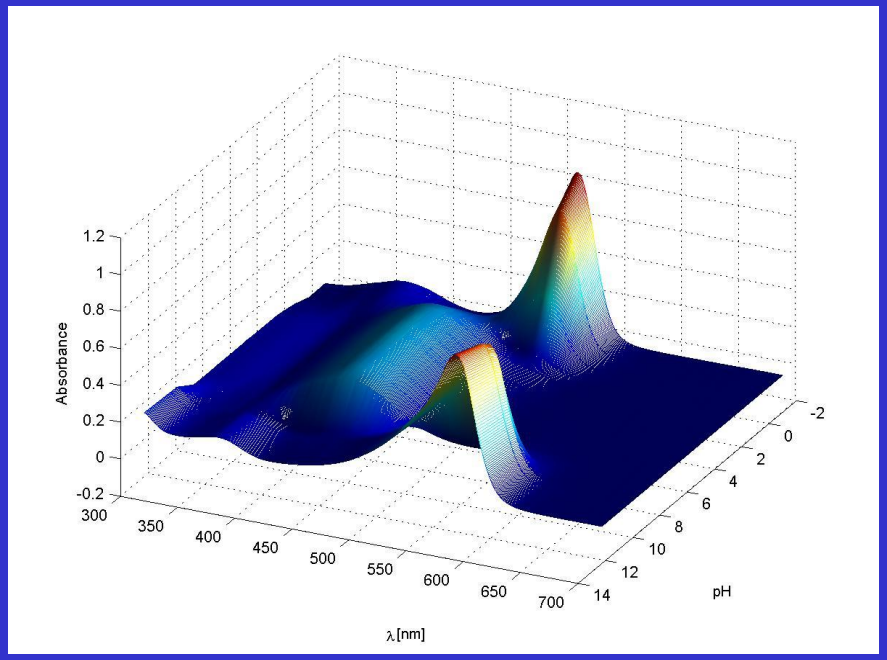
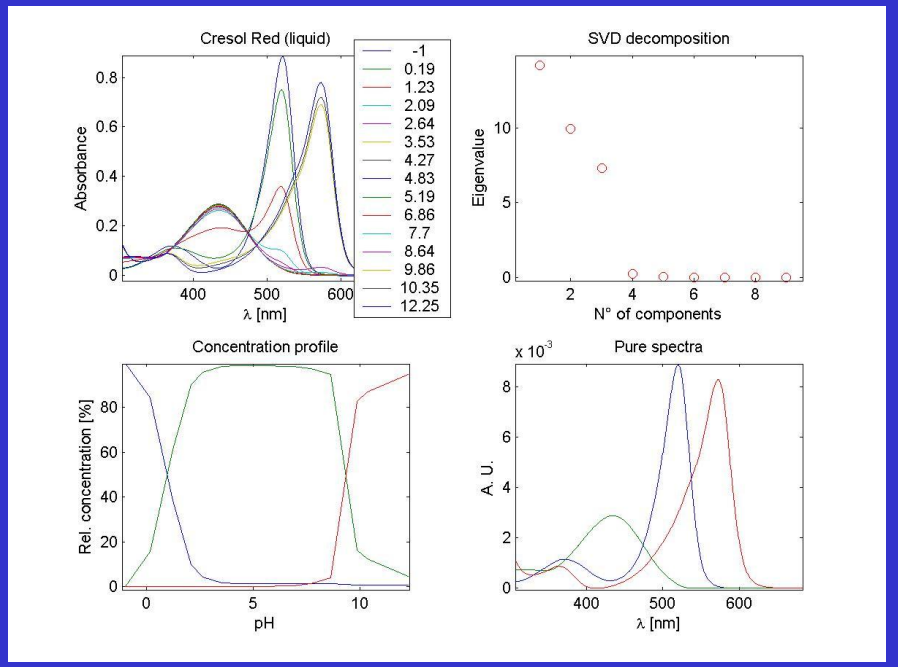
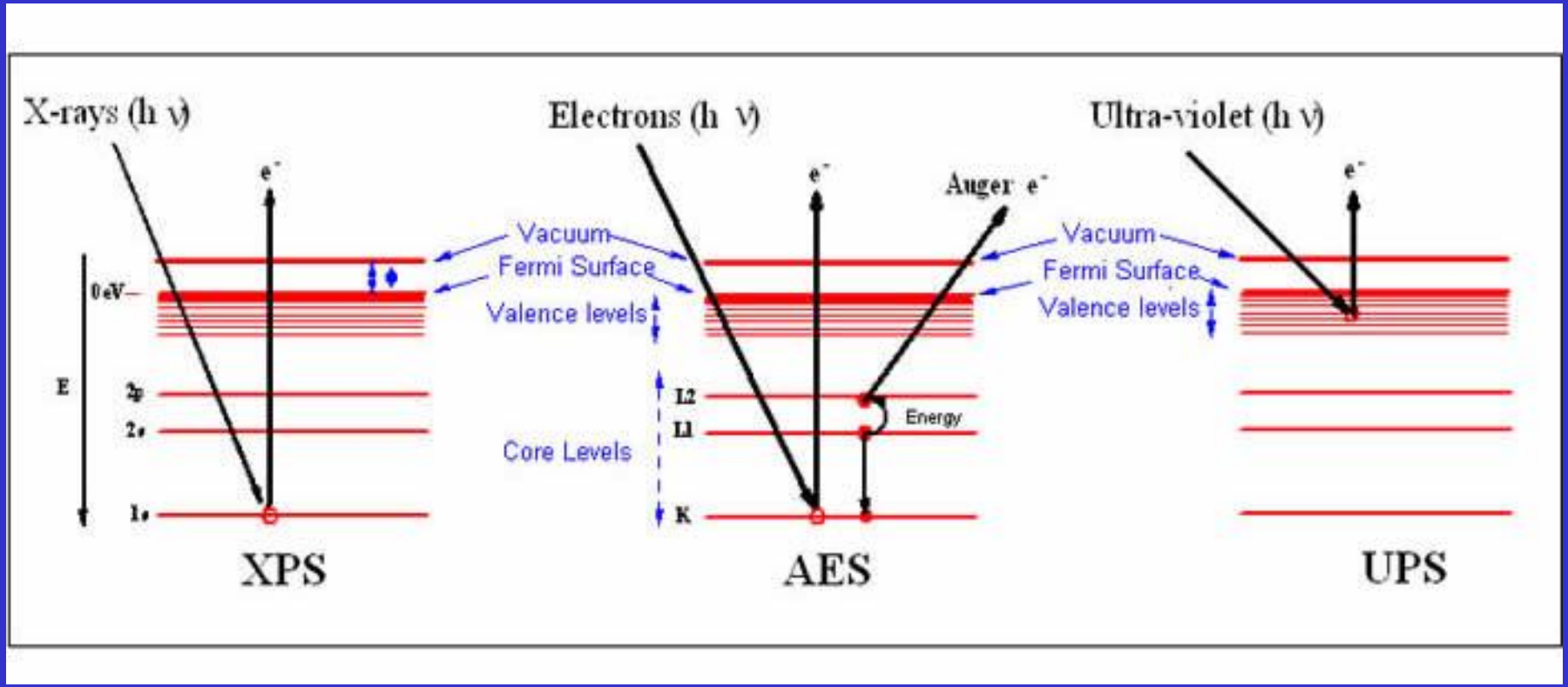
Ultrafialová a viditelná spetroskopie

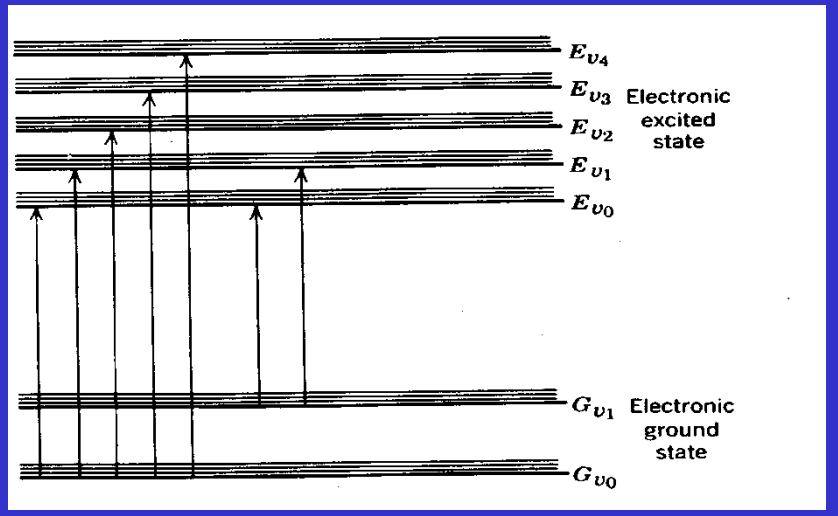


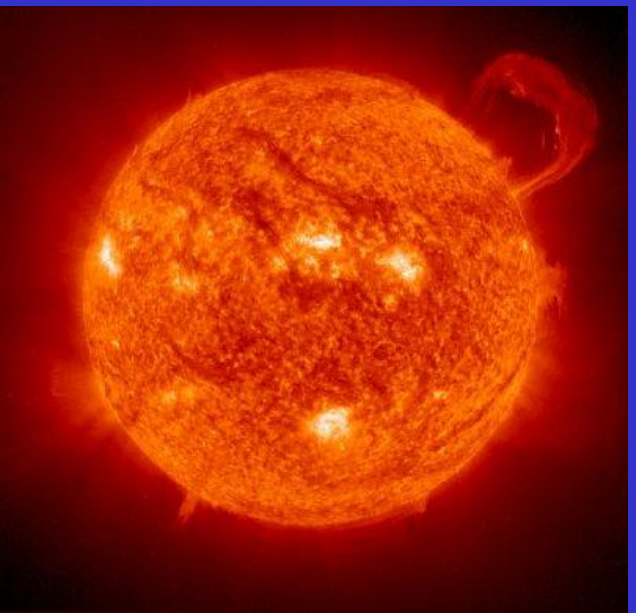


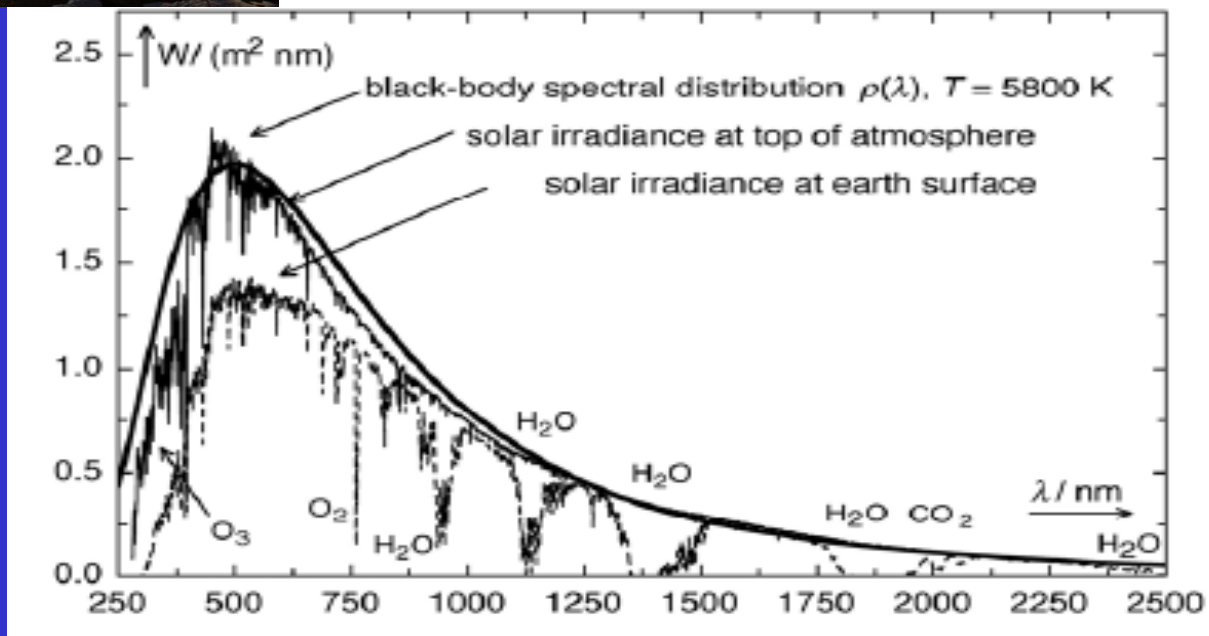
Elektronová spektroskopie



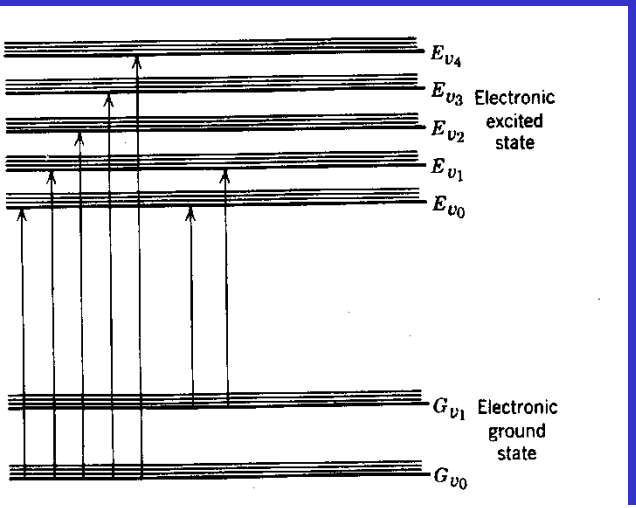
Sluneční světlo







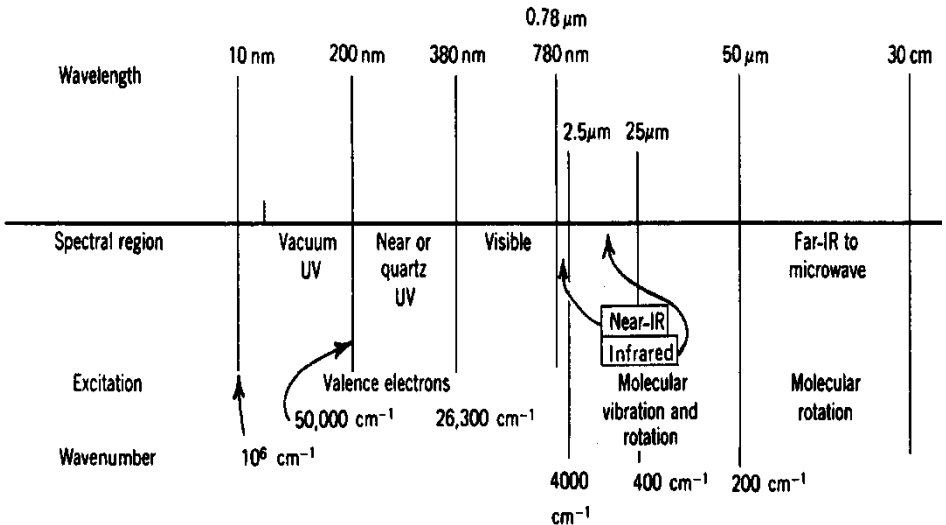
Co měří UV-VIS spetroskopie? fyzikální podstata

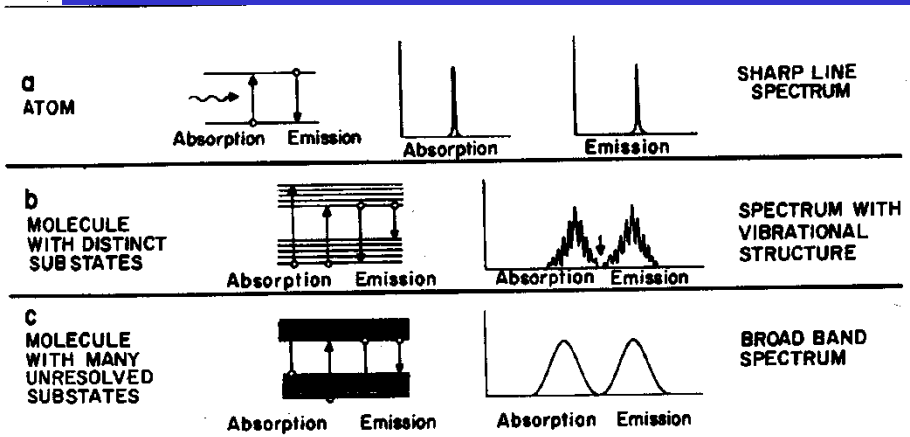


λ / nm	
185 - 200	Vacuum-UV
200 – 380	Near-UV (quartz)
380 – 780	Visible

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

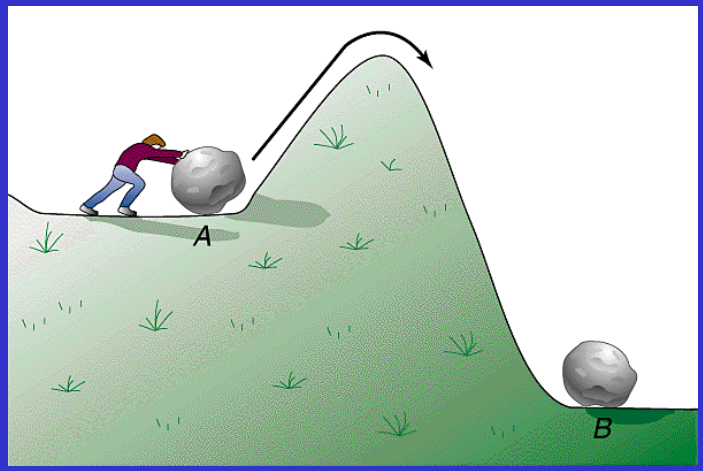
$$E = h\,\nu$$

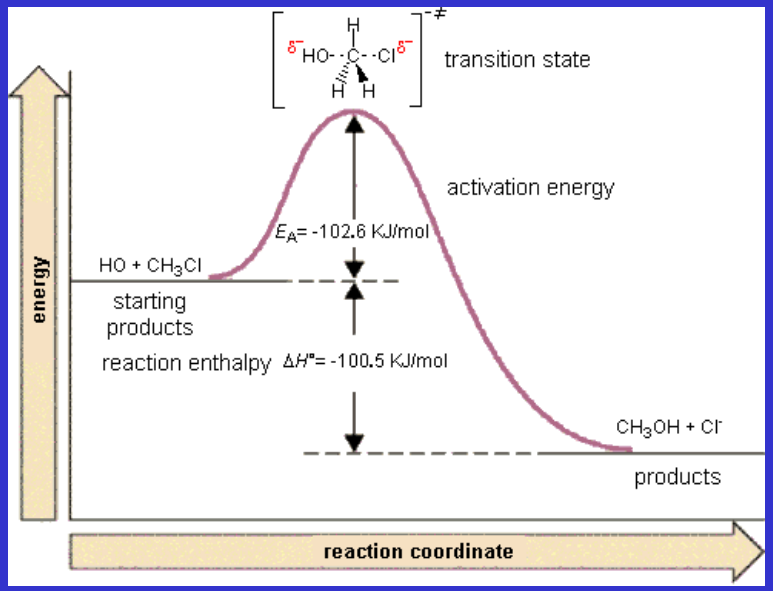




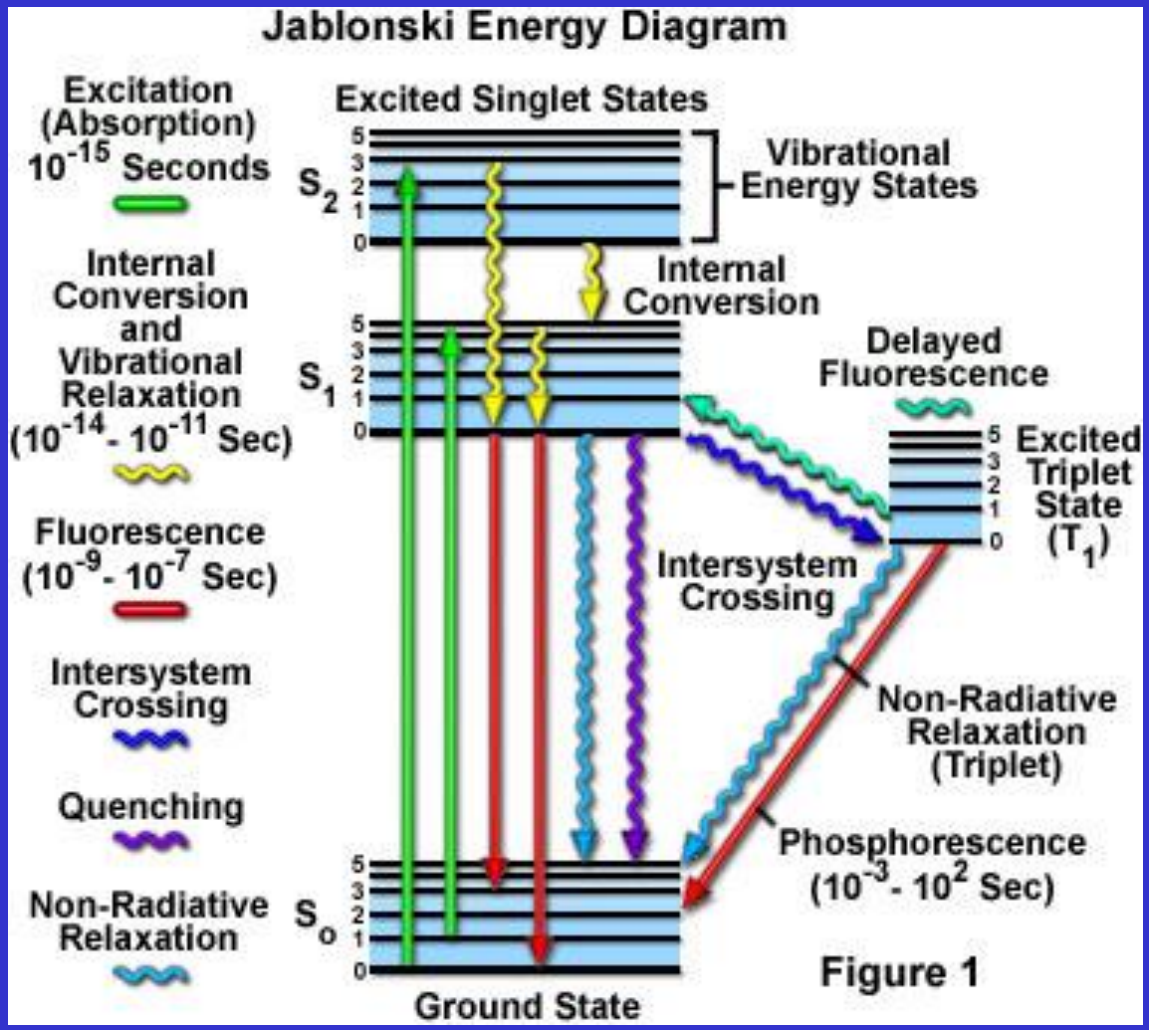
PES

Plochy potenciální energie

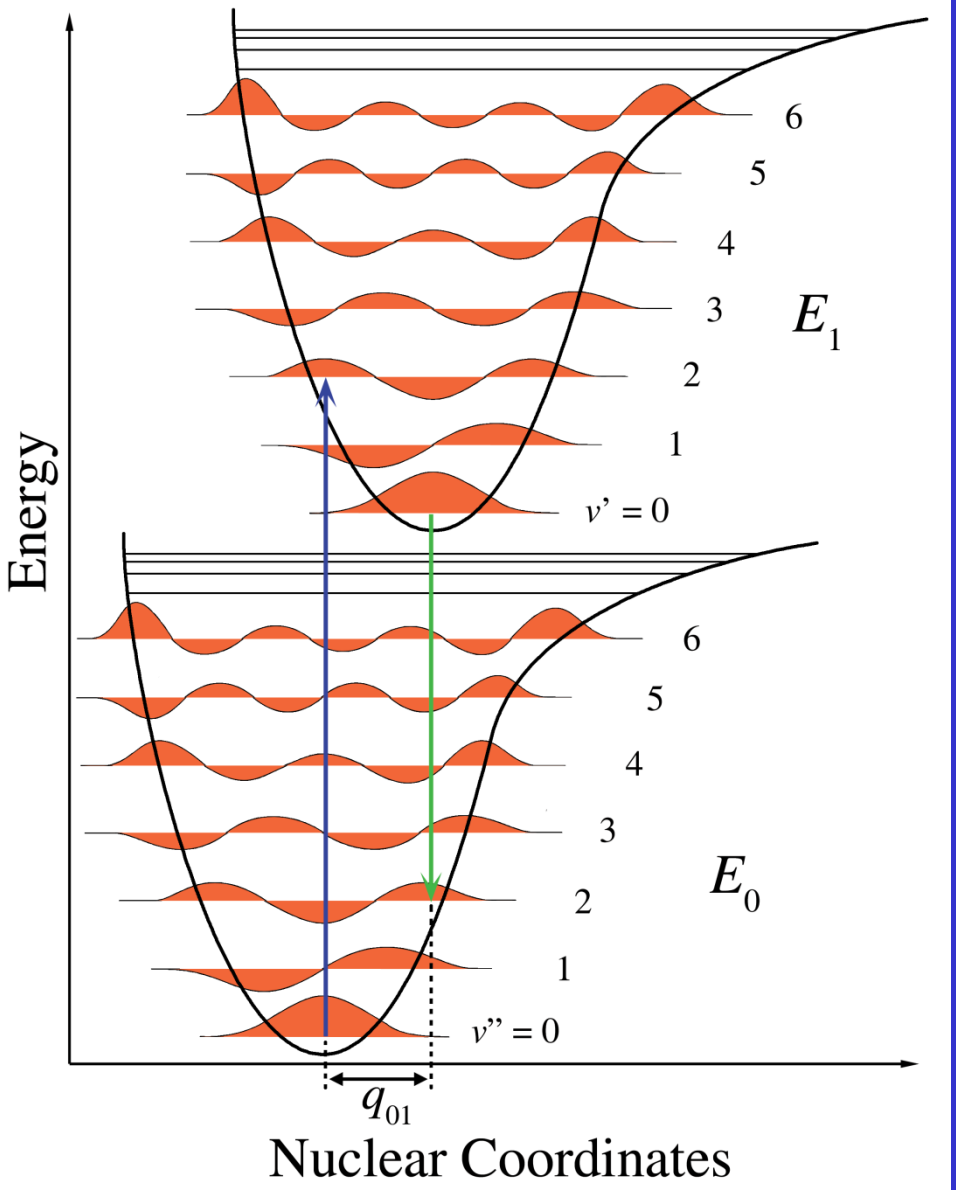


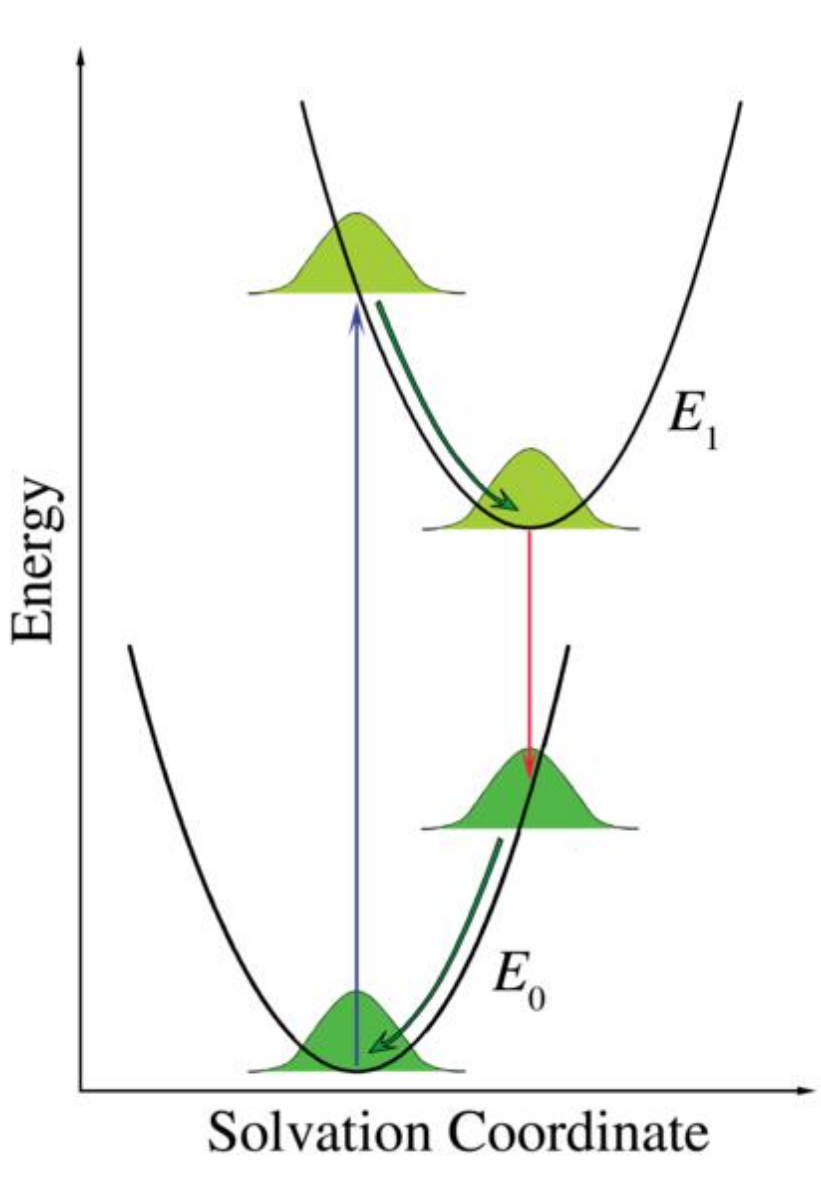


Jablonskiho energetický diagram

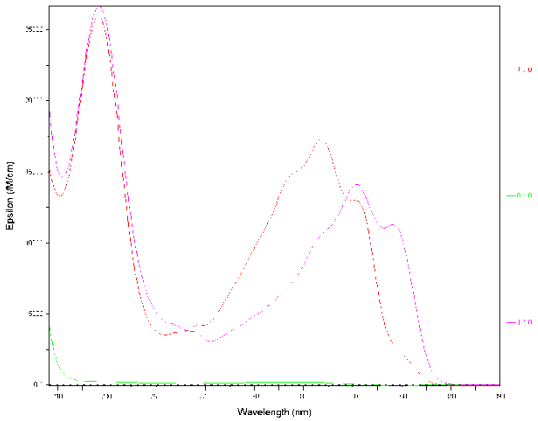


Franck-Condon Principle





Spektrum

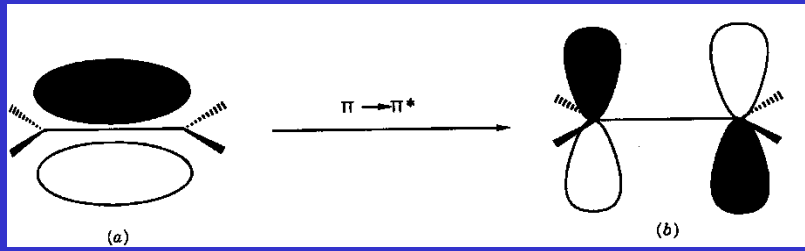


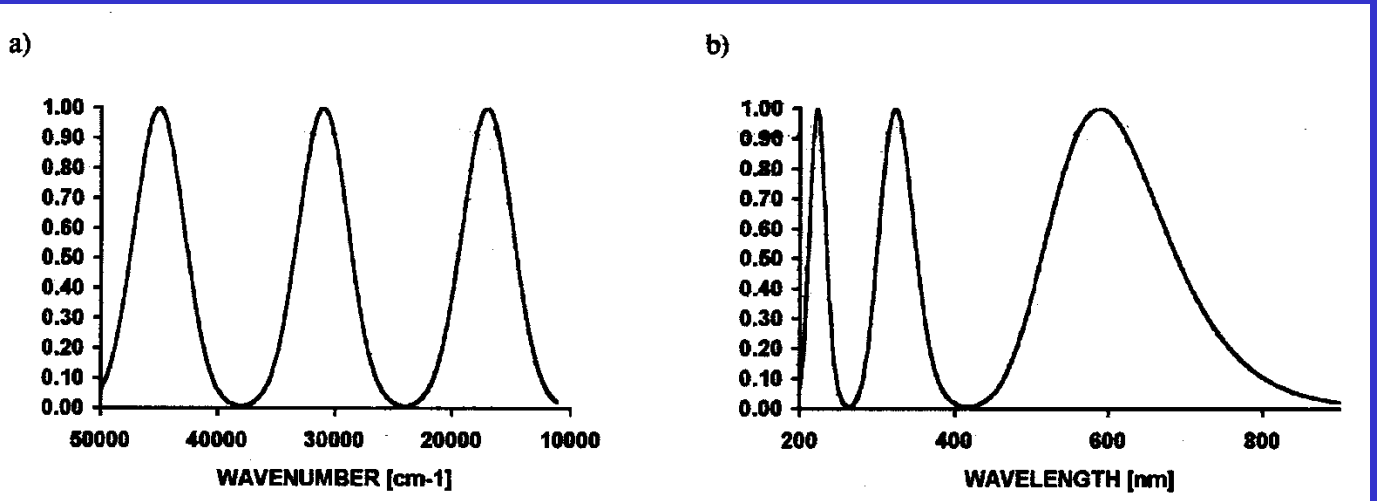
x ~ E ~ $\tilde{\nu}$ ~ $1/\lambda$

y ~ intenzita ~ pravděpodobnost přechodu → síla oscilátoru

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

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





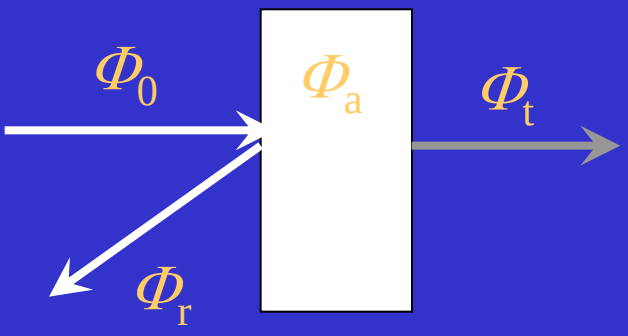
Beer – Lambert – Bouguer law

$$-\log \Phi_t/\Phi_0 = -\log \tau_i = \varepsilon c b = A$$

$\tau_i = \Phi_t/\Phi_0$ vnitřní transmitance (transimisní faktor)

$\rho = \Phi_r/\Phi_0$ reflektance, reflexní faktor

$\alpha = \Phi_a/\Phi_0 = 1 - \tau$ absorptance, absorpční faktor



Veličina	Symbol	Jednotka
monochromatický zářivý tok	Φ	W
(dekadická) vnitřní absorbance	A	1
molární (dekadický) absorpční koeficient	ε	L mol^{-1} cm^{-1}
absorpční dráha	b	cm^{-1}
optická dráha kyvety	l	cm^{-1}

Jednopaprskový UV – vis spektrometr

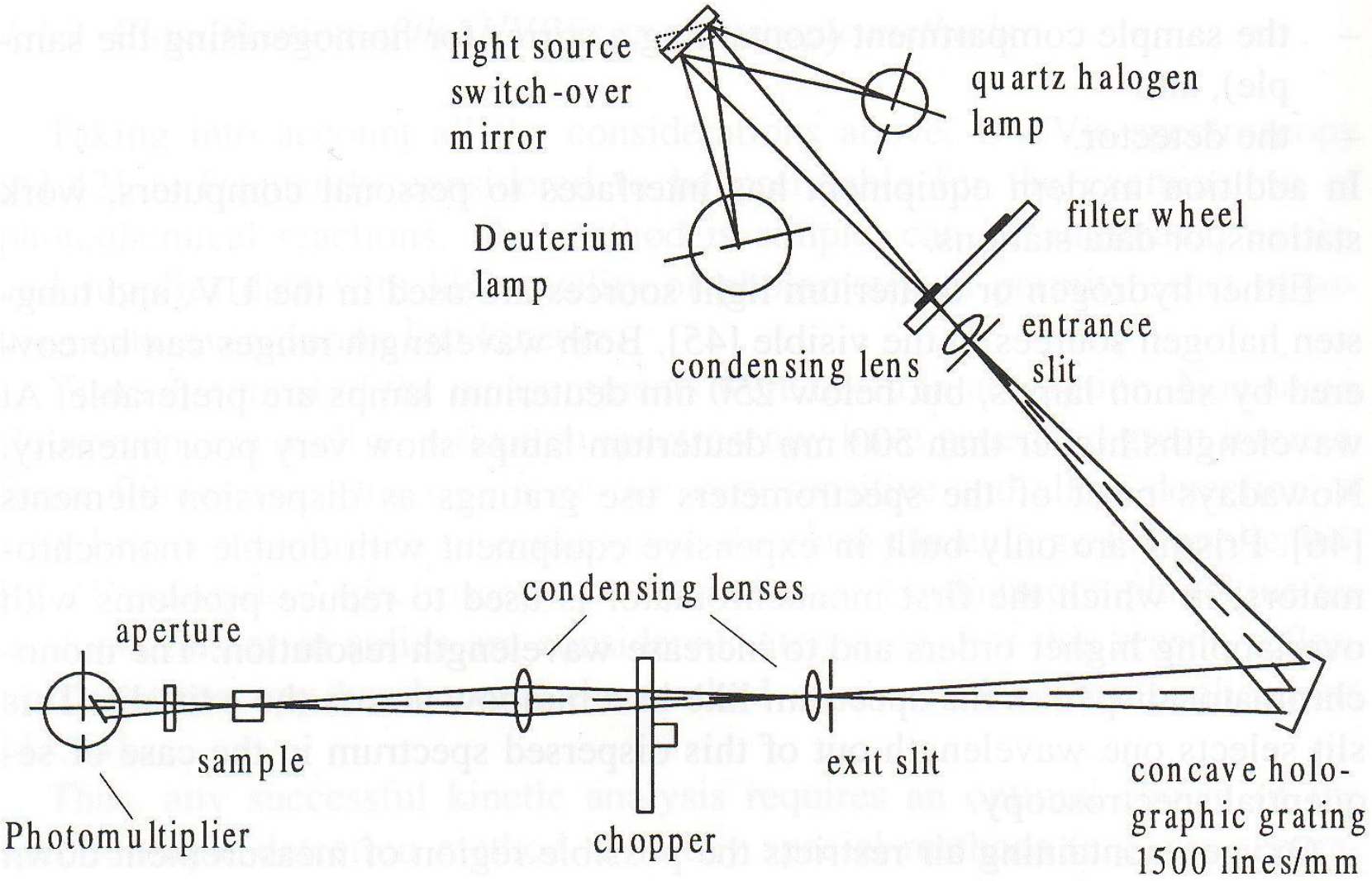


Fig. 4.1. Optical geometry of a single beam instrument, the Uvikon 710 by Kontron Instruments, Eching.

Dvoupaprskový UV – vis spektrometr

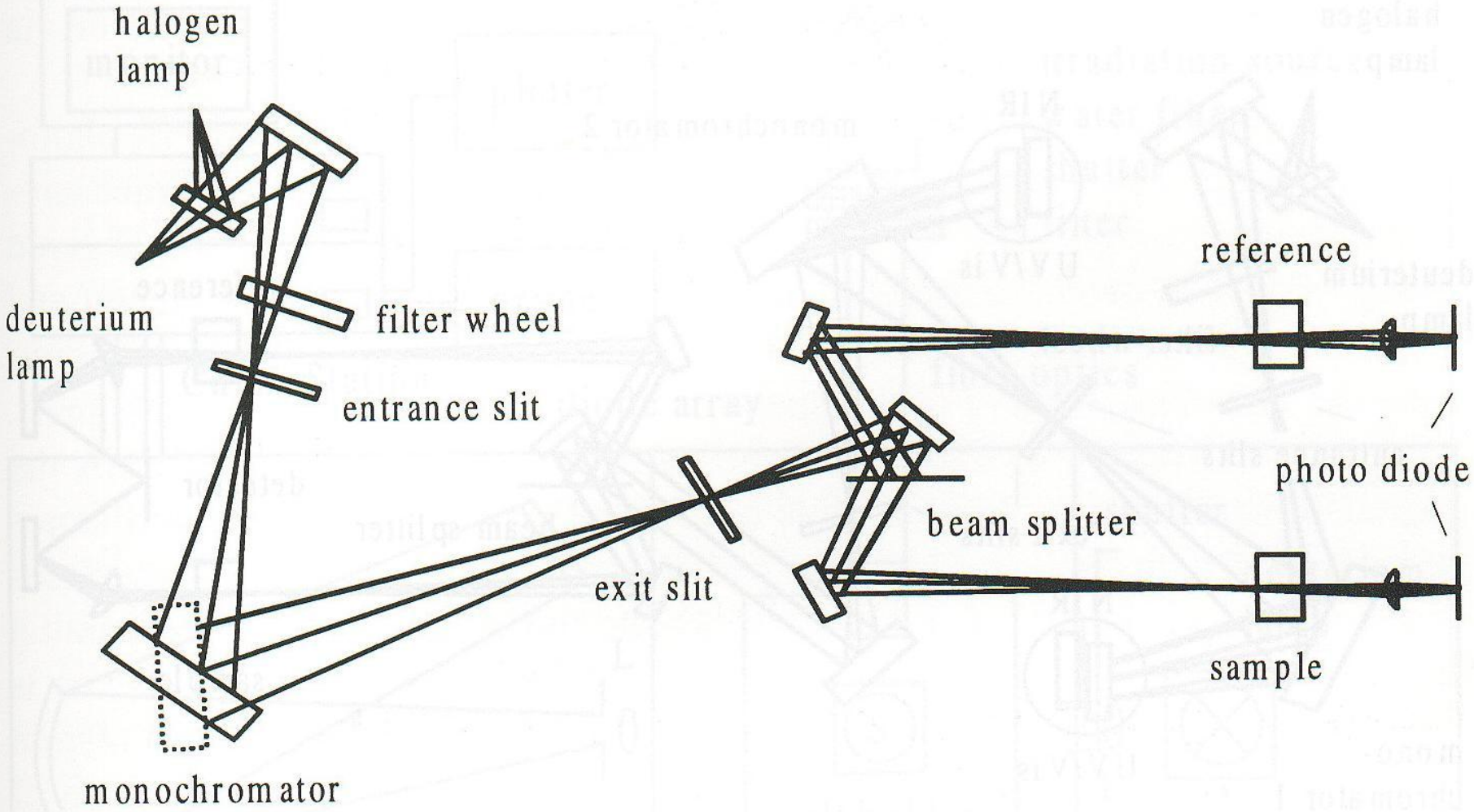


Fig. 4.2. Schematic diagram of the optical pathway in a double beam instrument Lambda 2, Perkin Elmer, Überlingen.

Dvoupaprskový, dvoumřížkový UV – vis spektrometr

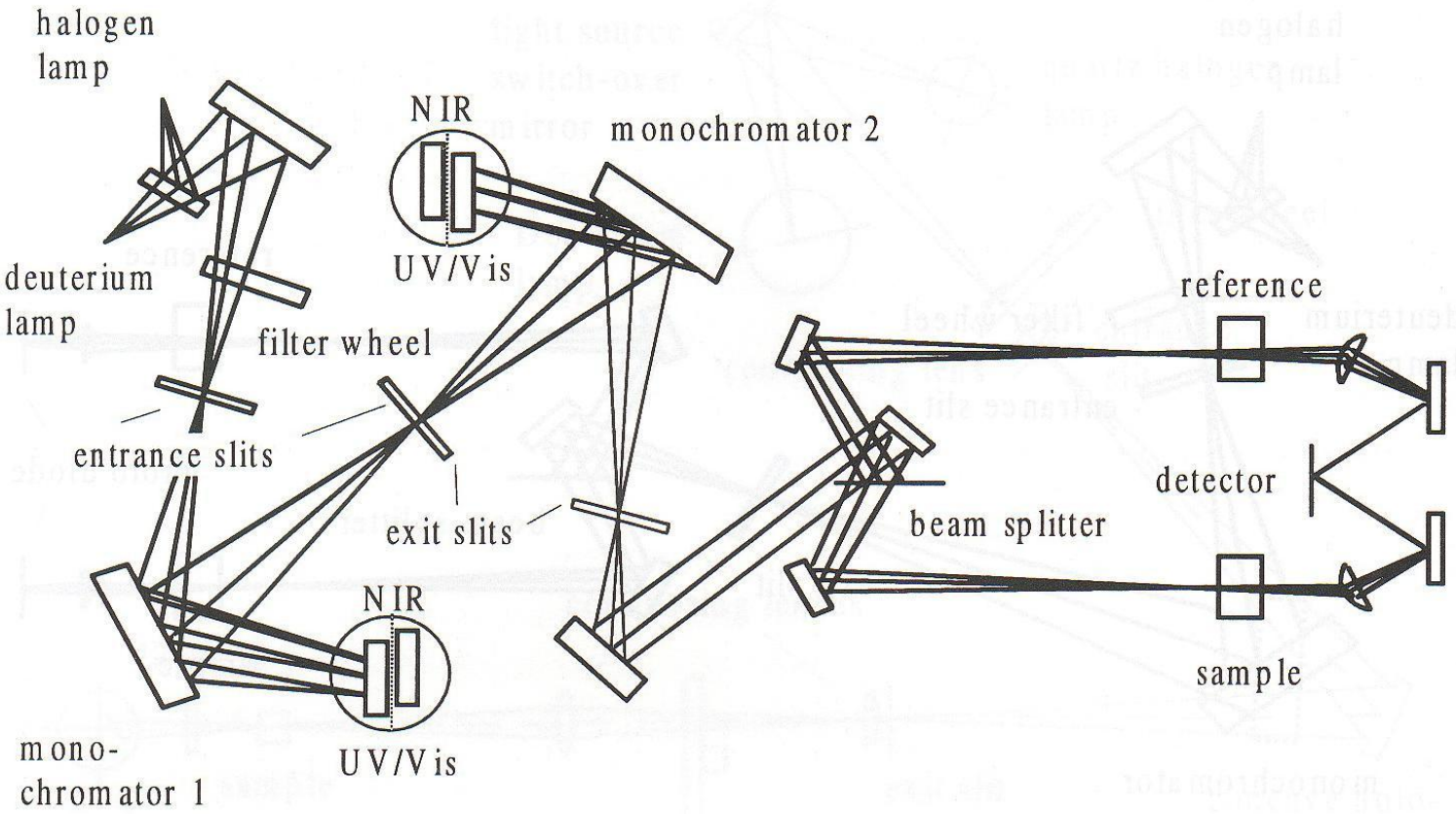
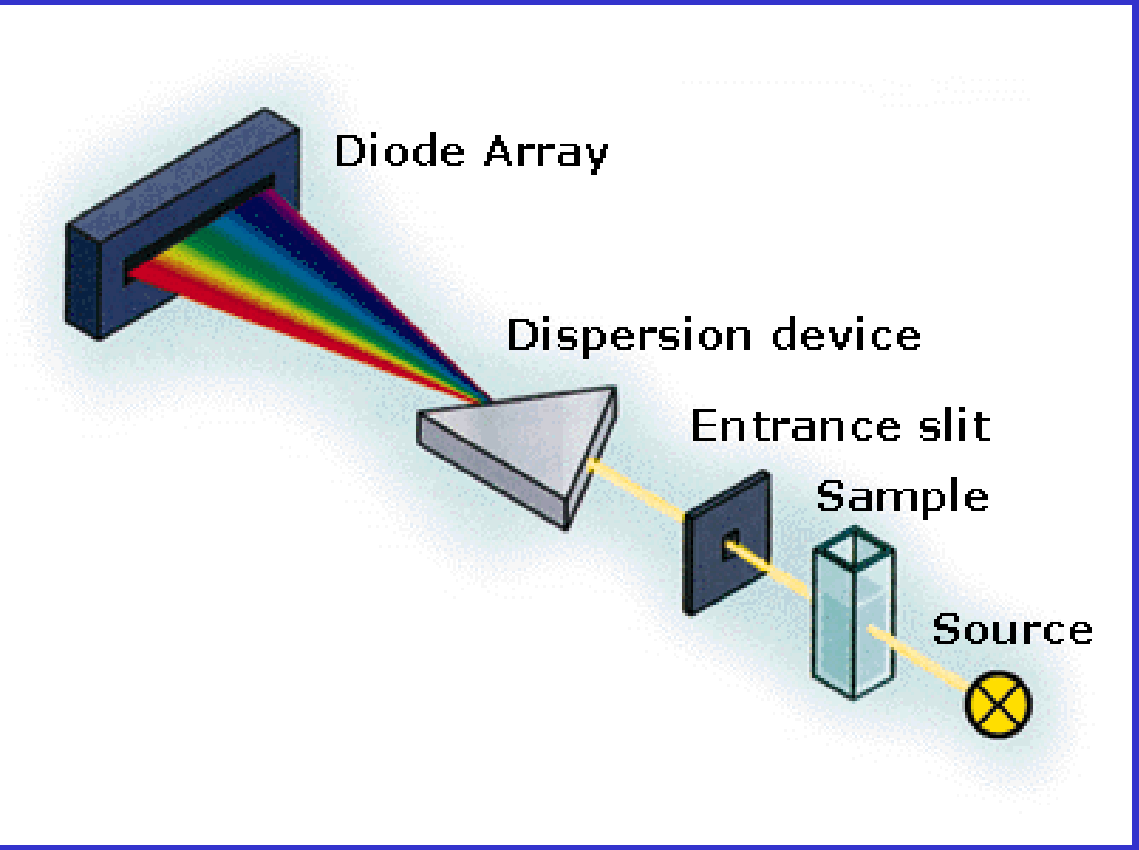
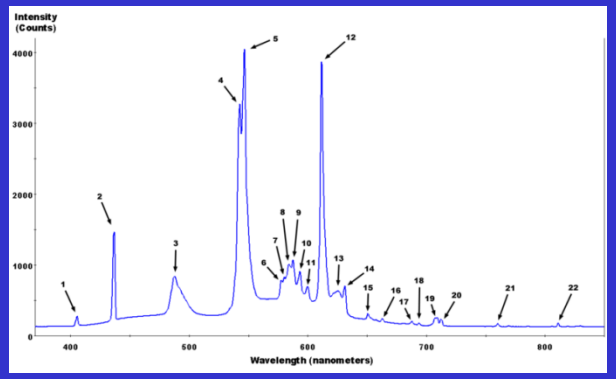


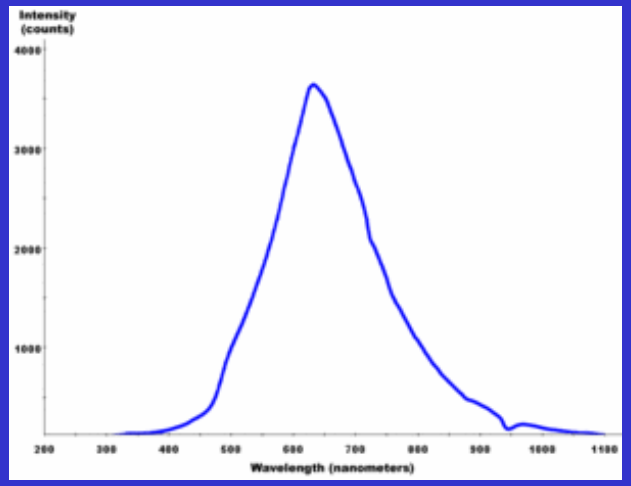
Fig. 4.3. Double beam set-up with a double monochromator for very precise photometric measurements and the possibility of taking high resolution spectra (Lambda 9, Perkin Elmer, Überlingen). This instrument covers the wavelength range from the UV until the near infrared (NIR).

Jednopaprskový UV – vis spektrometr s diodovým polem



Jak funguje spektrometr?





UV – vis spektrometr

Zdroj

- čarový x spojitý
- rtuťová-halogenová výbojka <330; 1200) nm
- D_2 lampa <UV; 330> nm
- Xe výbojka <190; 1000> nm

Spektrometr

- jednopaprskový x dvoupaprskový
- sekvenční x simultální

Detektory

- foto-emisní detektory (vakuované fotonky, fotonásobiče ...)
- polovodičové detektory (fotovodivostní detektory, fotodiody, fotonásobiče; detektory s prostorovým rozlišením – CCD –charge-coupled device)

Kyvety

- tvar
- objem
- materiál

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

Lampy

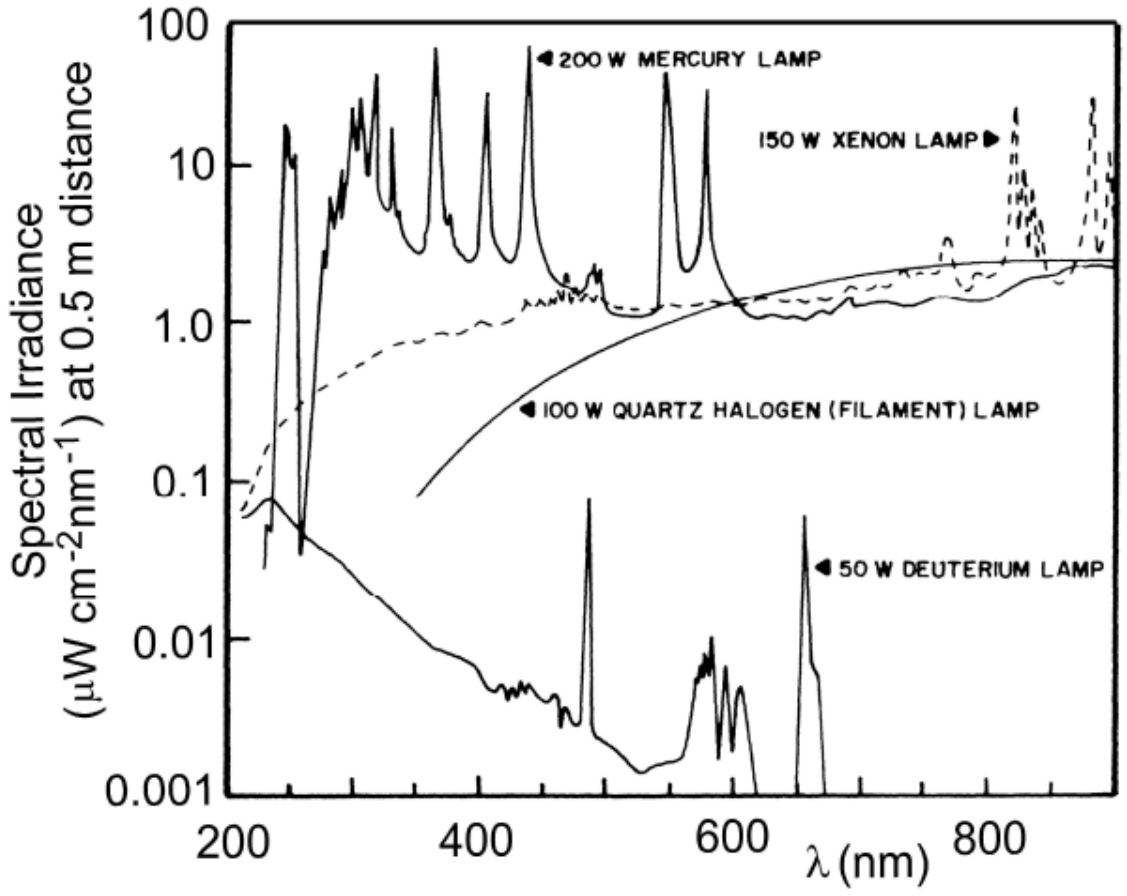


Fig. 11a-2. Spectral irradiance of some arc lamp sources. Reprinted by permission from LOT-Oriel catalogue.

Absorpční pásy organických molekul

Efekty

hyperchromní

Posuny

hypsochromní

bathochromní

hypochromní

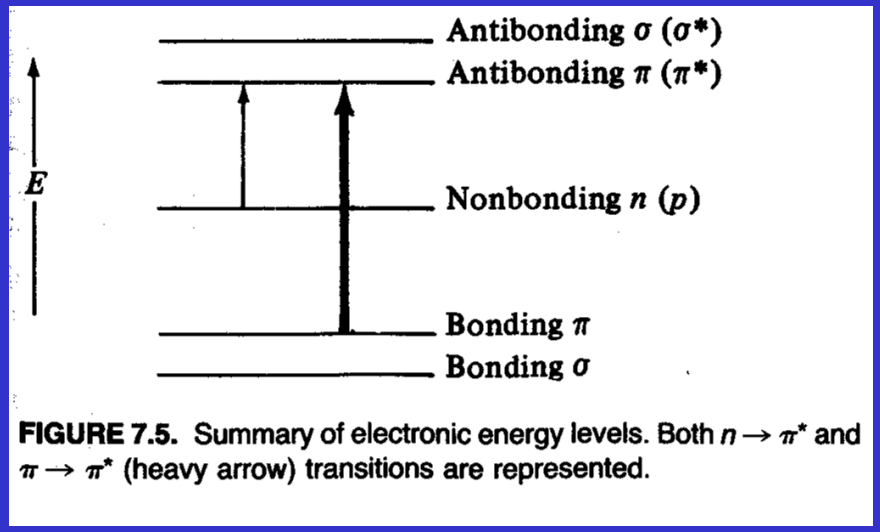
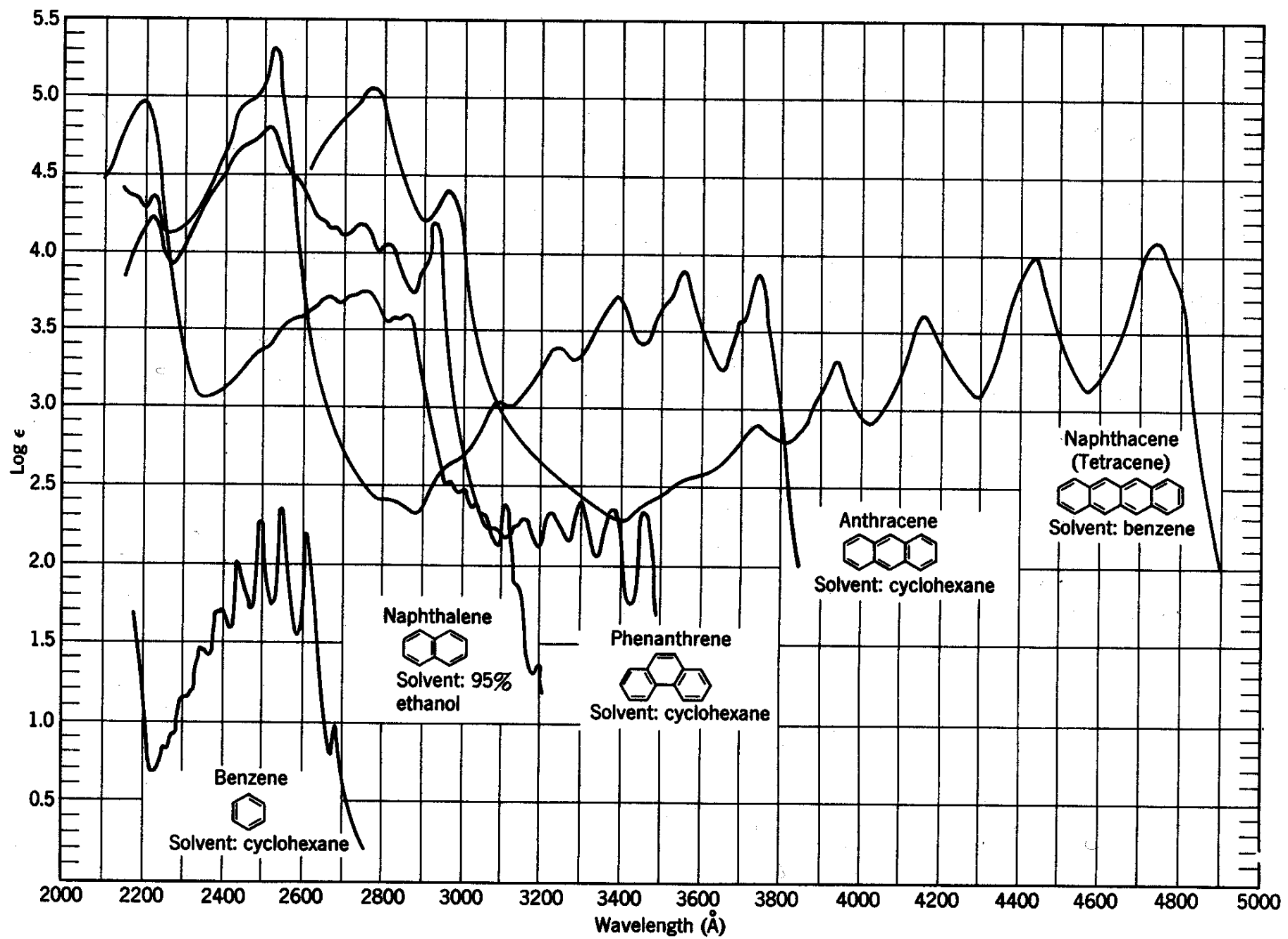


FIGURE 7.5. Summary of electronic energy levels. Both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (heavy arrow) transitions are represented.

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


Log ε
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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

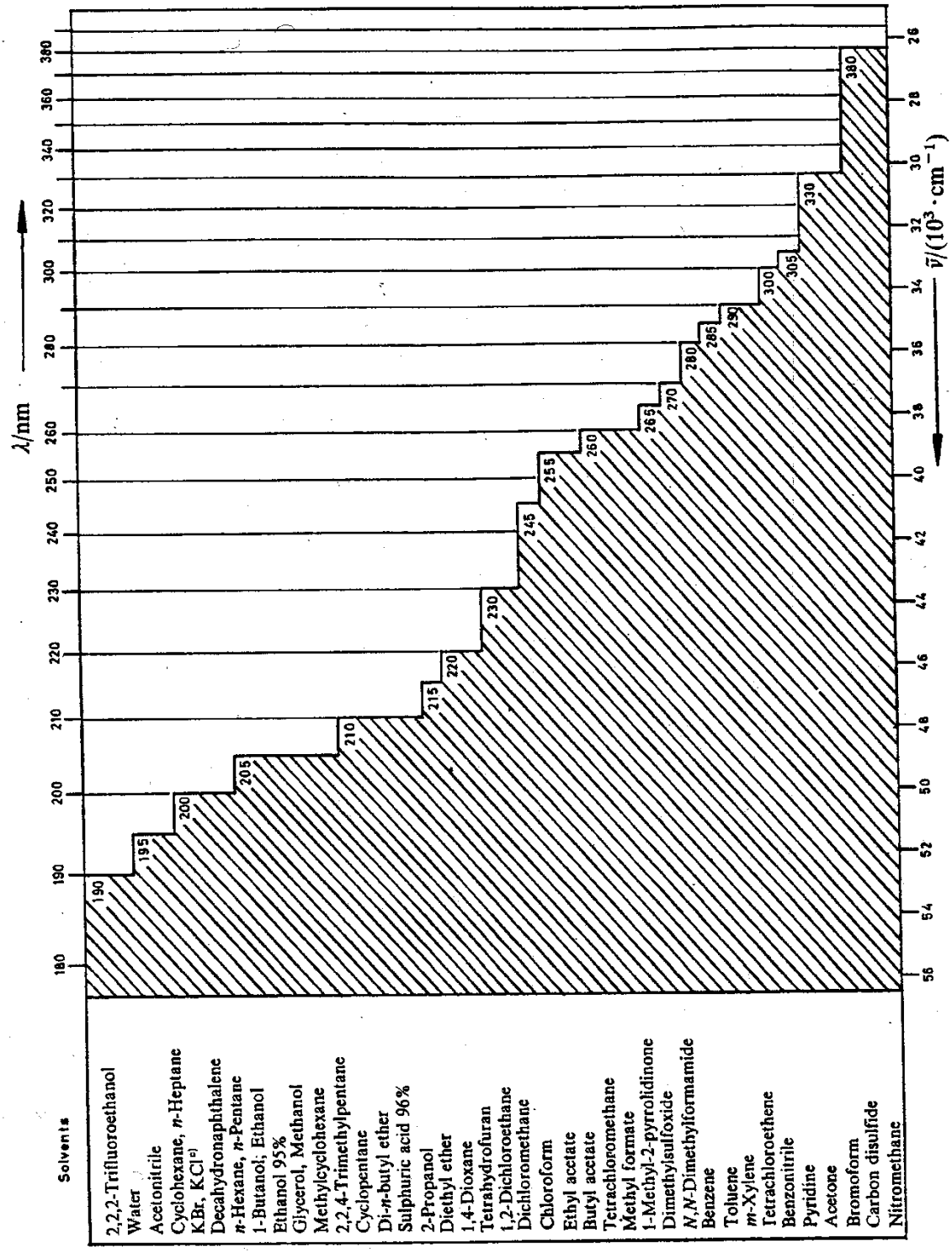


Table A-4. Ultraviolet "cut-off points"[a] of spectroquality solvents commonly used in UV/Vis-Spectroscopy, for 1 cm pathlengths (accuracy *ca.* ± 5 nm)[b].

[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.

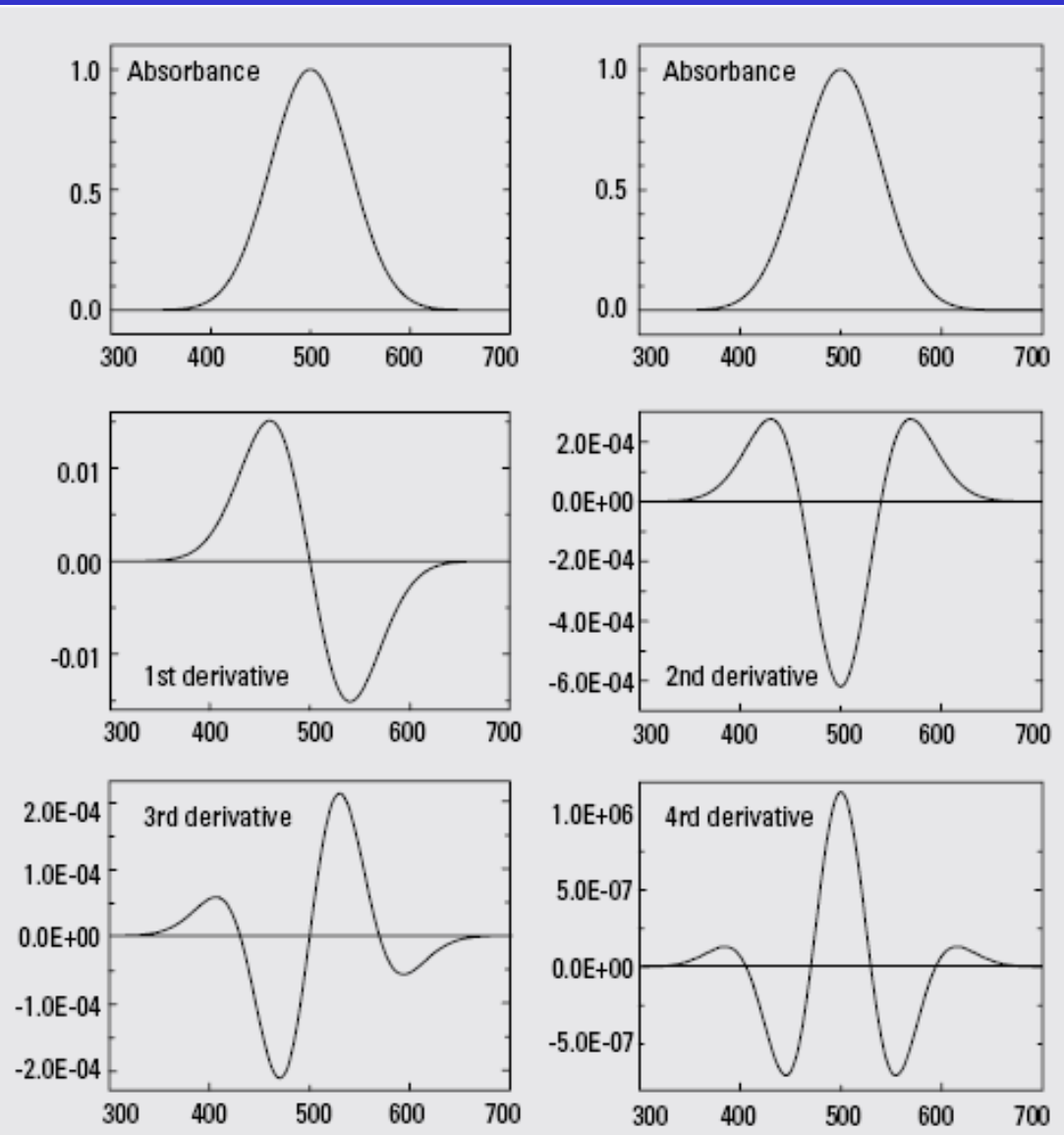
[b] Compiled from the following references:
(1) Eastman Kodak Company: *Spectrophotometric Solvents*. Dataservice Catalog JJ-282, Rochester, New York 14650, USA, 1977;
(2) E. Merck: *UVASOLE® – Lösungsmittel und Substanzen für die Spektroskopie*. D-6100 Darmstadt, Fed. Rep. Germany;
(3) and from the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

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

Vyhodnocení spekter – kvantitativní

- Nalezení maxim – Antonov – Step by step filter (SBSF) – Derivační spektroskopie
- Fitování Gaussových (či jiných) křivek
- Neparametrické metody
  - Singular Value Decomposition, Target Factoral Analysis

Derivační spektroskopie



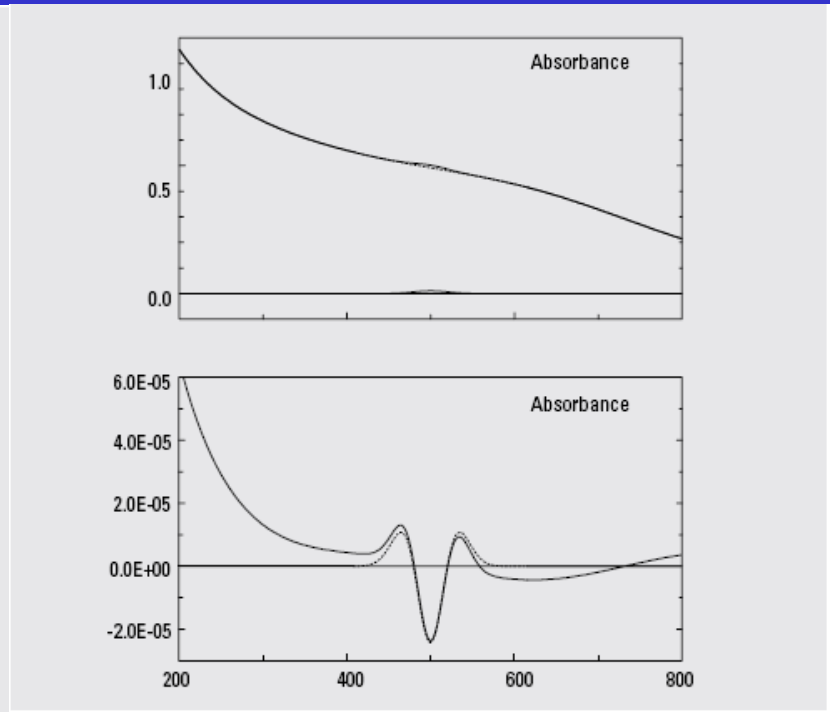
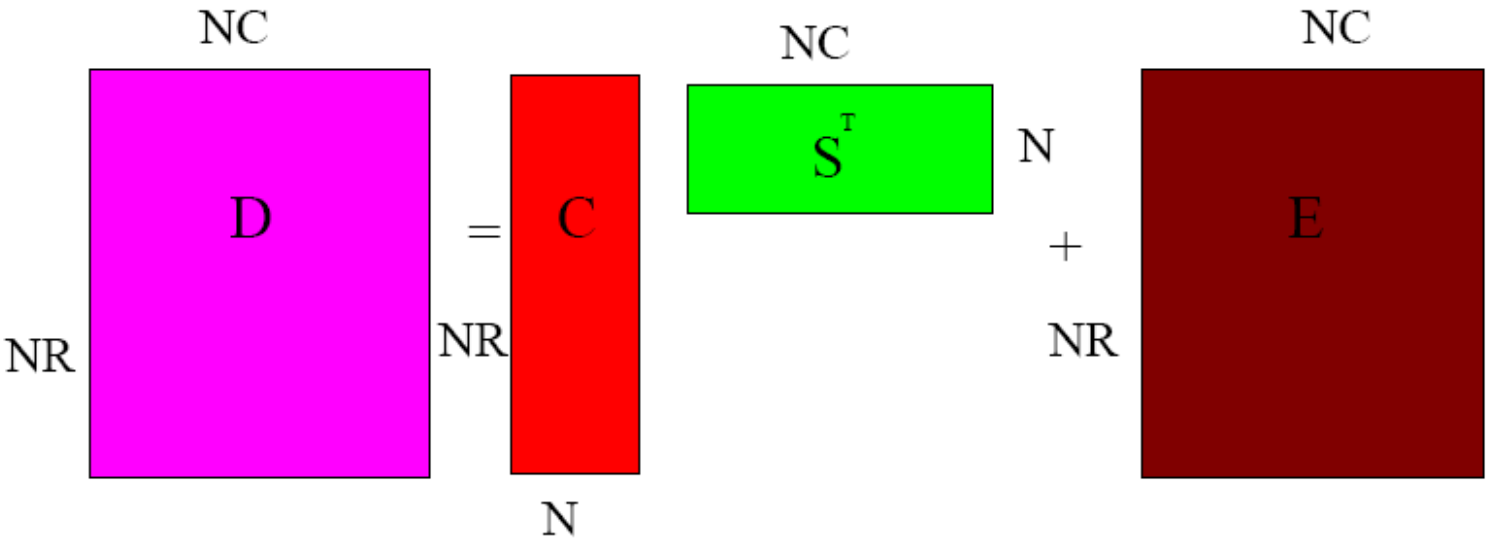


Figure 6
Matrix supression

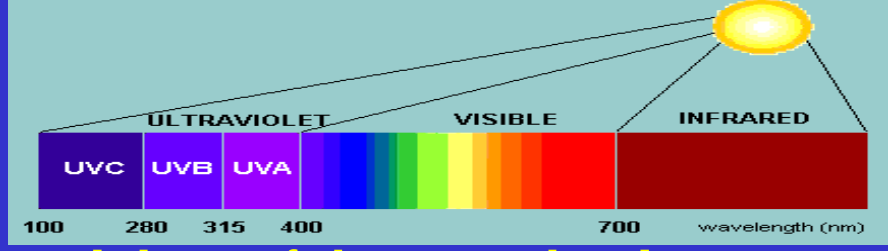
Multivariate Curve Resolution (MCR)

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

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



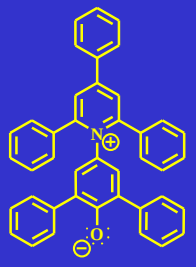
solvatochromism

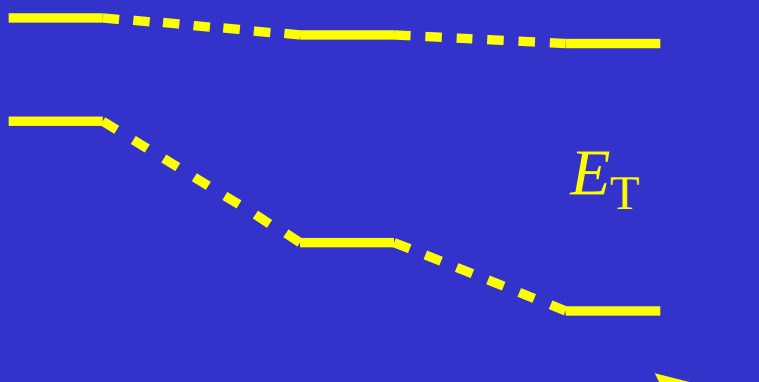
change in the position, intensity, and shape of absorption bands due to the surrounding medium

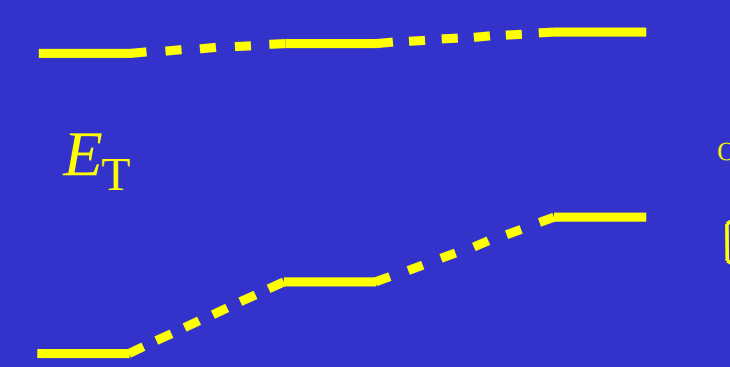
= perichromism (peri - around)

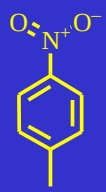
surrounding medium - liquids, solids, glasses, and surfaces

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







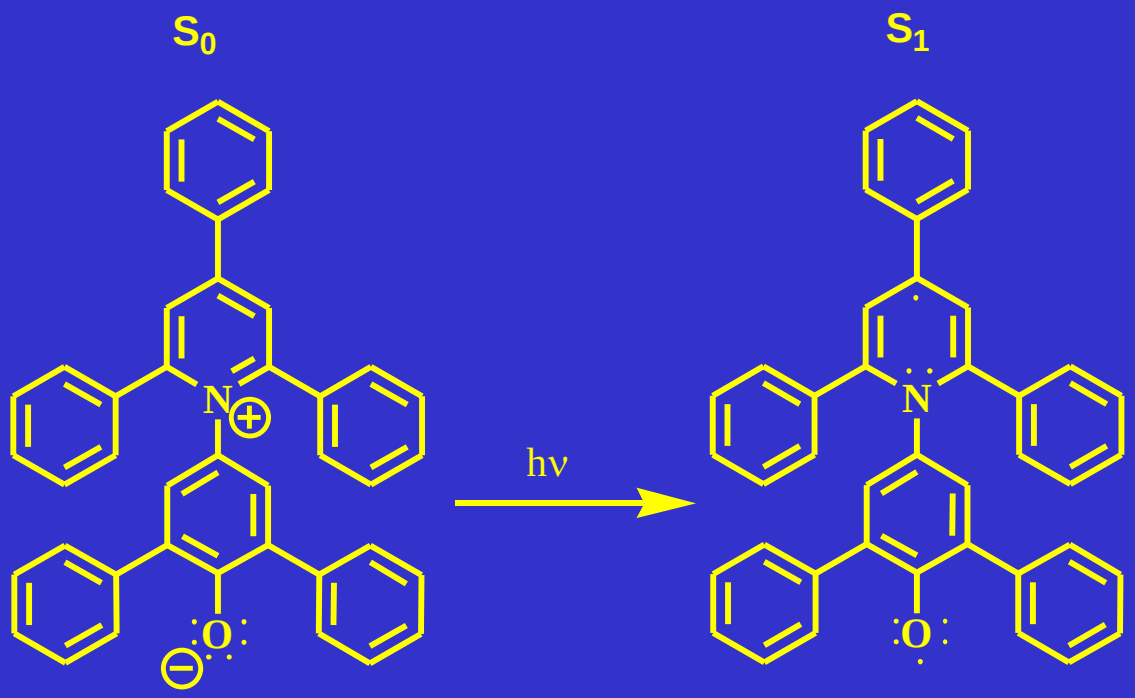


Reichardt's dye

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

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

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

$E_T^N = (E_T(solvent)-E_T(TMS))/(E_T(water)-E_T(TMS))$

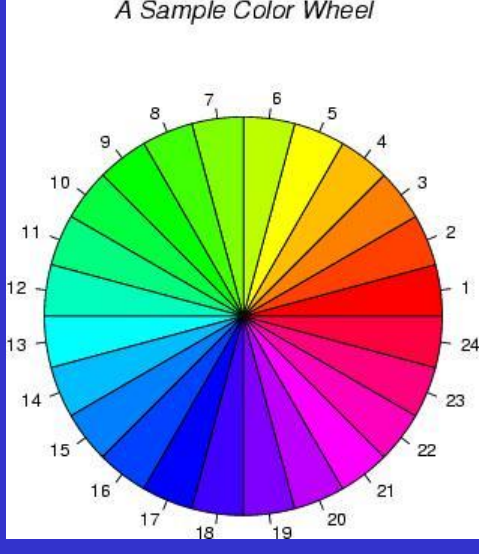
$= (E_T(solvent) - 30.7)/32.4$

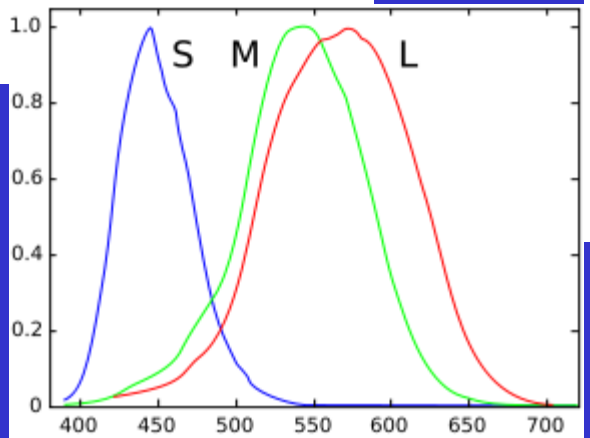
$E_T^N(TMS) = 0.000$ $E_T^N(H_2O) = 1.000$

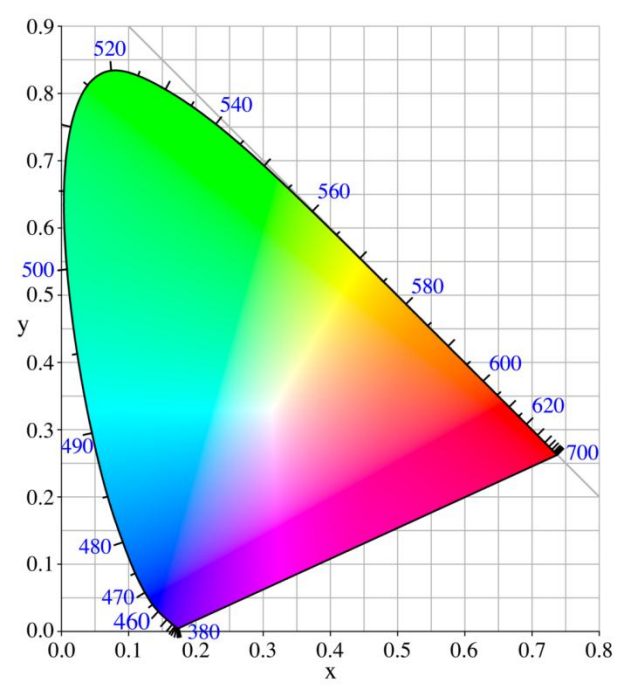
TMS = Tetramethylsilane

SPLIT COMPLEMENT
orange with blue-violet and blue-green

Vincent Van Gogh
The Starry Night, 1889







Normalizovaná odezva lidských čípků

Odkazy, literatura

- http://www.iupac.org/reports/VII/spectro/contents.html
- http://webbook.nist.gov/chemistry/name-ser.html
- Silverstein R. M. et all: Spectrometric indentification of organic compounds, John Wiley & Sons, inc.
- Reichardt, C. (1994). "Solvatochromic Dyes as Solvent Polarity Indicators." Chemical Reviews 94(8): 2319-2358.
- http://www.hellmaoptik.com/en/kuevetten/
- http://www.orgchm.bas.bg/~lantonov/