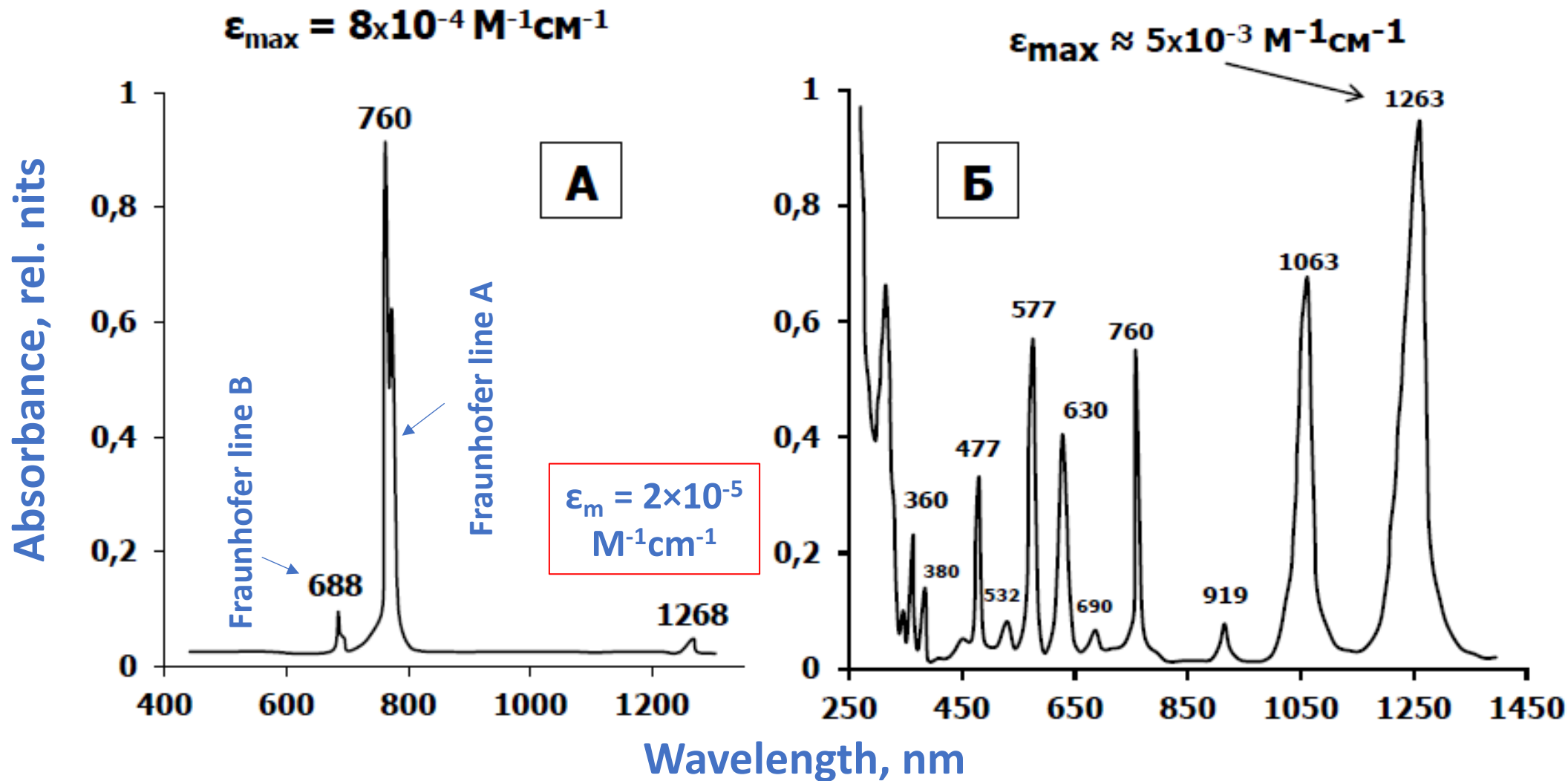
Mulliken-Herzberg lines

Vibronic transitions corresponding to the main atmospheric oxygen absorption bands

Absorption spectra of gaseous oxygen



Dianov-Klokov, Opt. Spektrosc. 20, № 6, 954-962, 1966



Absorption spectrum of oxygen in Earth Atmosphere

Absorption spectrum of compressed oxygen at 150 atm

Absorption spectrum of oxygen dissolved at high pressure (130 atm, 3.5 M) in freon 113

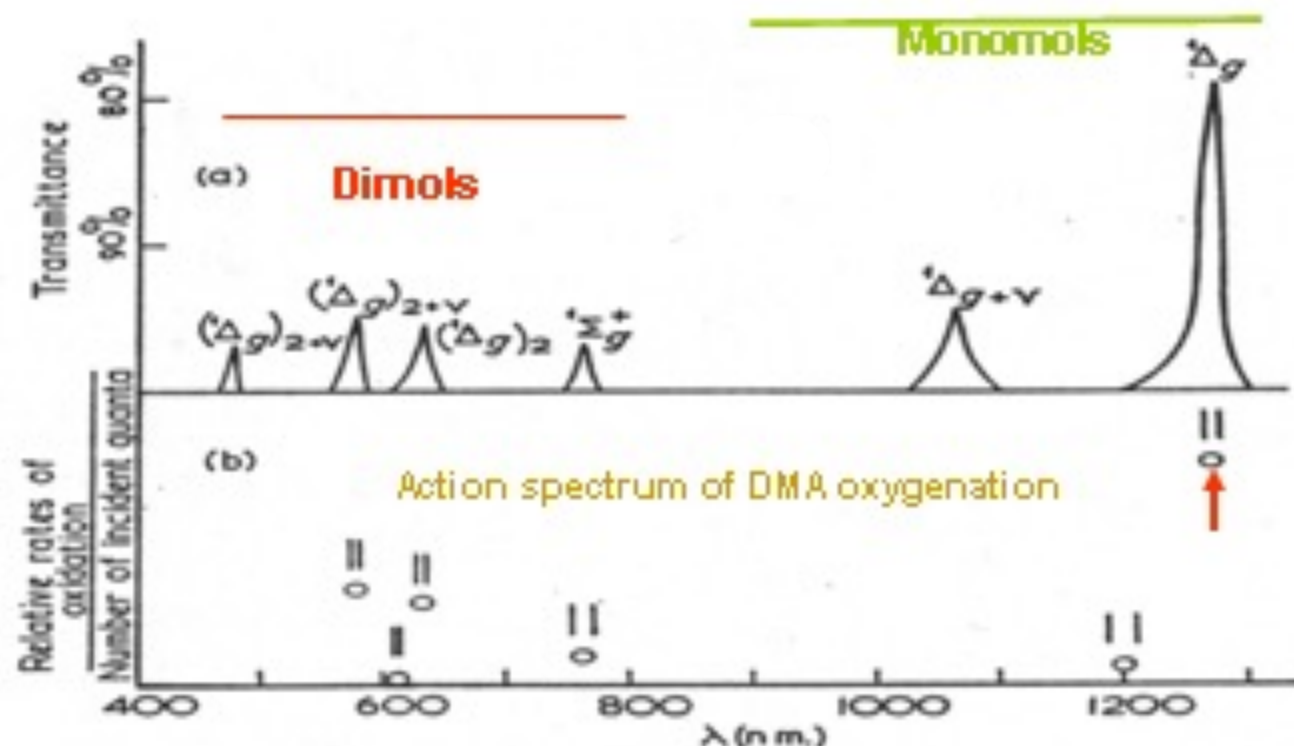
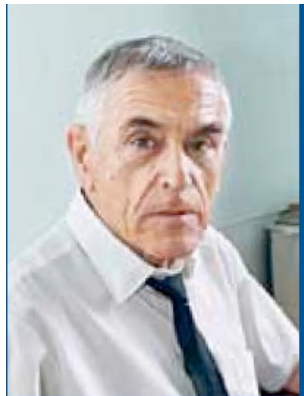


FIGURE. (a) The absorption spectrum of oxygen at 2000 lb./sq. in. dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane.

(b) The relative rates of photo-oxidation of a 4×10^{-6} M-solution of 9,10-dimethylantracene saturated with oxygen at 2000 lb./sq. in., divided by the number of quanta incident upon the cell. The vertical lines indicate the approximate widths at half-intensity of the interference filters used.



Н.Ф. Гамалея



В.С. Летохов



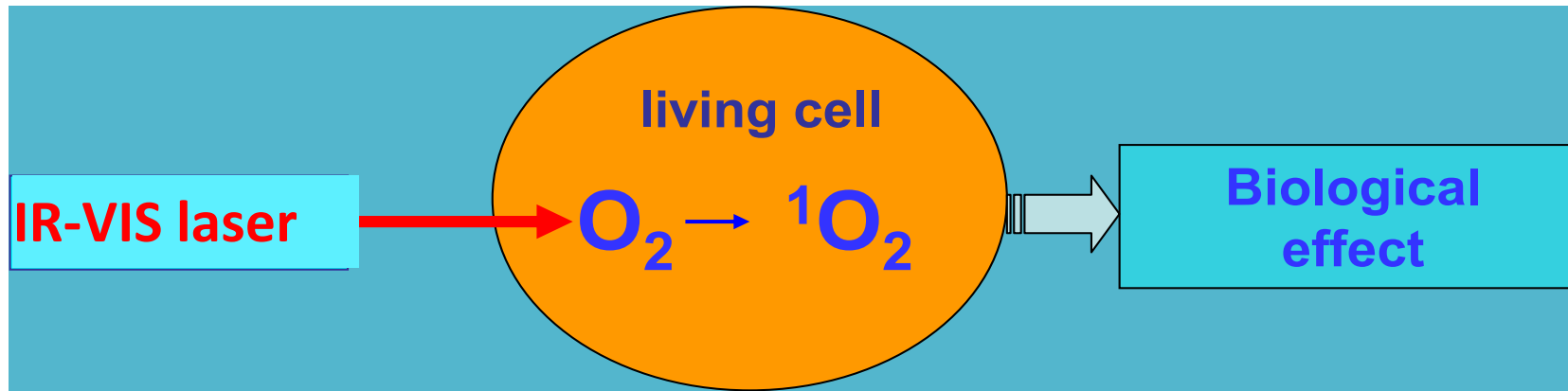
Т.Й. Кару

Низкоинтенсивная лазерная терапия (Low level laser therapy, LLLT)

1965-1990

Первые лазеры, пригодные для использования в биологии,
(гелий неоновый и рубиновый) были сделаны в 1960 г.

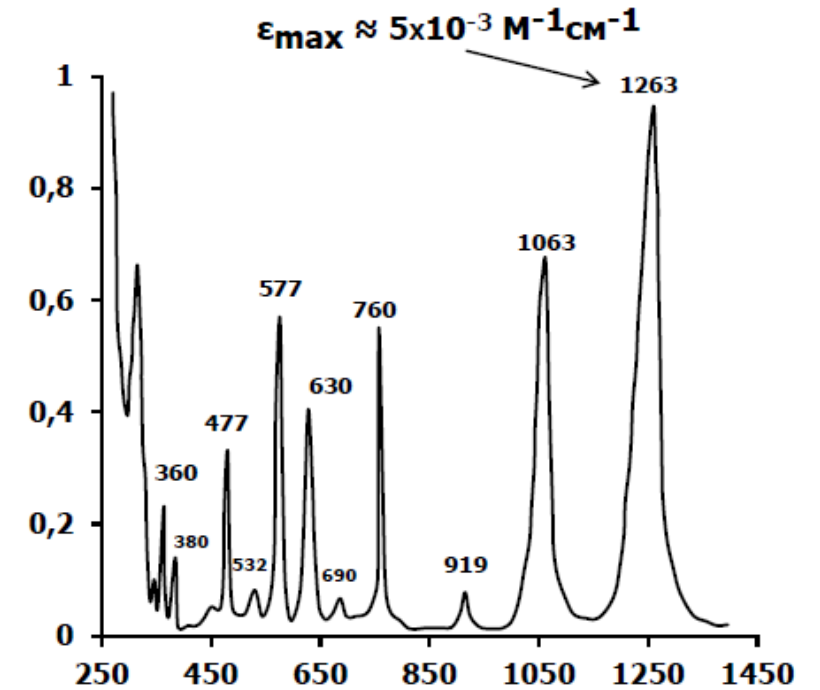
НЛТ (LLLT) эффективна при лечении боли в мышцах, зубной боли, дерматитов, ревматизма, способствует лечению суставов и заживлению ран, широко применяется в ветеринарной медицине, например, для лечения беговых лошадей, в спортивной медицине и в реабилитационных клиниках



Светокислородный эффект
Light oxygen effect



Ambartzumian R.V. PROC. SPIE, V. 701, p. 341-343, 1986

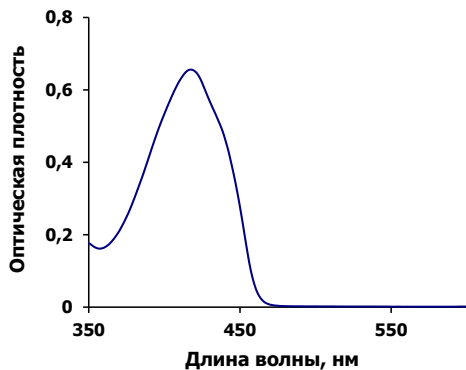
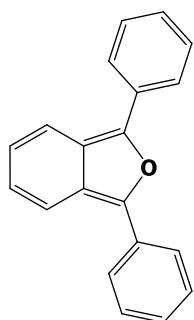


Absorption spectrum of compressed oxygen

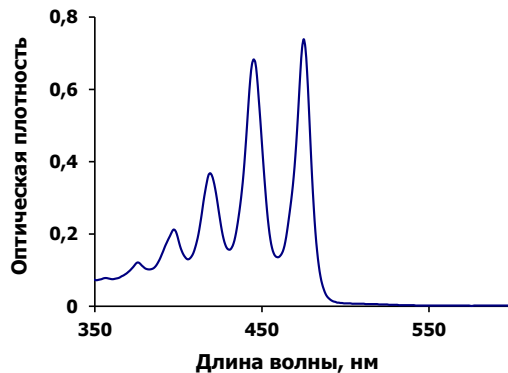
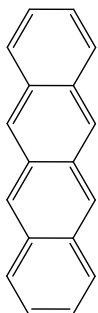
Моделирование светокислородного эффекта в аэрированных растворителях

Излучение лазера \longrightarrow $^3\text{O}_2$ \longrightarrow $^1\text{O}_2$ + ловушка \longrightarrow Окисление ловушки

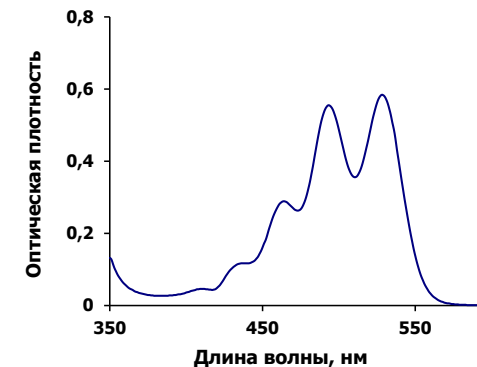
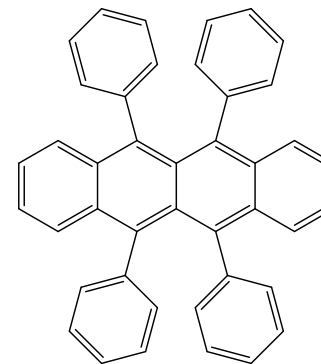
Основные химические ловушки синглетного кислорода (СК) и их спектры поглощения в четыреххлористом углероде



1,3-дифенилизобензофуран (ДФИБФ)

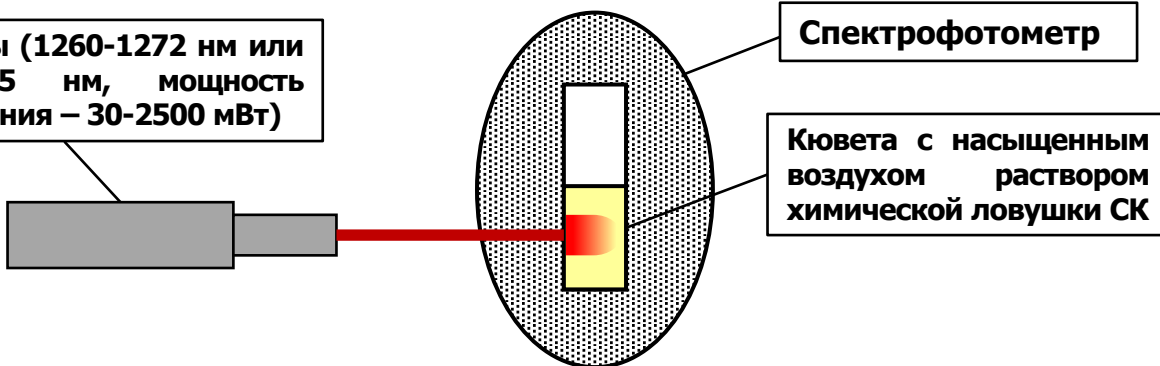


Тетрацен



Рубрен

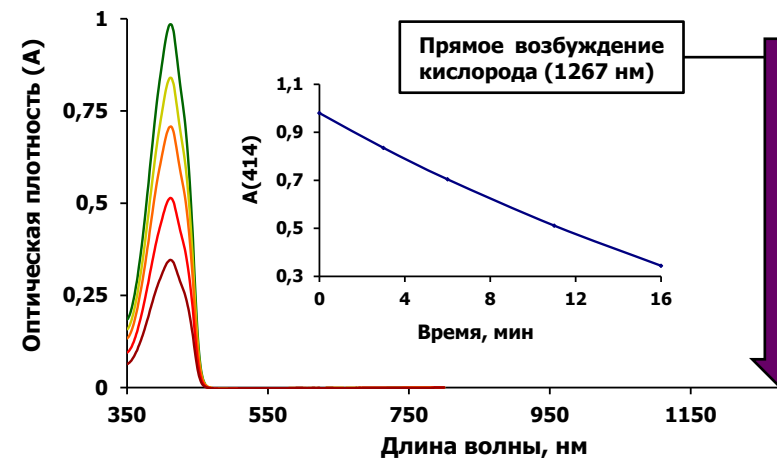
Лазеры (1260-1272 нм или 755-765 нм, мощность излучения – 30-2500 мВт)



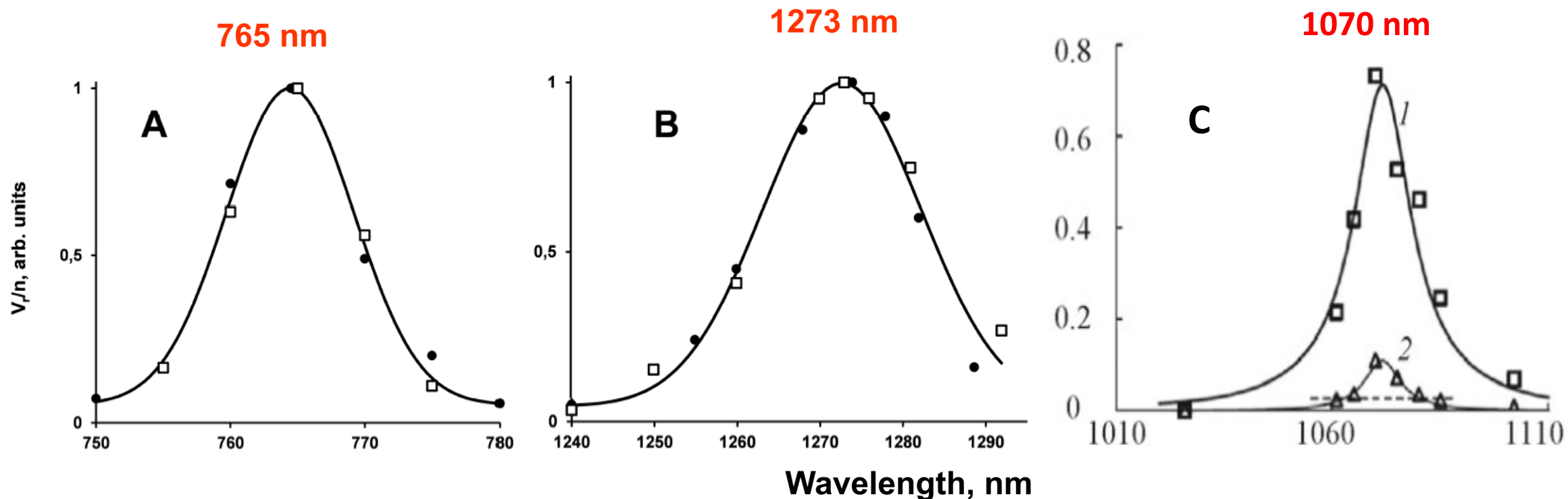
Спектрофотометр

Кювета с насыщенным воздухом раствором химической ловушки СК

Выцветание ДФИБФ в ацетоне при действии ИК лазера, возбуждающего растворенные молекулы кислорода



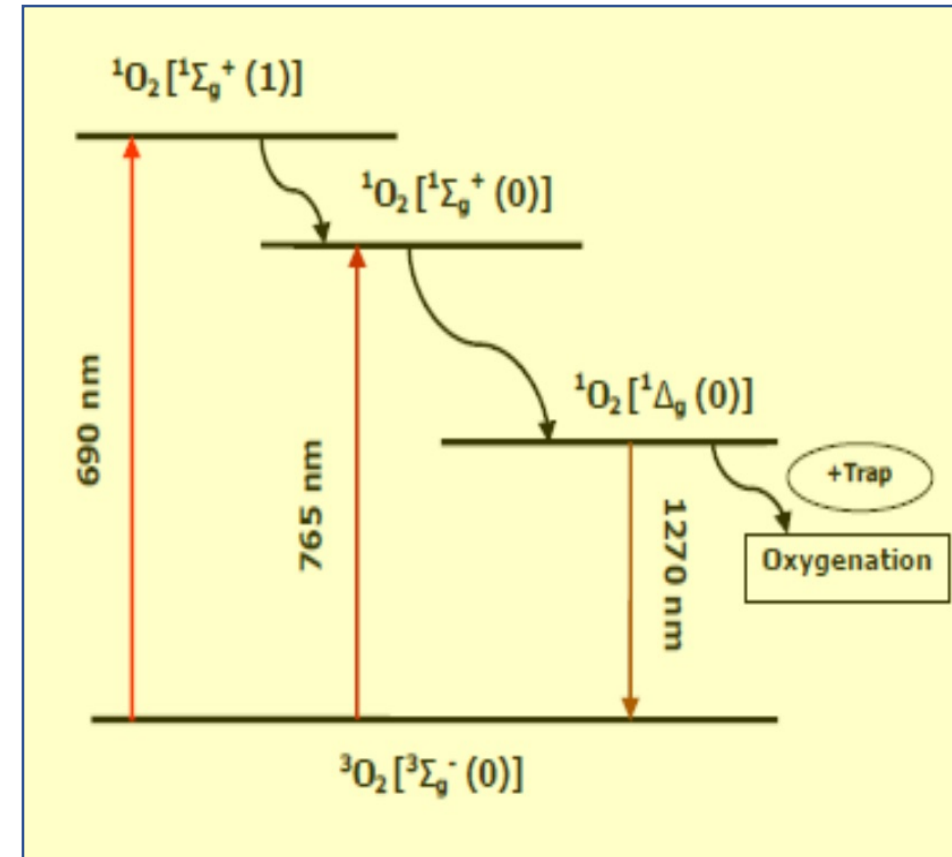
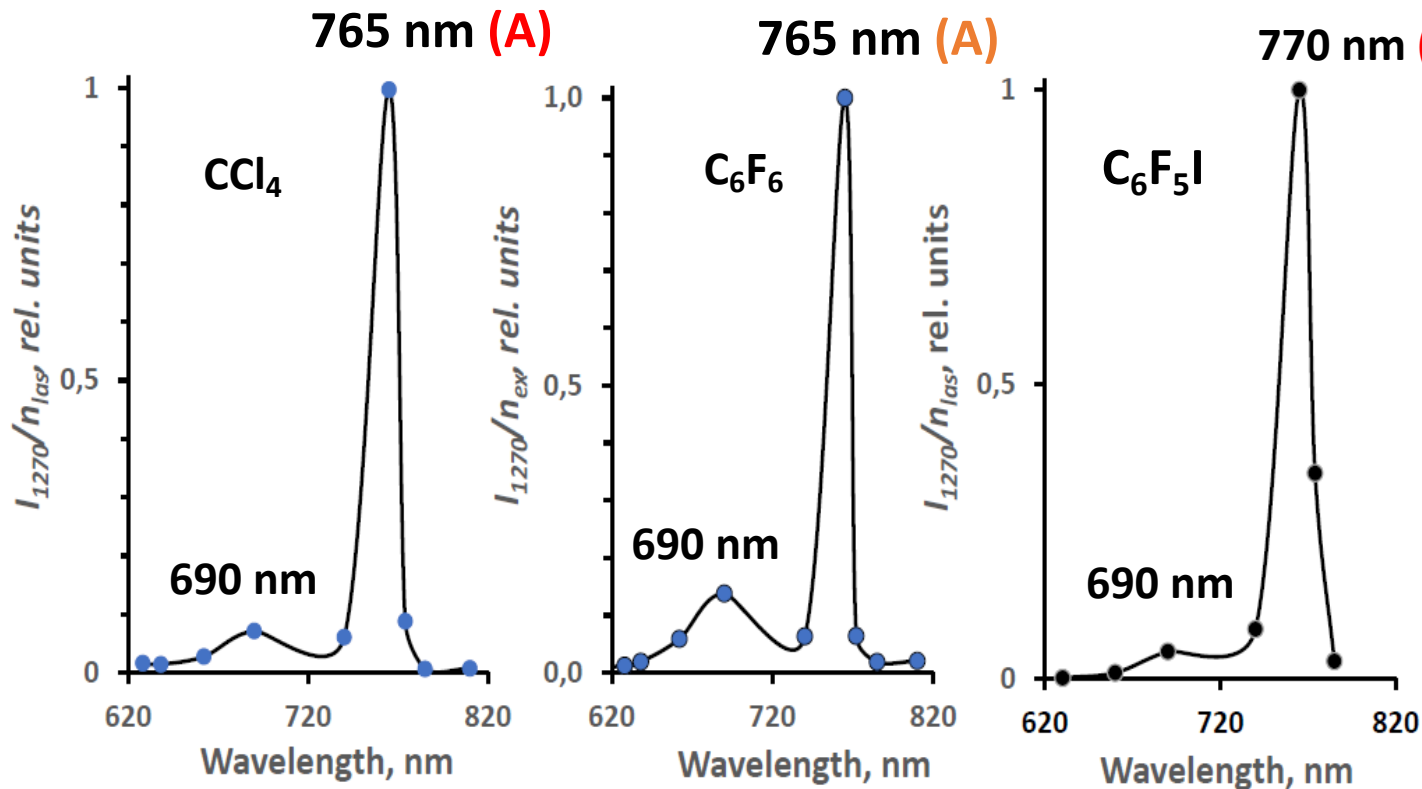
Krasnovsky A.A., Jr., Drozdova N.N., Ivanov A.V., Ambartsumian R.V.,
Biochemistry (Moscow), v. 68, № 9, pp. 963-966 (2003)



Action spectra of oxygenation of the singlet oxygen traps under direct excitation of oxygen molecules by IR laser radiation obtained using tunable titan-sapphire (A), forsterite laser (B) and GTW optical fiber laser (C) in aerated solutions

Krasnovsky, Abartzumian Chem. Phys. Lett., 2004, 400, 511
 Krasnovsky, Kozlov, Biofizika, 2014, 59, 199
 Krasnovsky, Kozlov, J. Photochem. Photobiol. A:, 2016, 329, 167
 Kozlov, Egorova et al. Optics lett. USA 2021, 46, 556-558
 Kozlov, Krasnovsky et al, J. Appl. Spektr., Minsk, 2023, 90, 493-498

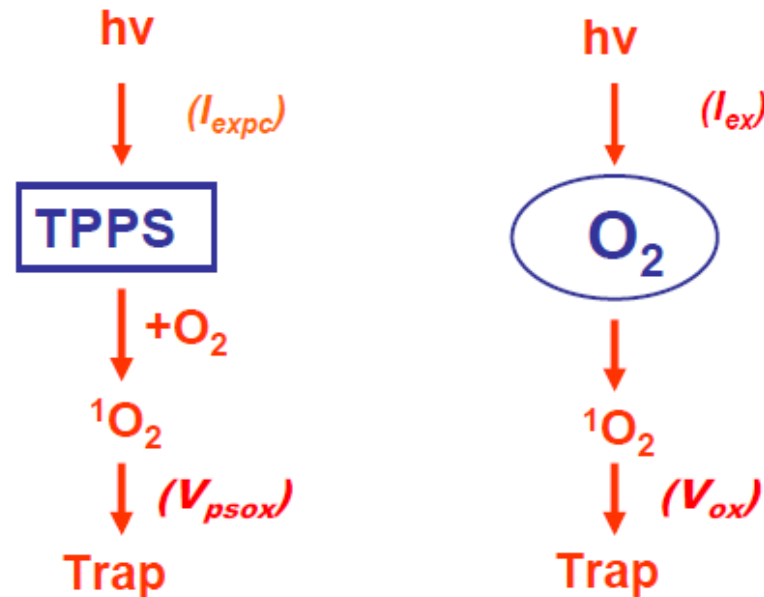
Excitation of Fraunhofer lines **A** and **B** of dissolved oxygen in aerated solvents



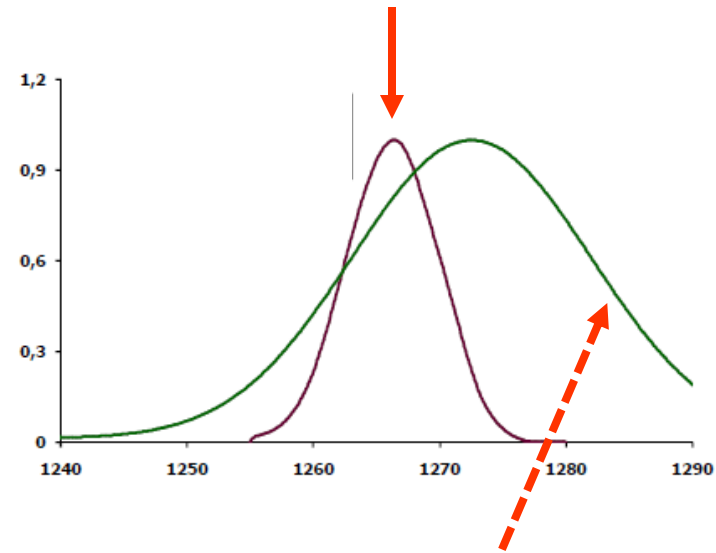
Excitation spectra of $^1\text{O}_2$ phosphorescence in aerated solvents using cw lasers with fixed wavelengths.

$$V_{ox}/V_{psox} = I_{ex} \alpha A_{max} / I_{exp} \Phi_{\Delta} (1 - 10^{-A_{ps}})$$

Comparison of V_{ox} and V_{pcox}



Diode laser



Oxygen excitation spectrum

Krasnovsky, Kozlov, Roumbal. Photochem. Photobiol. Sci., 11, 988-997, 2012

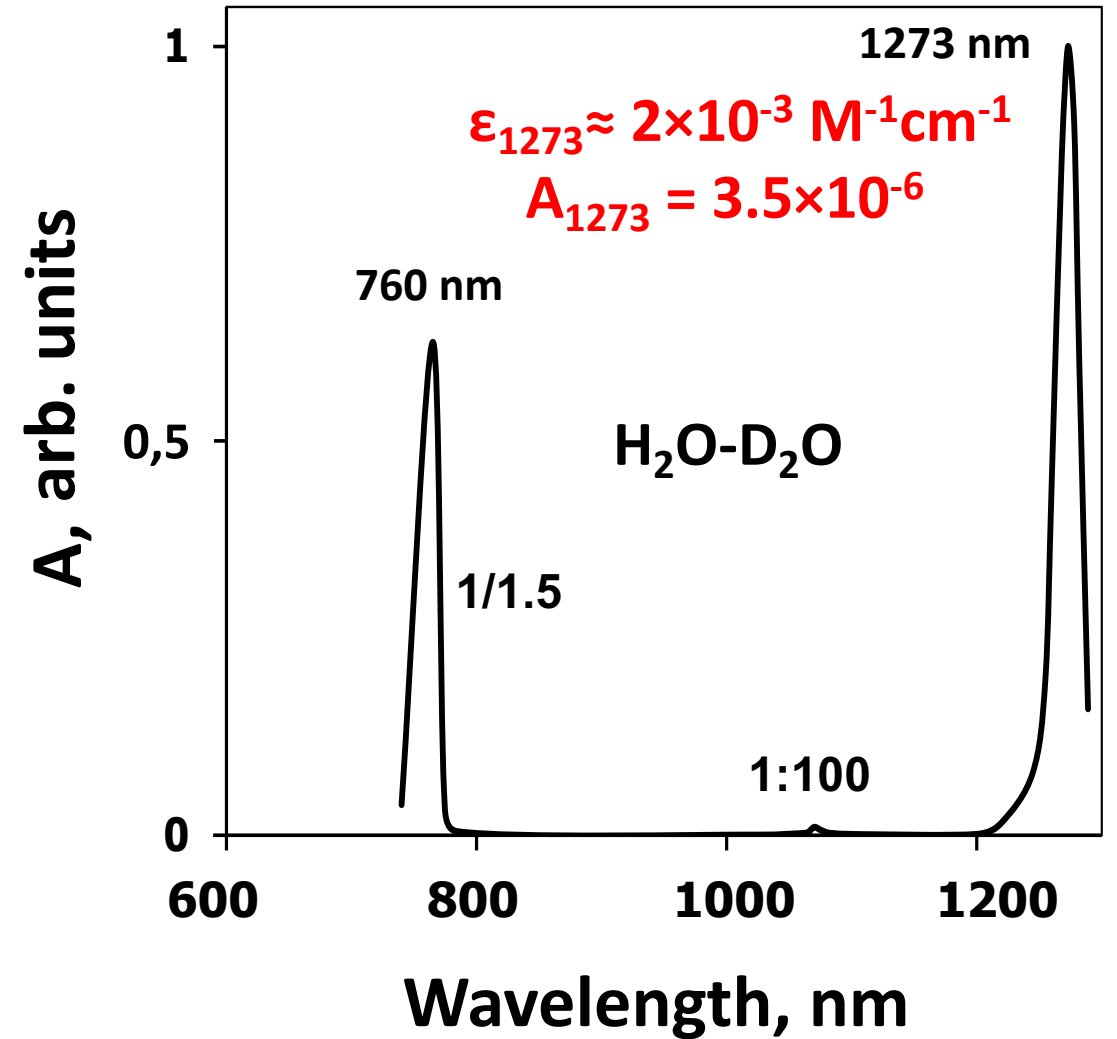
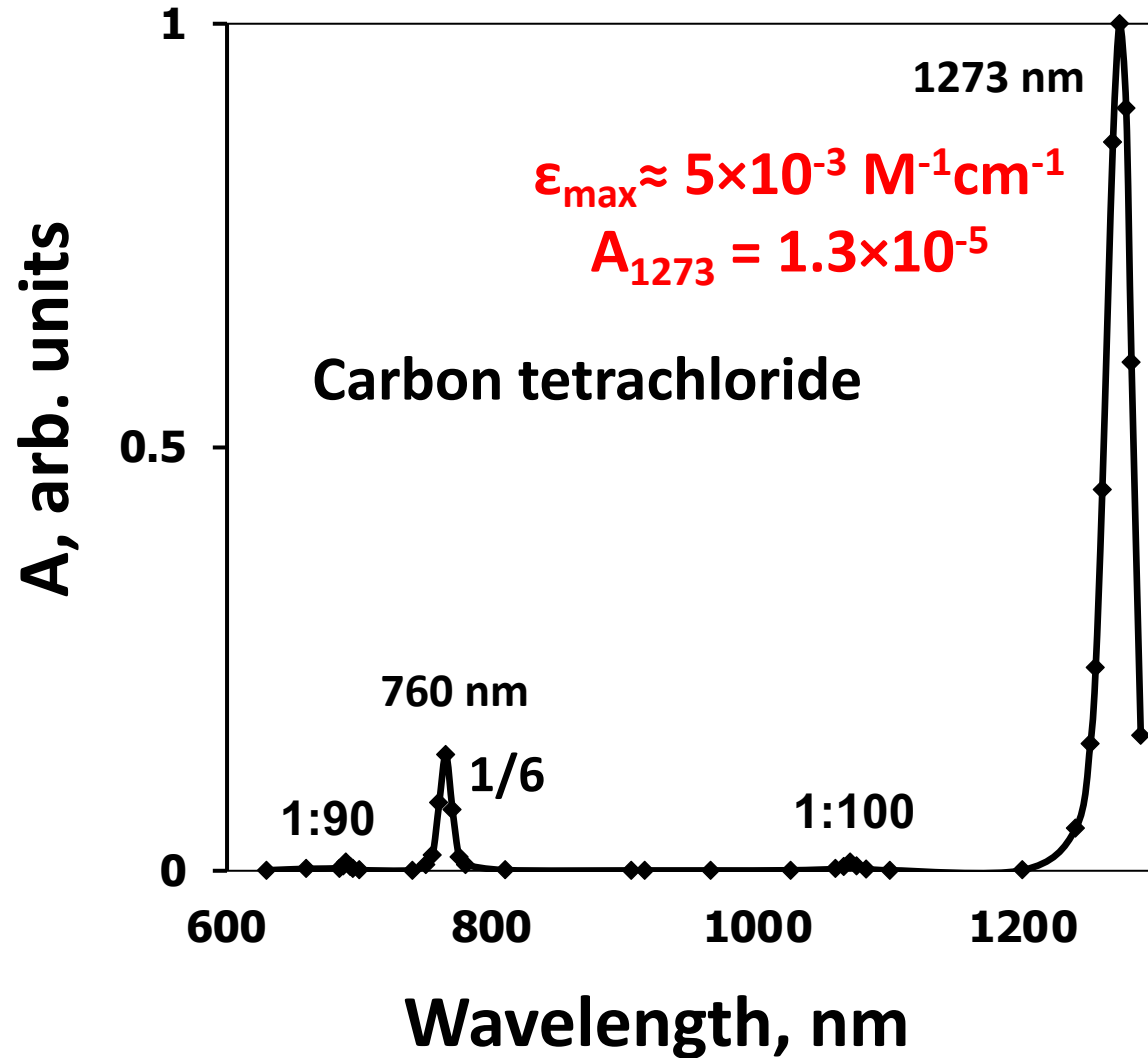
Krasnovsky, Kozlov. Biofizika, 59, 199–205, 2014

Krasnovsky, Kozlov. J. Photochem. Photobiol. A., 329, 167-174, 2016

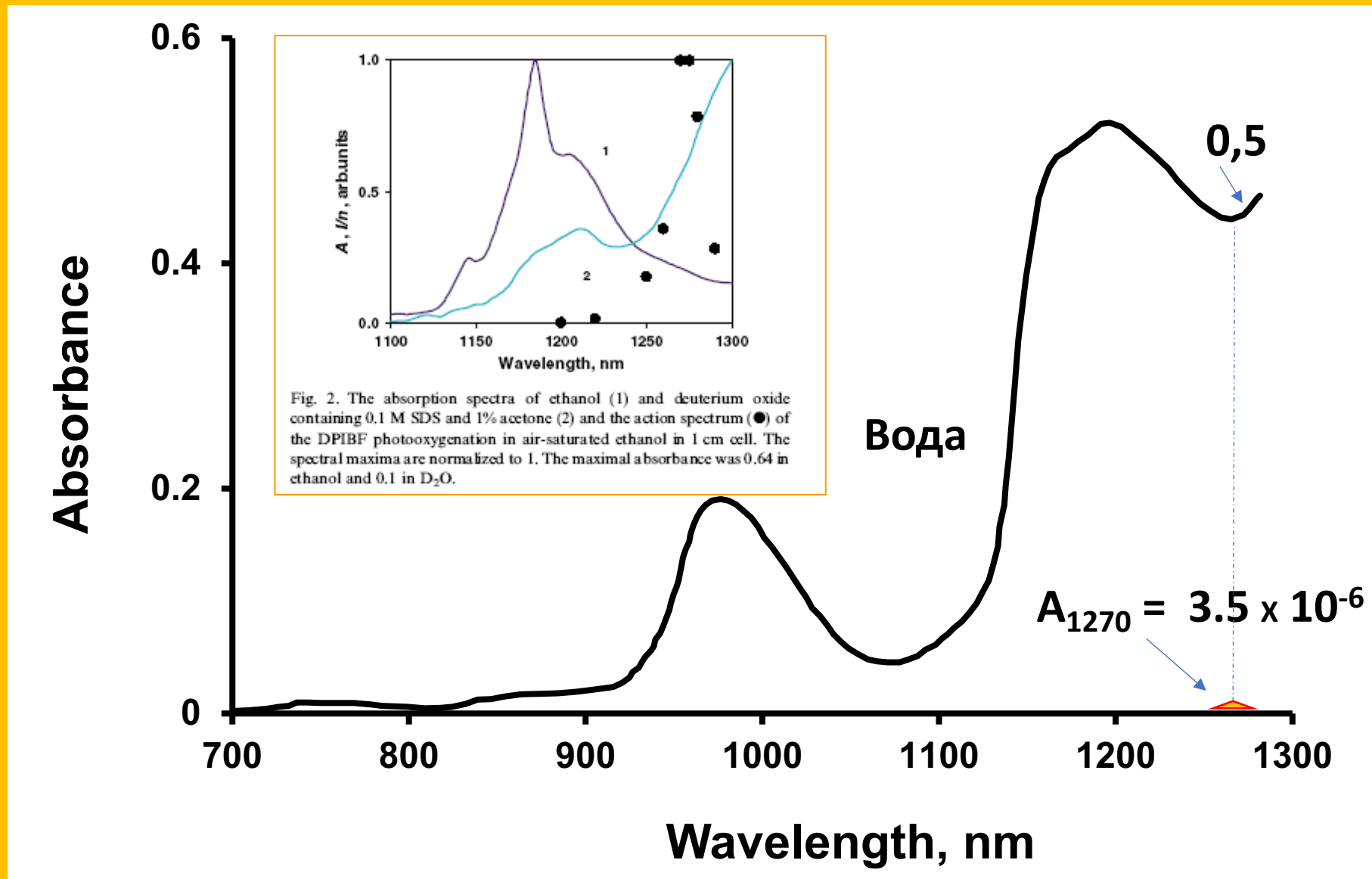
Krasnovsky, Kozlov. J. Biomed. Photonics & Engineering, 3(1) 1-10, 2017

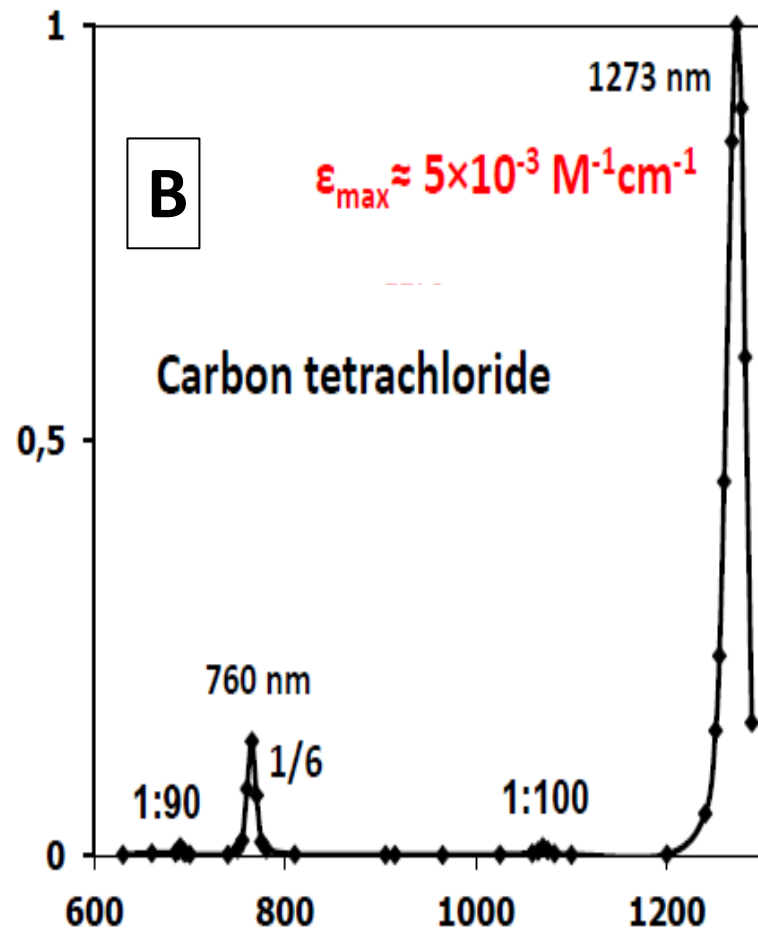
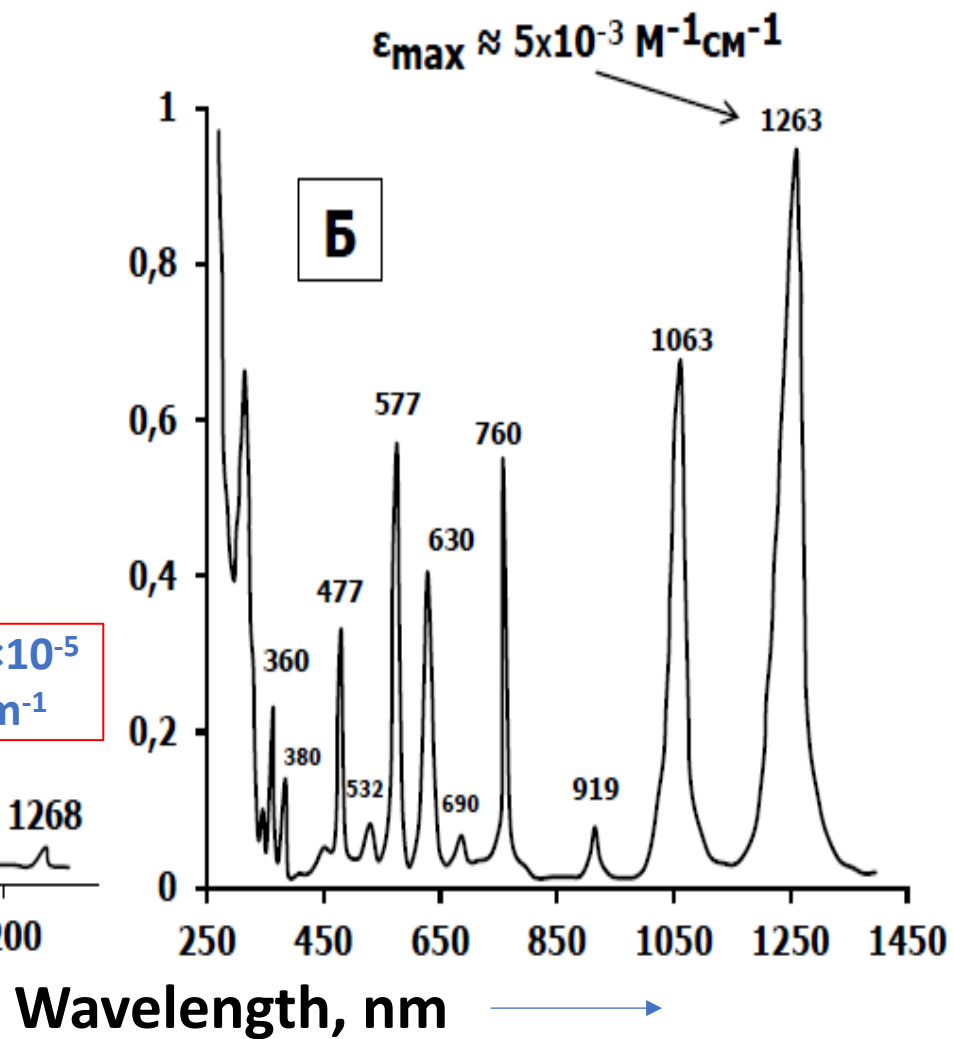
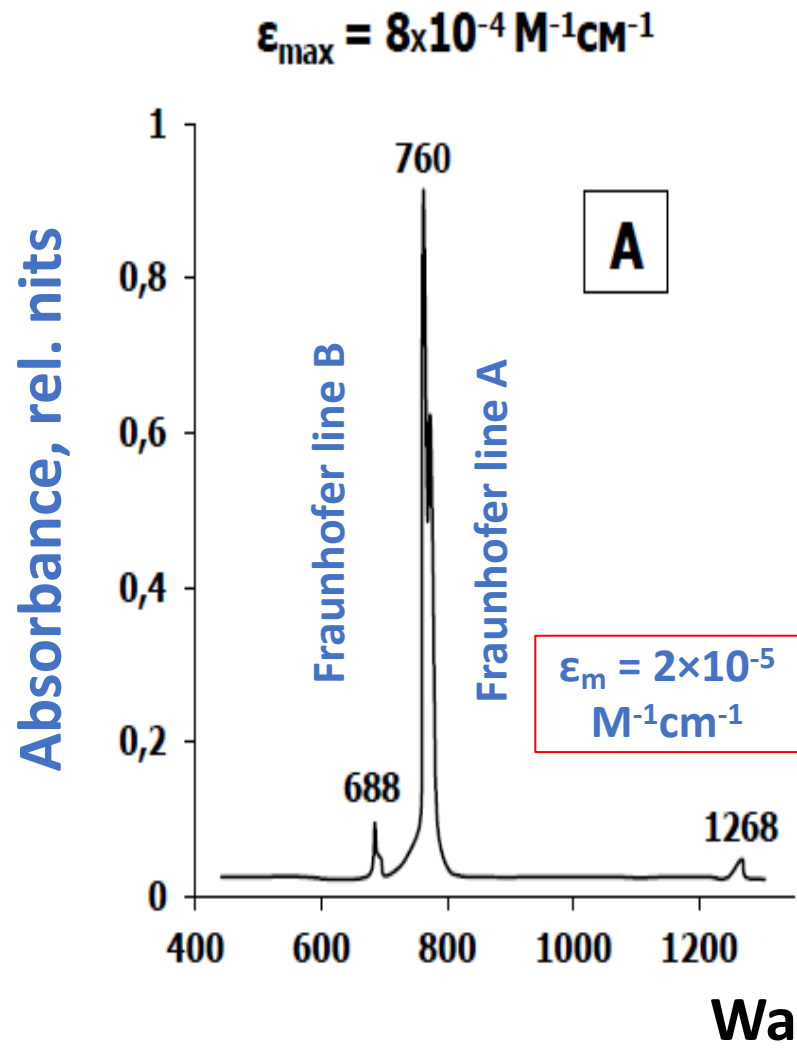
Krasnovsky, Kozlov, Benditkis, Rus. Phys. Journal, 64, 2035-2045, 2022

Absorption spectra of oxygen in aerated CCl_4 and water



Сравнение спектра поглощения воды и растворенного кислорода в 1 см слое



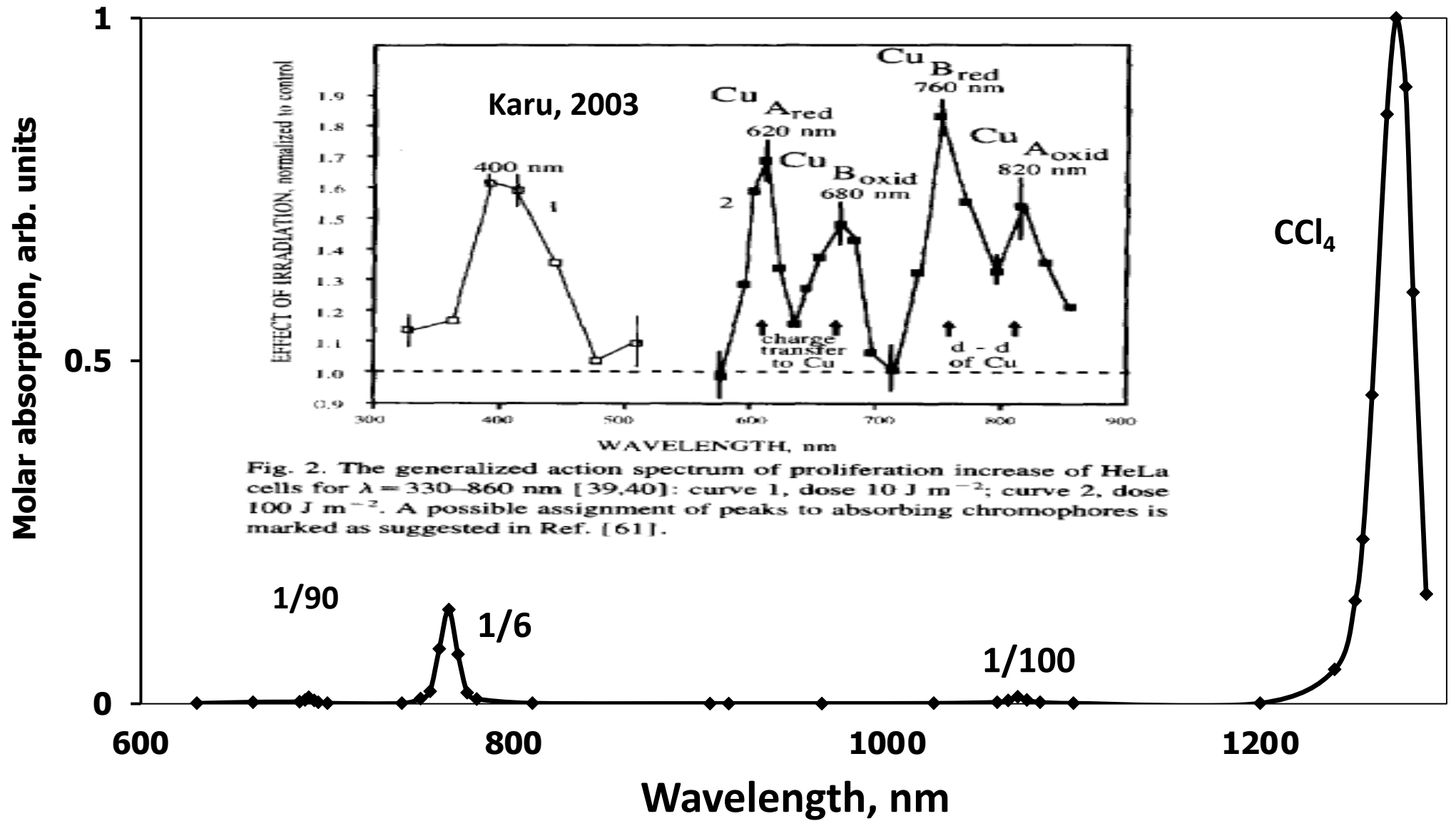


Absorption spectrum of oxygen
in Earth Atmosphere

Absorption spectrum of compressed
oxygen at 150 atm

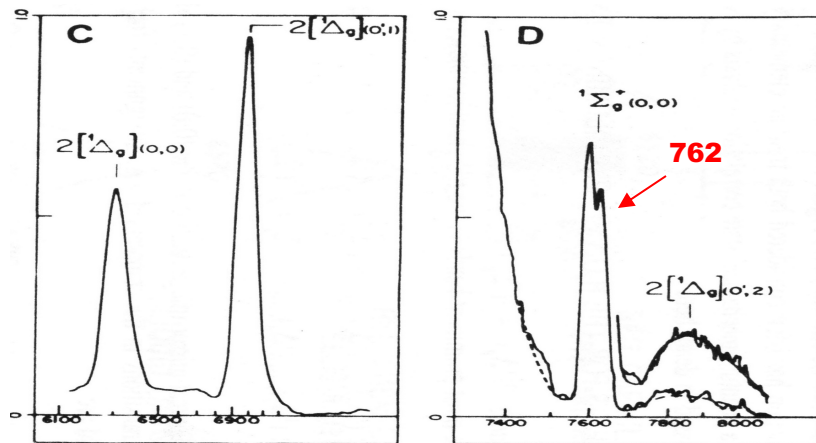
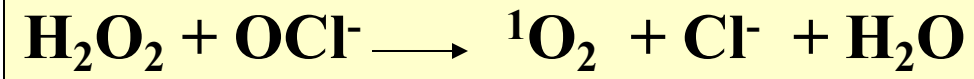
Absorption spectrum of
oxygen in aerated CCl_4

$$\epsilon \approx 5 \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$$

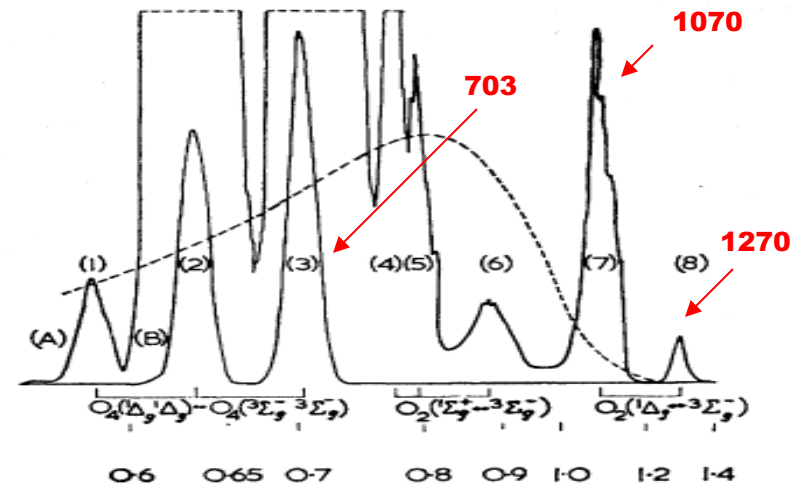


Luminescence kinetics and spectroscopy

Singlet oxygen formed in chemical reaction between H_2O_2 and OCl^- or by electric discharge in oxygen flow produces bright luminescence in visible, red and infrared

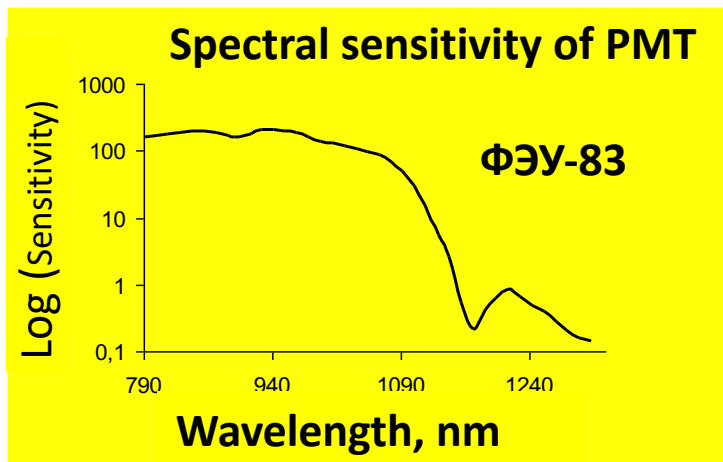
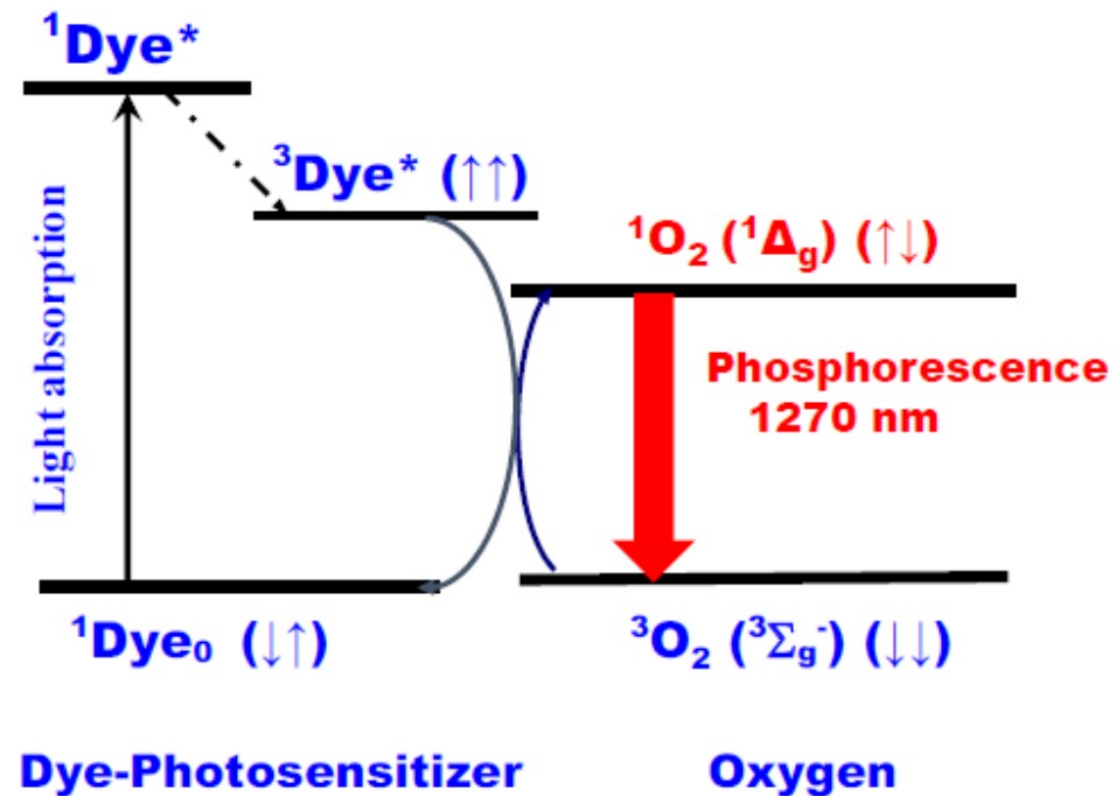
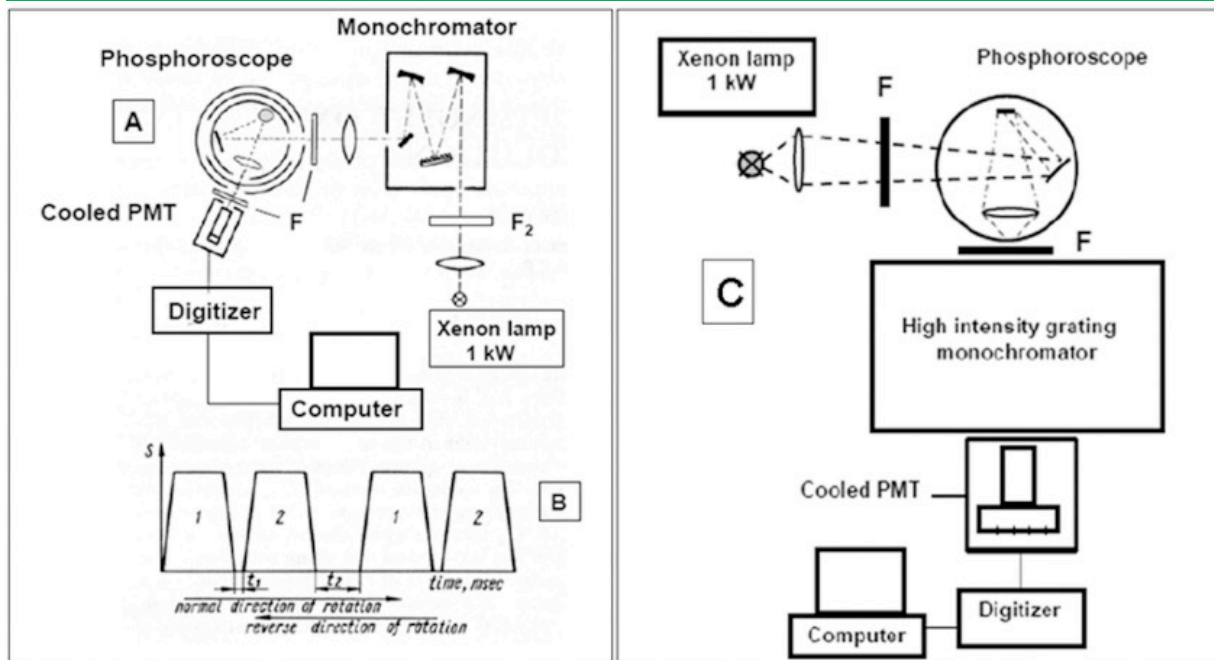


Khan A.U., Kasha M. J. Chem. Phys. 39, 2105, 1963



Brown R.J., Ogryzlo E.A. Proc. Chem. Soc., p. 117, 1964

Set-ups with mechanical phosphoroscope, S-1 PMT and 0.1 ms time resolution



- Krasnovsky A.A. *Biofizika*, 1976, v. 21, p. 748-749
- Krasnovsky A.A. *Biofizika*, 1977, v. 22, p. 927
- Krasnovsky A.A. *Izv. AN SSSR, ser phys.* 1978, v. 42, p. 343
- Krasnovsky A.A. *Photochem. Photobiol.*, 1979, v. 29, p. 29-36

Photosensitized luminescence of singlet oxygen

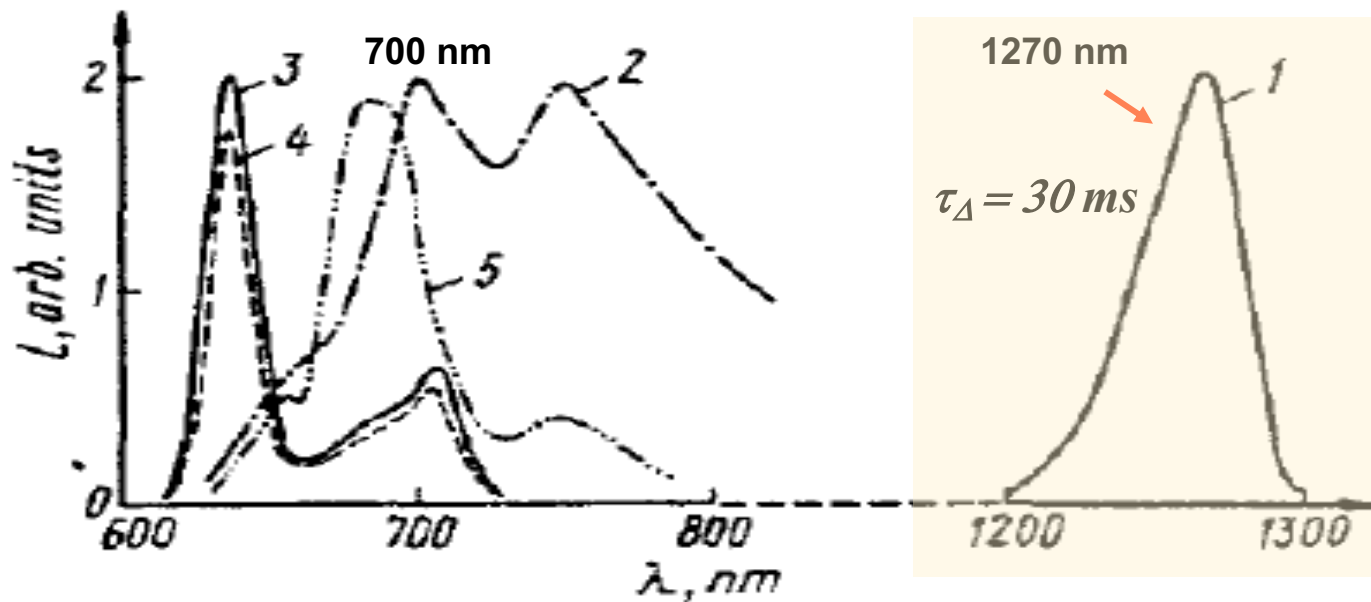


Figure 3. Normalized spectra of delayed luminescence of protoporphyrin solutions in aerobic (1,2) and anaerobic (3) conditions at 20°C (solvent is CCl_4). 4,5 fluorescence spectra of the solutions before (4) and after (5) protoporphyrin oxidation by oxygen. Photooxidation was carried out by prolonged (30–60 min) illumination of air saturated solutions with red light $\approx 10^6 \text{ J} \times \text{m}^{-2} \times \text{s}^{-1}$.

Krasnovsky AA. *Biofizika*, 1976, V. 21, No 4, p. 748-749;
Izv. AN SSSR, ser. Phys., 42, 343-348, 1978.
Photochem. Photobiol. 29, 29-37, 1979

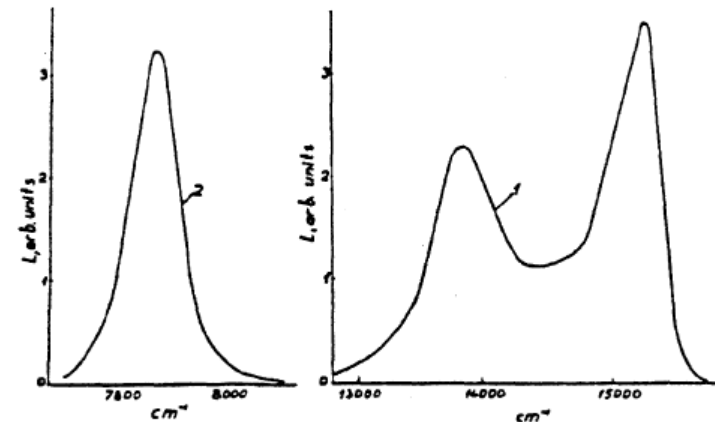
$$\Phi_{ph} = \Phi_{\Delta} p_r = \Phi_{\Delta} \tau_{\Delta} / \tau_r$$

$$\tau_r = \tau_{\Delta} / p_r = 4 \pm 2 \text{ s in CCl}_4$$

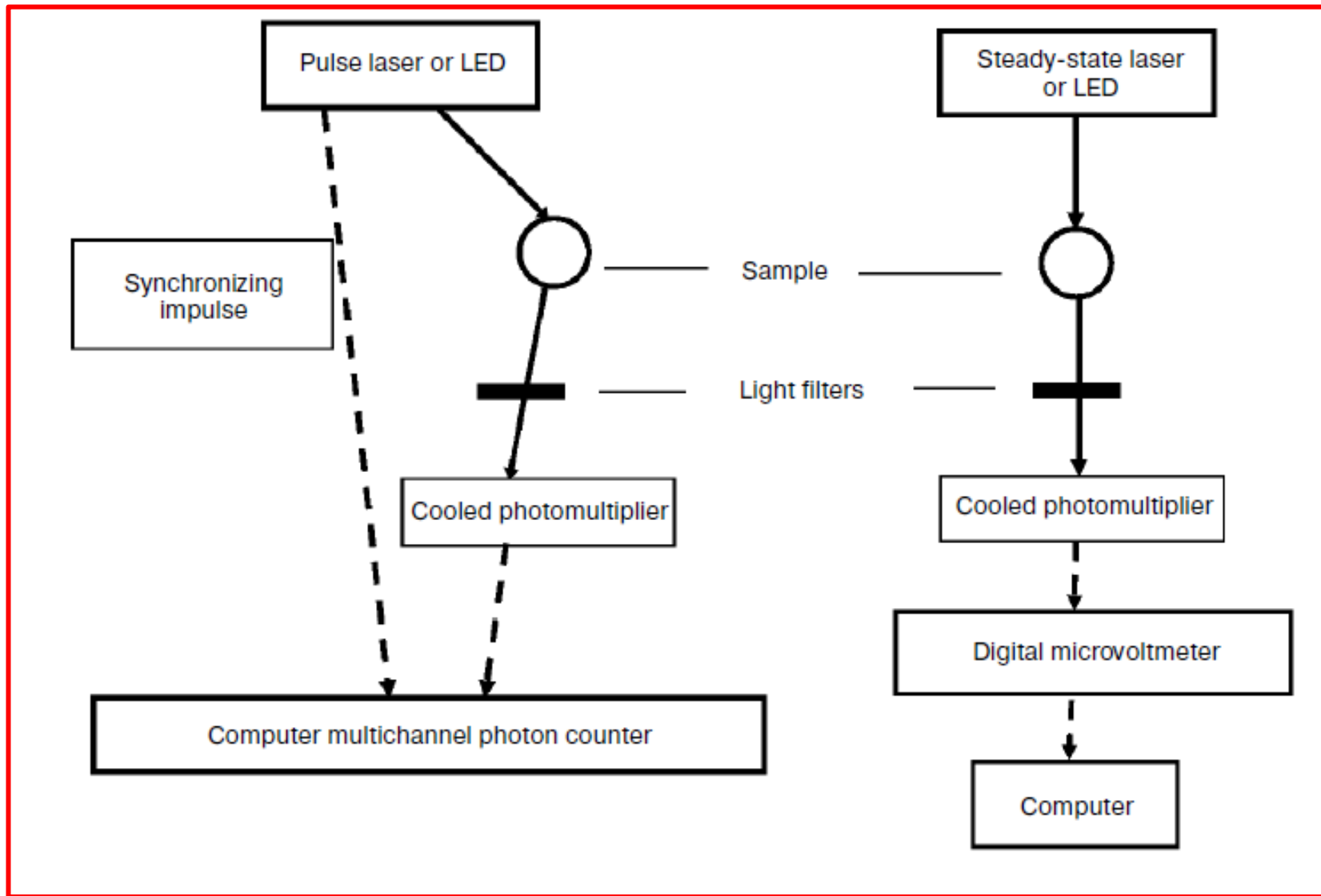
(Compare $\tau_r \sim 4000$ s in the gas phase in the Earth atmosphere!)

Table 1
Values of τ_r and p_r in different solvents

Solvent	τ_0 (ms)		p_r (arb. units)	τ_r (arb. units)
	this work ^{a)}	literature		
CCl ₄	26000	26000 [6,7]	1	1
chloroform	210	250 [6,7]	1/110	0.9-1.06
acetone	50	51 [6,7]	1/600	1.15



Krasnovsky, Chem. Phys. Lett, 81, No 3, p. 443-445, 1981
Krasnovsky, Dokl. AN SSSR, 257, No 6, p. 1360-1362, 1981



New laser (LED) spectrometers for phosphorescence detection

Krasnovsky, Benditkis, Kozlov. Biochemistry Moscow, 84, 240-251, 2019

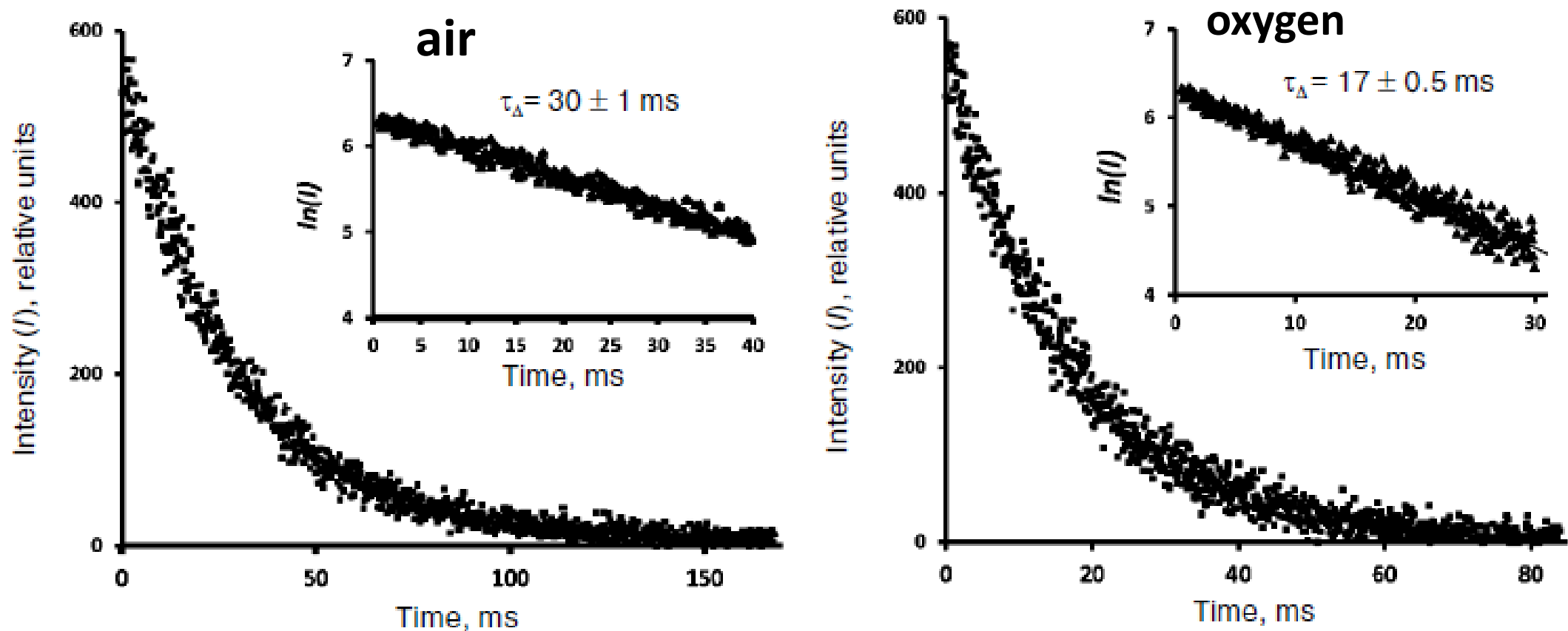
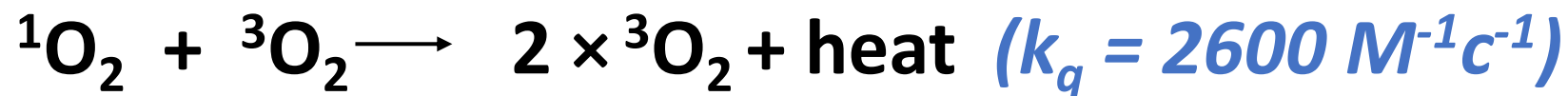
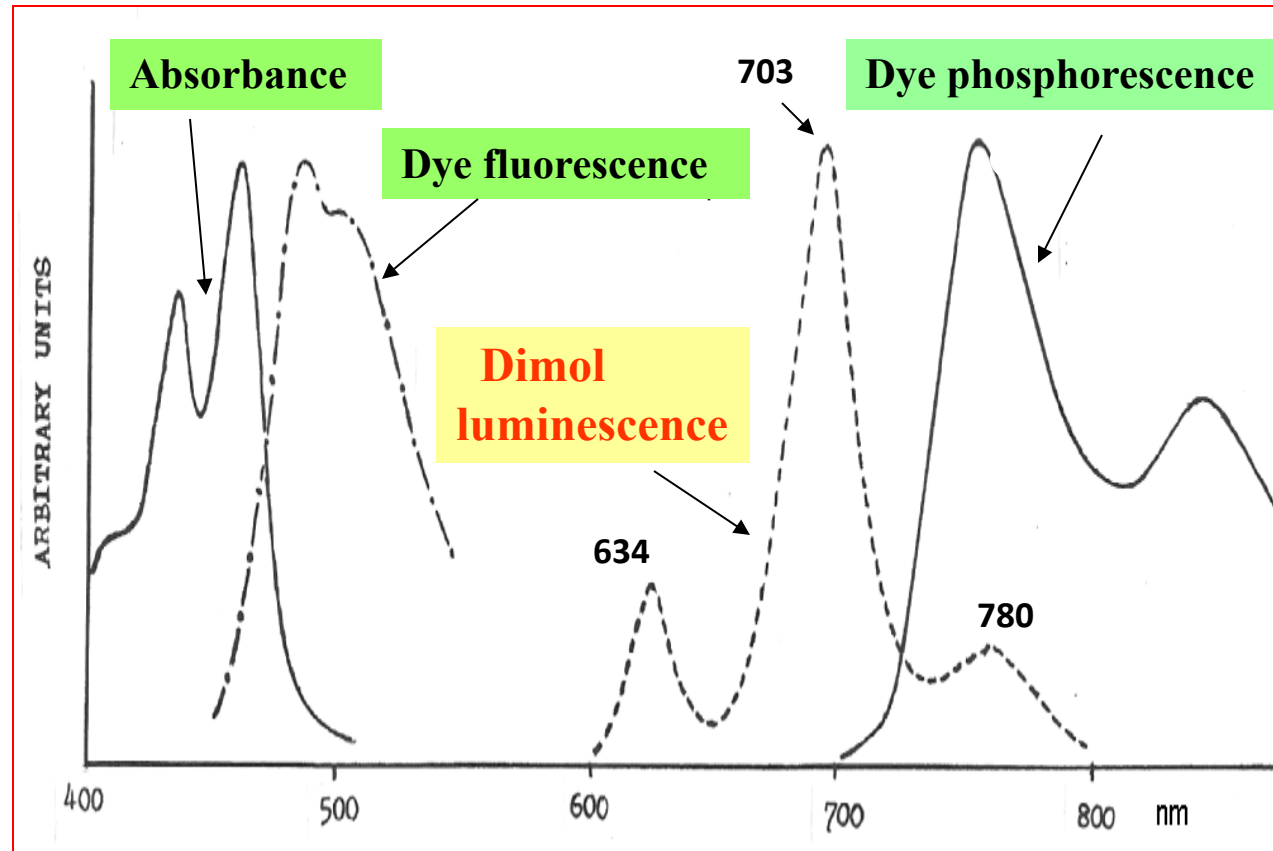


Fig. 4. Decays of $^1\text{O}_2$ phosphorescence in phenalenone ($35 \mu\text{M}$) solutions in CCl_4 after irradiation by $10 \mu\text{s}$ pulses of LED (405 nm) in the presence of air (a) and after saturation with oxygen (b). The curves were obtained at a pulse repetition rate of 5 Hz as a result of 30-min signal accumulation; duration of one channel, $164 \mu\text{s}$; average excitation power, $15 \mu\text{W}$. Insets: decay curves in the semi-log scale.



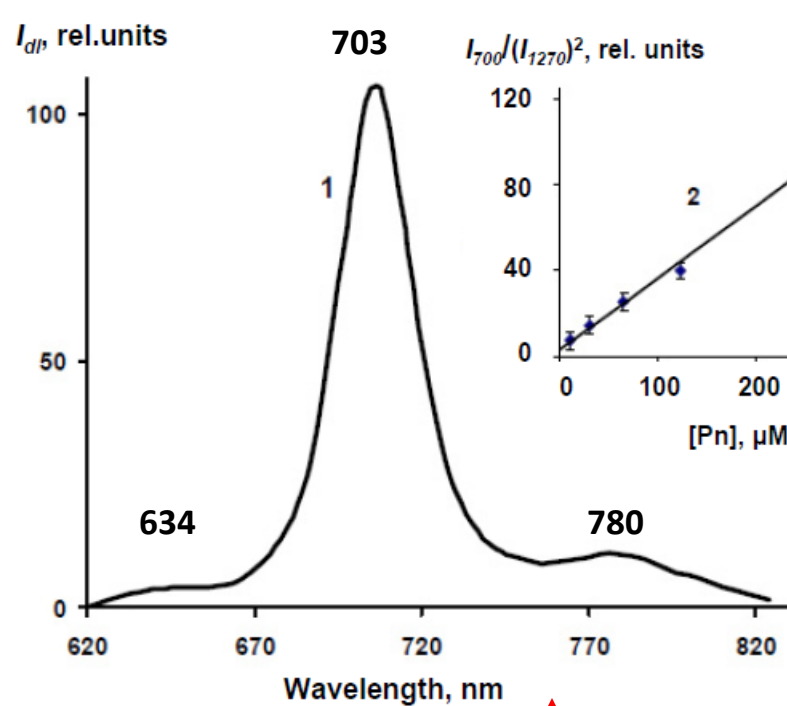
Photosensitized luminescence of singlet oxygen dimols and luminescence properties of the photosensitizer DBPQ



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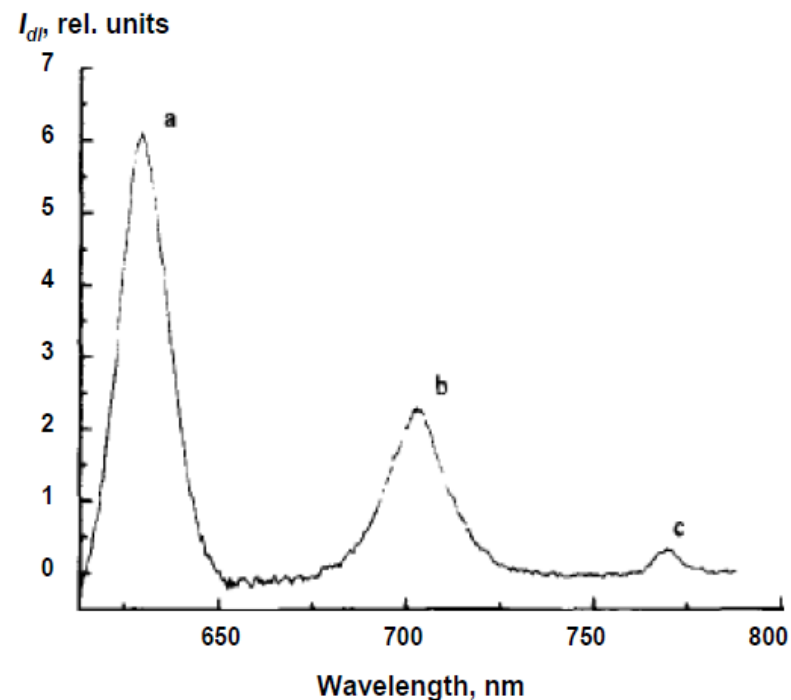
Maallem et. al. Dokl. AN SSSR (Physical Chemistry), 1990, V. 313, No 4, p. 893-897.

Photosensitized luminescence of singlet oxygen dimols in phenaleneone (PH) solutions in carbon tetrachloride



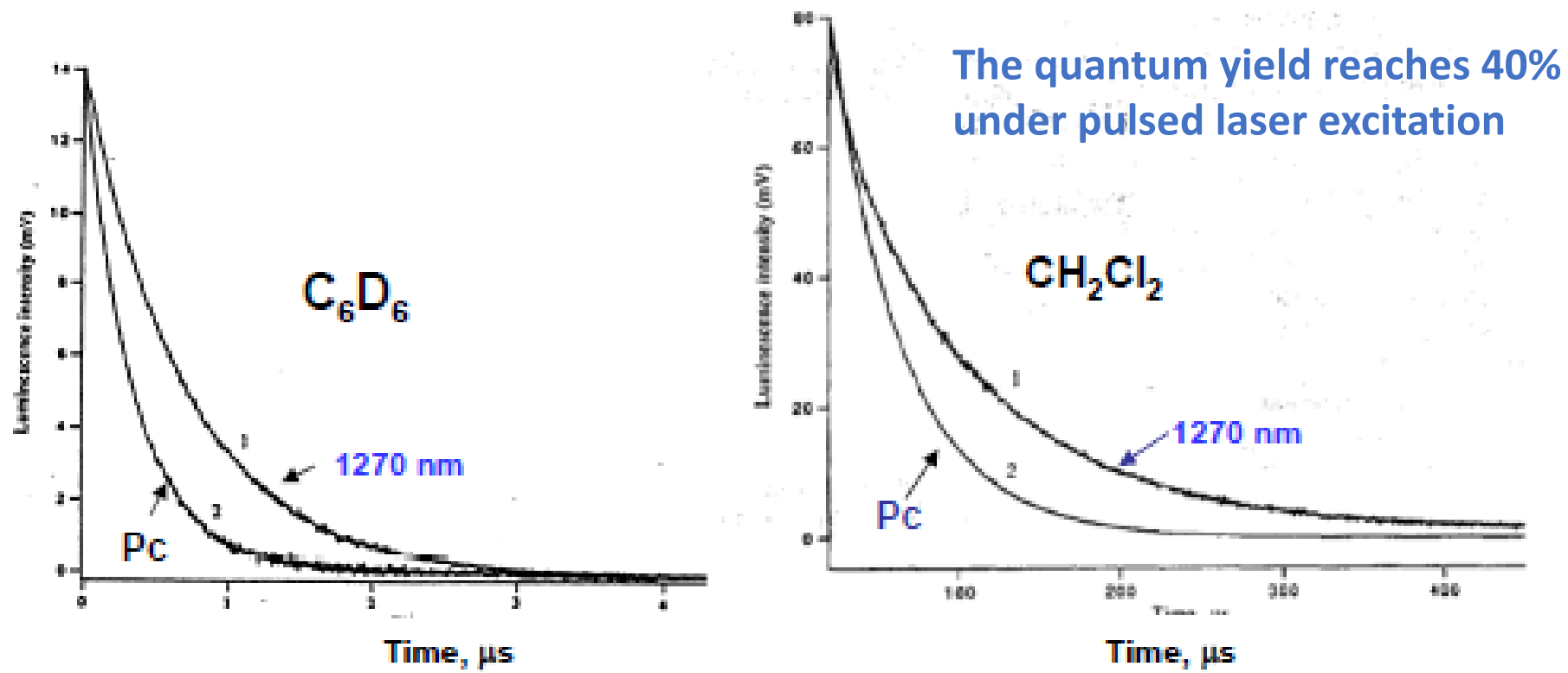
Krasnovsky, Neverov. Biofizika, 55, 389, 2010

$$DI \sim [^1O_2]^2 \times [PH]$$



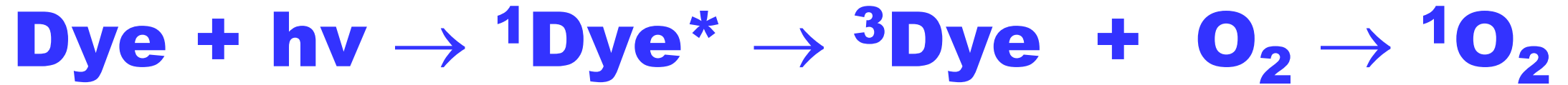
Chow et al. JACS 1996, 118, 3031-3032

$$DI \sim [^1O_2]^2$$



Decays of photosensitized phosphorescence of singlet oxygen at 1270 nm (1) and photosensitized delayed fluorescence of Pc (2) after 532-nm laser shots in C_6D_6 and CH_2Cl_2 . Photosensitizer was fullerene C_{70} ($10 \mu M$); $[Pc] = 0.4 \mu M$.

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