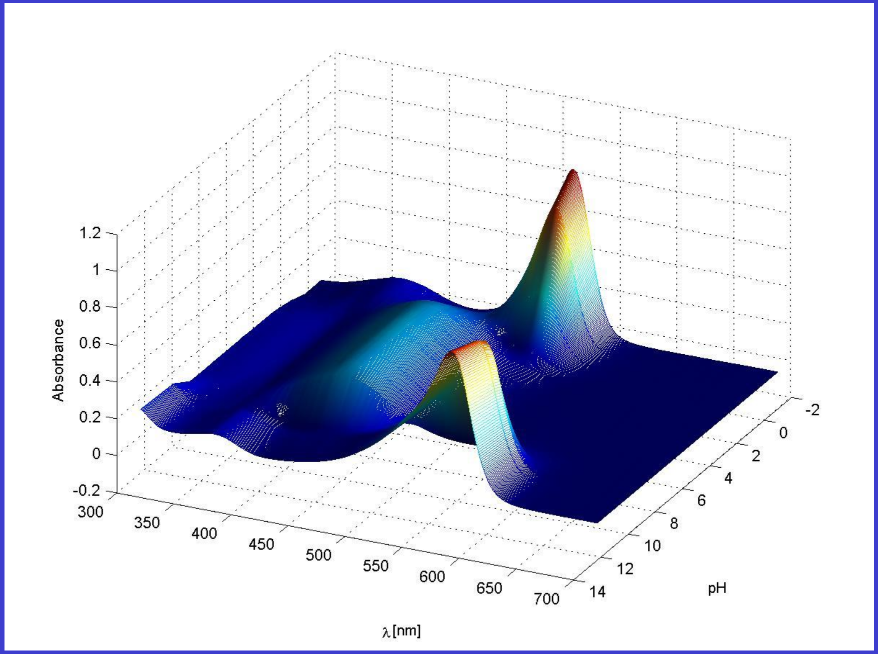
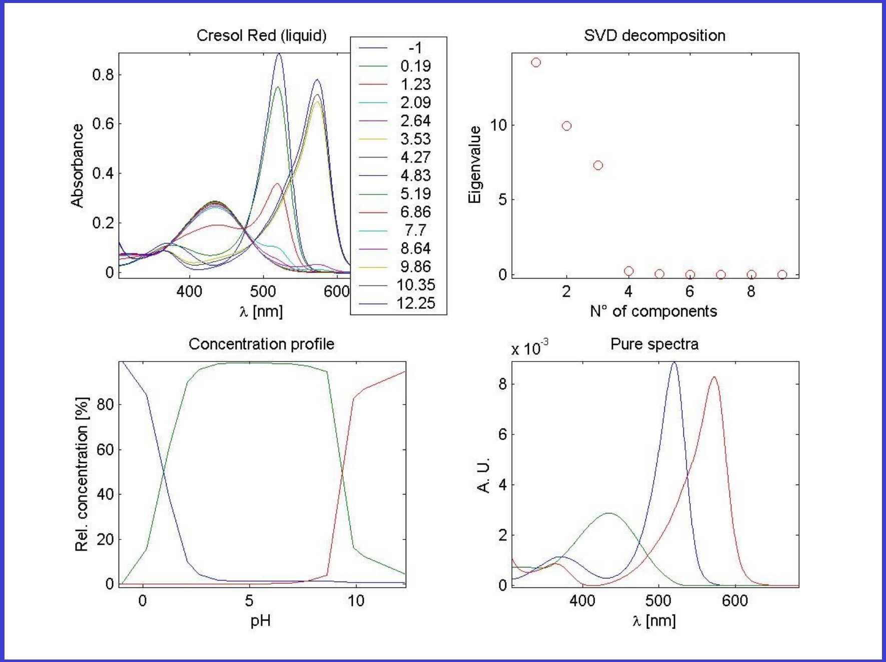
Ultrafialová a viditelná spektroskopie

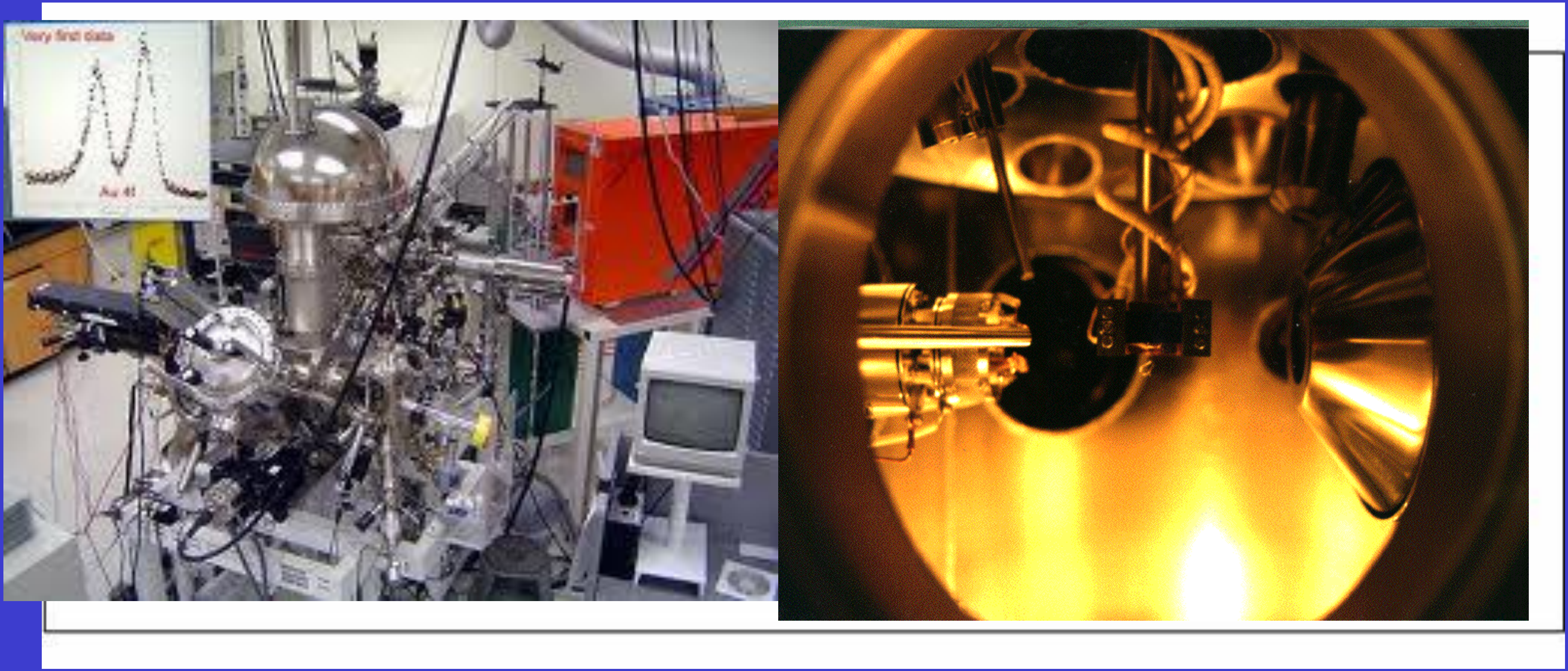




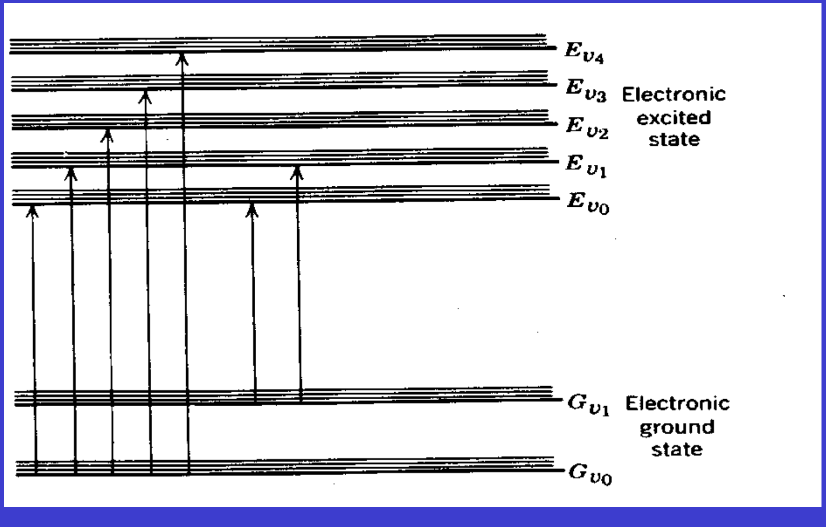
Ústav chemie, MU

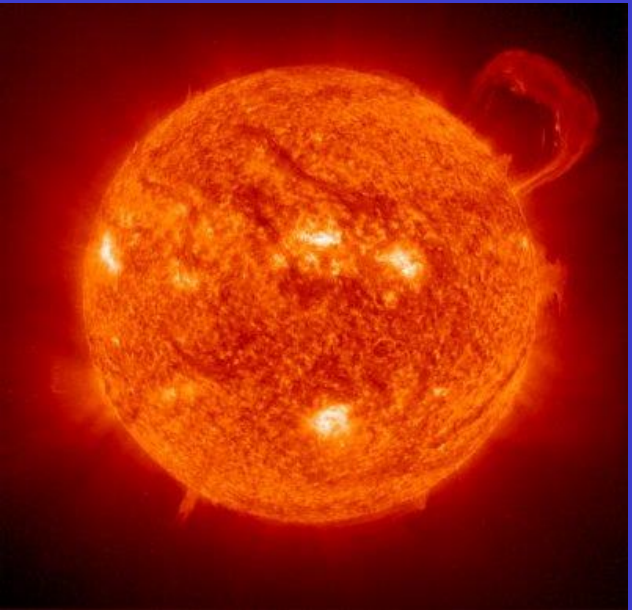
Brno 2015, Dominik Heger

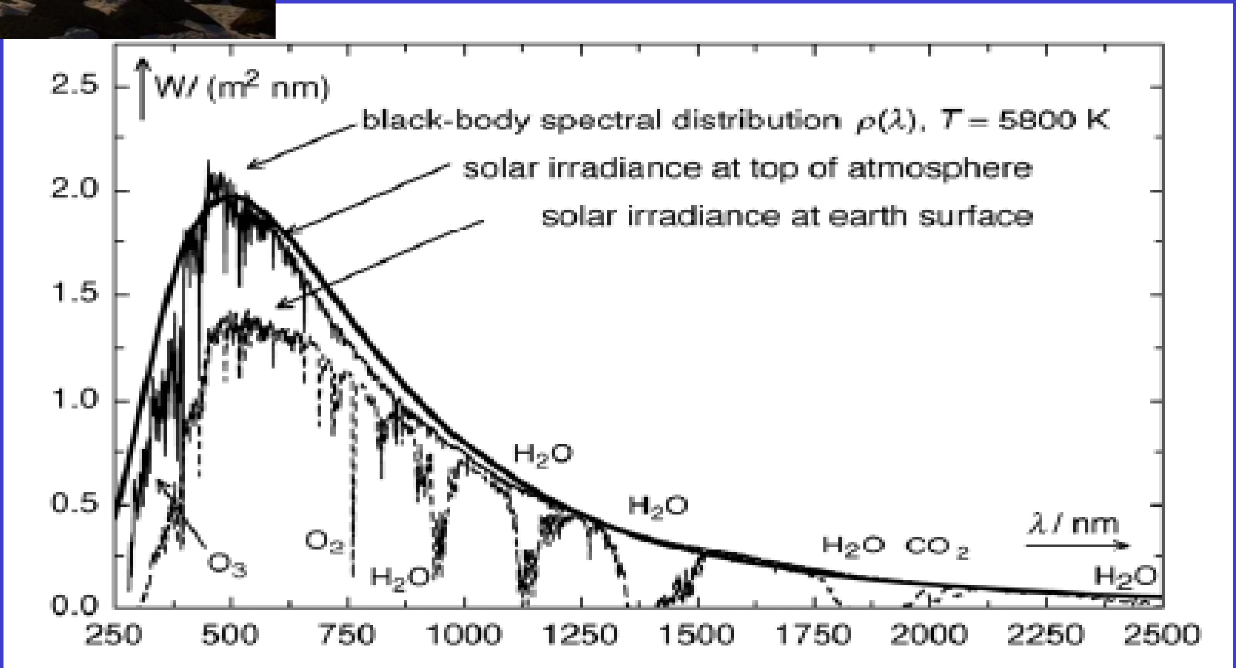
Elektronová spektroskopie



Sluneční světlo





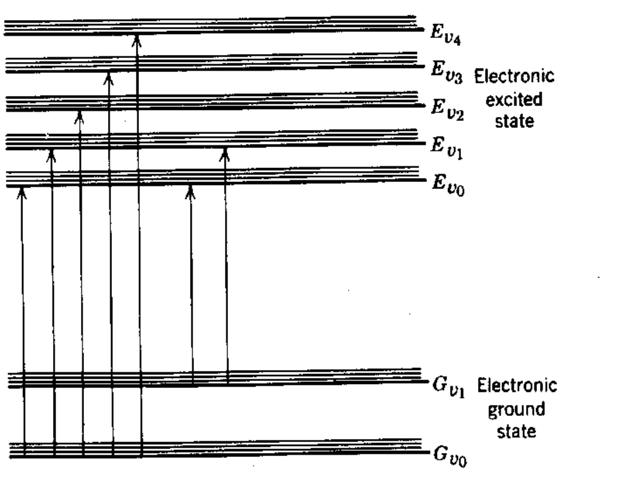


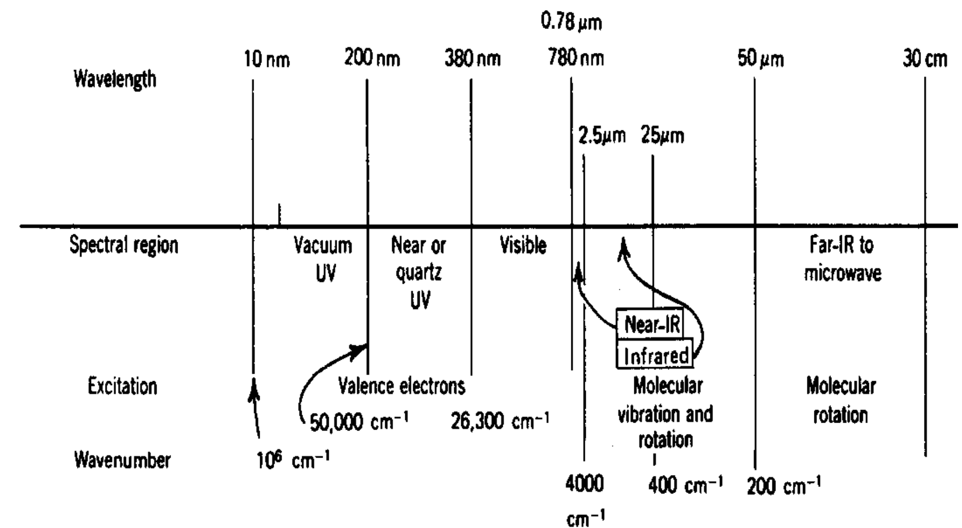
What is UV-VIS spectroscopy measuring? Electronic transitions.

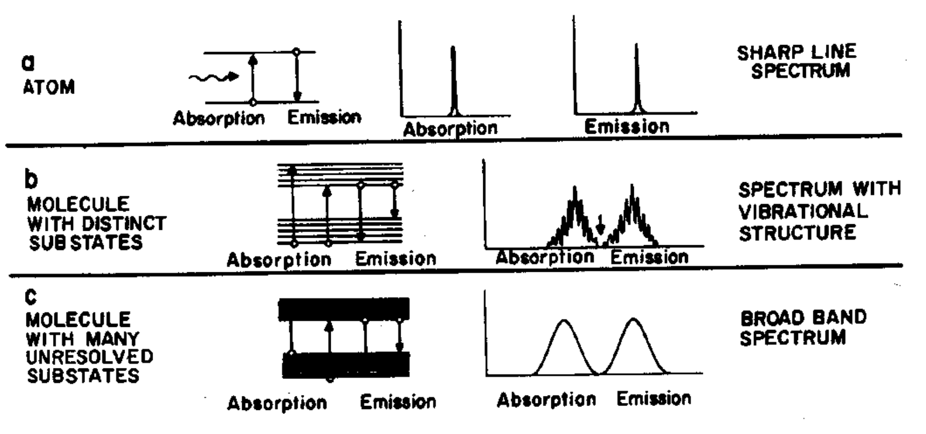
λ / nm	
185 - 200	Vacuum-UV
200 – 380	Near-UV (quartz)
380 – 780	Visible

$$E_{\text{int}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}$$

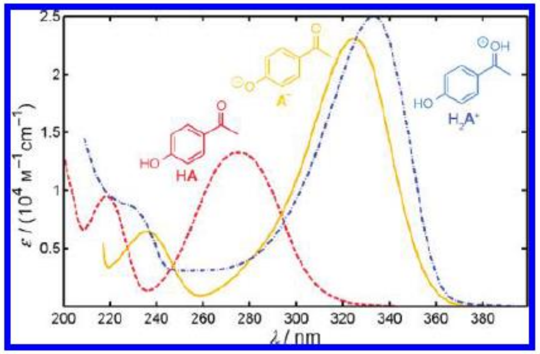
$$\Delta E = h\,\nu$$







Spectrum

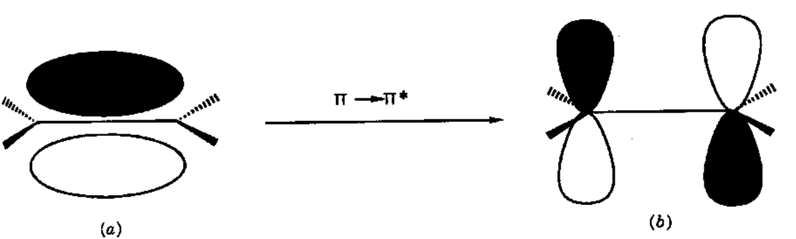


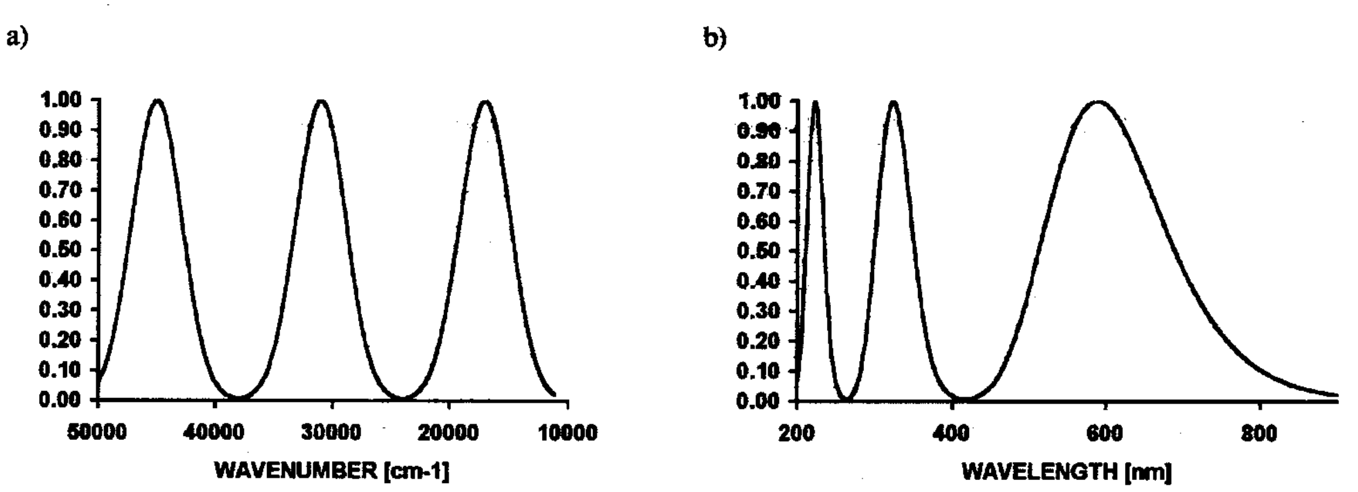
Abscissa (x) ~ $\Delta E \sim \tilde{\nu} \sim 1/\lambda$

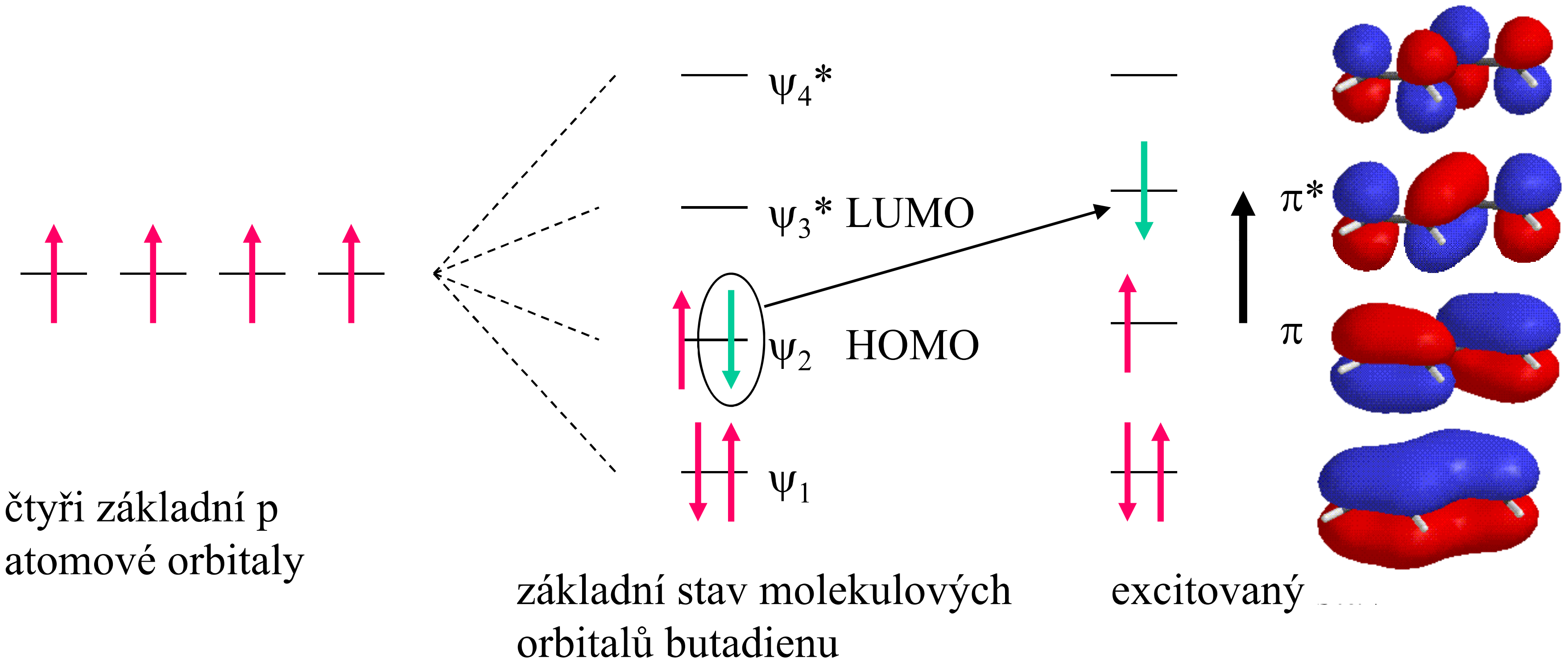
Ordinat (y) ~ intensity ~ probability of transition → the oscillator strength

$$f \equiv 4.3\text{e-}9 \int \varepsilon \, d\tilde{\nu} \sim 4.3\text{e-}9 \; \varepsilon_{\max} \, \Delta \tilde{\nu}_{1/2}$$

$$\Delta E = h\nu = hc/\lambda = hc\tilde{\nu}$$







čtyři základní p atomové orbitaly

základní stav molekulových orbitalů butadienu

excitovaný

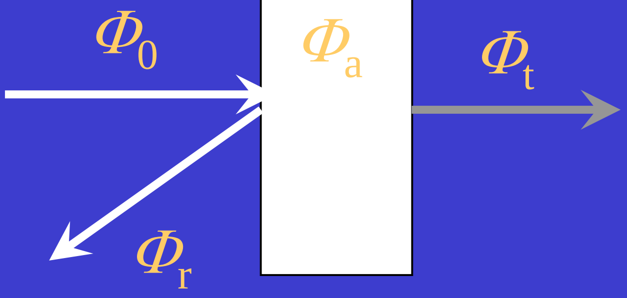
LUMO – Lowest Unoccupied Molecular Orbital (nejnižší neobsazený MO)
HOMO – Highest Occupied Molecular Orbital (nejvyšší obsazený MO)

- Překryvový integrál
- Dipólový moment

Beer – Lambert – Bouguer law

$$-\log(\Phi_t/\Phi_0) = -\log\,\tau_i = \varepsilon c b = A(\lambda)$$

$\tau_i = \Phi_t/\Phi_0$	internal transmittance (transmission factor)
$\rho = \Phi_r/\Phi_0$	reflectance (reflection factor)
$\alpha = \Phi_a/\Phi_0 = 1 - \tau$	absorptance (absorption faktor)



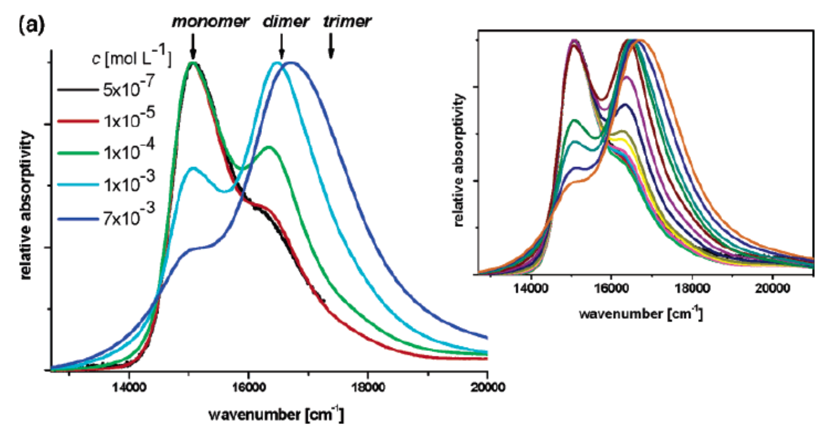
Term	Symbol	Unit
Monochromatic radiant power	Φ	W
(decadic) internal absorbance	A	1
Molar (decadic) absorption coefficient	ε	L mol^{-1} cm^{-1}
Absorption pathlength	b	cm^{-1}
Cell pathlength	l	cm^{-1}

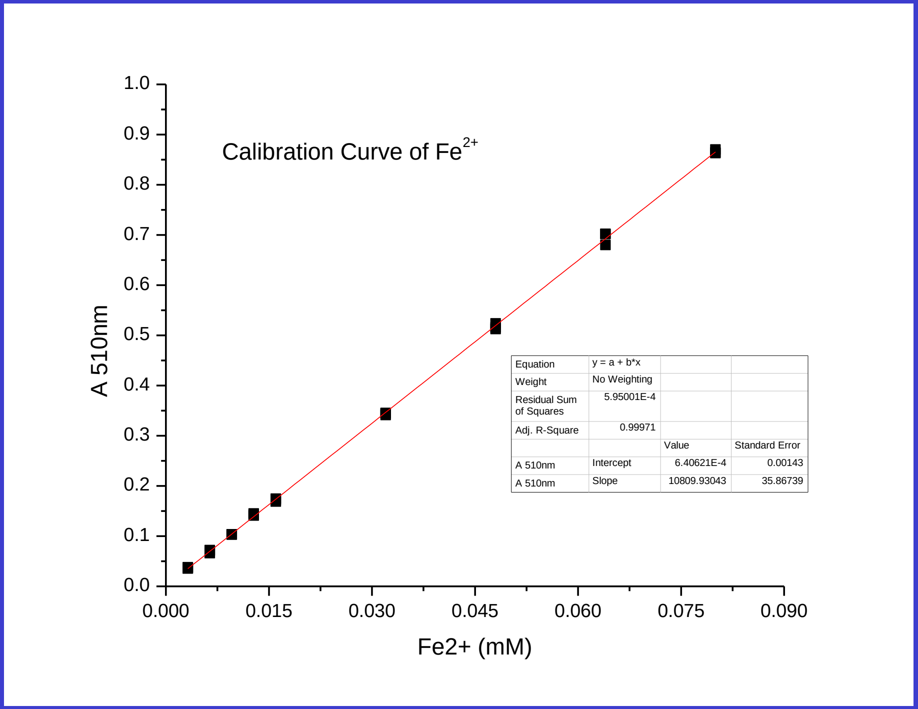
Extinction – sum of absoption, scattering and luminescence.

http://old.iupac.org/reports/V/spectro/partVII.pdf

Beer – Lambert – Bouguer law

$$A(\lambda) = \varepsilon(\lambda)cl$$





Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	5.95001E-4		
Adj. R-Square	0.99971		
		Value	Standard Error
A 510nm	Intercept	6.40621E-4	0.00143
A 510nm	Slope	10809.93043	35.86739

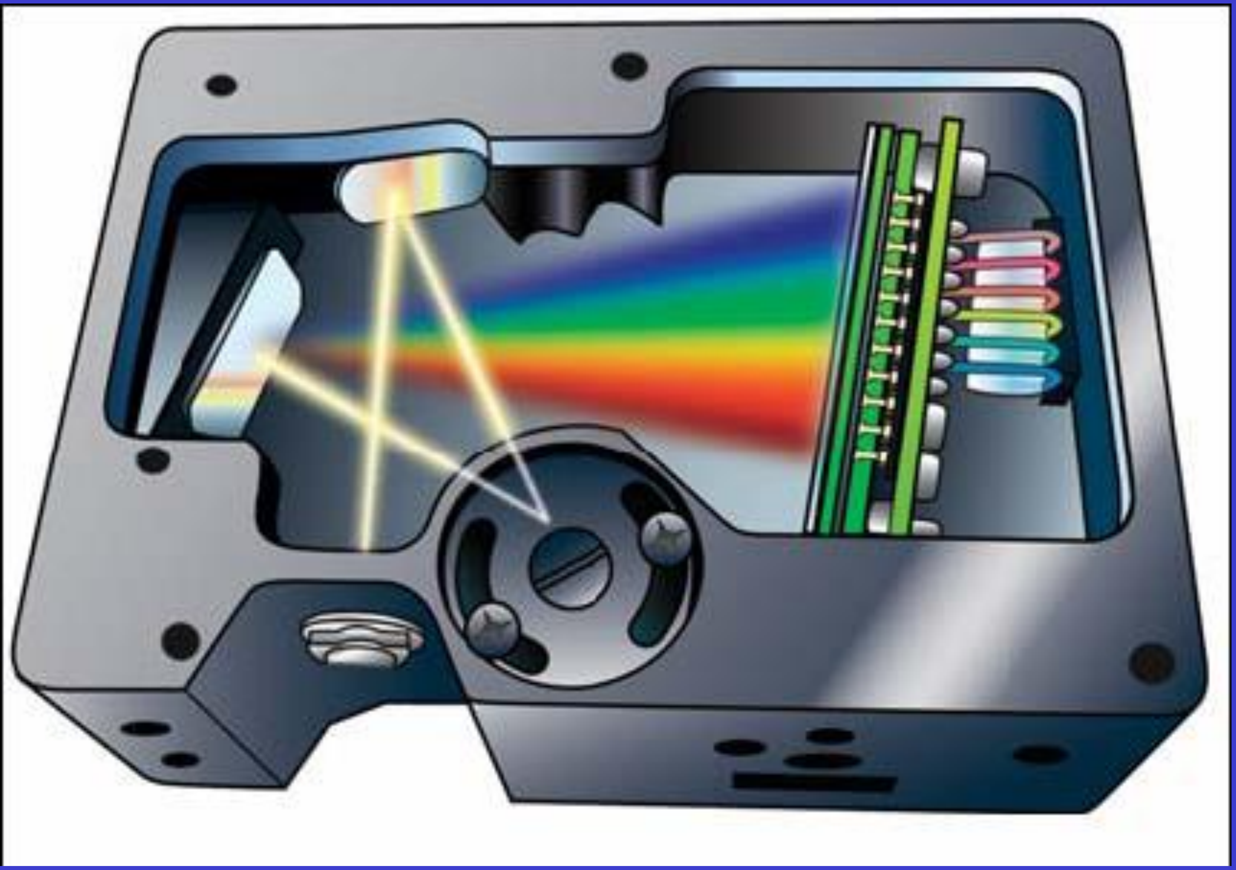
$$A(\lambda) = \sum_{i=1}^{n} A_i(\lambda) = l \sum_{i=1}^{n} \varepsilon_i(\lambda) c_i$$

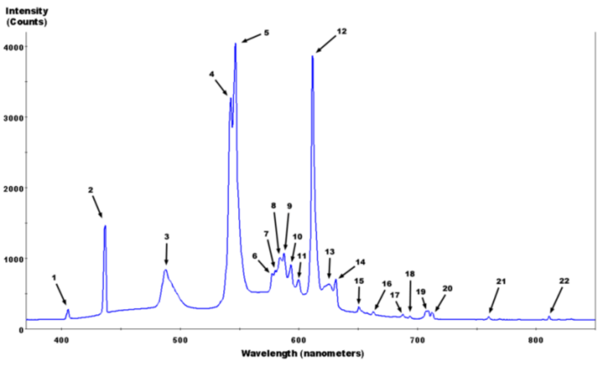
J. Phys. Chem. A, Vol. 109, No. 30, 2005

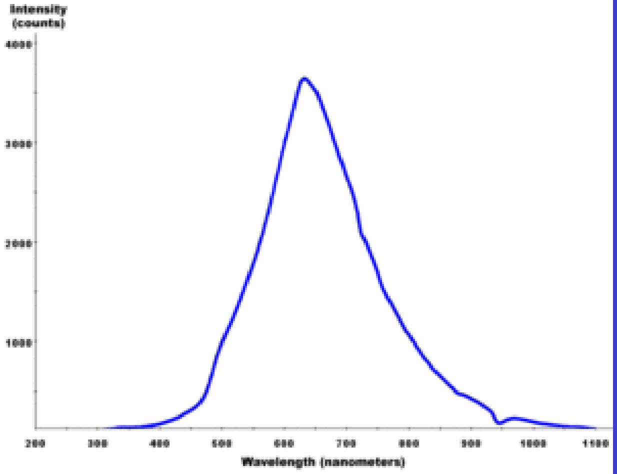
Beer – Lambert – Bouguer law limitations

- Chemical reasons – chemical equilibria (acid-base reaction, self-association, complexation, thermal reaction, photochemical reaction, inhomogenous samples)
- Physical reasons – thermochromism, saturation effects – depletion of the ground state, incident radiation must be parallel

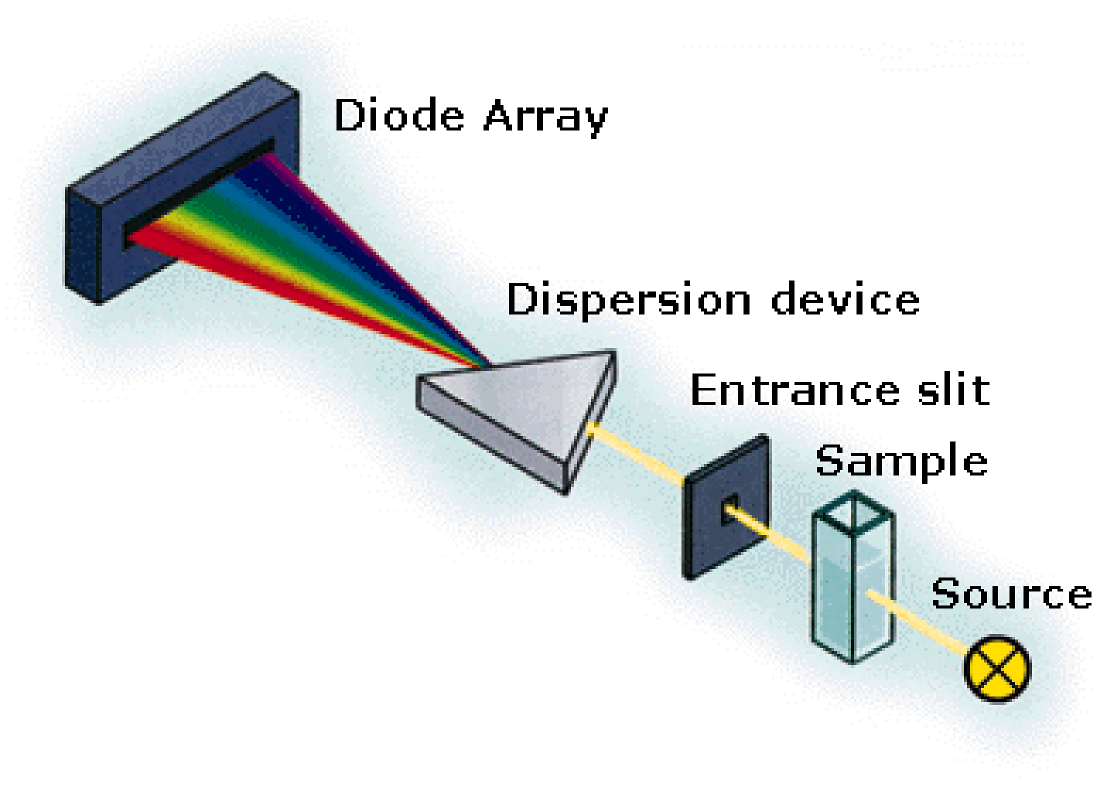
Jak funguje spektrometr?







Single beam UV – VIS spectrophotometer with diod array detector



Single beam UV – VIS spectrophotometer

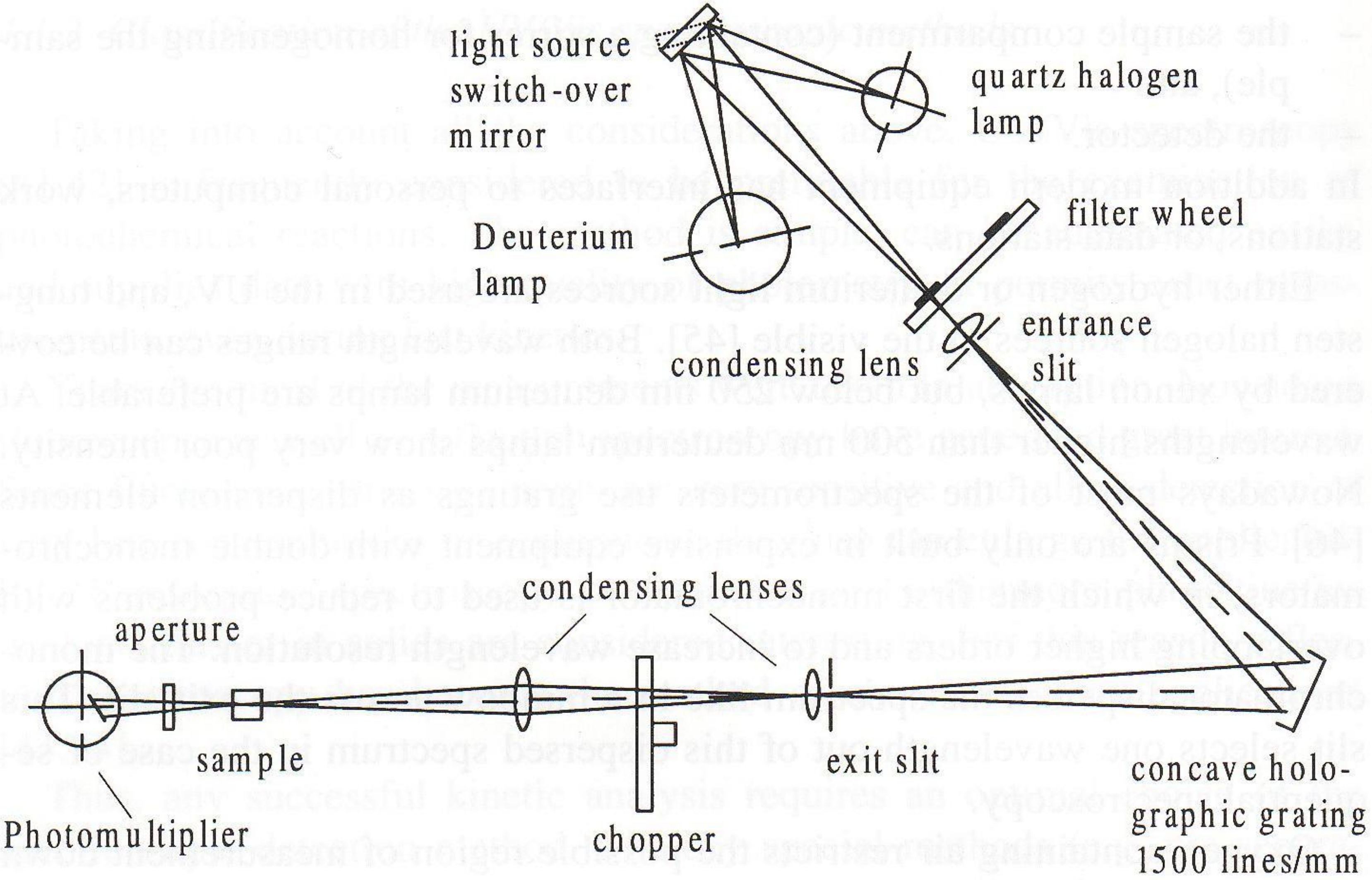


Fig. 4.1. Optical geometry of a single beam instrument, the Uvikon 710 by Kontron Instruments, Eching.

Double beam UV – VIS spectrophotometer

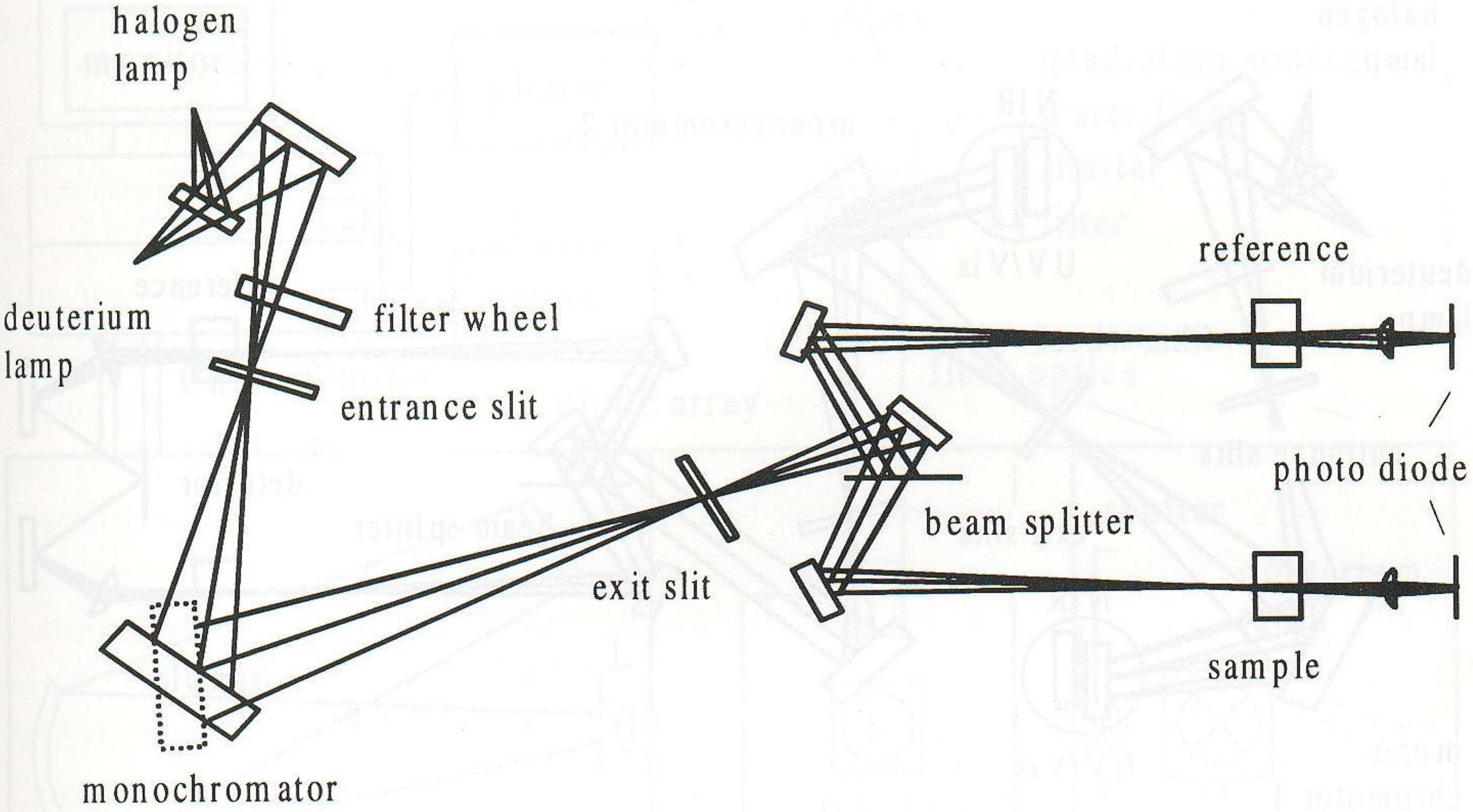


Fig. 4.2. Schematic diagram of the optical pathway in a double beam instrument Lambda 2, Perkin Elmer, Überlingen.

Double beam, double monochromators UV – VIS spectrophotometer

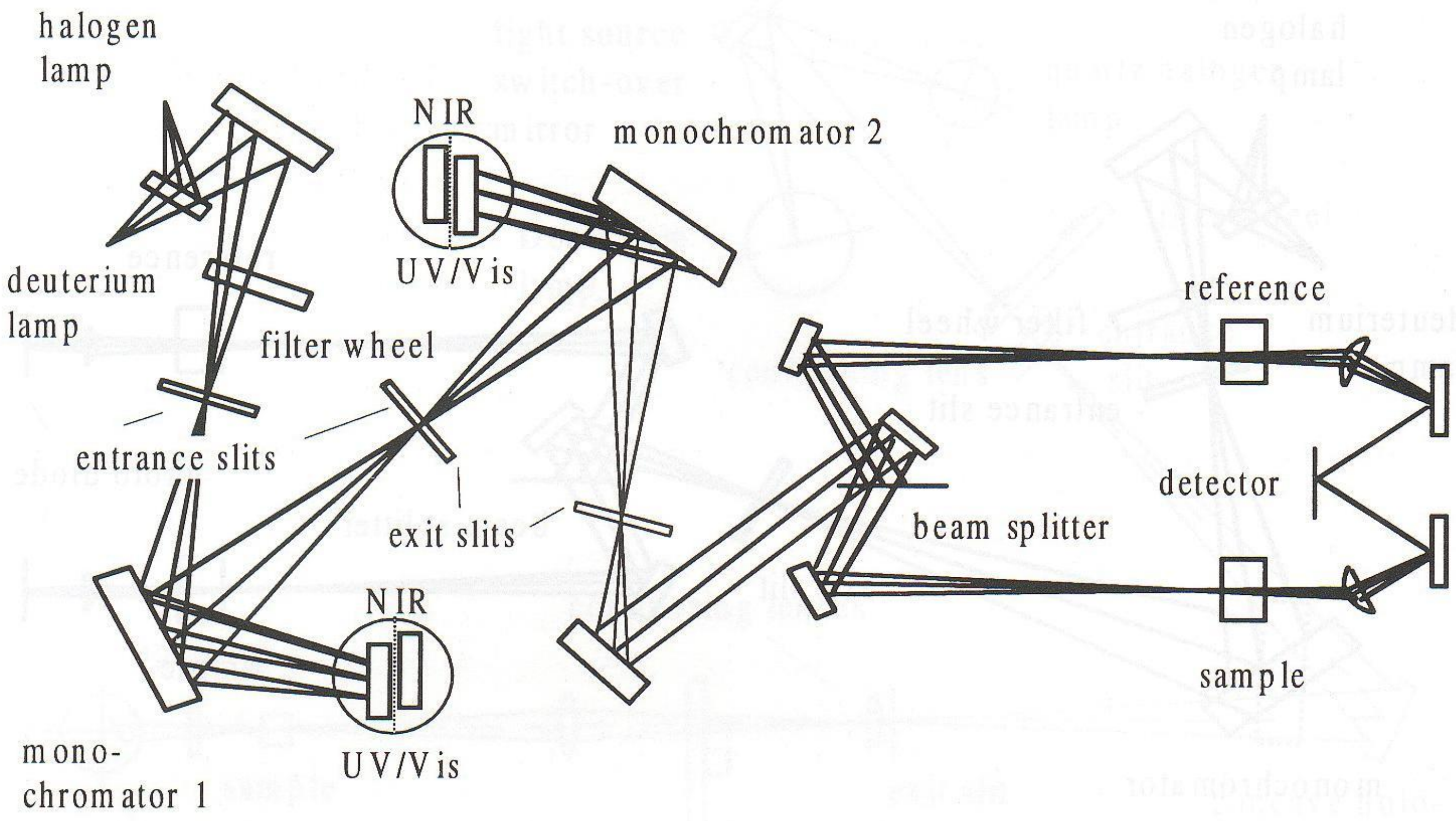


Fig. 4.3. Double beam set-up with a double monochromator for very precise photometric measurements and the possibility of taking high resolution spectra (Lambda 9, Perkin Elmer, Überlingen). This instrument covers the wavelength range from the UV until the near infrared (NIR).

UV – VIS spectrophotometer

Light source

- Continuuu × spectral-line source
- Hg-halogen lamp <330; 1200) nm
- D_2 lamp <UV; 330> nm
- Xe arc lamp <190; 1000> nm

Spectrometer

- Single beam × double beam
- Sequential × simultaneous

Cuvettes

- shape
- volume
- material
- use of matched cells

Detectors

- photo-emisive detectors (evacuated phototubes, photomultiplier...)
- semiconuctive detectors (photodiods; detectors with a spacial resolution– CCD –charge-coupled device)

http://www.hellmaoptik.com/en/kuevetten/

Lamps

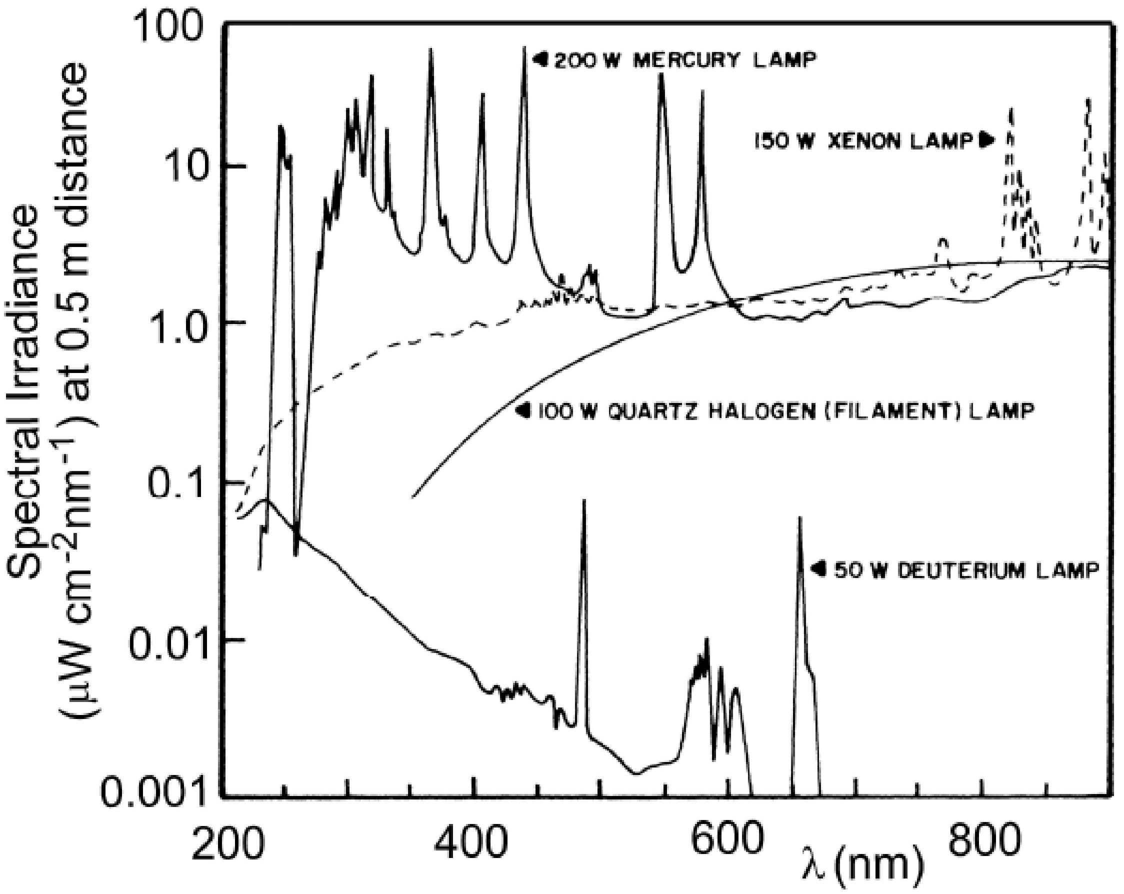
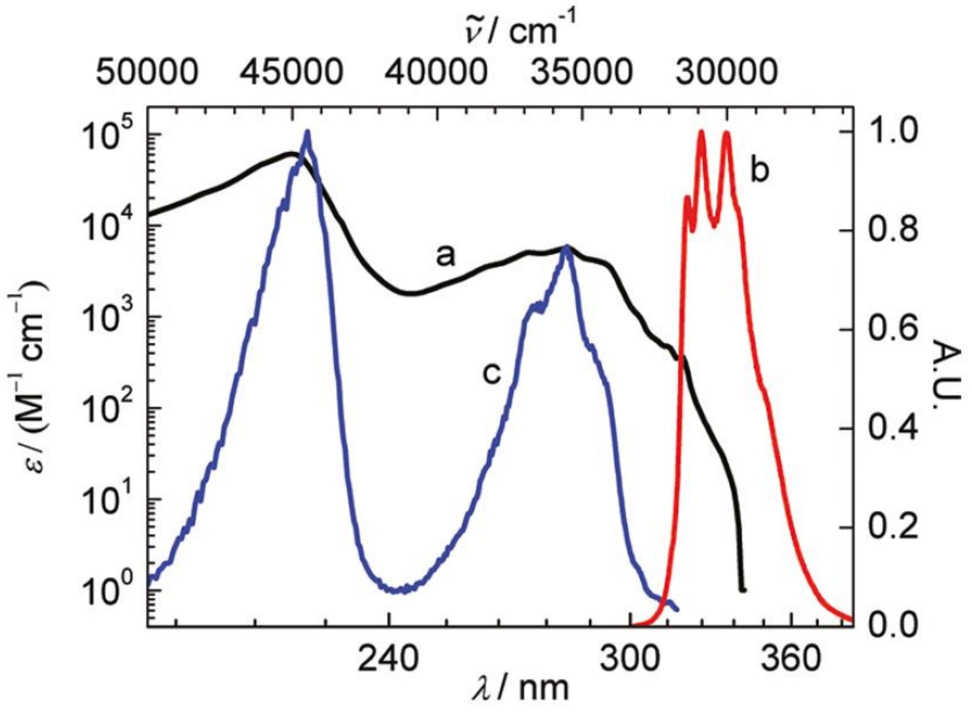


Fig. 11a-2. Spectral irradiance of some arc lamp sources. Reprinted by permission from LOT-Oriel catalogue.

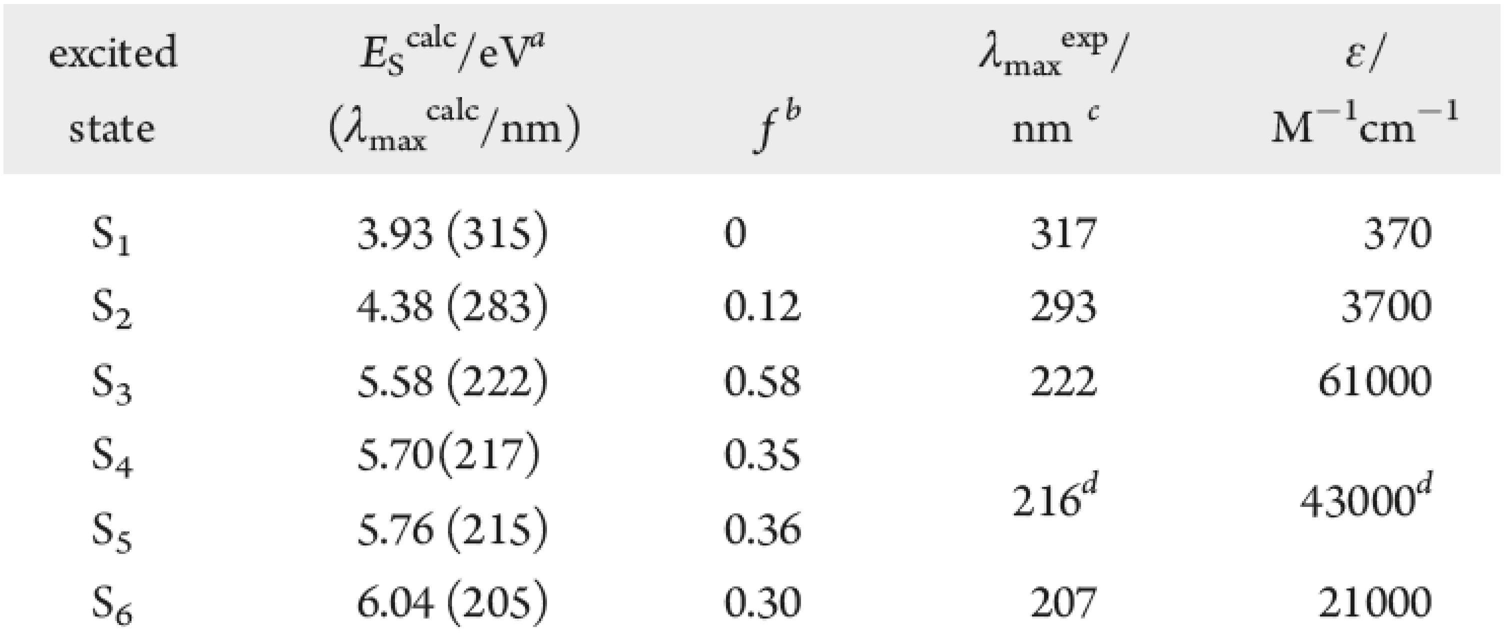
Methyl-Naftalen



$0.1 \leq A \leq 1.5$

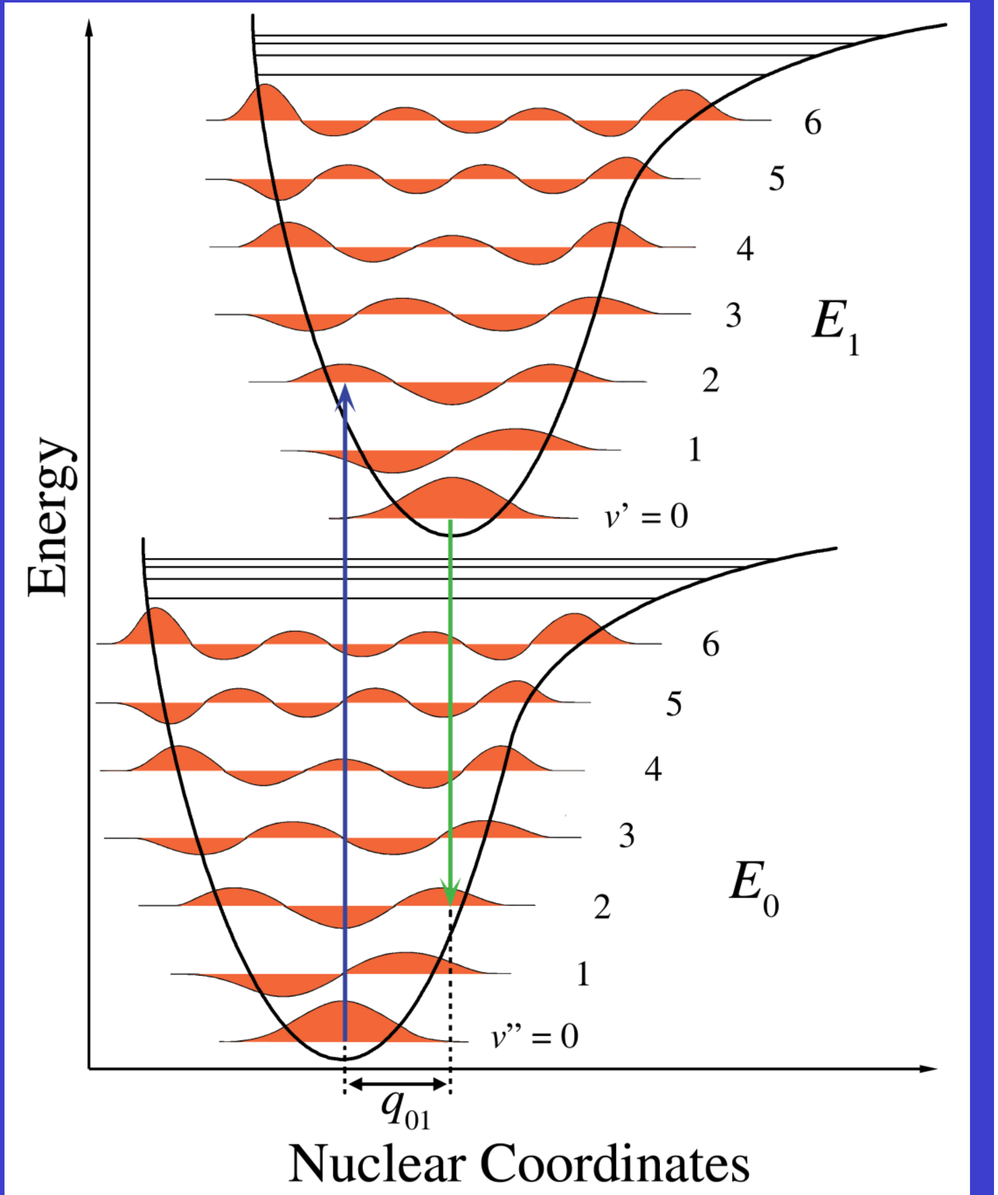
A	τ
0.001	0.998
0.010	0.977
0.046	0.900
0.100	0.794
0.430	0.370
0.500	0.316
1.000	0.100
1.500	0.032
2.000	0.010
3.000	0.001
4.0000	0.0001

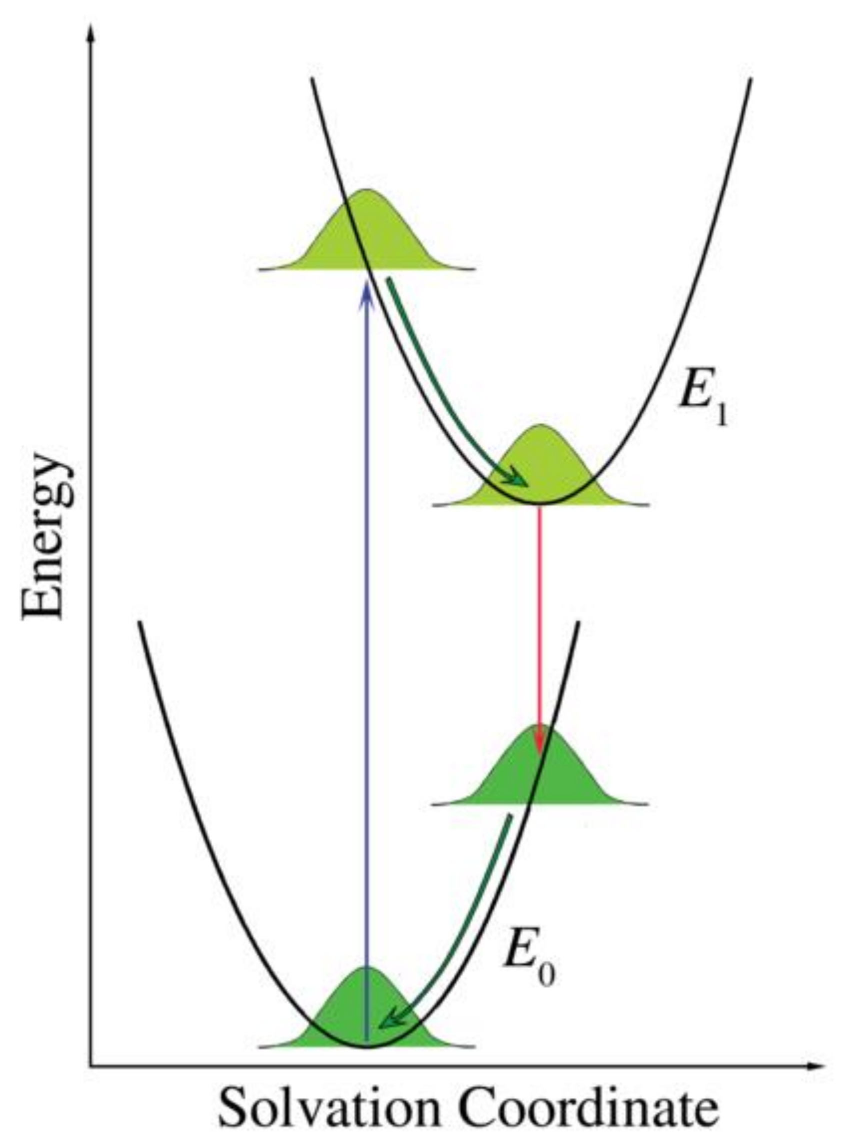
$$-\log\left(\Phi_t/\Phi_0\right) = -\log\ \tau_i = \varepsilon c b = A(\lambda)$$



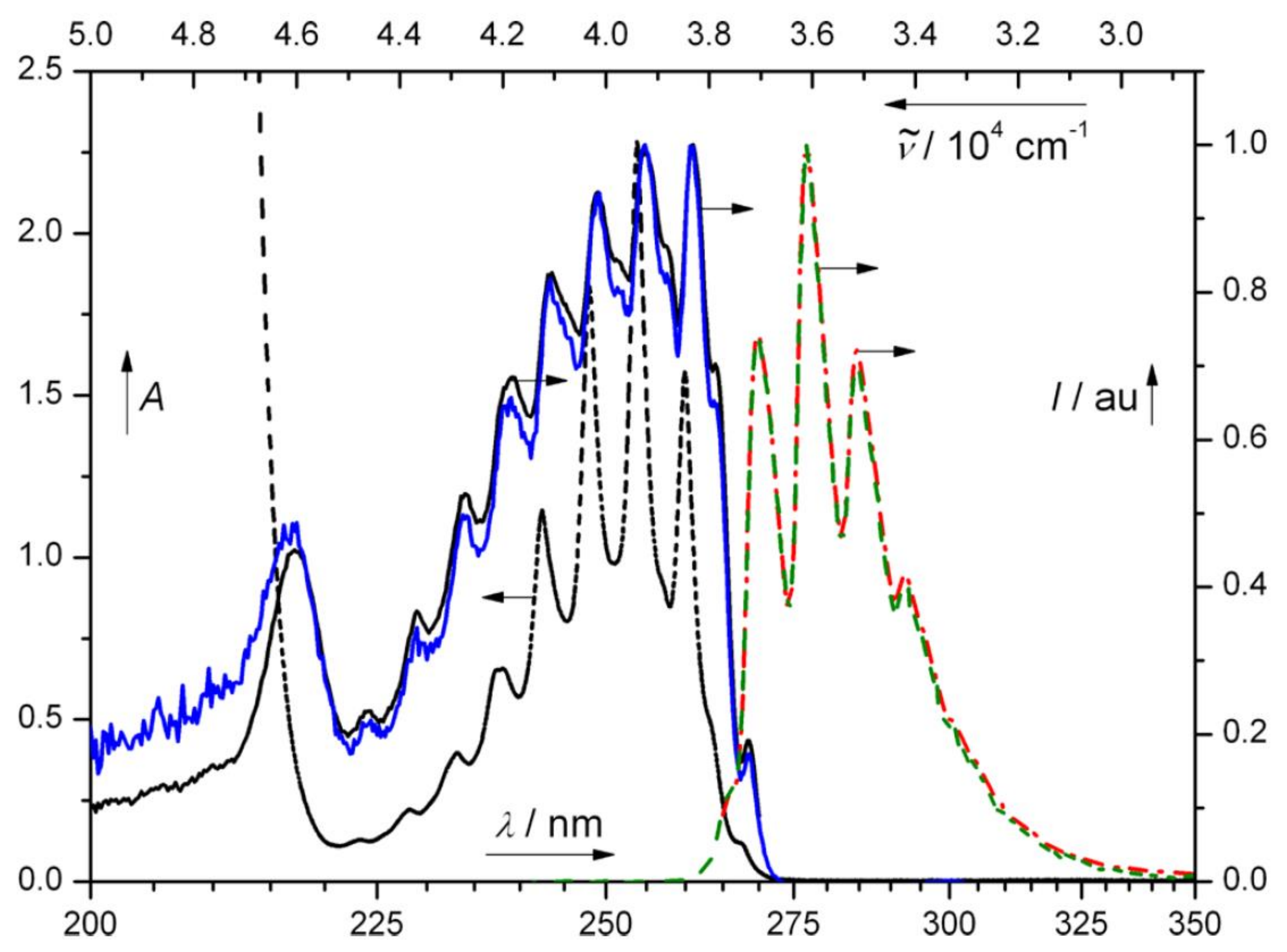
excited state	E_S^{calc}/eV^a (λ_{max}^{calc}/nm)	$f^{\,b}$	λ_{max}^{exp}/ nm ^{c}	ε/ M^{-1}cm^{-1}
S_1	3.93 (315)	0	317	370
S_2	4.38 (283)	0.12	293	3700
S_3	5.58 (222)	0.58	222	61000
S_4	5.70(217)	0.35	216^d	43000^d
S_5	5.76 (215)	0.36		
S_6	6.04 (205)	0.30	207	21000

Franck-Condon Principle; Vertical excitation





Benzene



J. Phys. Chem. A 2014, 118, 7535−7547

What is the vibrational progression in GS and in S1?

Application of derivative spectroscopy to benzene

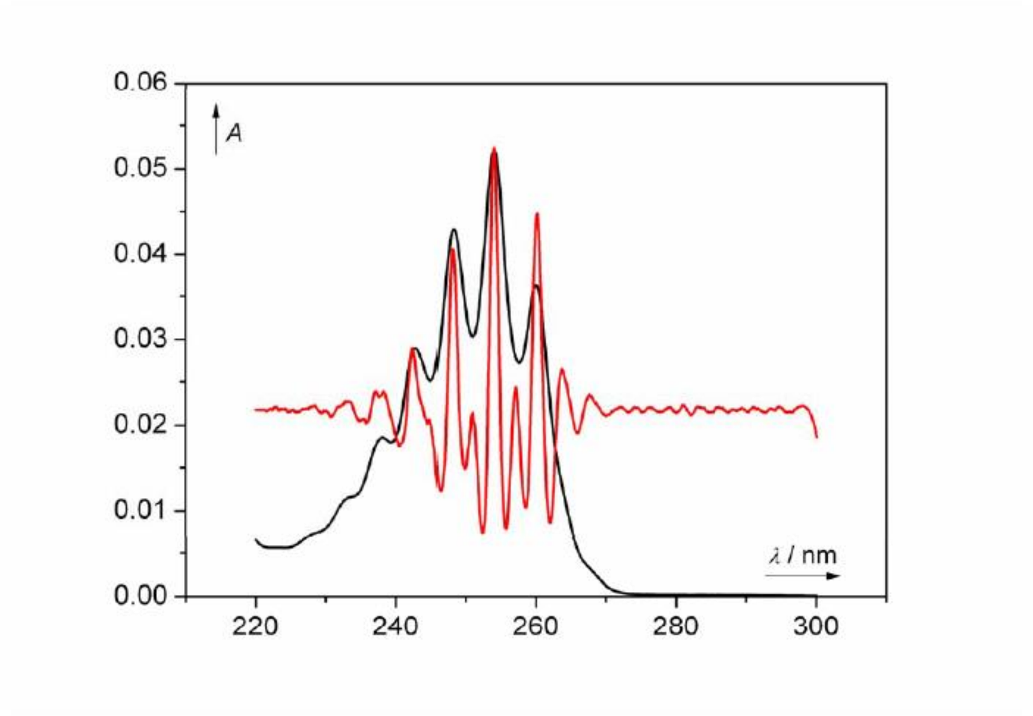
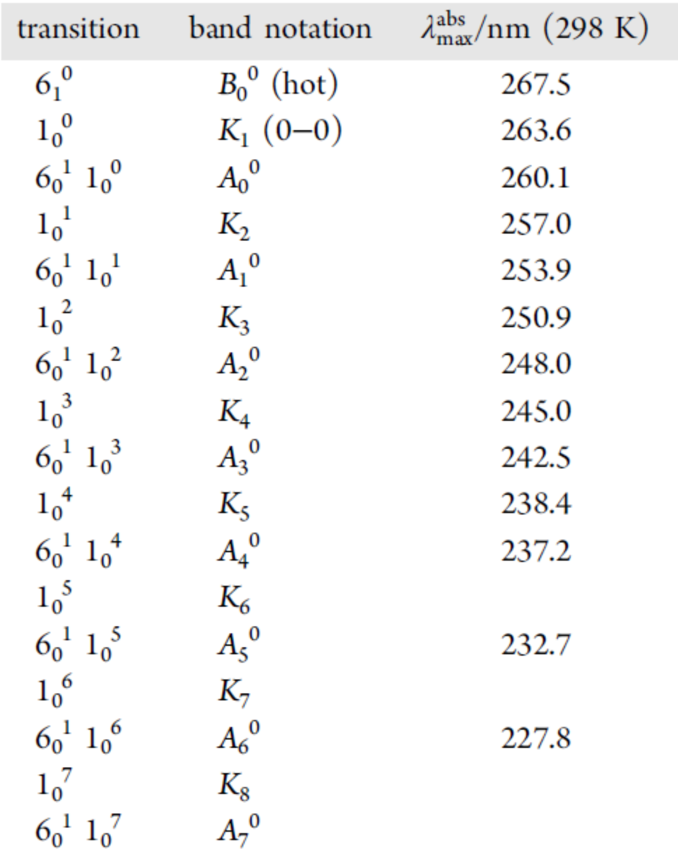


Figure S1. The absorption spectrum of benzene aq solution (black) with its 4th derivative (red).



transition	band notation	$\lambda_{\mathrm{max}}^{\mathrm{abs}}$/nm (298 K)
6_1^0	B_0^0 (hot)	267.5
1_0^0	K_1 (0–0)	263.6
$6_0^1\ 1_0^0$	A_0^0	260.1
1_0^1	K_2	257.0
$6_0^1\ 1_0^1$	A_1^0	253.9
1_0^2	K_3	250.9
$6_0^1\ 1_0^2$	A_2^0	248.0
1_0^3	K_4	245.0
$6_0^1\ 1_0^3$	A_3^0	242.5
1_0^4	K_5	238.4
$6_0^1\ 1_0^4$	A_4^0	237.2
1_0^5	K_6	
$6_0^1\ 1_0^5$	A_5^0	232.7
1_0^6	K_7	
$6_0^1\ 1_0^6$	A_6^0	227.8
1_0^7	K_8	
$6_0^1\ 1_0^7$	A_7^0	

Franck-Condon Principle

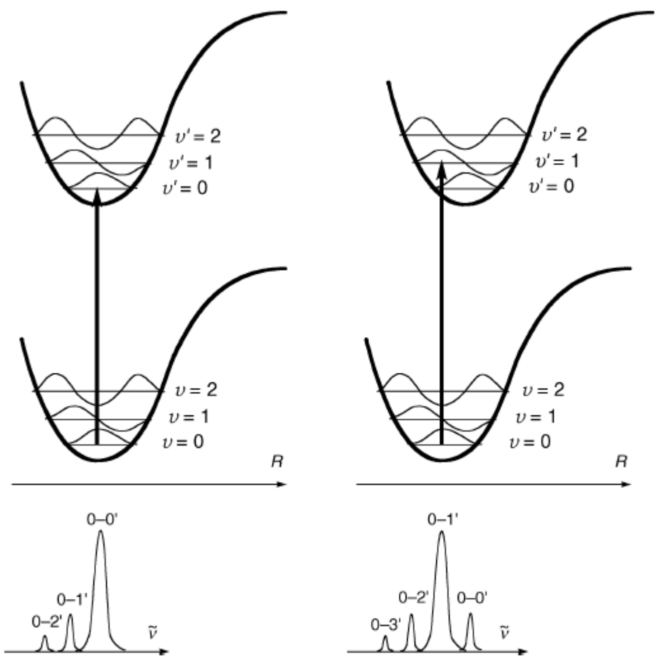
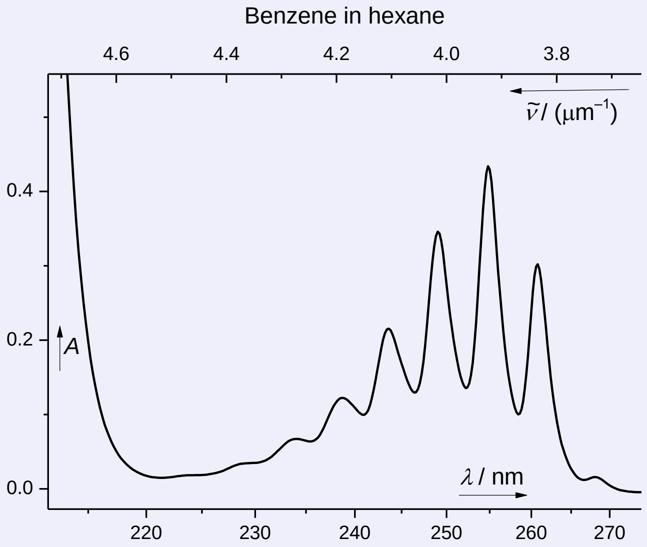
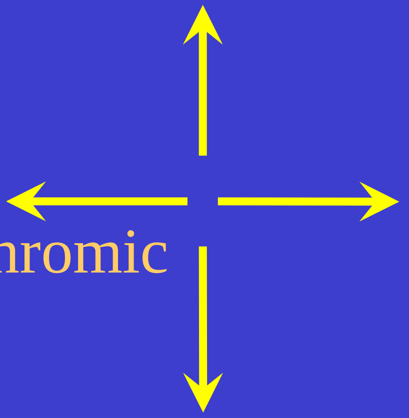


Figure 2.10 Illustration of the Franck–Condon principle. The bottom diagrams illustrate the vibrational structure of the absorption bands



Absorption bands of organic molecules



Effects

hyperchromic

Shifts

bathochromic

hypsochromic

hypochromic

Type of transition	ε_{max}
n → π^* (R)	< 100
π → π^* (K)	> 10 000
(B – benzenoid)	~ 500
(E - ethylenic)	2000 – 14 000

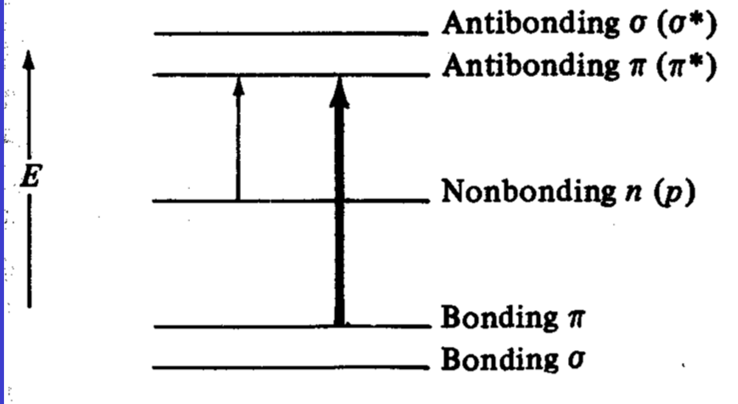
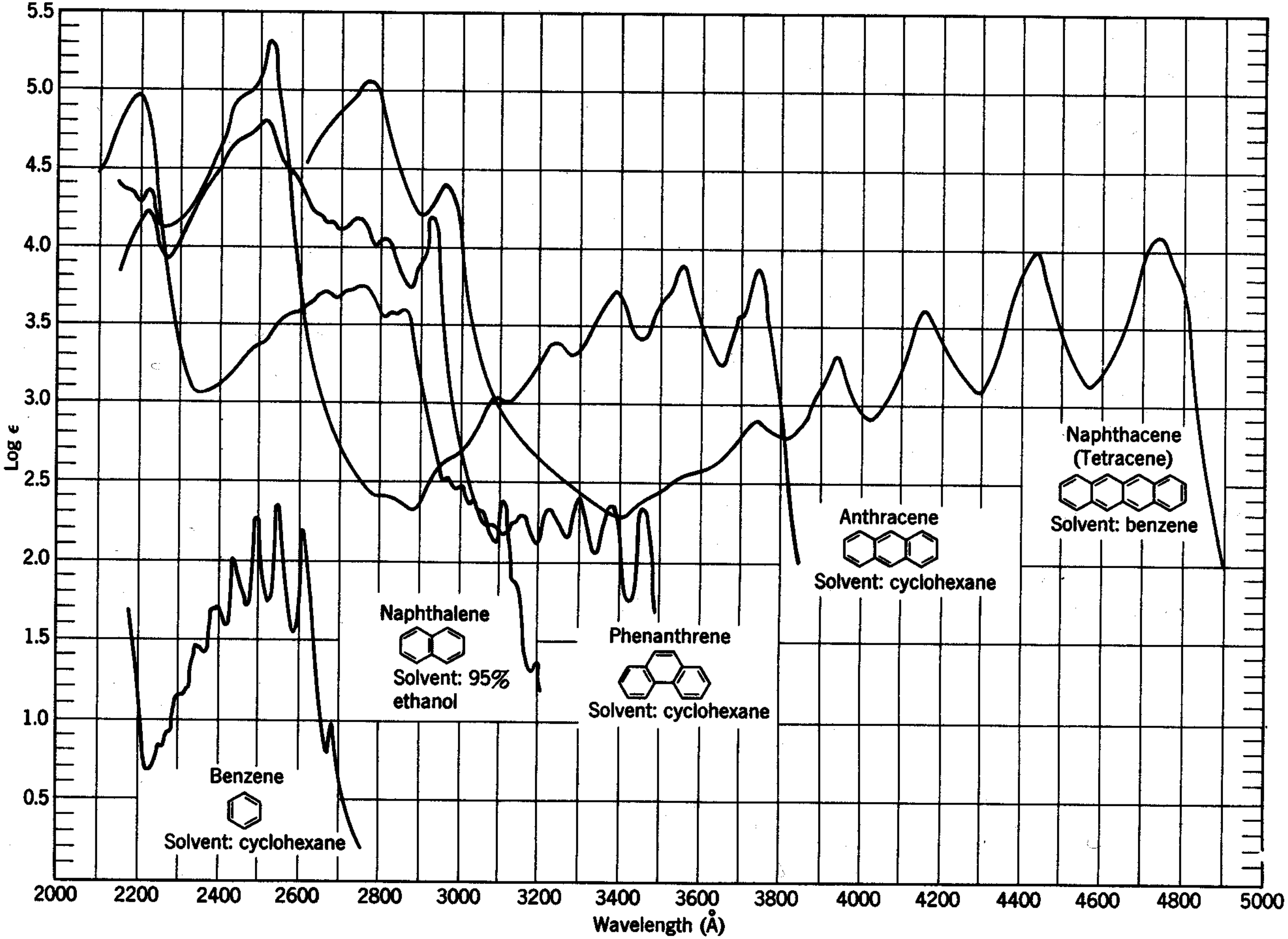


FIGURE 7.5. Summary of electronic energy levels. Both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (heavy arrow) transitions are represented.


5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Log ε
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
4400
4600
4800
5000
Wavelength (Å)
Benzene
Solvent: cyclohexane
Naphthalene
Solvent: 95% ethanol
Phenanthrene
Solvent: cyclohexane
Anthracene
Solvent: cyclohexane
Naphthacene (Tetracene)
Solvent: benzene

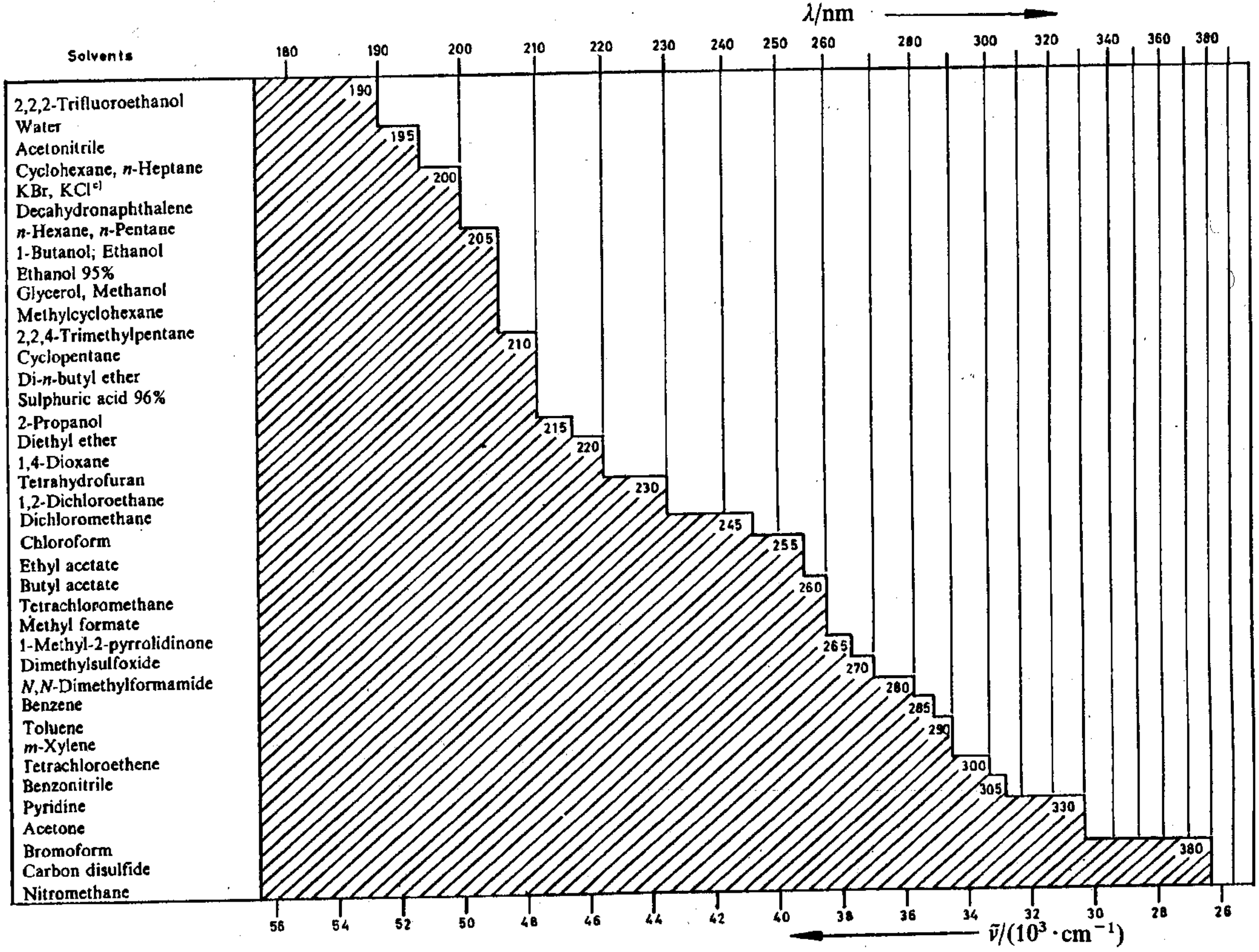


Table A-4. Ultraviolet "cut-off points"[a] of spectroquality solvents commonly used in UV/Vis-Spectroscopy, for 1 cm pathlengths (accuracy *ca.* ±5 nm)[b].

[a] The "cut-off point" in the ultraviolet region is the wavelength at which the absorbance approaches 1.0 using a 1-cm cell path with water as the reference. Solvents should not be used for measurements below the cut-off point, even though a compensating reference cell is employed. The cut-off points are very dependent on the purity of the solvent used. Most of the solvents listed above are available in highly purified "spectrograde" quality.

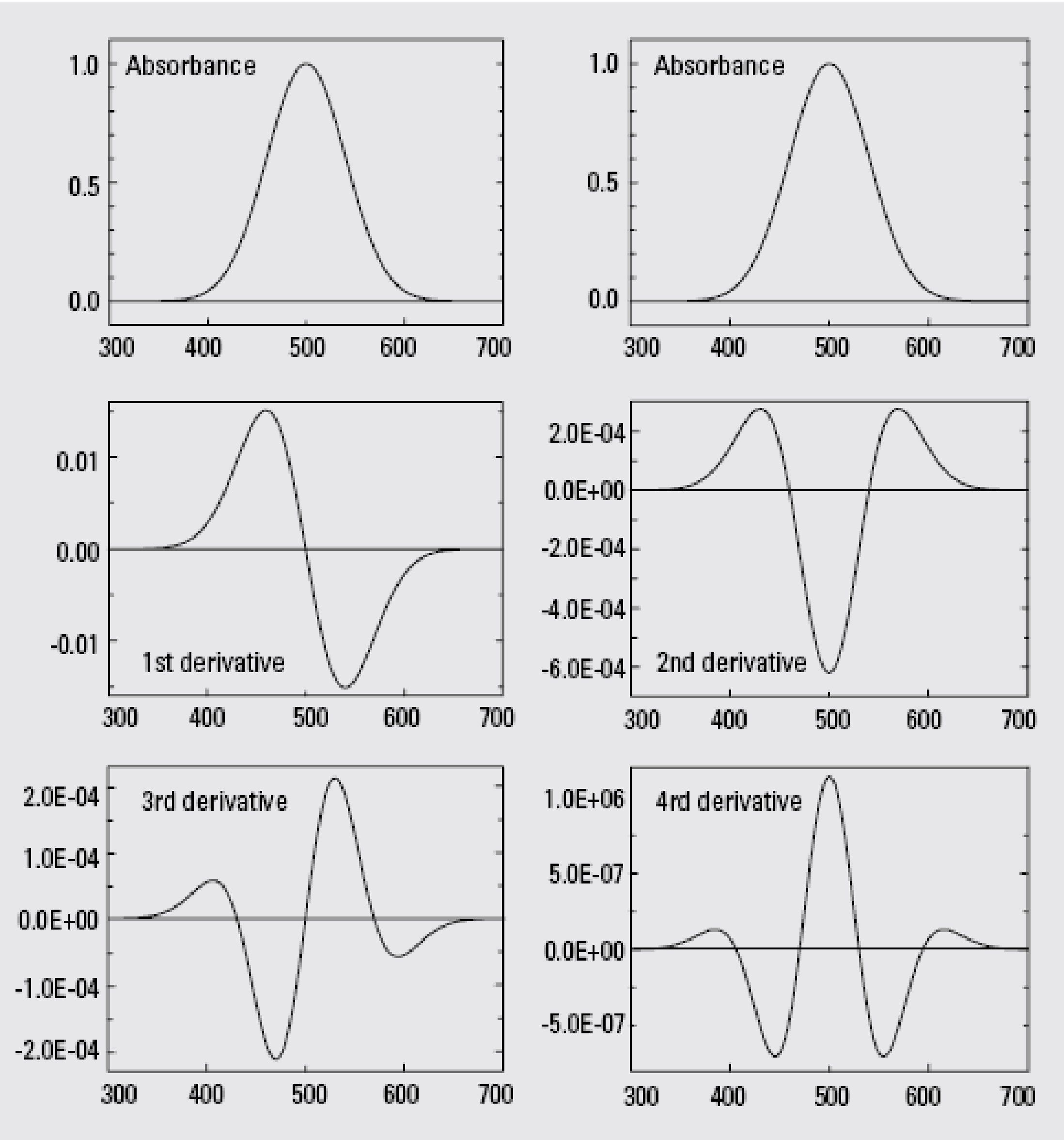
[b] Compiled from the following references:
(1) Eastman Kodak Company: *Spectrophotometric Solvents.* Dataservice Catalog JJ-282, Rochester, New York 14650, USA, 1977;
(2) E. Merck: *UVASOLE® – Lösungsmittel und Substanzen für die Spektroskopie.* D-6100 Darmstadt, Fed. Rep. Germany;
(3) and from the reviews of Gordon and Ford [4] (p. 167), Pestemer [25], and Hampel [34].

[c] Values for solid, as used in a pellet for example.

Measuring techniques

- Kvantitativní analýza
- Derivative spectroscopy-Finding of maxima– Antonov – Step by step filter (SBSF) –
- Resolution of overlapping bands (x deconvolution)
  - Curve fitting – Gaussian or others
  - Nonparametric methods
  - Singular Value Decomposition, Target Factoral Analysis
- Difference absorption spectroscopy
- Absorbance matching

Derivative spectroscopie



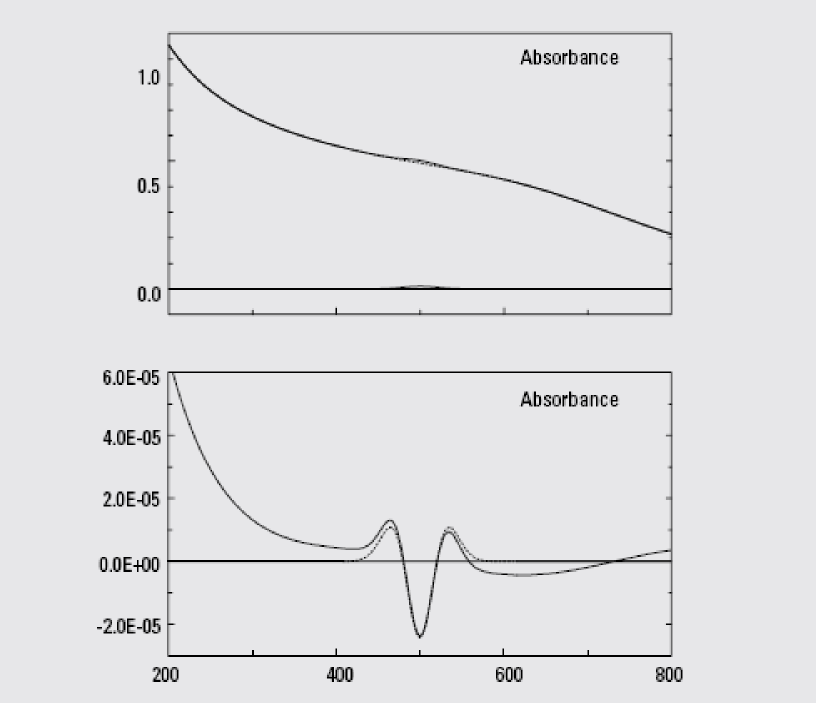
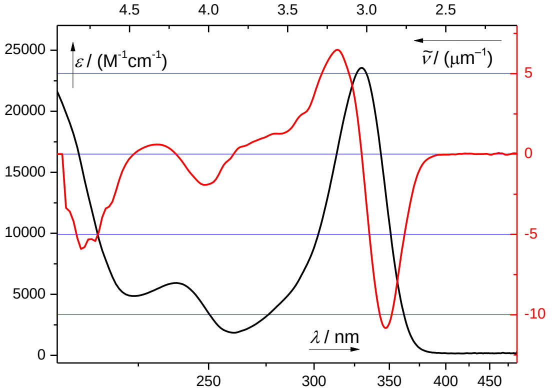


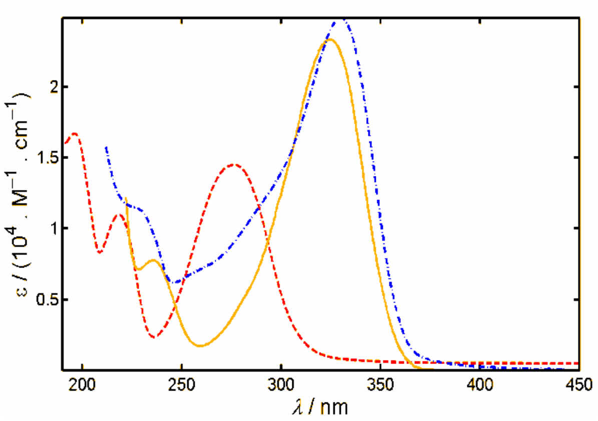
Figure 6
Matrix supression

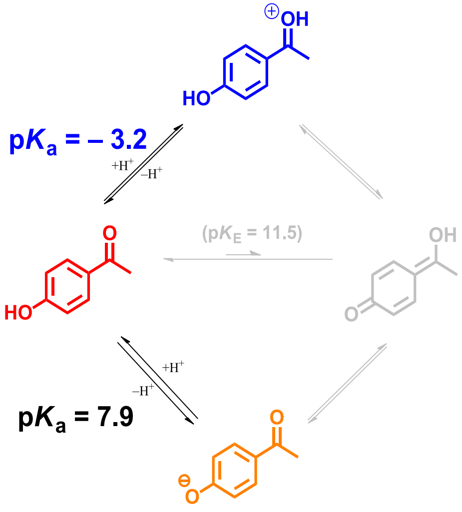
Antony J. Owen: Uses of Derivative Spectroscopy, Agilent Technologies, 1995

Derivative spectroscopie

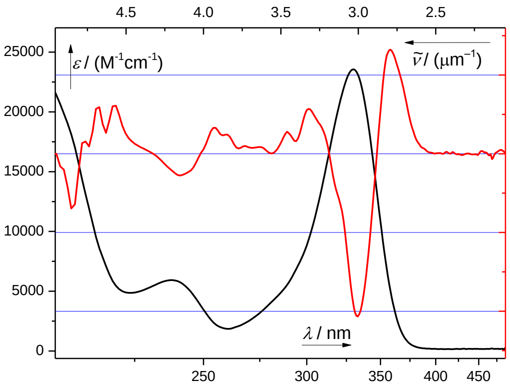
1st derivative



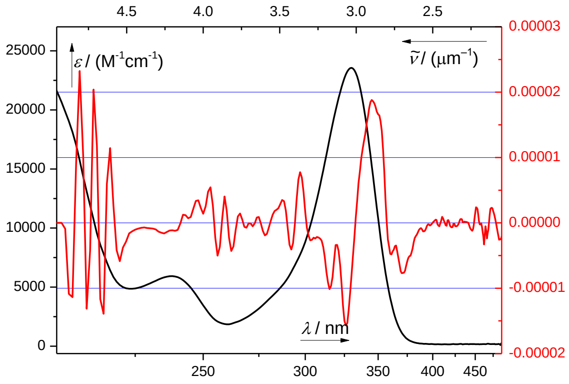




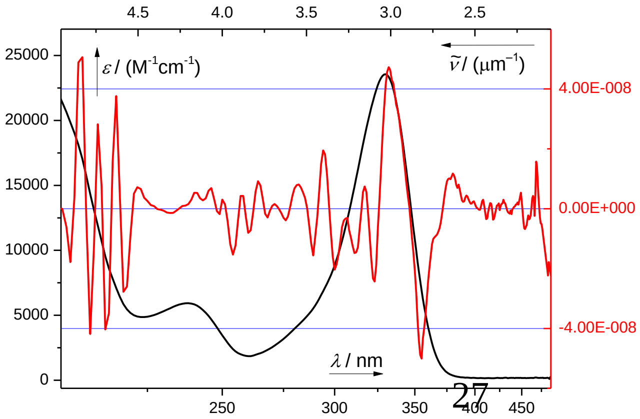
2nd derivative



3rd derivative



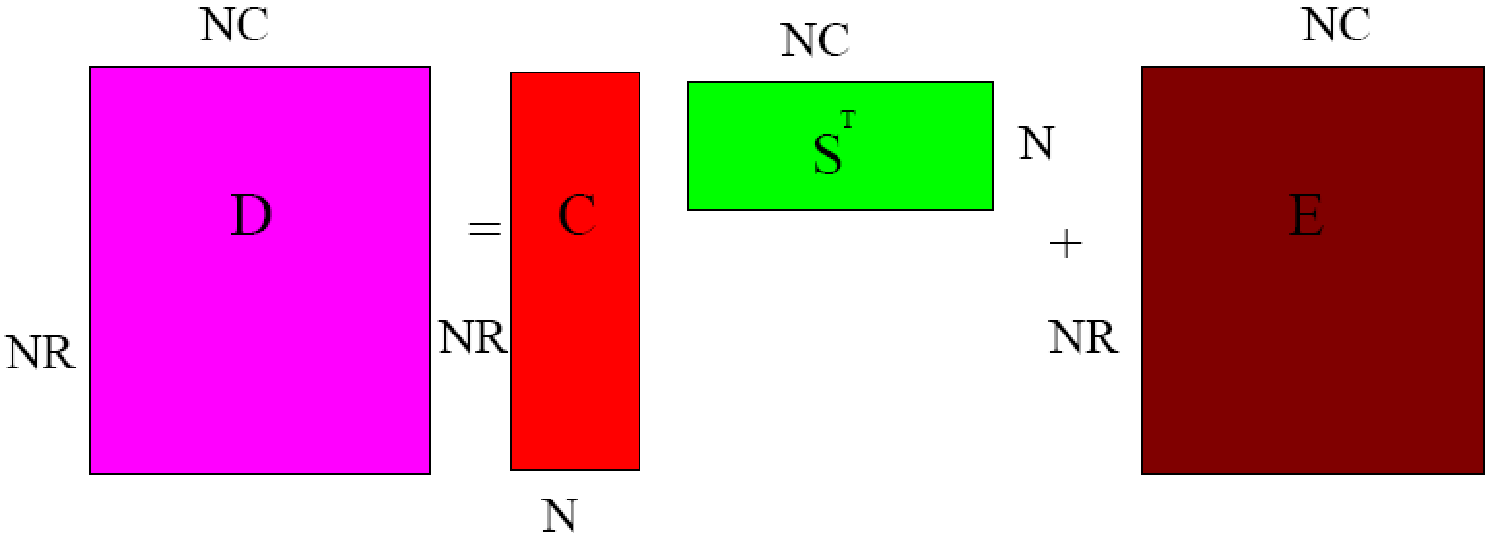
4th derivative



Multivariate Curve Resolution (MCR)

$$\boxed{d_{ij} = \sum_{k=1}^{N} c_{ik} s_{kj} + e_{ij}}$$

Bilinearity!



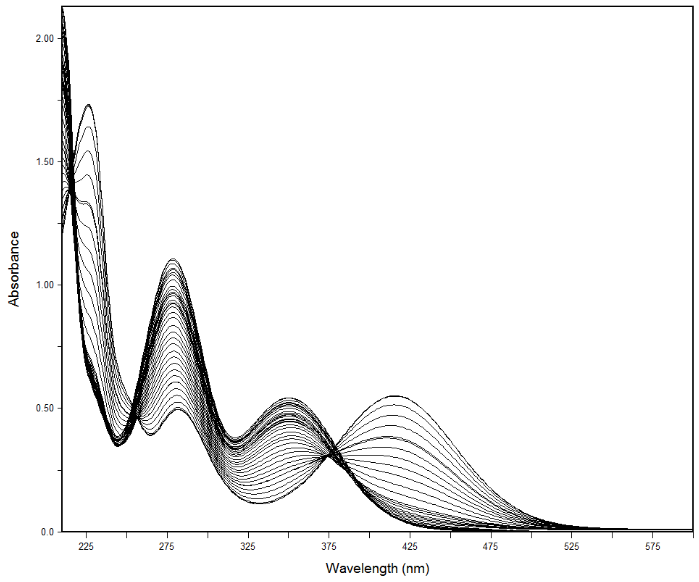
D(NR,NC) experimental data matrix

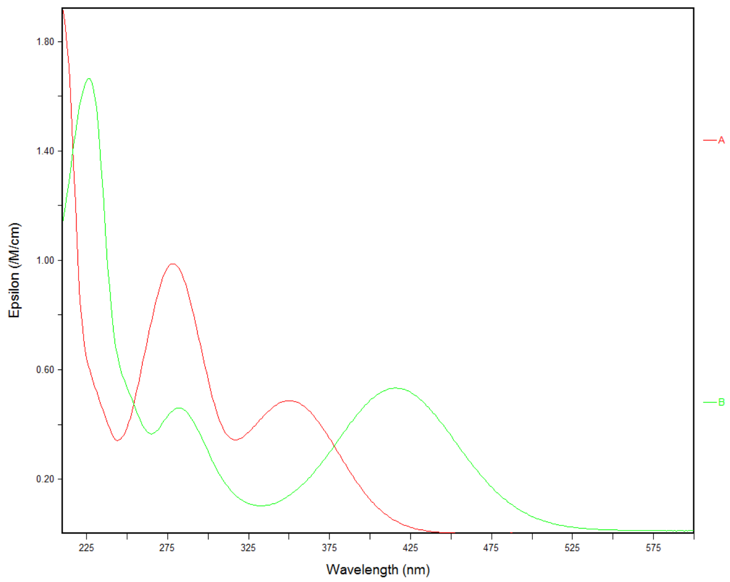
C(NR,N) row (concentration) profiles matrix

S(NC,N) column (spectra) profiles matrix

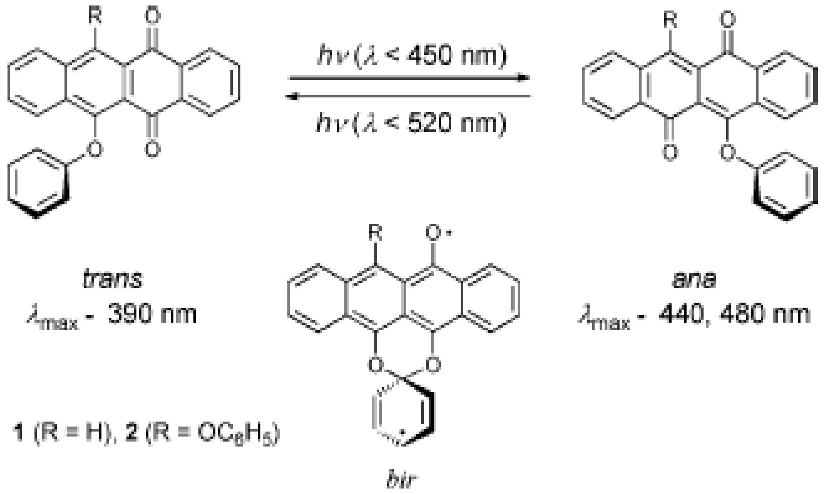
E(NR,NC) residual (noise, error) matrix

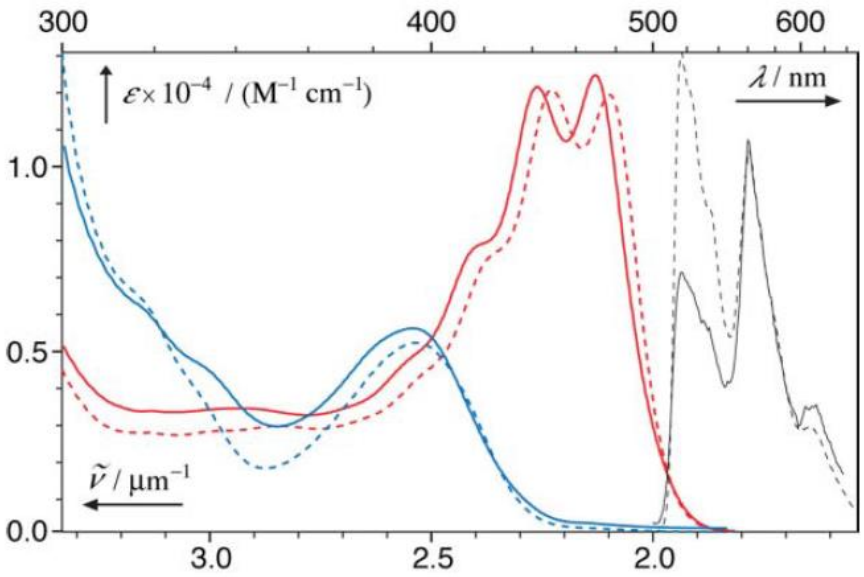
pH titration





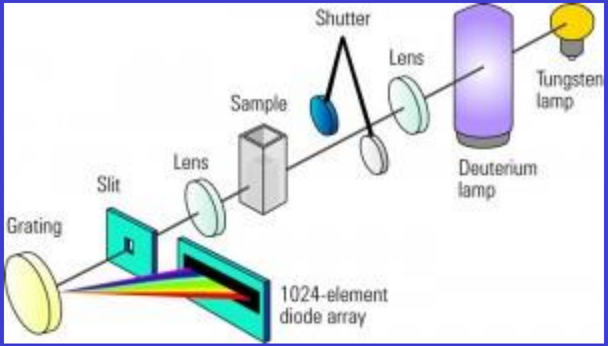
Photochromism

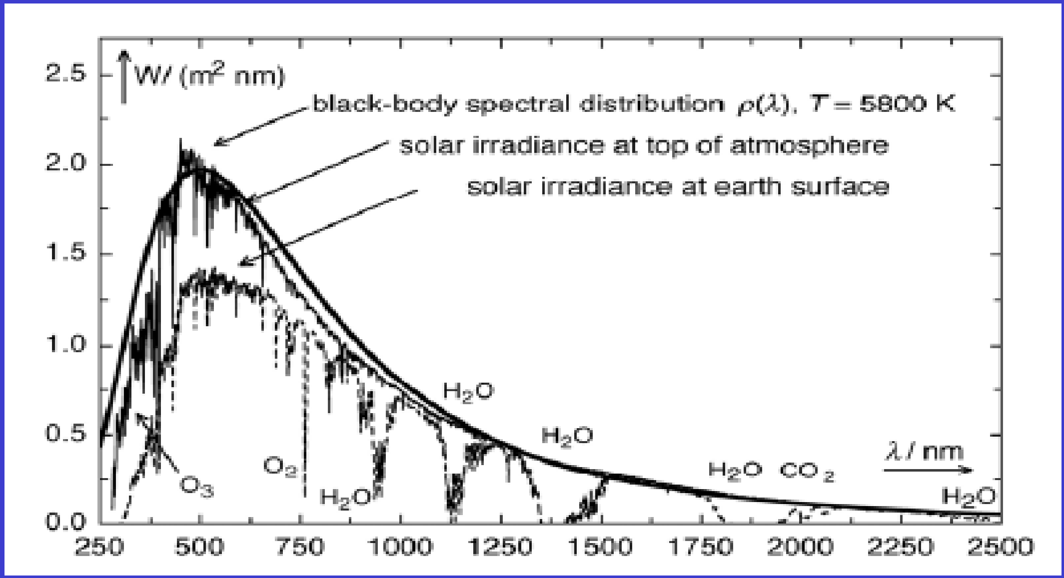




Photochem. Photobiol. Sci., 2007, 6, 552–559

Naše aplikace





- Přesné stanovení koncentrací (kvantové výtěžky)
- Speciace v roztoku
- Rovnovážné konstanty (p*K*a)
- Solvatochromismus
- První informace o molekule v excitovaném stavu (E_S, p*K*a v excitovaném stavu)

Excimers

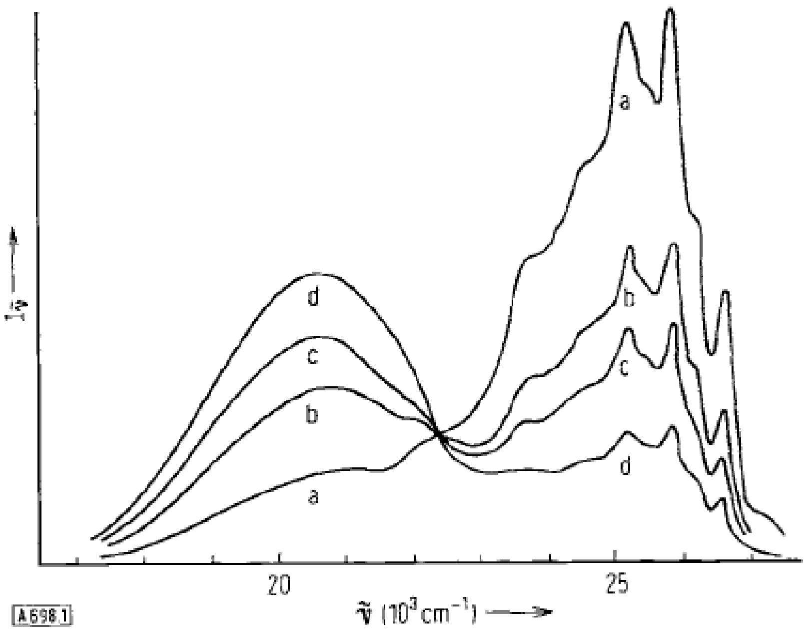


Fig. 1. Fluorescence spectra of pyrene in *n*-heptane. $t = 20\ ^\circ C$, c (mole/l): 5×10^{-5} (a), 1.8×10^{-4} (b), 3.1×10^{-4} (c), 7.0×10^{-4} (d).

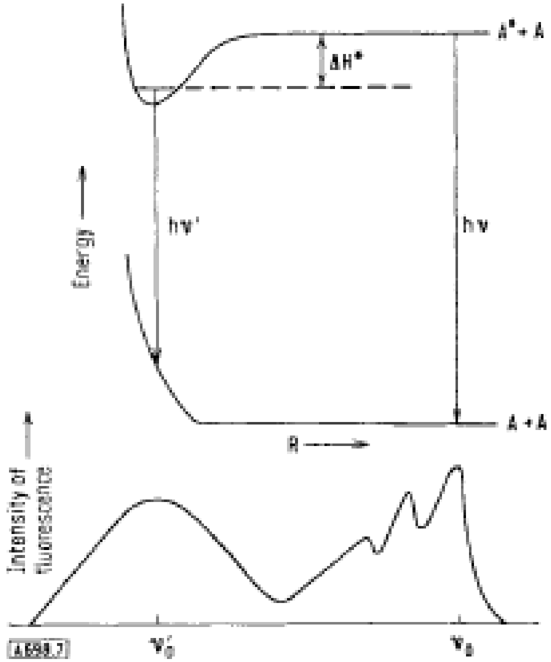


Fig. 7. Potential energy diagram for the formation of the excimer. R = distance between the molecular planes.

Theodor Foerster and K. Kasper: Z. physik. Cehm. N.F. J. 275 1954

Excimers in Ice

Naphthalene

Benzene

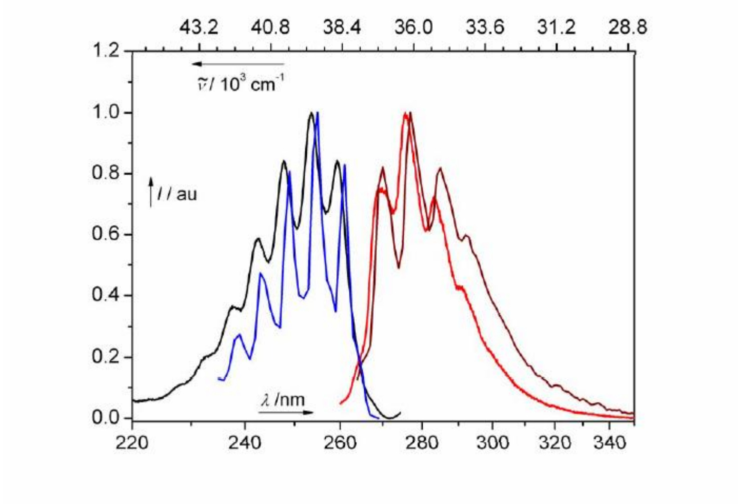


Figure S4. The fluorescence emission (λ_{exc} = 248 nm, red line) and excitation (λ_{em} = 283 nm, black line) spectra of aq benzene solution (c = 1.4 mM; 295 K), and the emission (λ_{exc} = 248 nm, brown line) and excitation (λ_{em} = 290 nm, blue line) spectra of benzene in artificial snow prepared by a SF method (253 K).

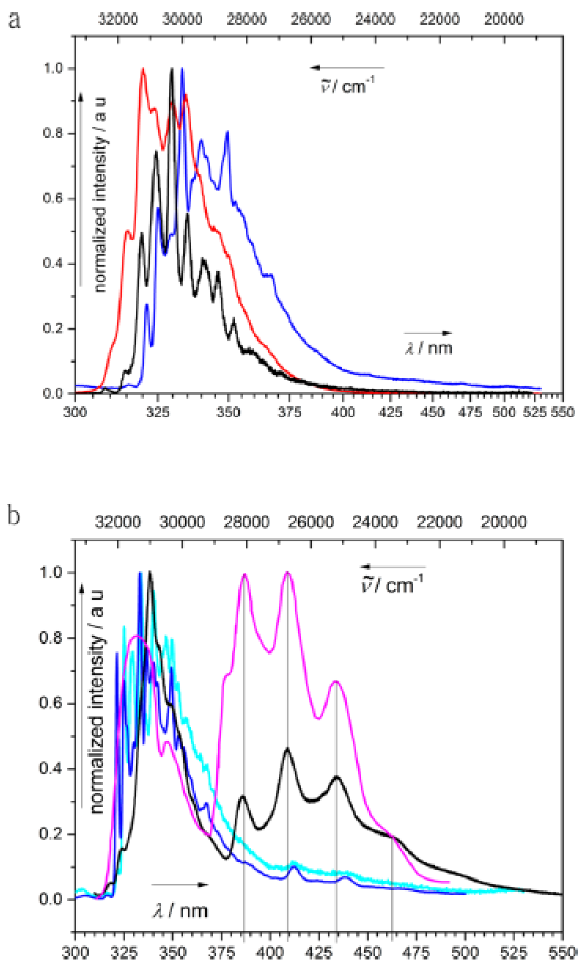
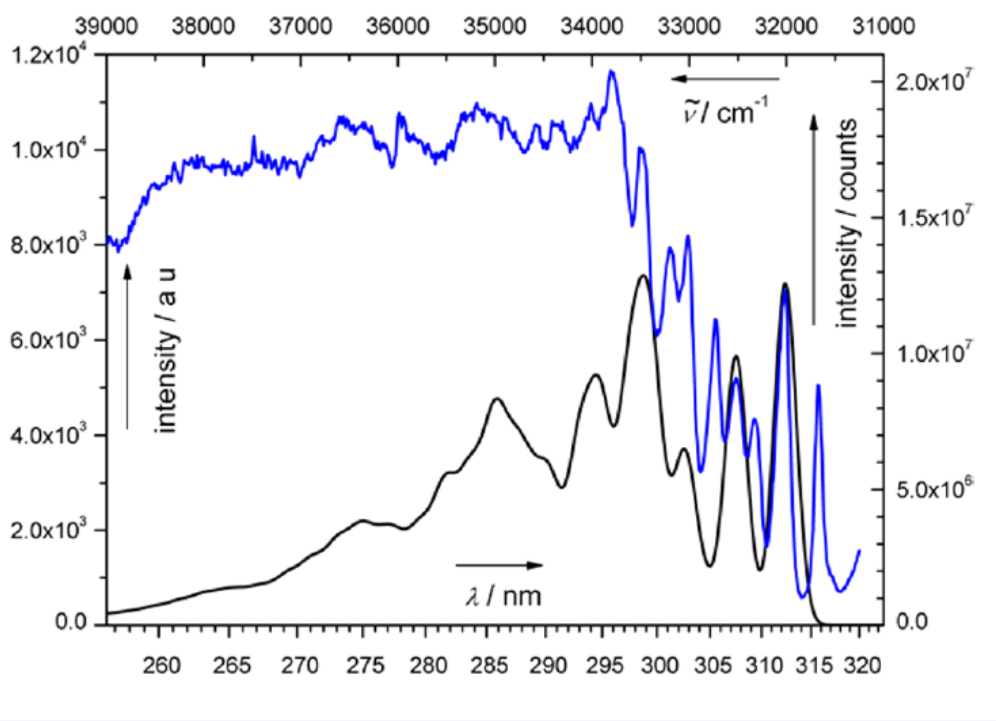


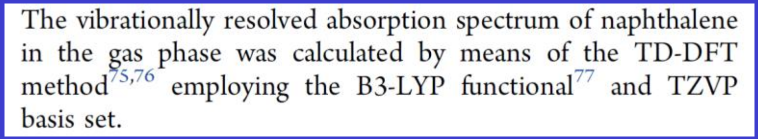
Figure 6. (a) Fluorescence emission spectra of naphthalene (Lachema): the aqueous solutions at room temperature (red, λ_{exc} = 274 nm) and frozen at 77 K (blue, λ_{exc} = 274 nm), both of c = 1.0 × 10^{-4} mol dm^{-3}, and of crystalline naphthalene at 77 K (black, λ_{exc} = 274 nm). (b) Fluorescence emission spectra of naphthalene (Fluka): the solution in water at 77 K (blue and cyan, λ_{exc} = 274 nm) and the crystals at 296 K (black, λ_{exc} = 274 nm) The emission spectrum from the frozen naphthalene solution digitized from ref 9 (magenta) is given for comparison.

J. Phys. Chem. A 2015, 119, 8565−8578

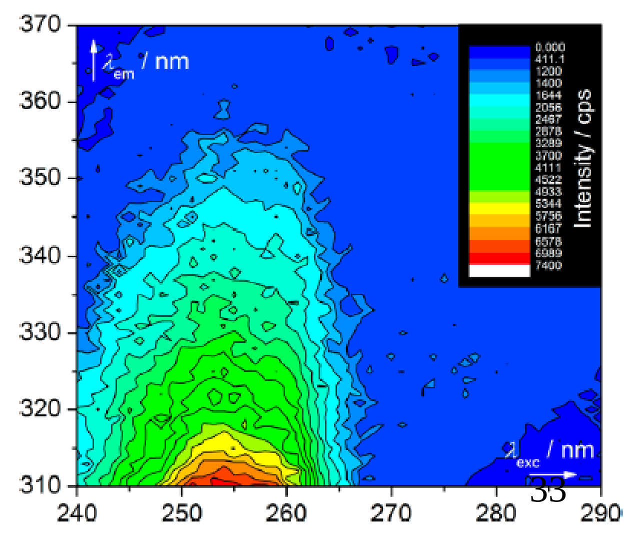
Does Bz and Np shifts bathochromicaly on ice?



Perfect match between: gas phase vibrations and solid state spectrum!

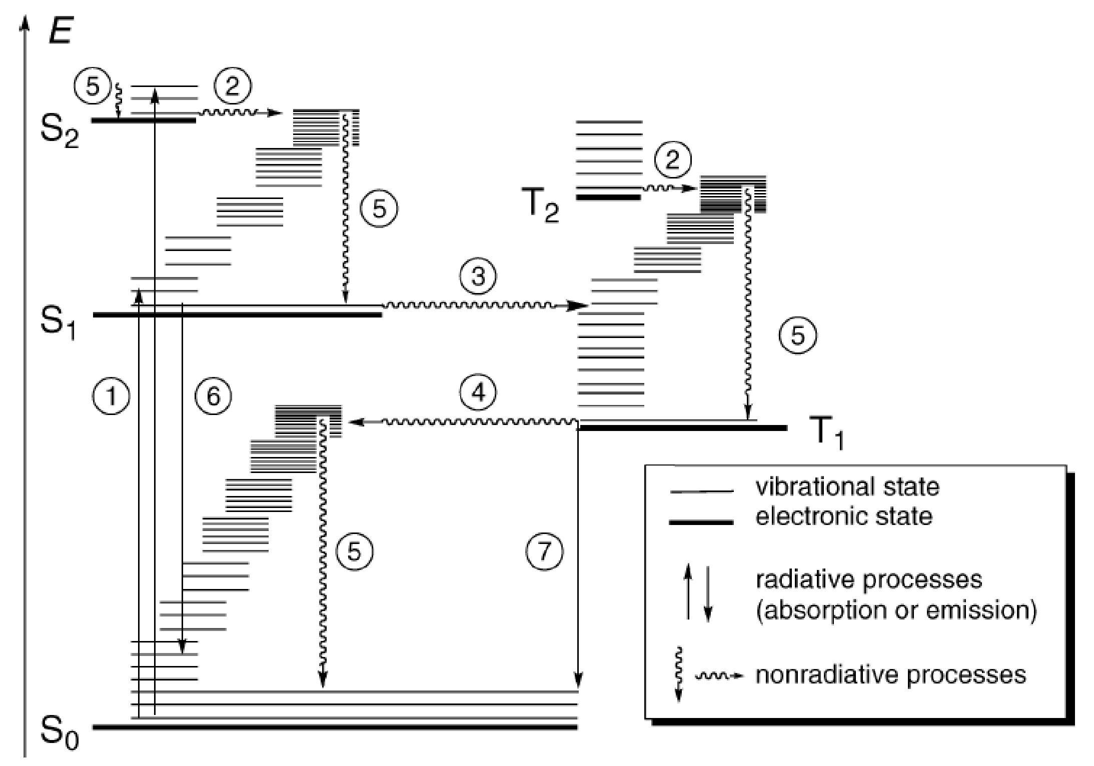


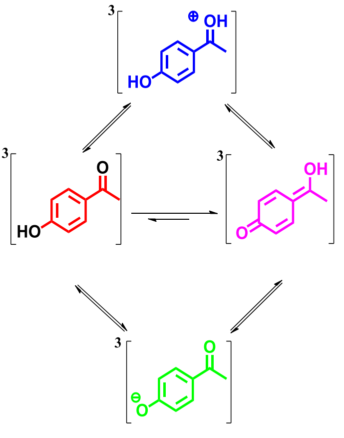
The vibrationally resolved absorption spectrum of naphthalene in the gas phase was calculated by means of the TD-DFT method[75,76] employing the B3-LYP functional[77] and TZVP basis set.



J. Phys. Chem. A 2015, 119, 8565−8578

Konečně nahoře! Legrace (fotochemie) teprve začíná.

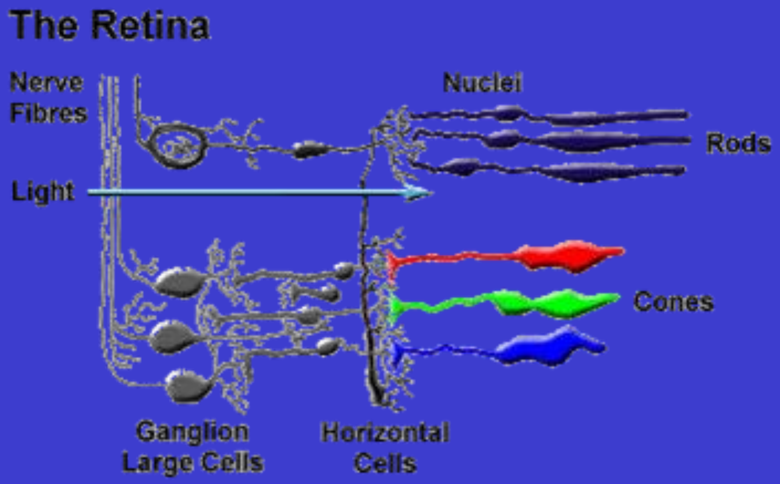


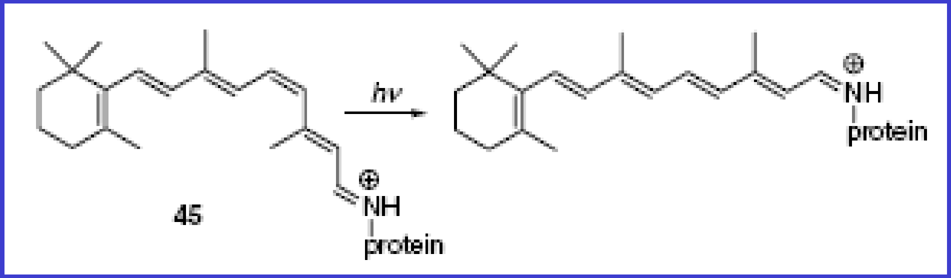


Fotochemie vidění

Mechanismus fototransdukce

Rhodopsin = 11 – *cis* retinal + opsin

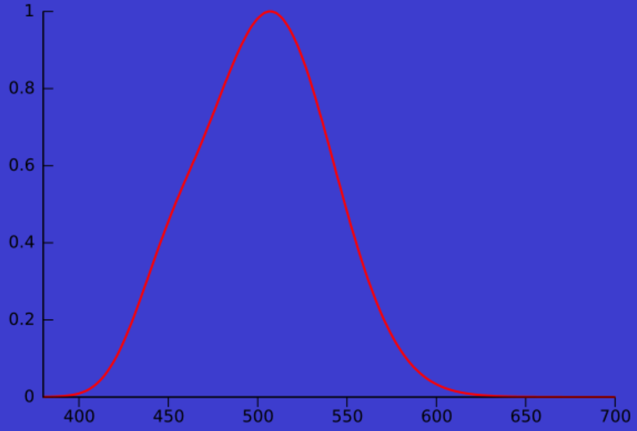




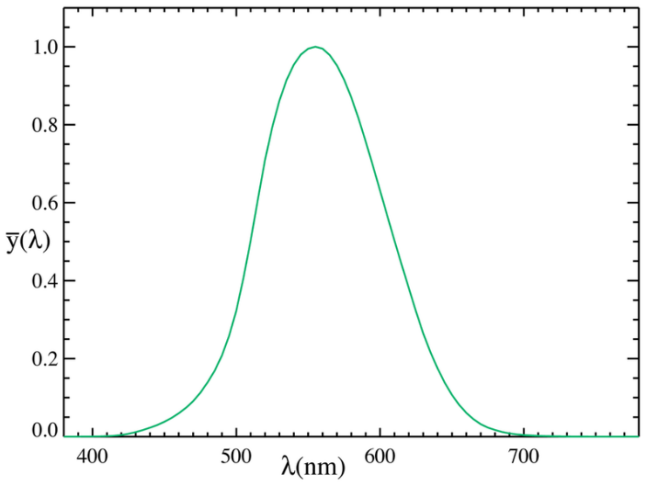
~ 200 fs

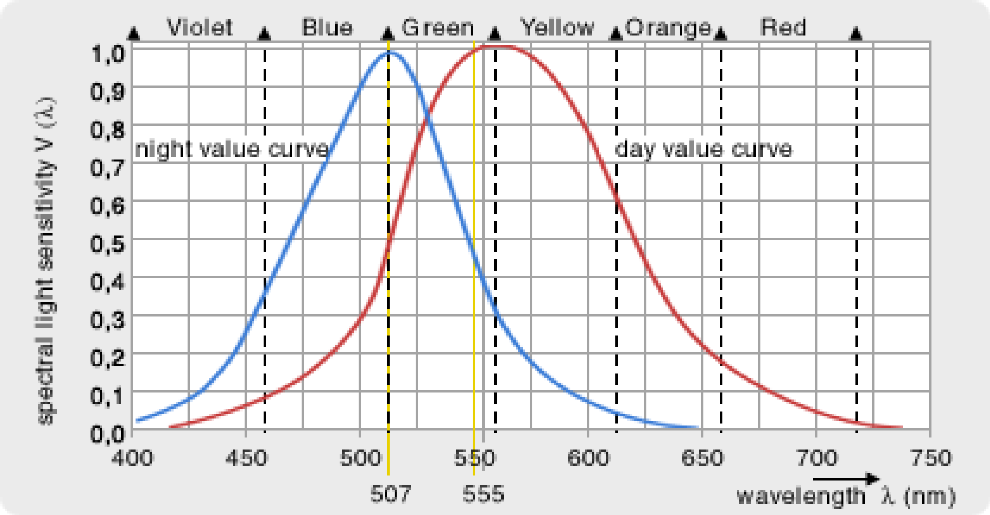
Lidské detektory světla

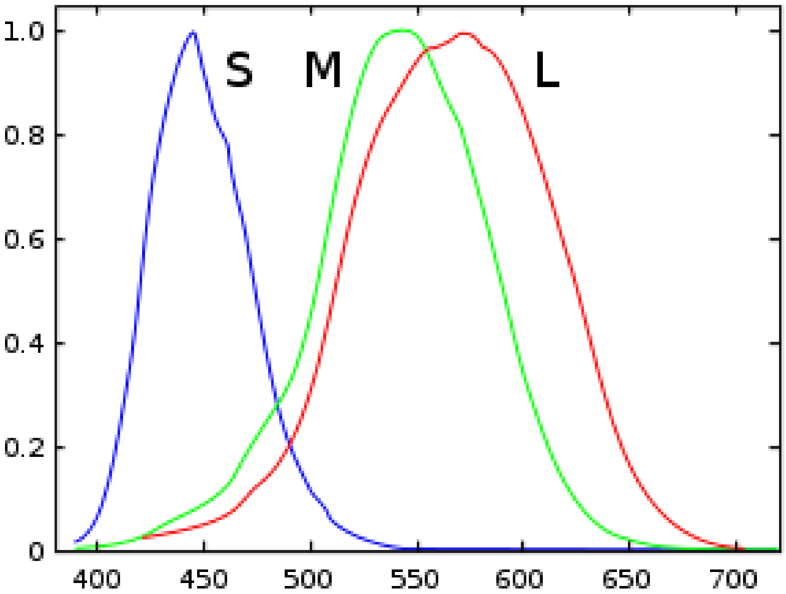
- Tyčinky - rhodopsin

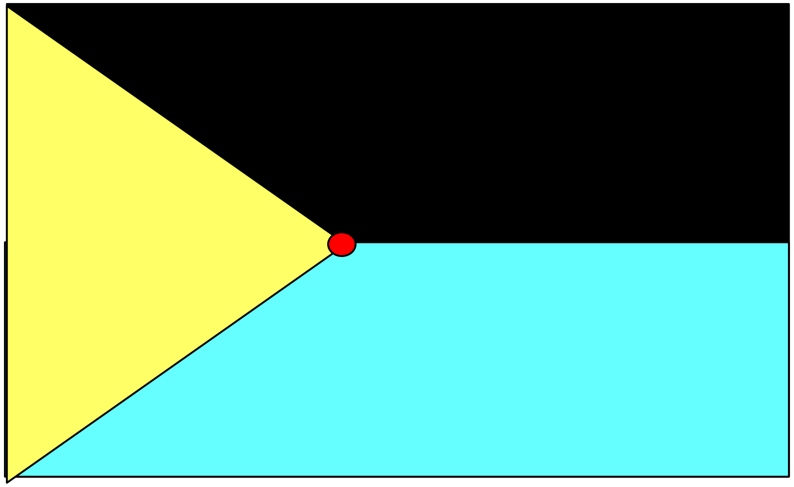


- Čípky – photopsiny, trichromatické vidění





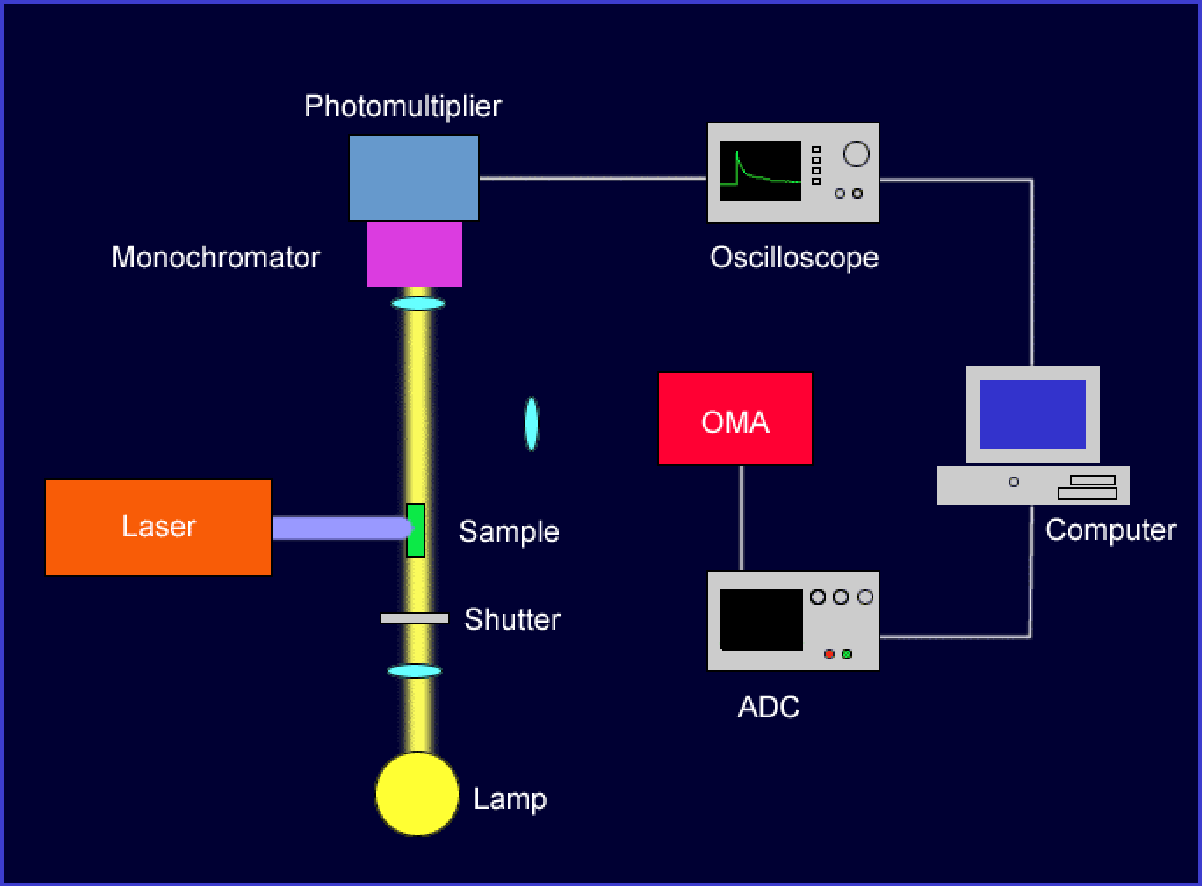


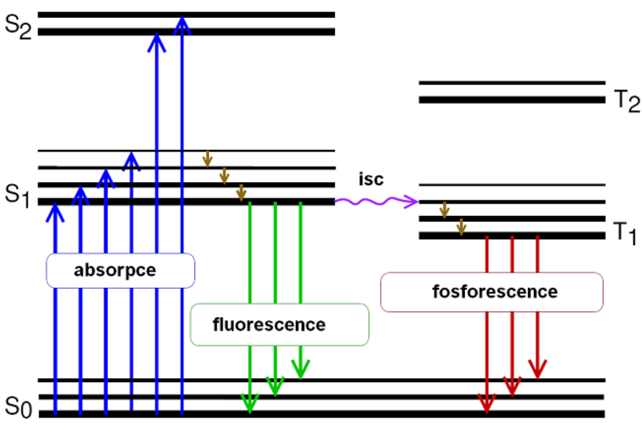


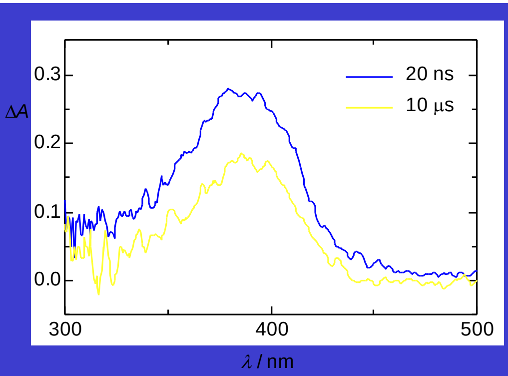
Záblesková fotolýza

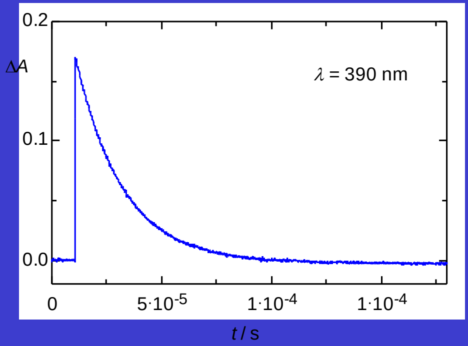
M. Eigen; R. G. W. Norrish; G. Porter (NP 1967)

A. Zewail (NP 1999)

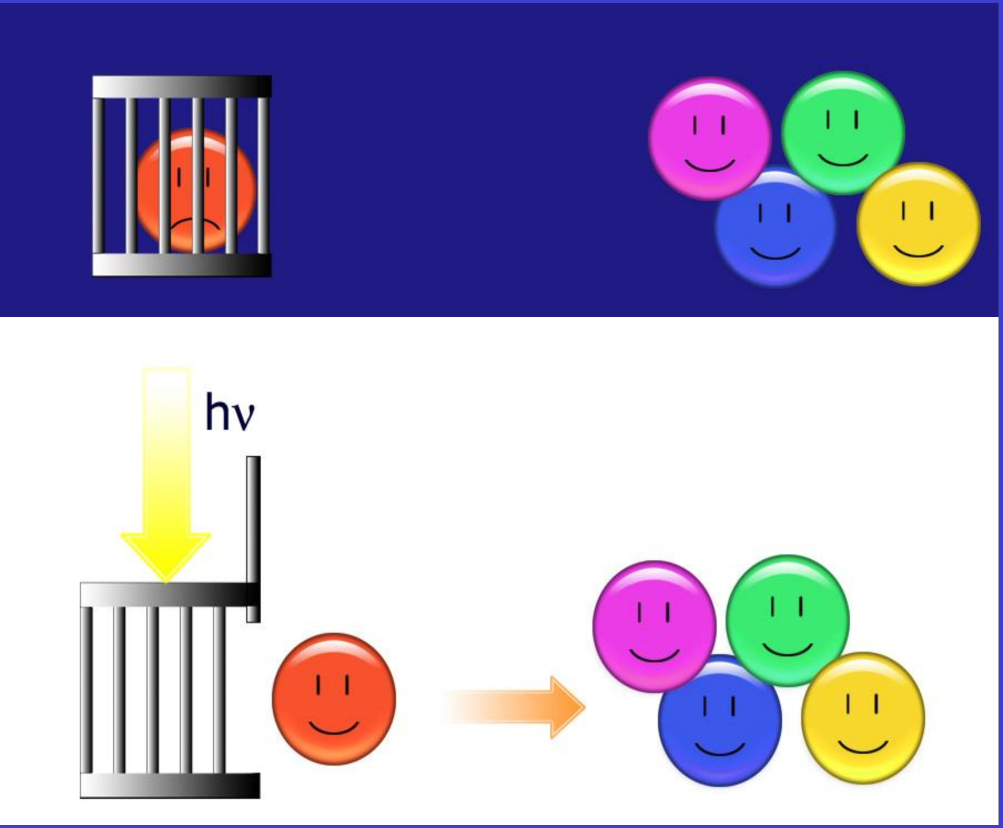


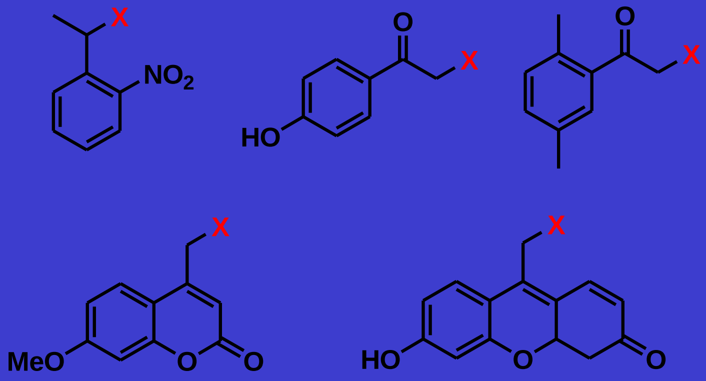


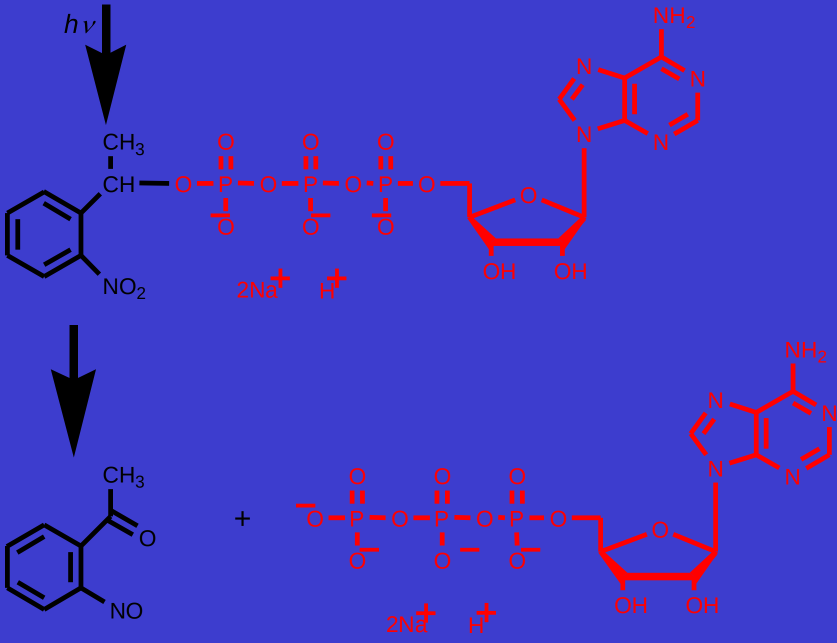




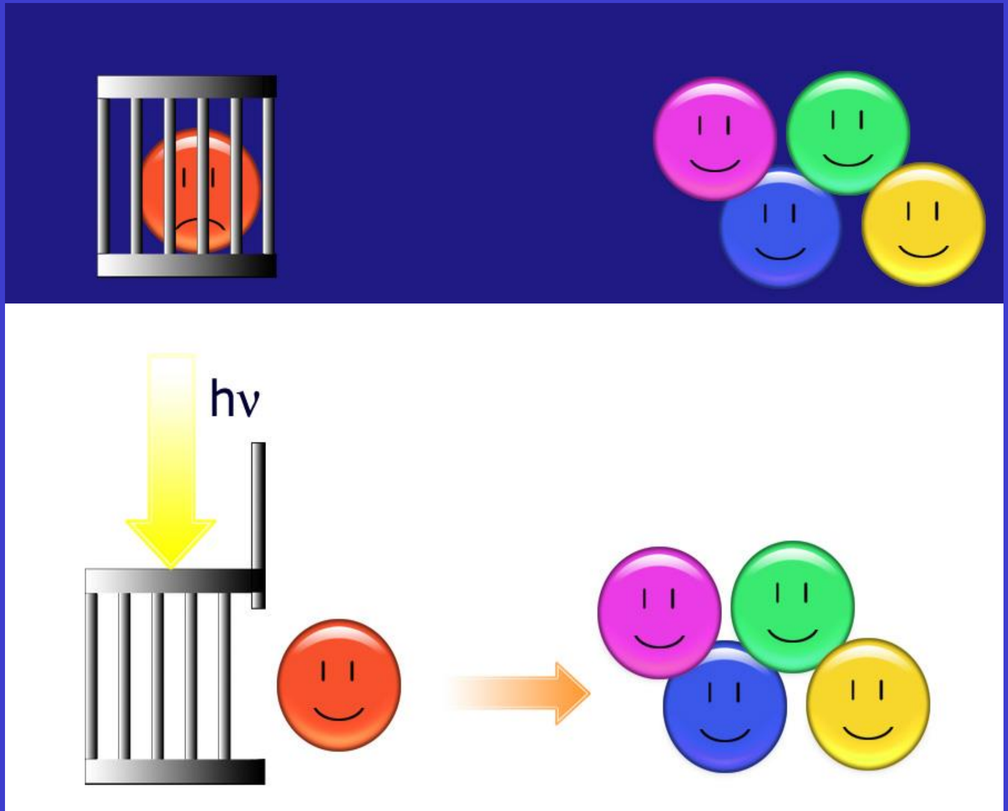
Fotoaktivovatelné molekuly chránicí skupiny



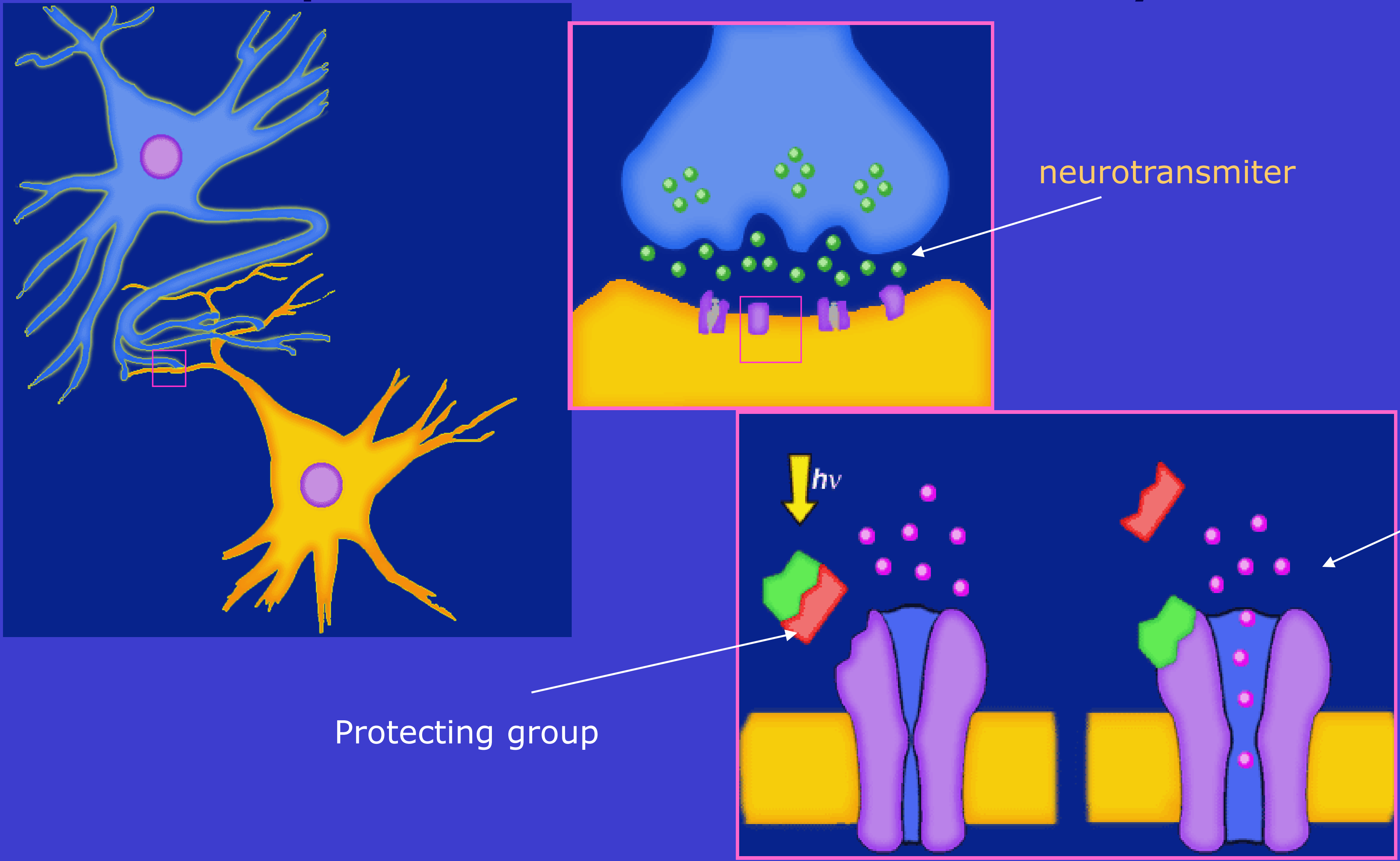




Fotoaktivovatelná cytostatika



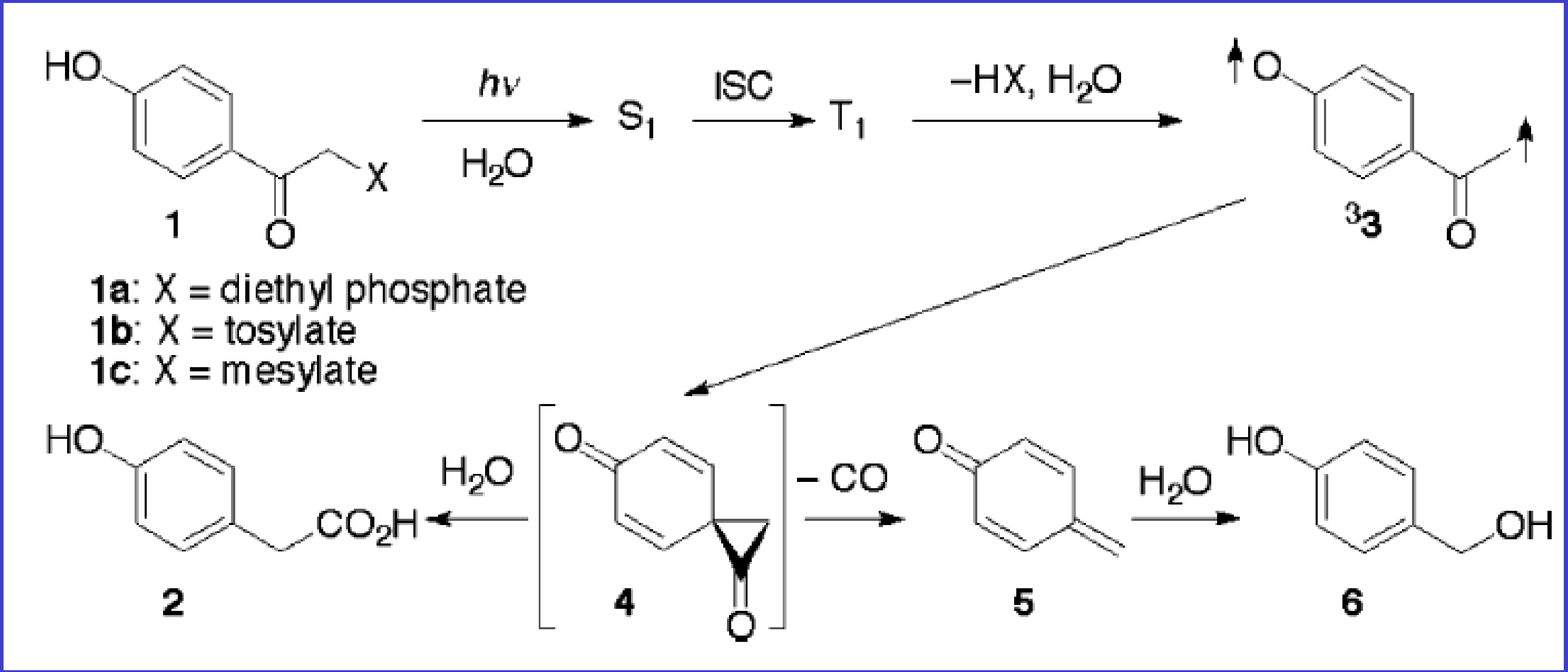
spoutané neurotrasmitery



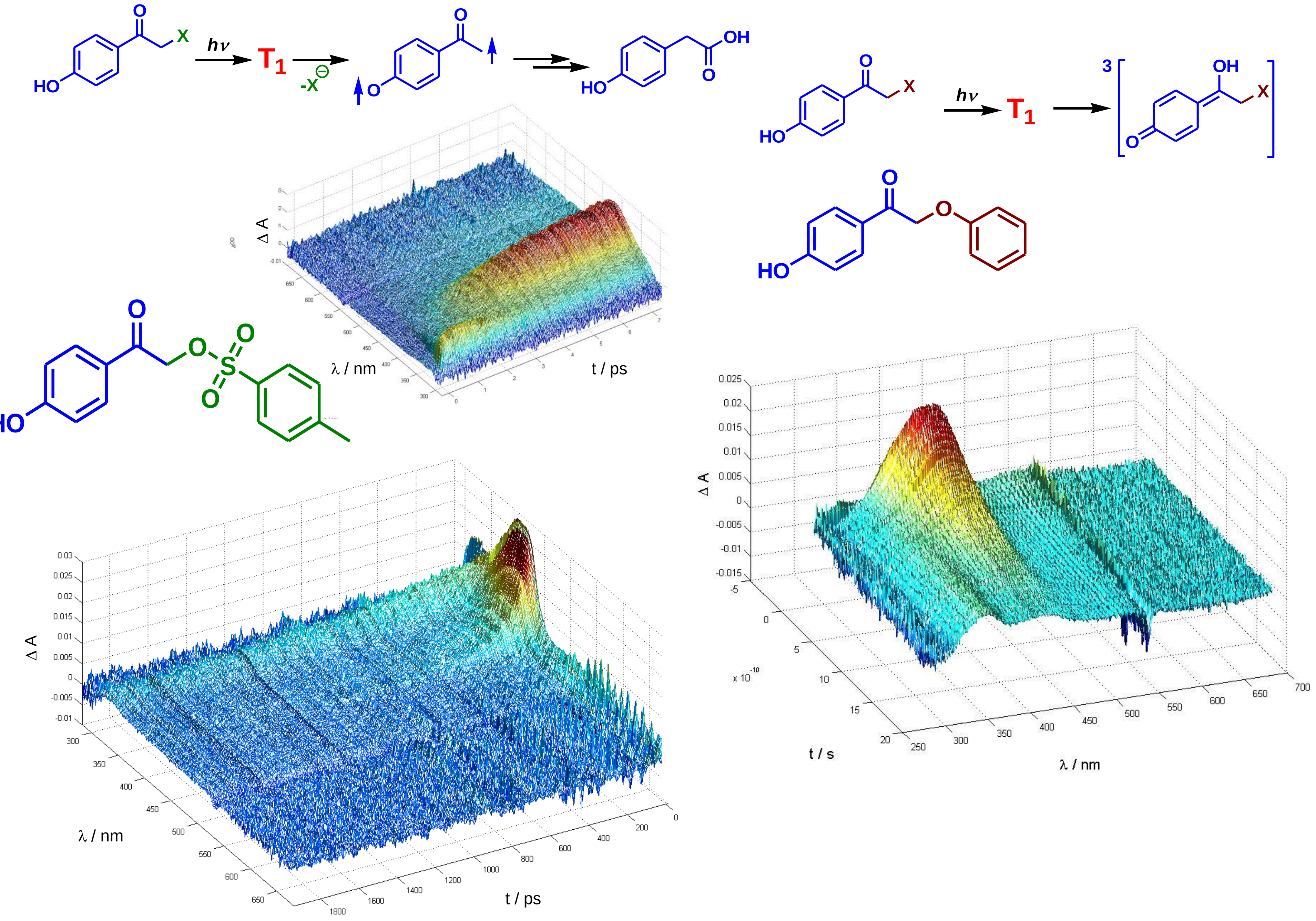
neurotransmiter

Protecting group

Deriváty *p*-hydroxyacetofenonu



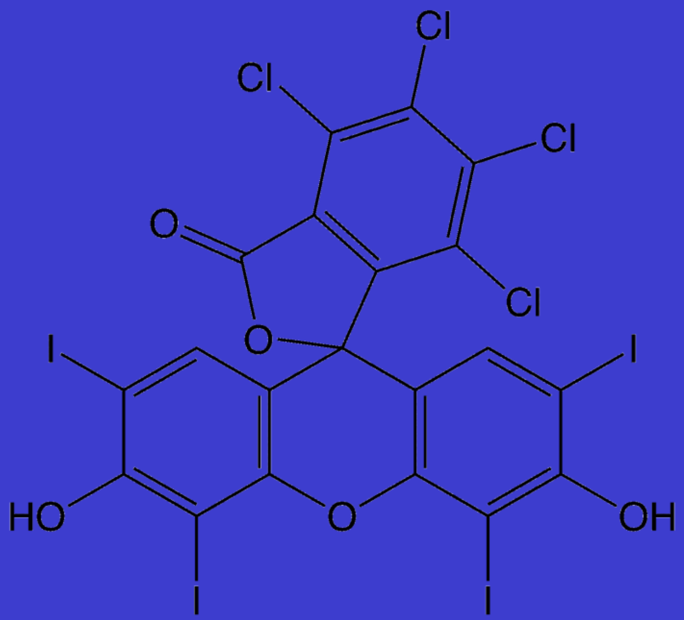
1a: X = diethyl phosphate
1b: X = tosylate
1c: X = mesylate



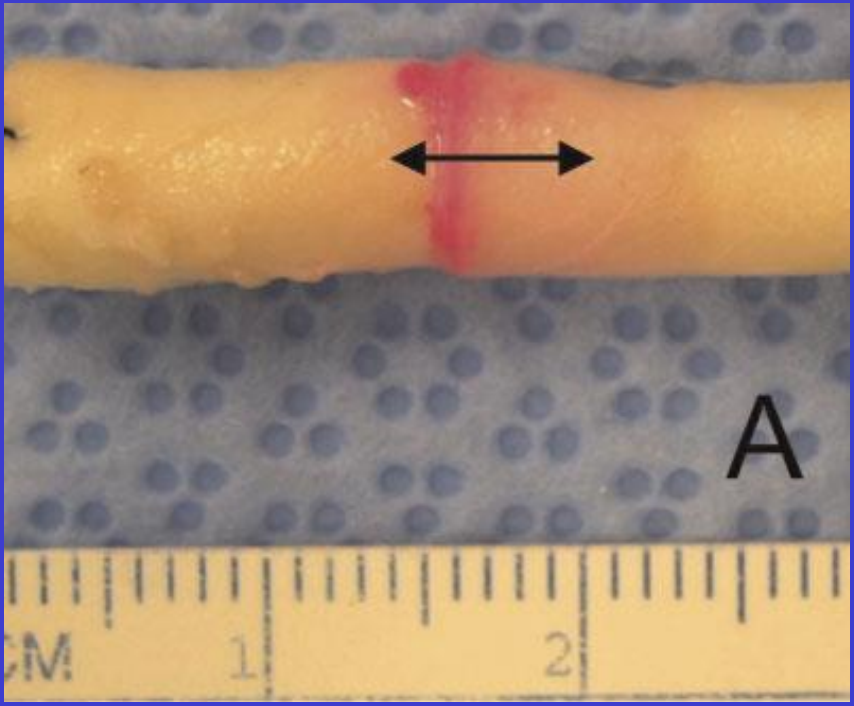
HO
O
X
hν
T1
-X⊖
O
OH
HO
O
X
hν
T1
3
OH
O
X
HO
O
O
HO
O
O
S
O
O
ΔA
λ / nm
t / ps
0
1
2
3
4
5
6
7
300
350
400
450
500
550
600
650
0.03
0.025
0.02
0.015
0.01
0.005
0
-0.005
-0.01
ΔA
λ / nm
300
350
400
450
500
550
600
650
t / ps
0
200
400
600
800
1000
1200
1400
1600
1800
0.025
0.02
0.015
0.01
0.005
0
-0.005
-0.01
-0.015
ΔA
-5
0
5
10
15
20
x 10^-10
t / s
250
300
350
400
450
500
550
600
650
700
λ / nm

Fotochemické šití tkáně

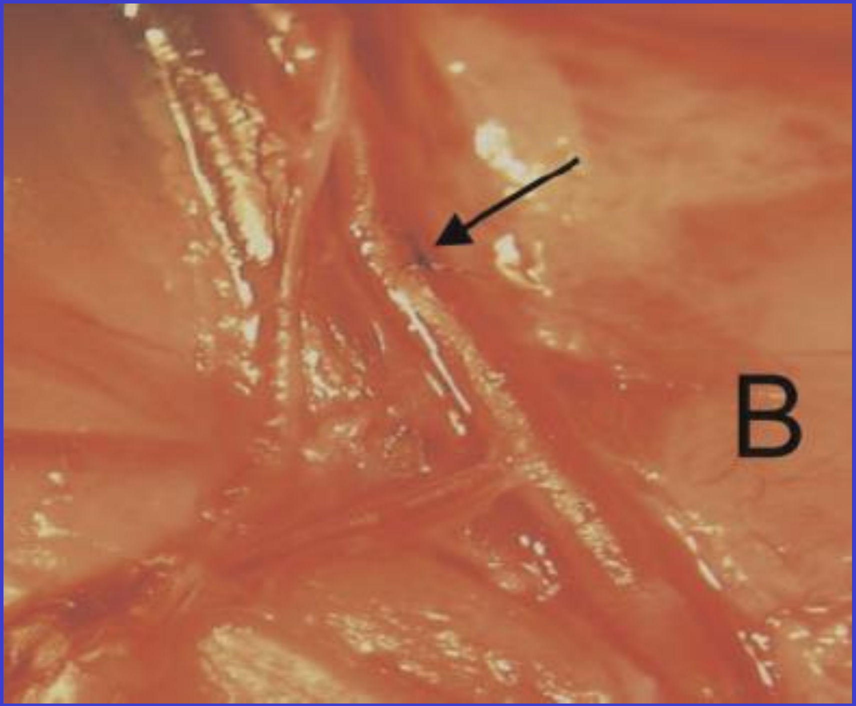
- Zesíťování kolagenových vláken
- Rychlé a nedestruktivní
- Bengálská červeň



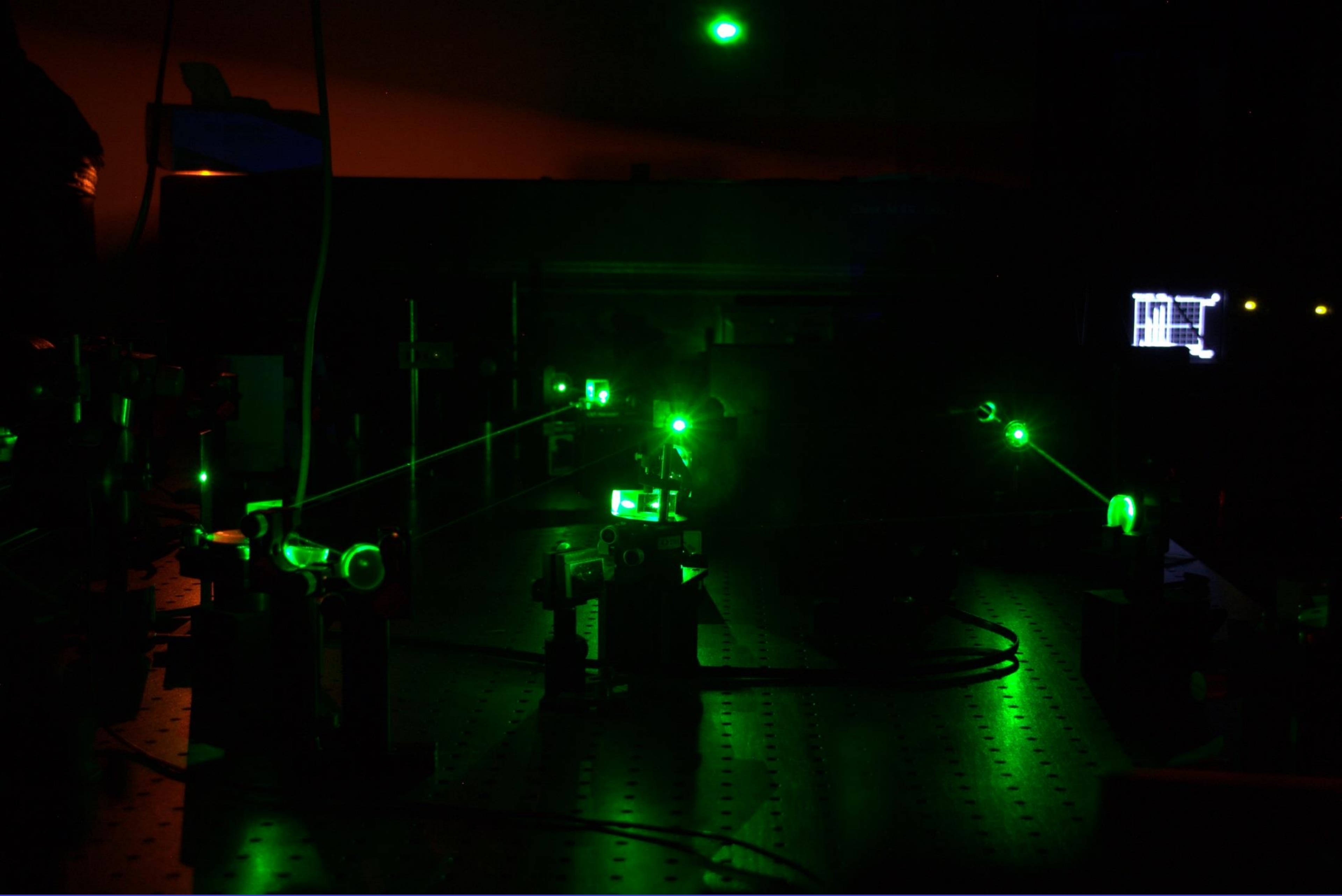
Fotochemické šití tkáně



Tepna prasete – ex vivo



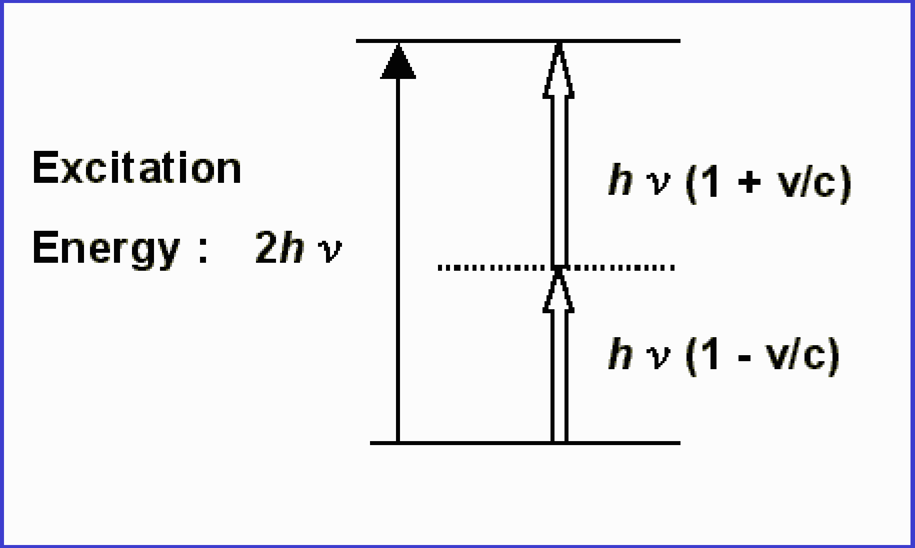
Tepna krysy – in vivo

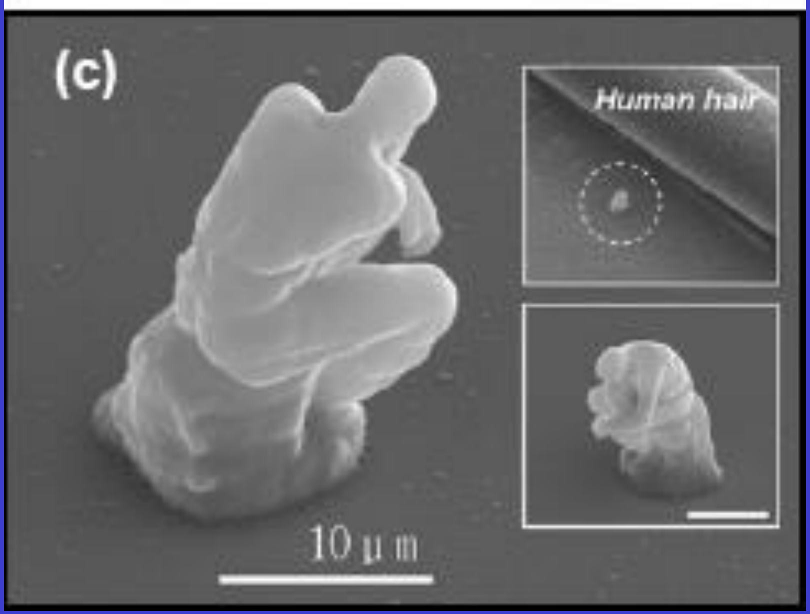


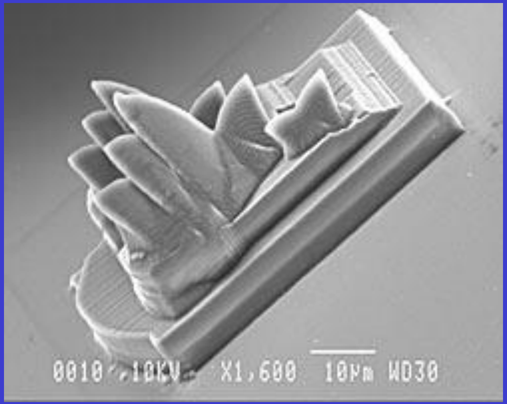
Scientia est potentia!

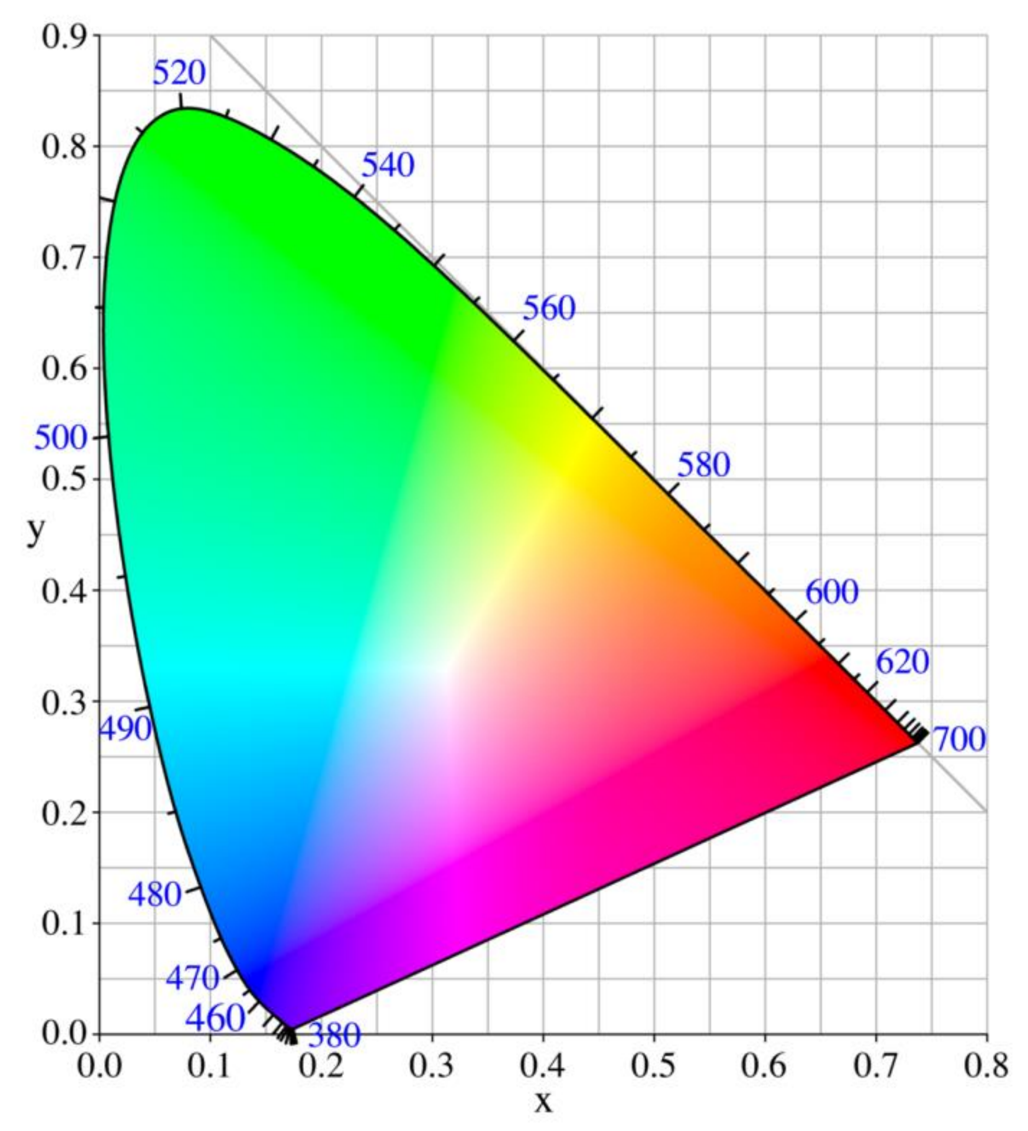
Dvoufotonová absorpce

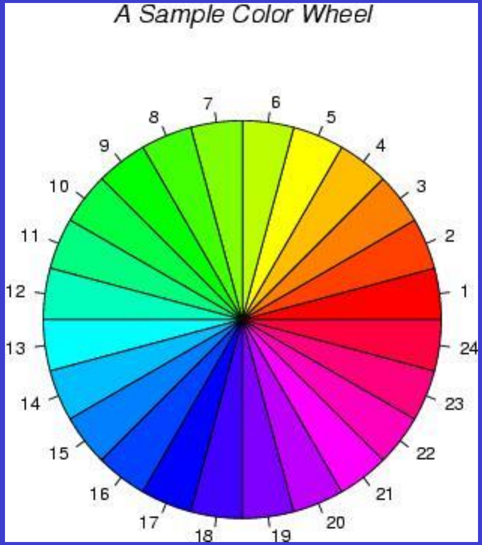
- 3D nanoobrábění = dvoufotonová fotopolymerizace

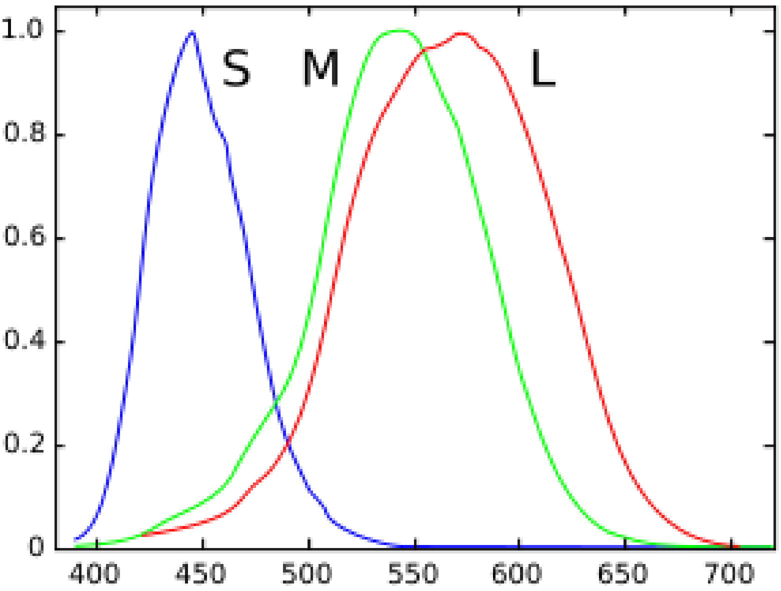






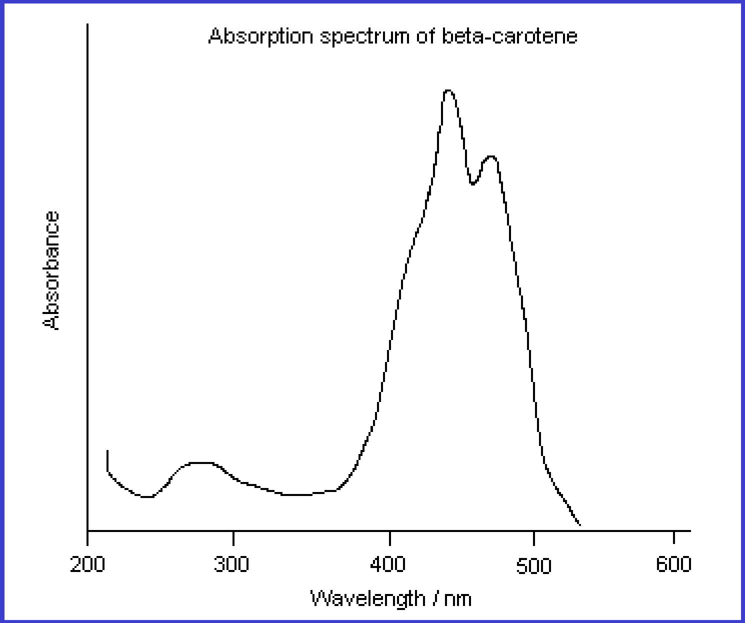


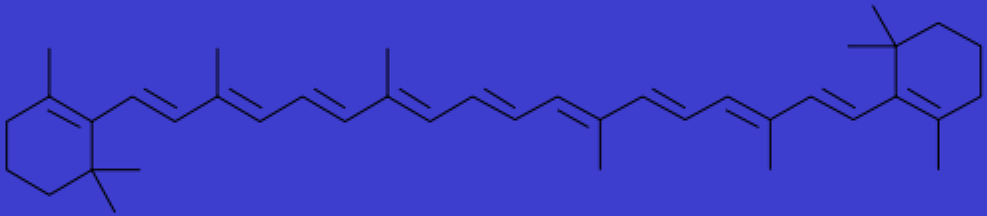




Normalizovaná odezva lidských čípků

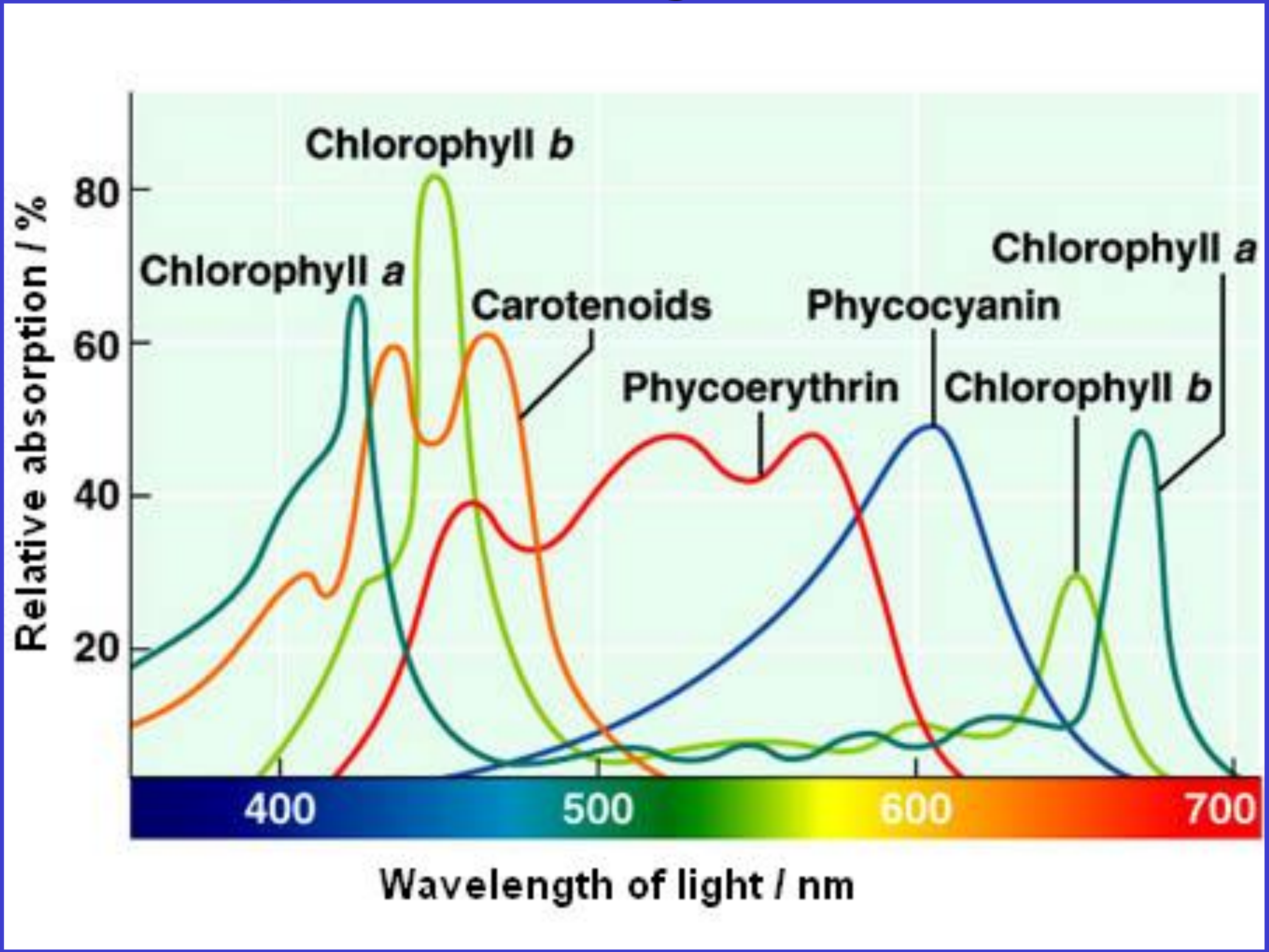
Proč je mrkev červená?





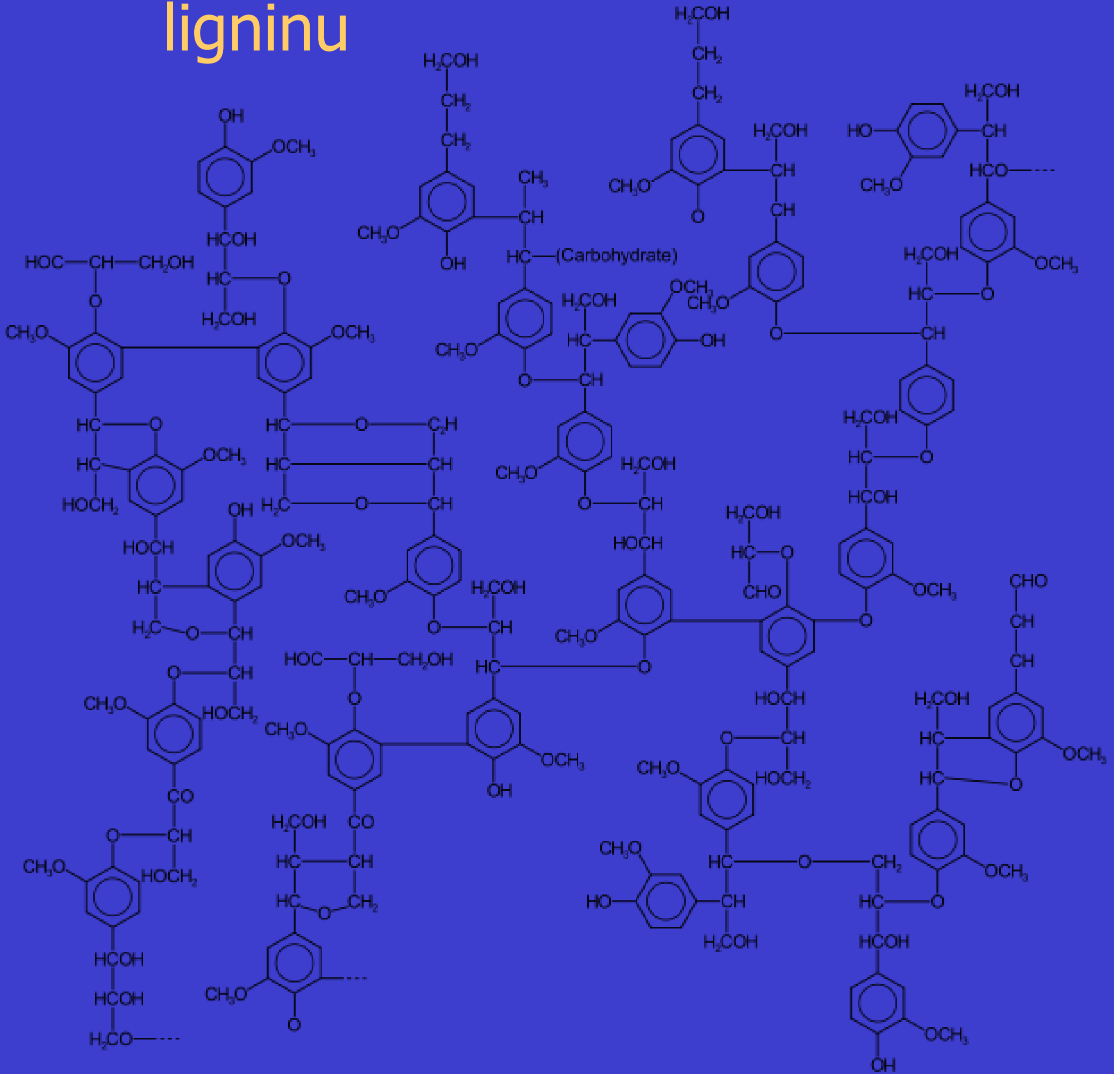
β-karoten

Fotosyntetizující barviva



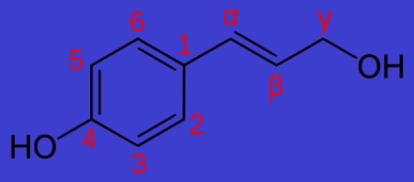
Proč papír žloutne?

Struktura ligninu

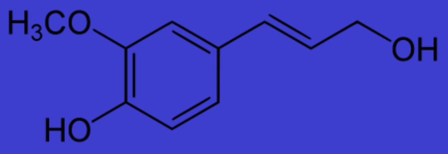


Základní jednotky - lignoly

1



2



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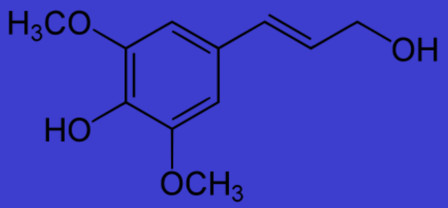
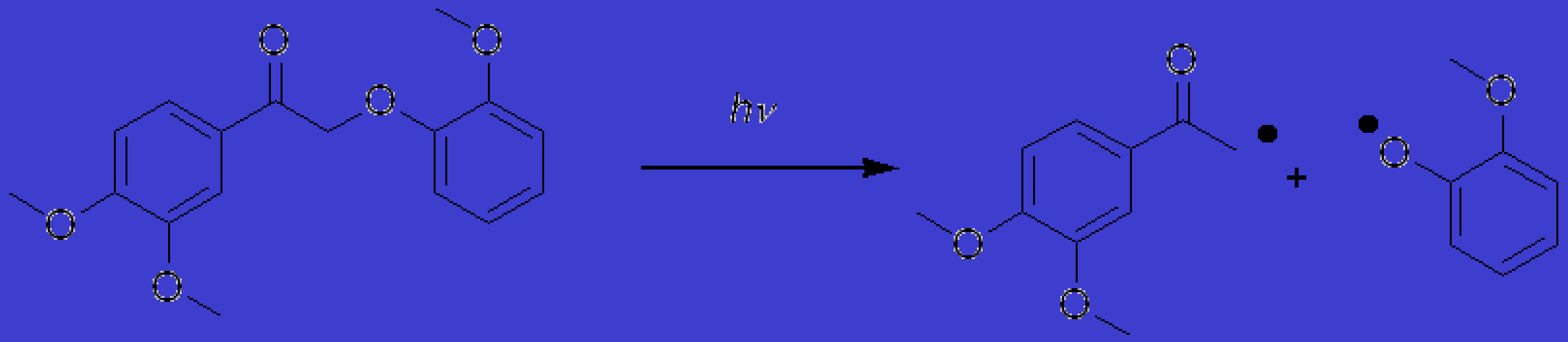
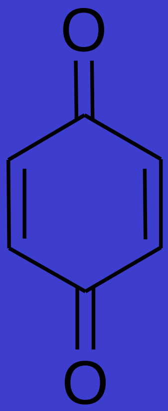


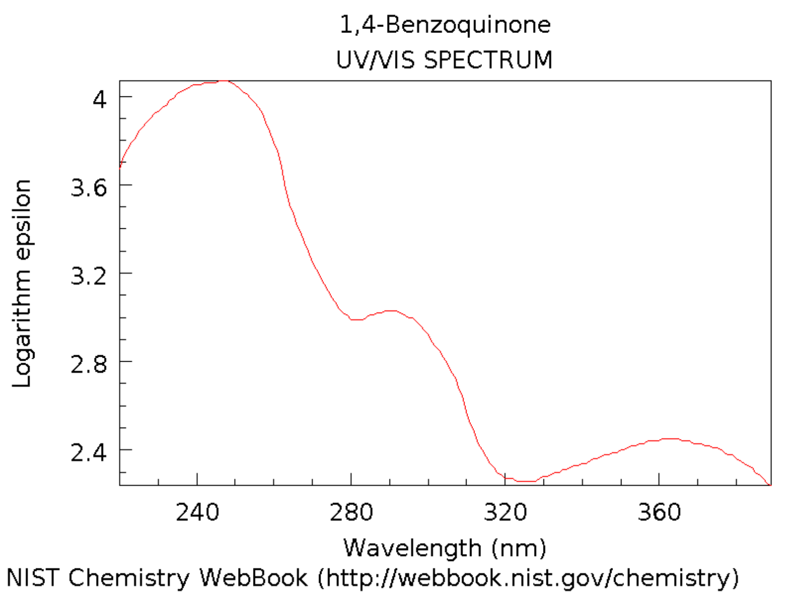
Proč býval papír nažloutlý?

- Fotodegradace ligninu



- Oxidace

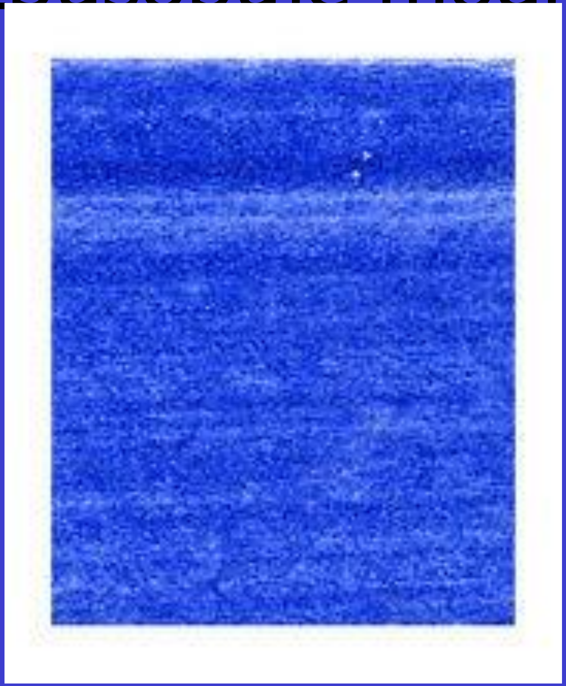



1,4-Benzoquinone
UV/VIS SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Jak se bělí (modří!) prádlo v Itálii?

- Modrá šmolka
  (hlinitokřemičitany sodné + síra)
- $S_3^{-\cdot}$ radikál způsobuje modrou barvu



Fluorescence

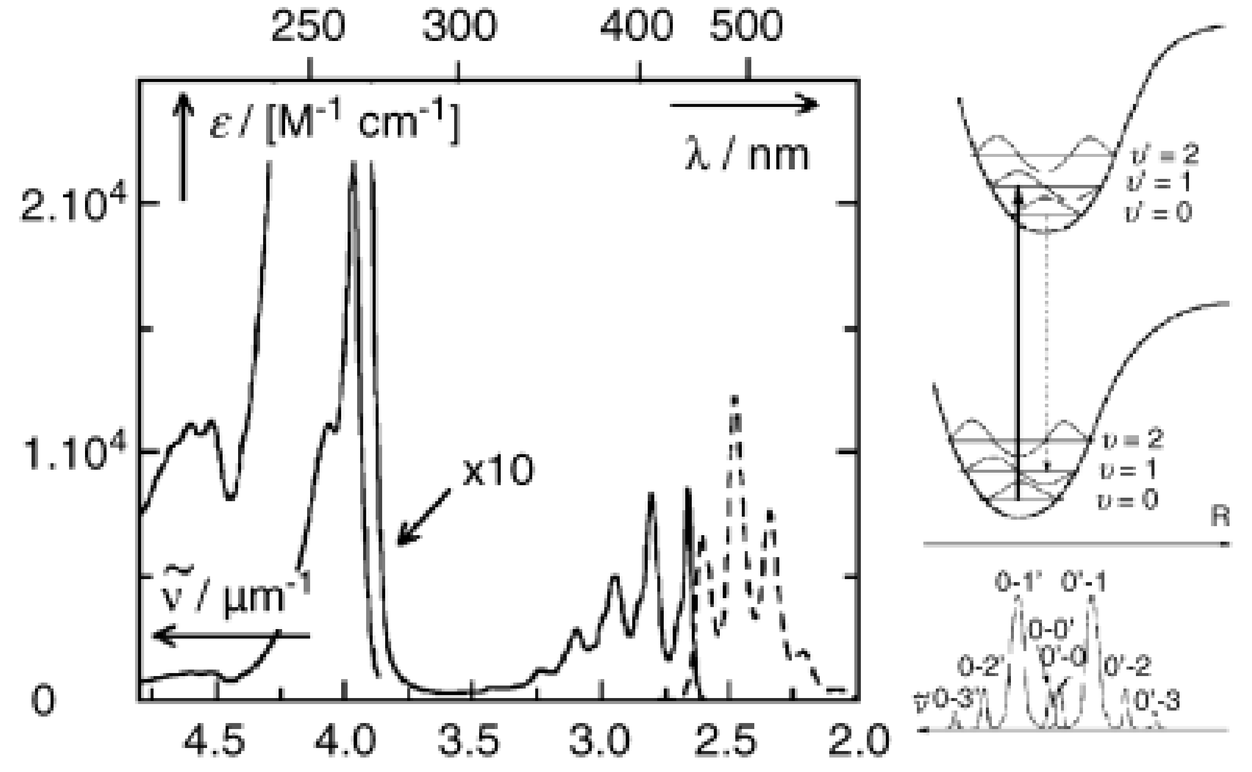
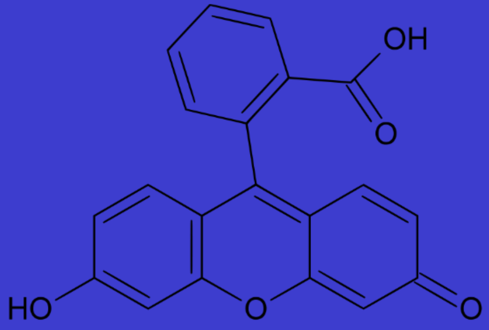
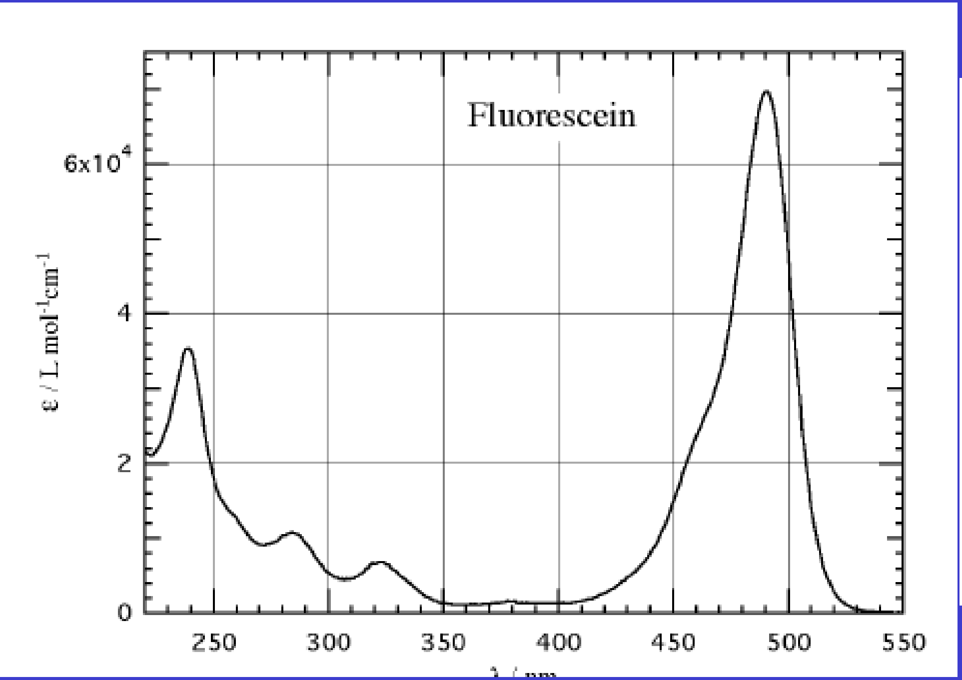


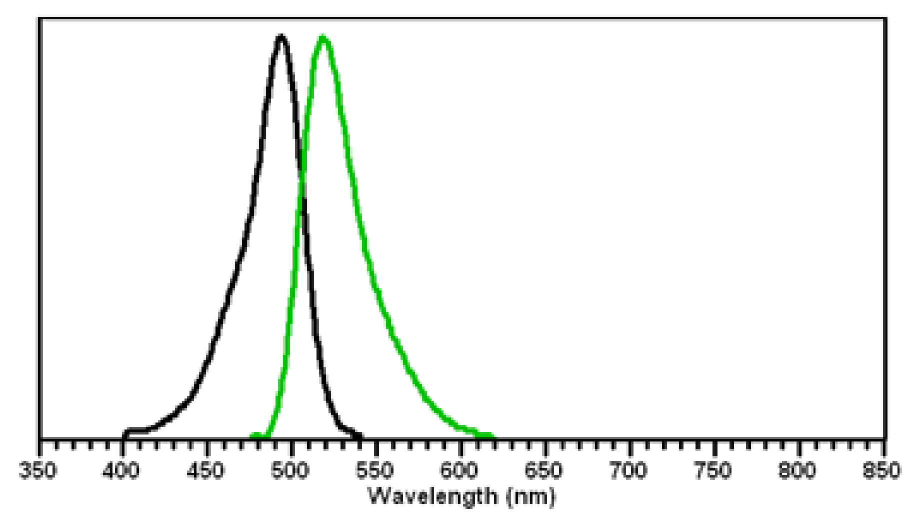
Figure 2.11 Absorption and fluorescence emission of anthracene

- látka emituje při delších vlnových délkách než absorbuje
- zvýrazňovače, cedulky na lyžařských svazích

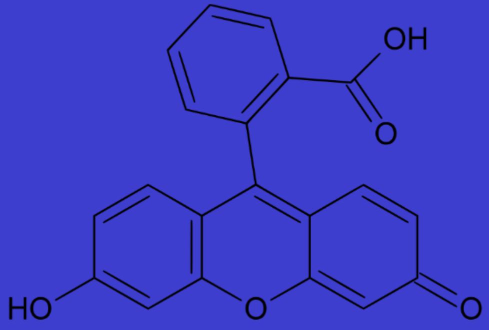
Fluorescence fluoresceinu

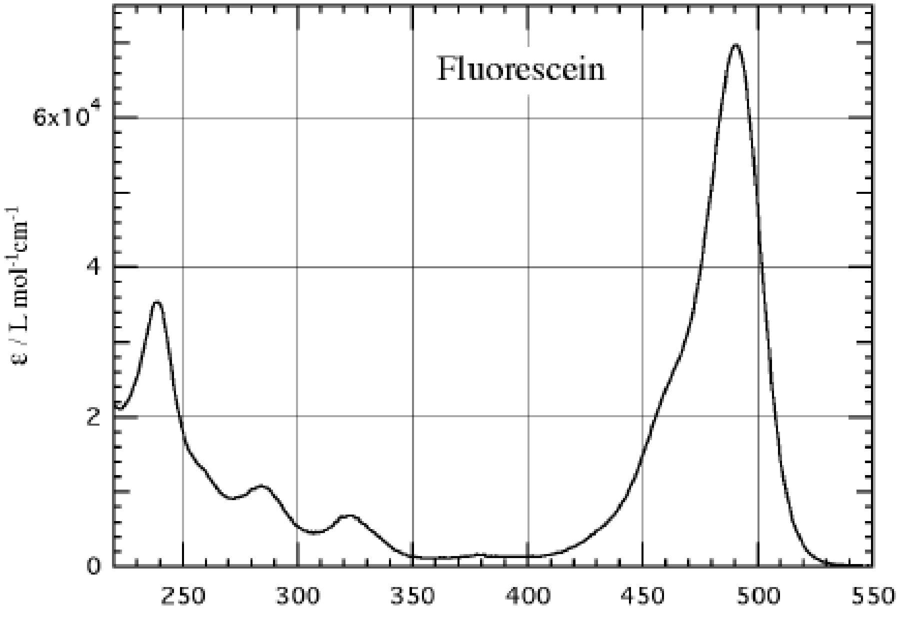


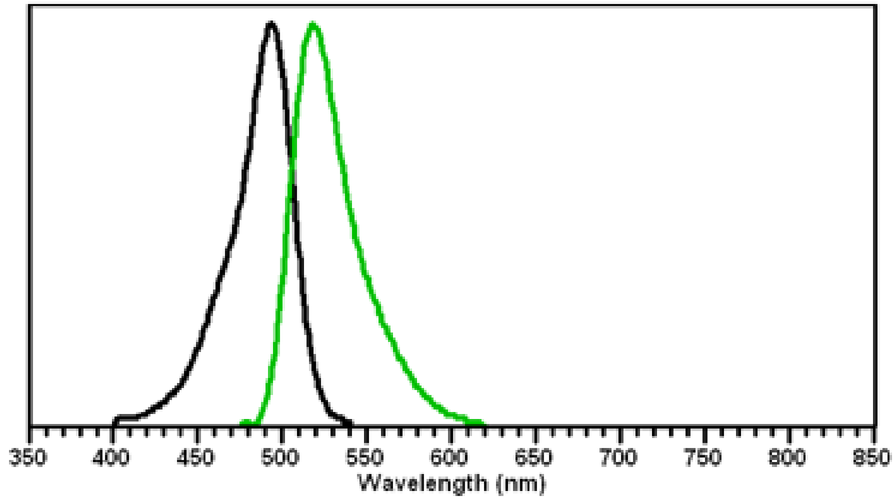




Fluorescence fluoresceinu







Literature

- http://old.iupac.org/reports/V/spectro/partVII.pdf
- Silverstein R. M. et all: Spectrometric indentification of organic compounds, John Wiley & Sons, inc.
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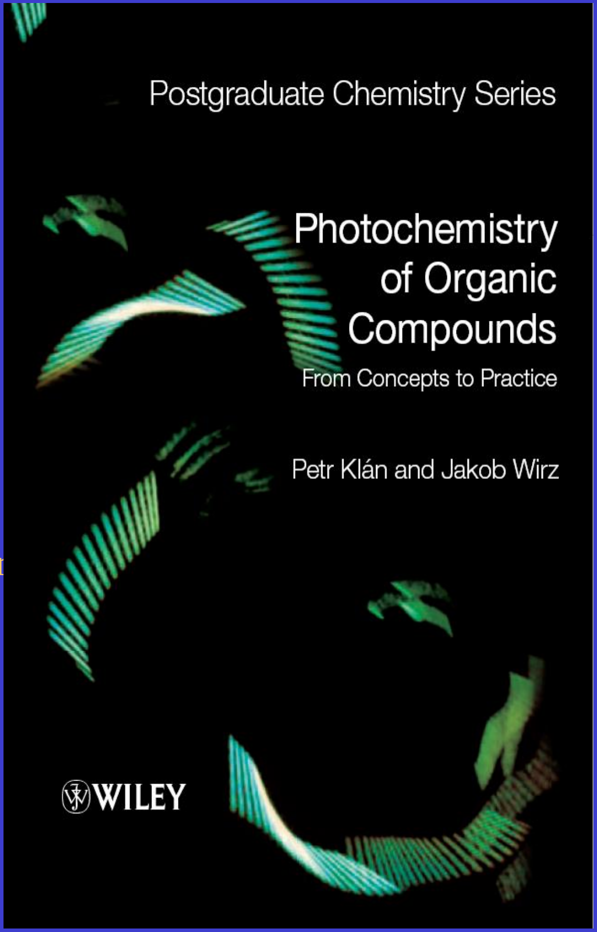


Postgraduate Chemistry Series

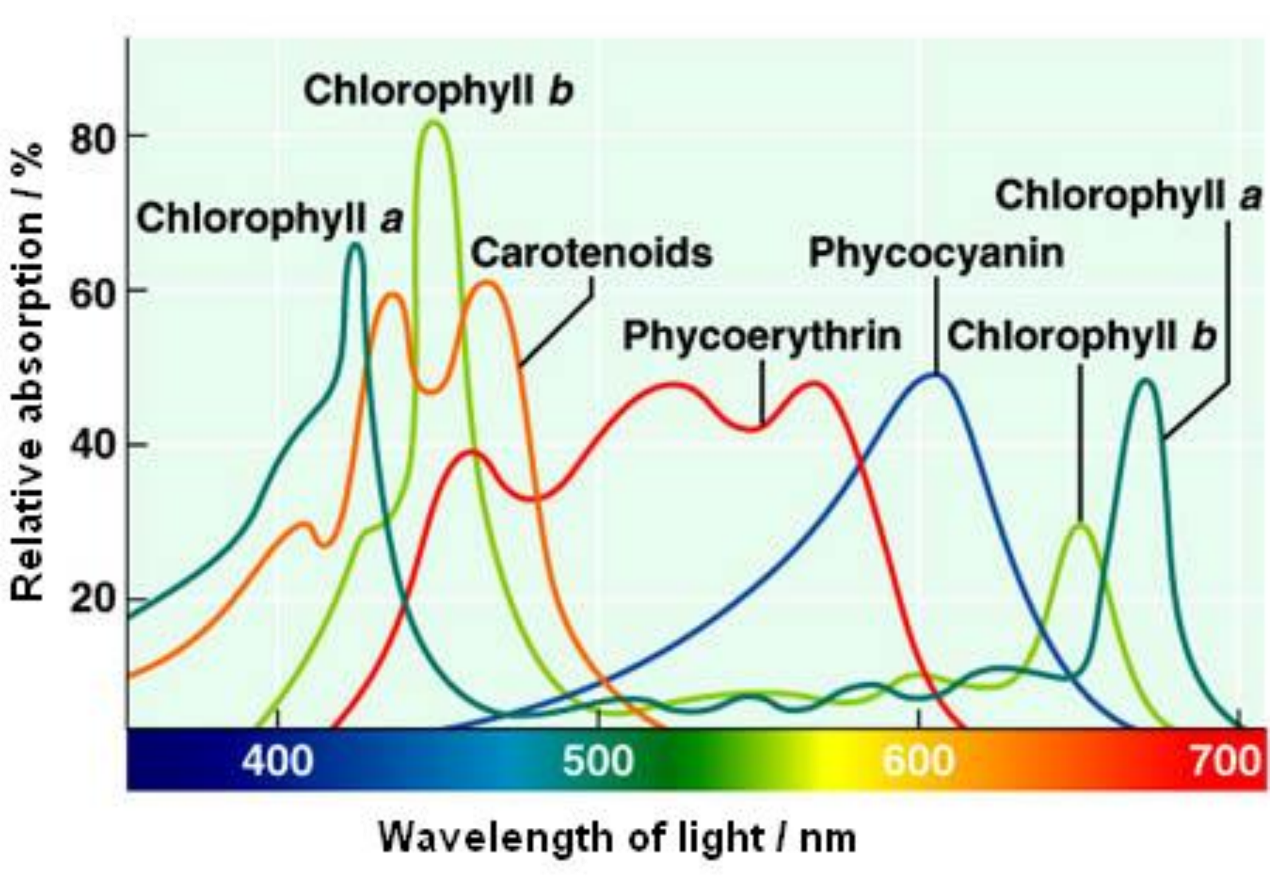
Photochemistry of Organic Compounds

From Concepts to Practice

Petr Klán and Jakob Wirz

WILEY

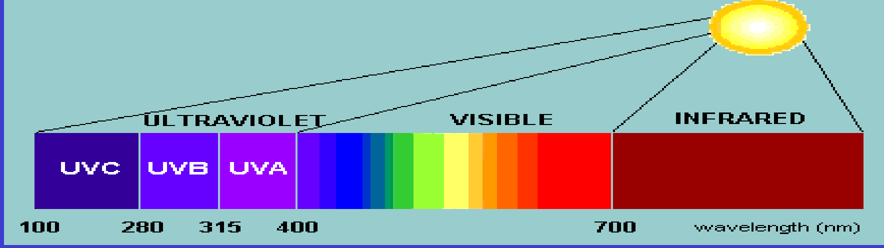
Fotosyntetizujicí barviva



Proč je obloha modrá a slunce žluté?

Proč při pohledu na oblohu nevidíme tmu?

- Rayleighův rozptyl ~ $1/\lambda^4$



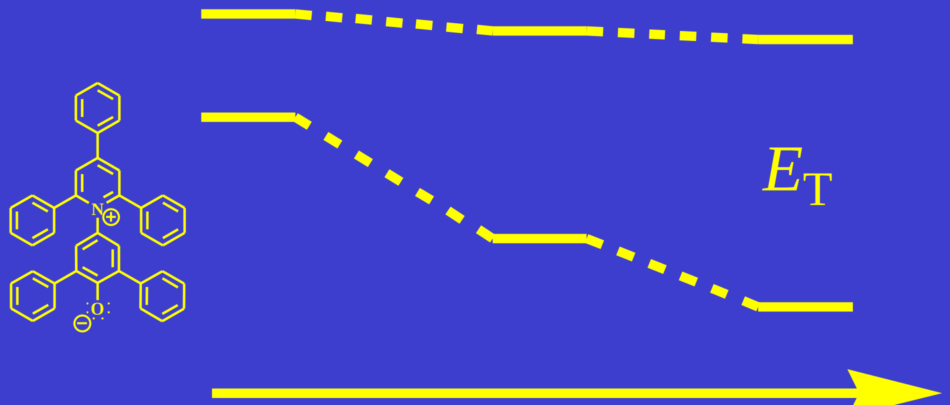
solvatochromism

change in the position, intensity, and shape of absorption bands due to the surrounding medium

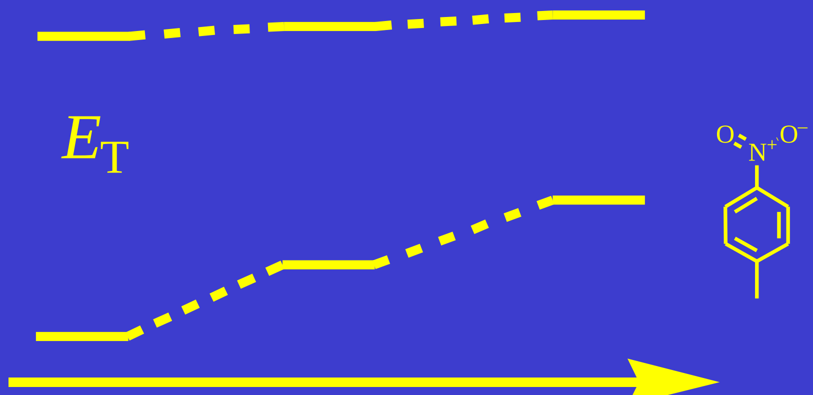
= perichromism (peri - around)

surrounding medium - liquids, solids, glasses, and surfaces

- negative solvatochromism
  a blue (hypsochromic) shift
- positive solvatochromism
  a red (bathochromic) shift



solvent polarity increases



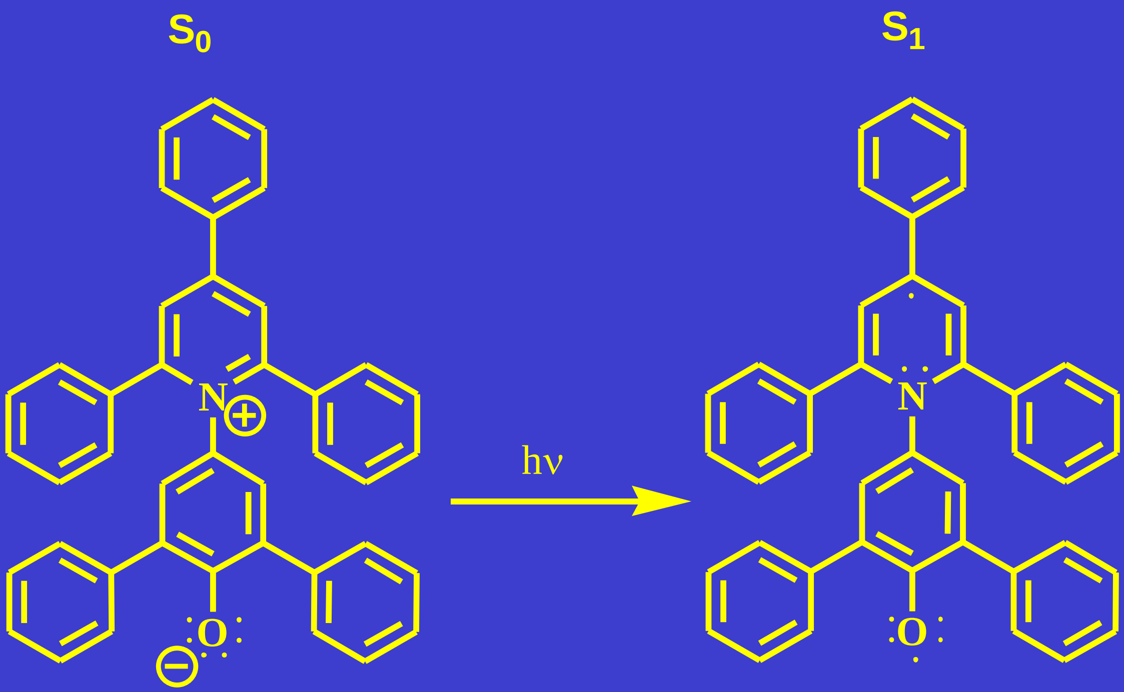
solvent polarity increases

Reichardt’s dye

betaine-30

2,6-diphenyl-4-(2,4,6-triphenyl-pyridium)phenolate

- dipol moment - dipol/dipol, dipol/induced dipol interaction
- π electron system - dispersion interaction
- phenolate oxygen - highly basic EPD ceter



dipol moment
in 1,4-dioxane

μ_g = 14.8+-1.2 D

μ_e = 6.2+-0.3 D

E_T(30) and E_T^N scale of solvent polarity

E_T - molar electronic transition energy

$[E_T]$ = kcal/mol

$[E_T^N] = 1$

Látka	E_T^N
n-hexan	0.009
Dichlor methan	0.309
EtOH	0.608
Voda	1

$$E_T(\mathbf{30}) = hc\,\tilde{\nu}_{max}N_A = (2.8591\ \mathrm{E}\ {-3})(\,\tilde{\nu}_{max}\ /\ \mathrm{cm}^{-1})$$

$$= 28591/(\lambda_{max}\ /\ \mathrm{nm})$$

$$E_T^N = (E_T(\mathrm{solvent}) - E_T(\mathrm{TMS}))/(E_T(\mathrm{water}) - E_T(\mathrm{TMS}))$$

$$= (E_T(\mathrm{solvent}) - 30.7)/32.4$$

E_T^N (TMS) = 0.000 E_T^N (H_2O) = 1.000

TMS = Tetramethylsilane

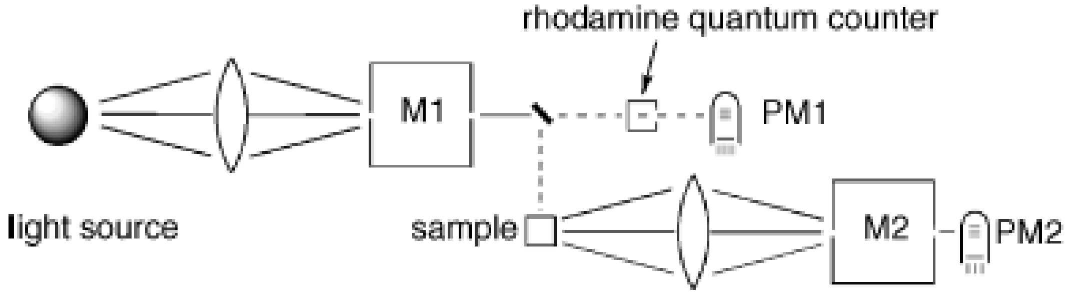


Figure 3.12 Basic components of a steady-state fluorescence spectrophotometer. The boxes M1 and M2 are monochromators and the detectors PM1 and PM2 are photomultipliers