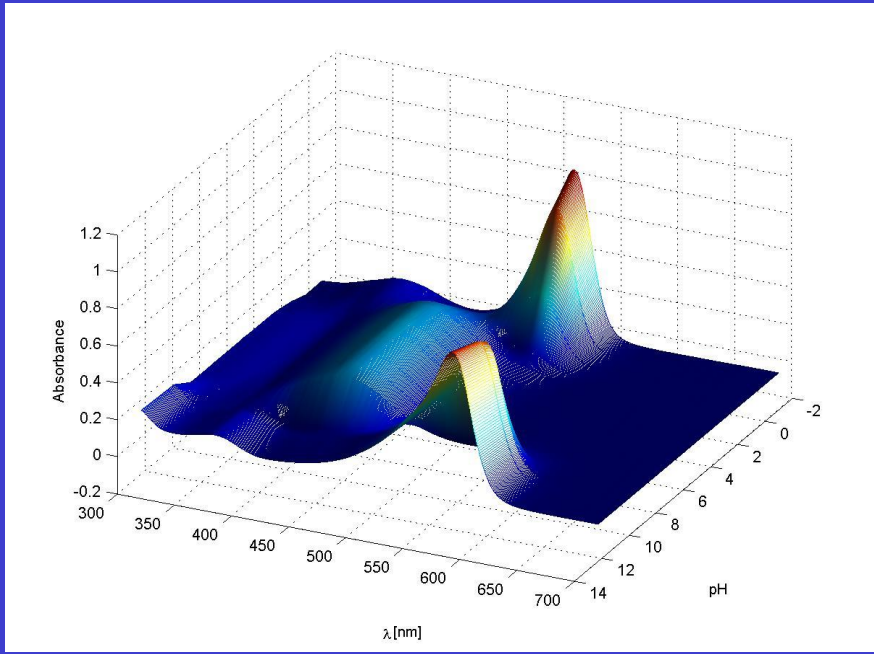
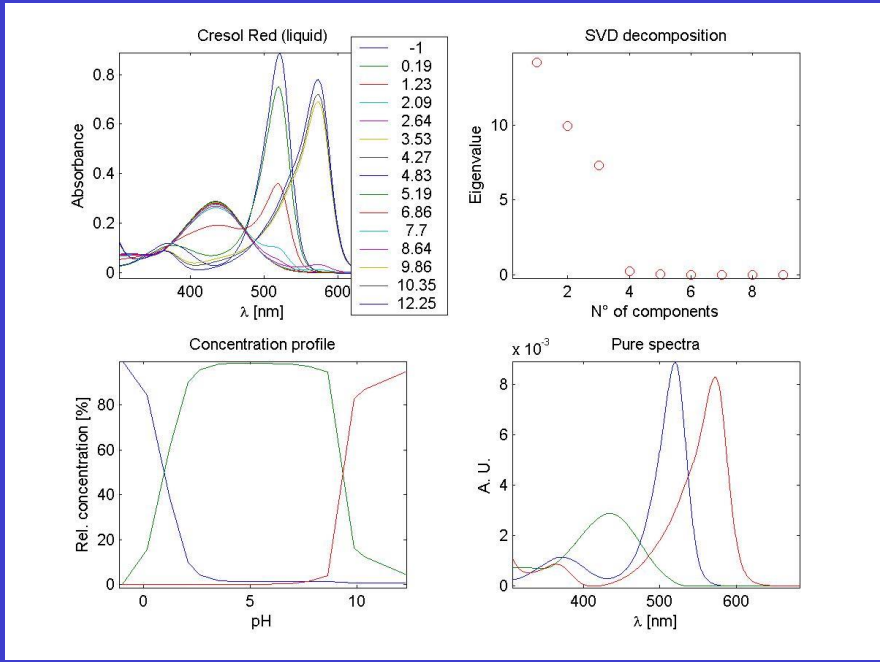
UV-Vis spektrometrie





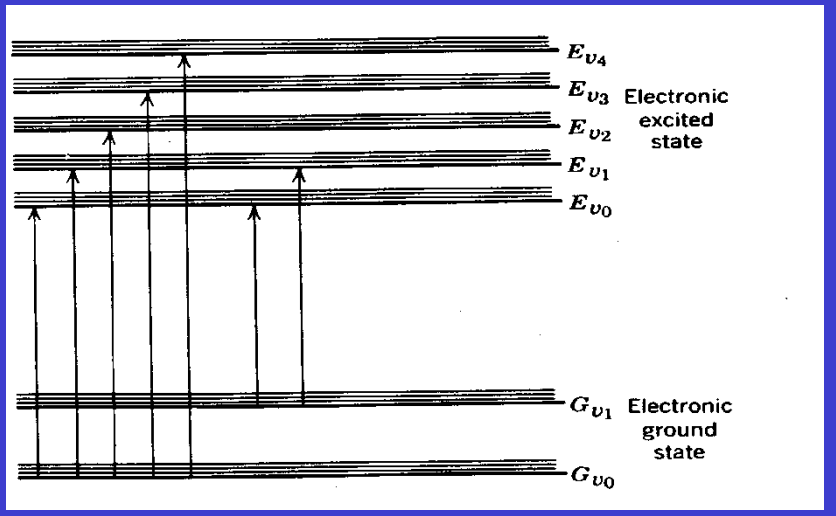
Brno 2016, Dominik Heger, http://hegerd.sci.muni.cz/

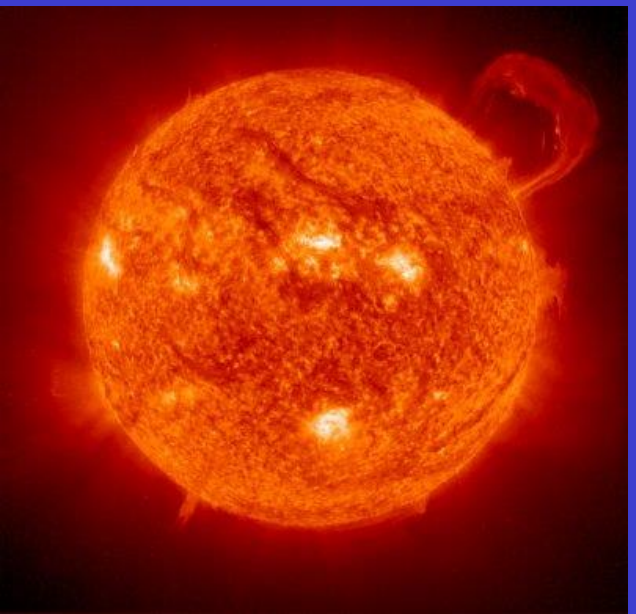
Ústav chemie a RECETOX, MU

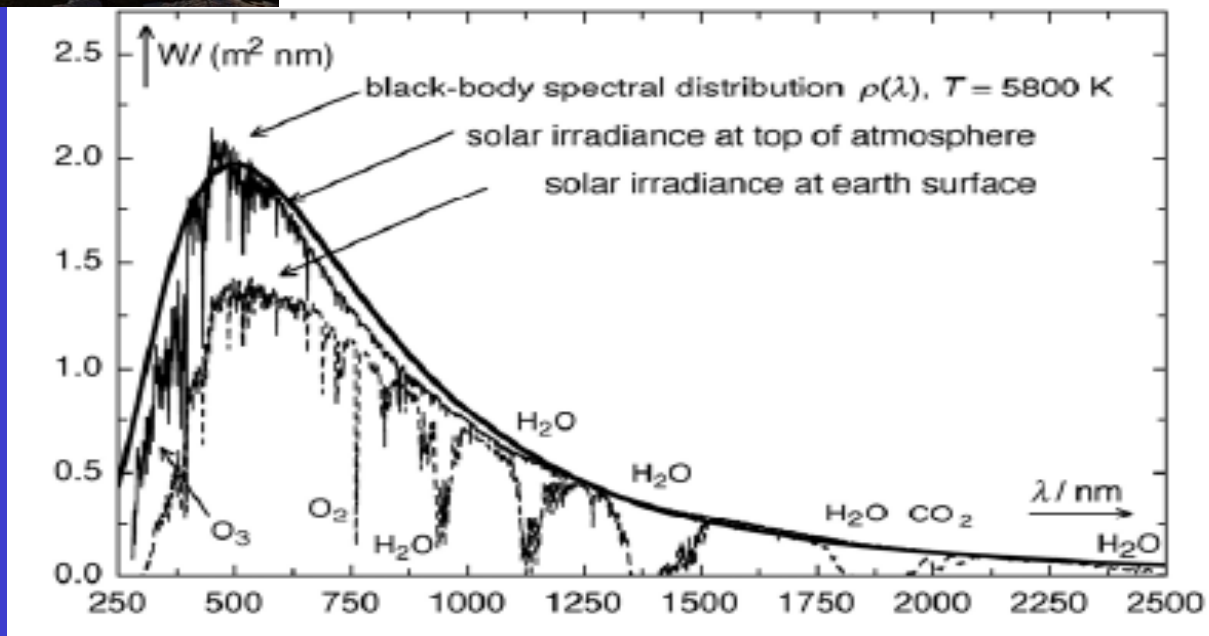




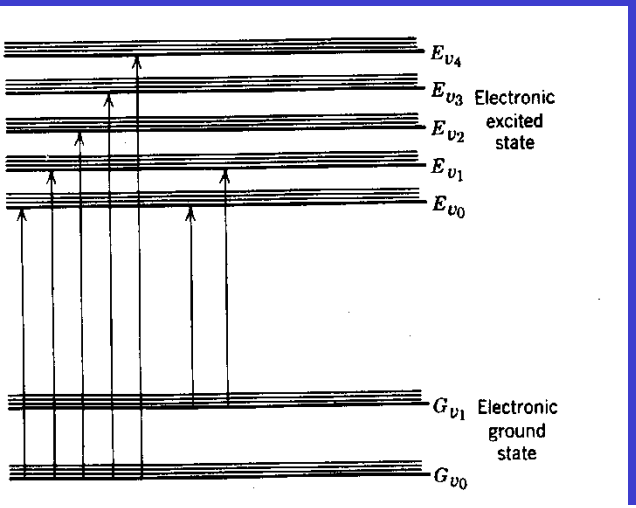

Sluneční světlo







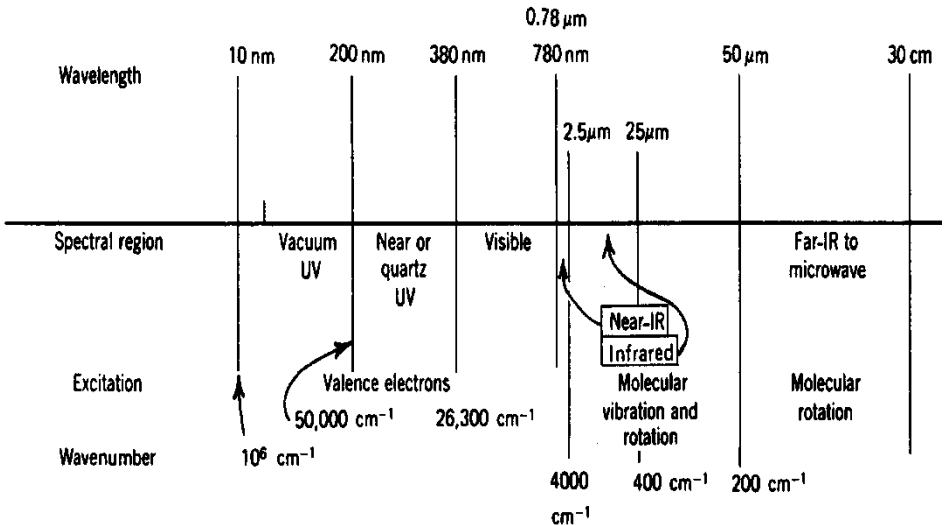
What is UV-VIS spectroscopy measuring? Electronic transitions.

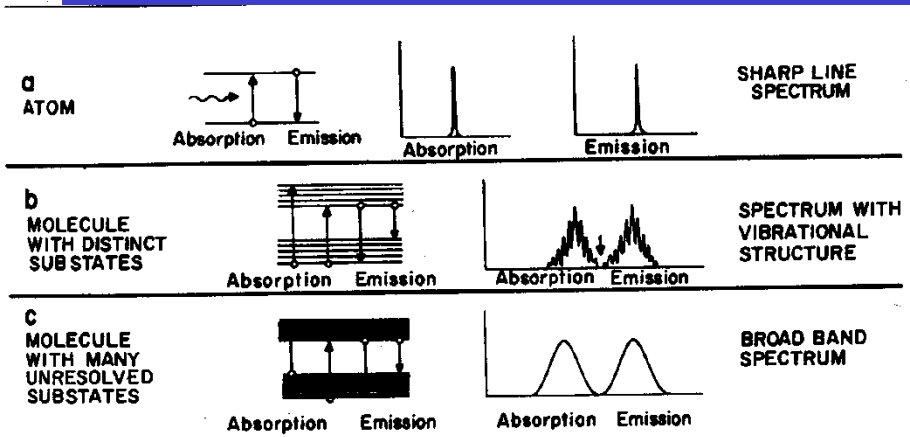


λ / nm	
185 - 200	Vacuum-UV
200 – 380	Near-UV (quartz)
380 – 780	Visible

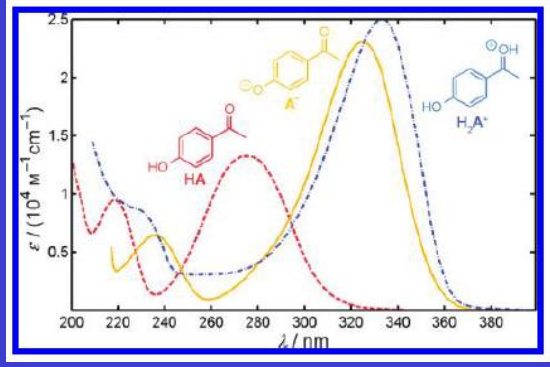
$$E_{\text{int}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}$$

$$\Delta E = h \nu$$





Spectrum



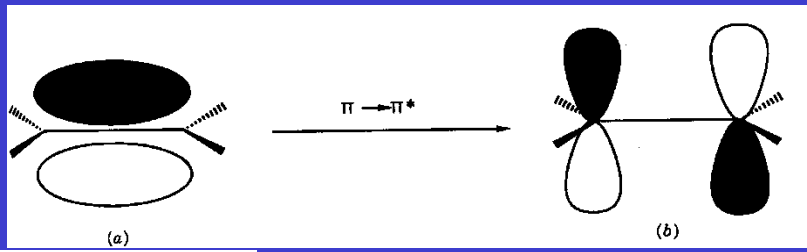
Abscissa (x) ~ $\Delta E \sim \tilde{\nu} \sim 1/\lambda$

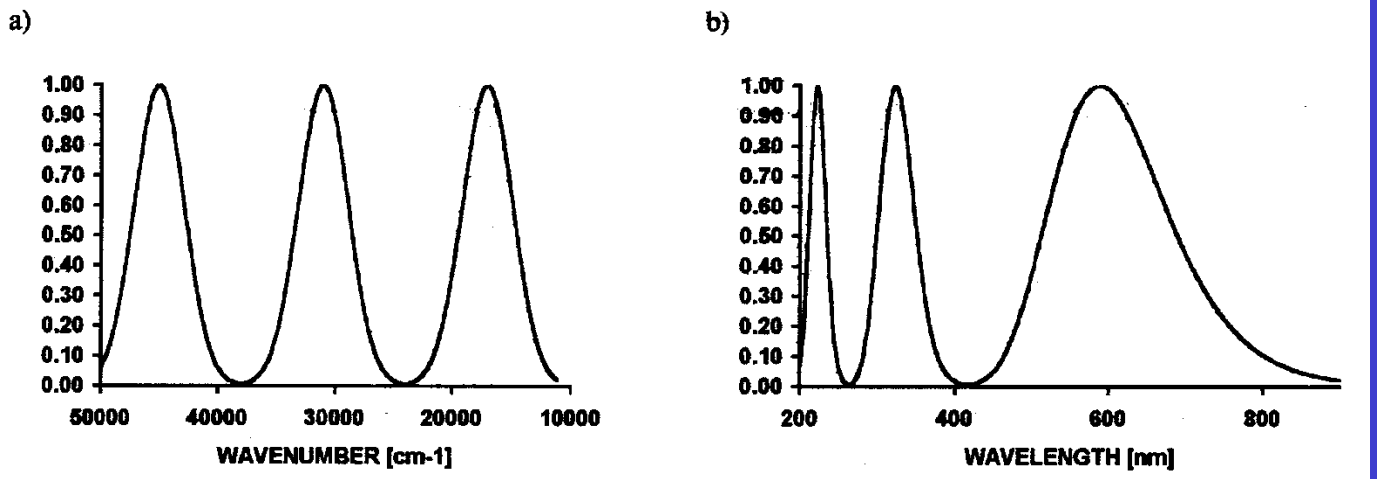
Ordinat (y) ~ intensity ~ probability of transition →

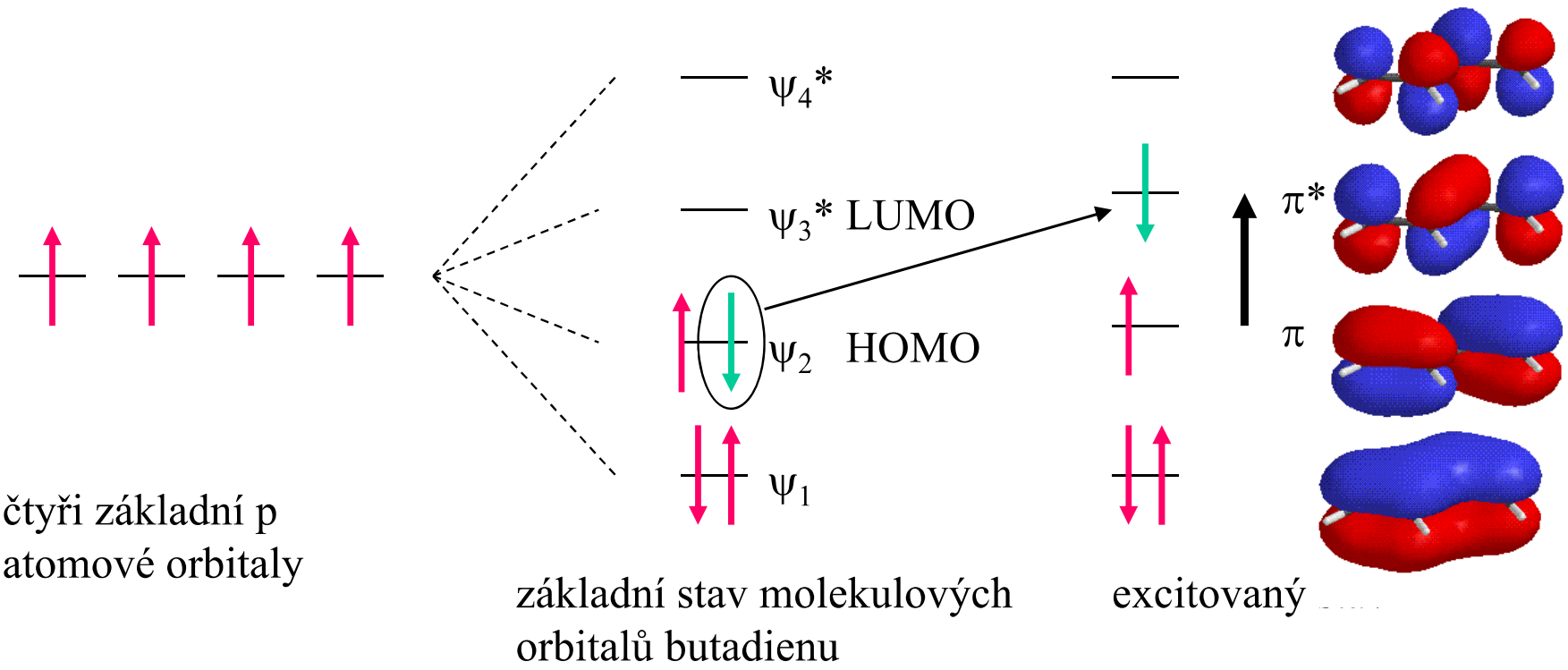
the oscillator strength

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

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





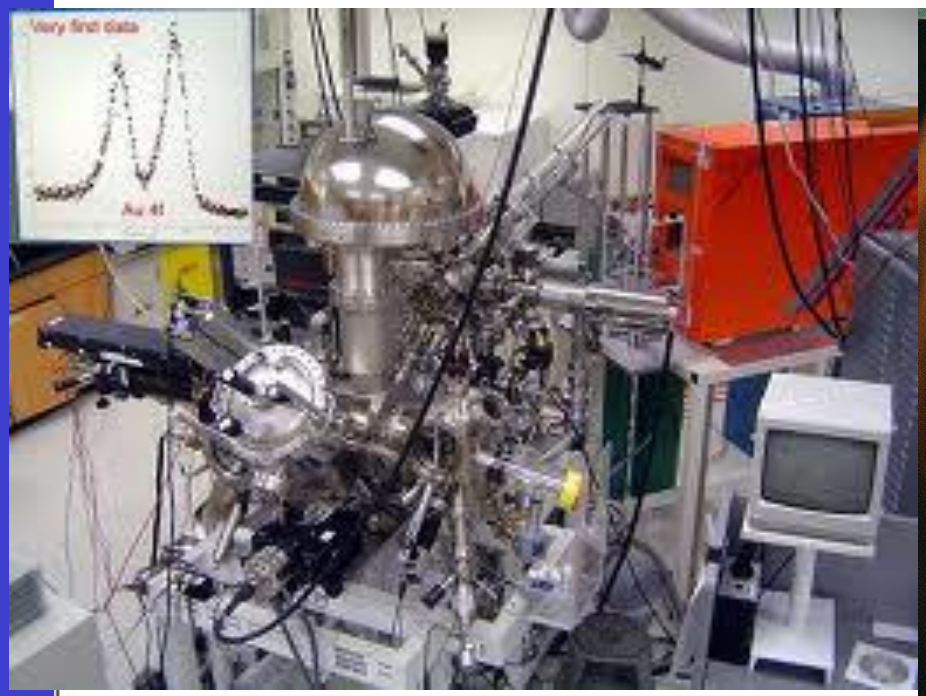


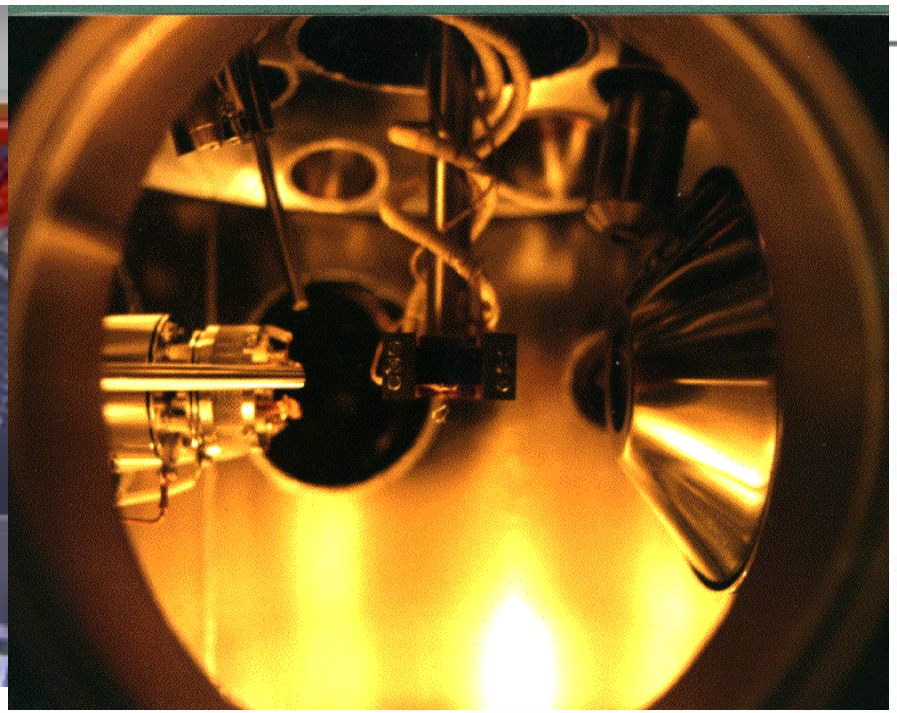
LUMO – Lowest Unoccupied Molecular Orbital (nejnižší neobsazený MO)
HOMO – Highest Occupied Molecular Orbital (nejvyšší obsazený MO)

- Překryvový integrál
- Dipólový moment

Hueckel molecular orbital method (HMO)

Elektronová spektroskopie





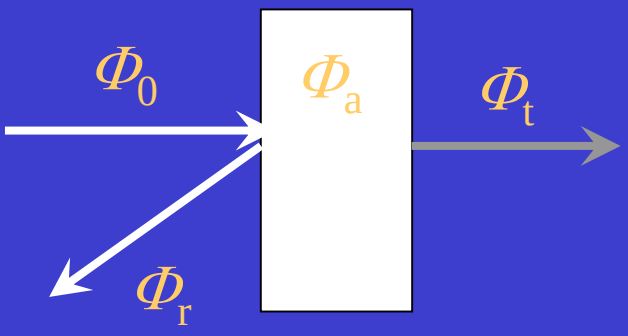
Beer – Lambert – Bouguer law

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

$\tau_i = \Phi_t/\Phi_0$ internal transmittance (transmission factor)

$\rho = \Phi_r/\Phi_0$ reflectance (reflection factor)

$\alpha = \Phi_a/\Phi_0 = 1 - \tau$ absorptance (absorption faktor)



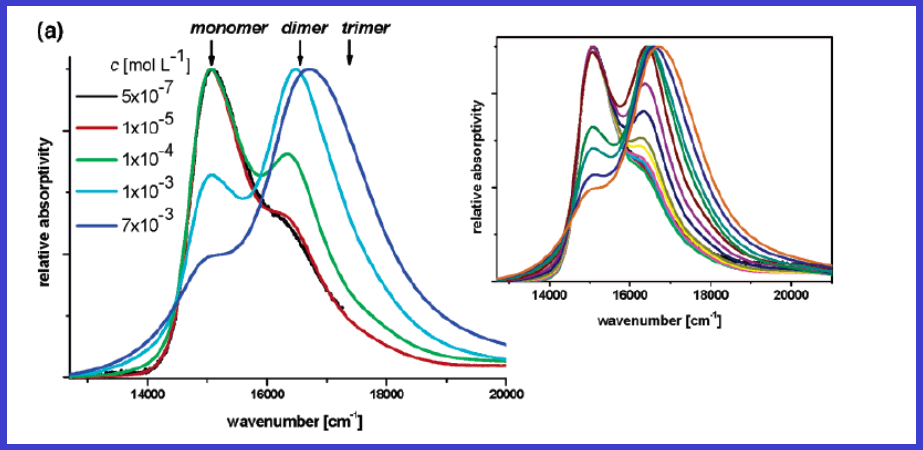
Term	Symbol	Unit
Monochromatic radiant power	Φ	W
(decadic) internal absorbance	A	1
Molar (decadic) absorption coefficient	ε	L mol^{-1} cm^{-1}
Absorption pathlength	b	cm^{-1}
Cell pathlength	l	cm^{-1}

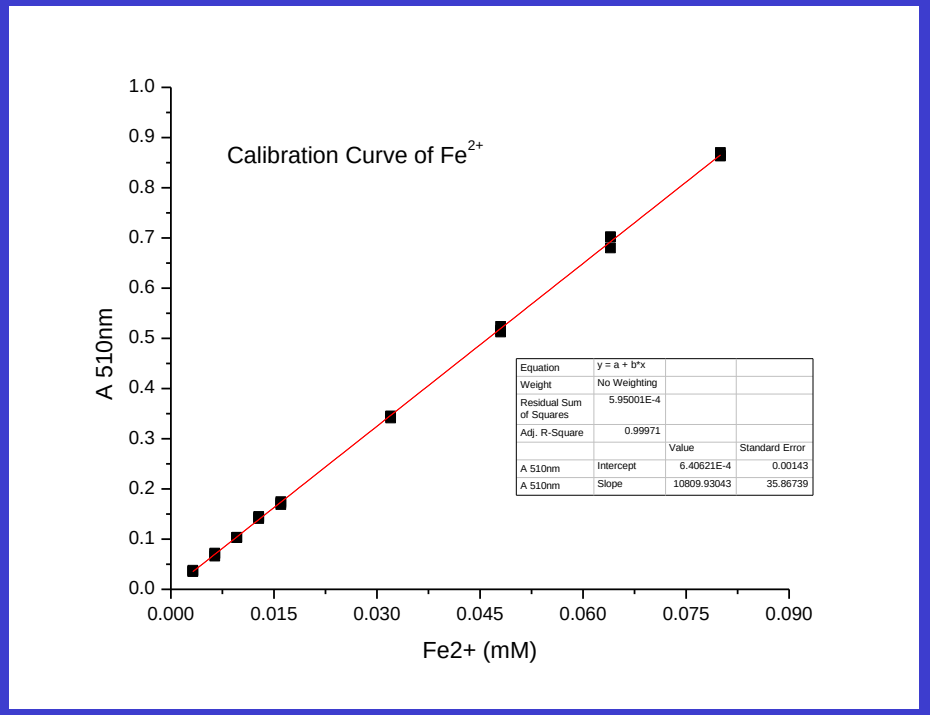
http://old.iupac.org/reports/V/spectro/partVII.pdf

Extinction – sum of absoption, scattering and luminescence.

Beer – Lambert – Bouguer law

$$A(\lambda) = \varepsilon(\lambda) c l$$





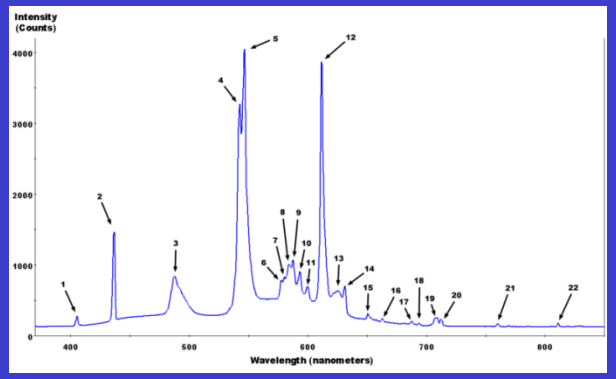
$$A(\lambda) = \sum_{i=1}^{n} A_i(\lambda) = l \sum_{i=1}^{n} \varepsilon_i(\lambda) c_i$$

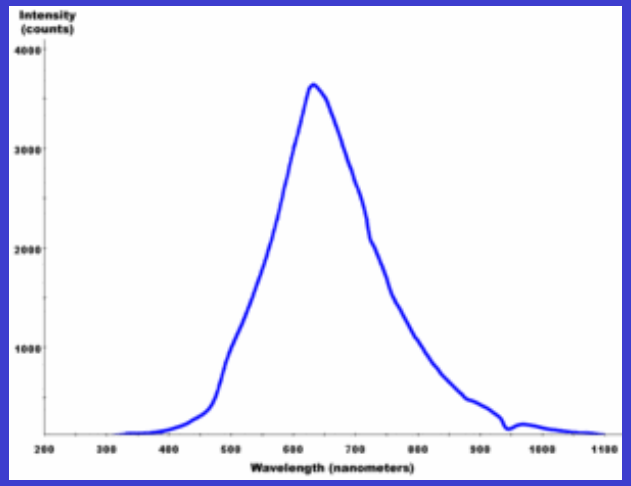
J. Phys. Chem. A, Vol. 109, No. 30, 2005

Beer – Lambert – Bouguer law limitations

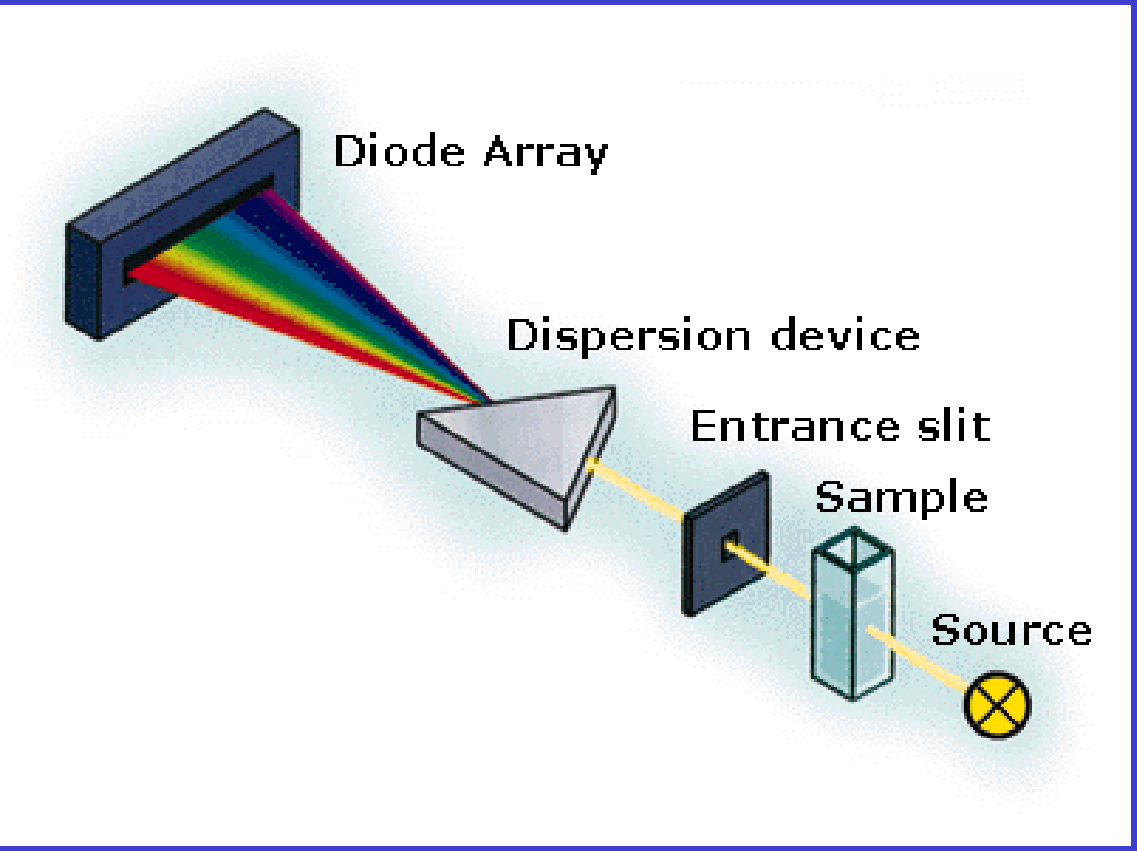
- Chemical reasons – chemical equilibria (acid-base reaction, self-association, complexation, thermal reaction, photochemical reaction, inhomogenous samples)
- Physical reasons – thermochromism, saturation effects – depletion of the ground state, incident radiation must be parallel

Jak funguje spektrometr?





Single beam UV – VIS spectrophotometer with diod array detector



Single beam UV – VIS spectrophotometer

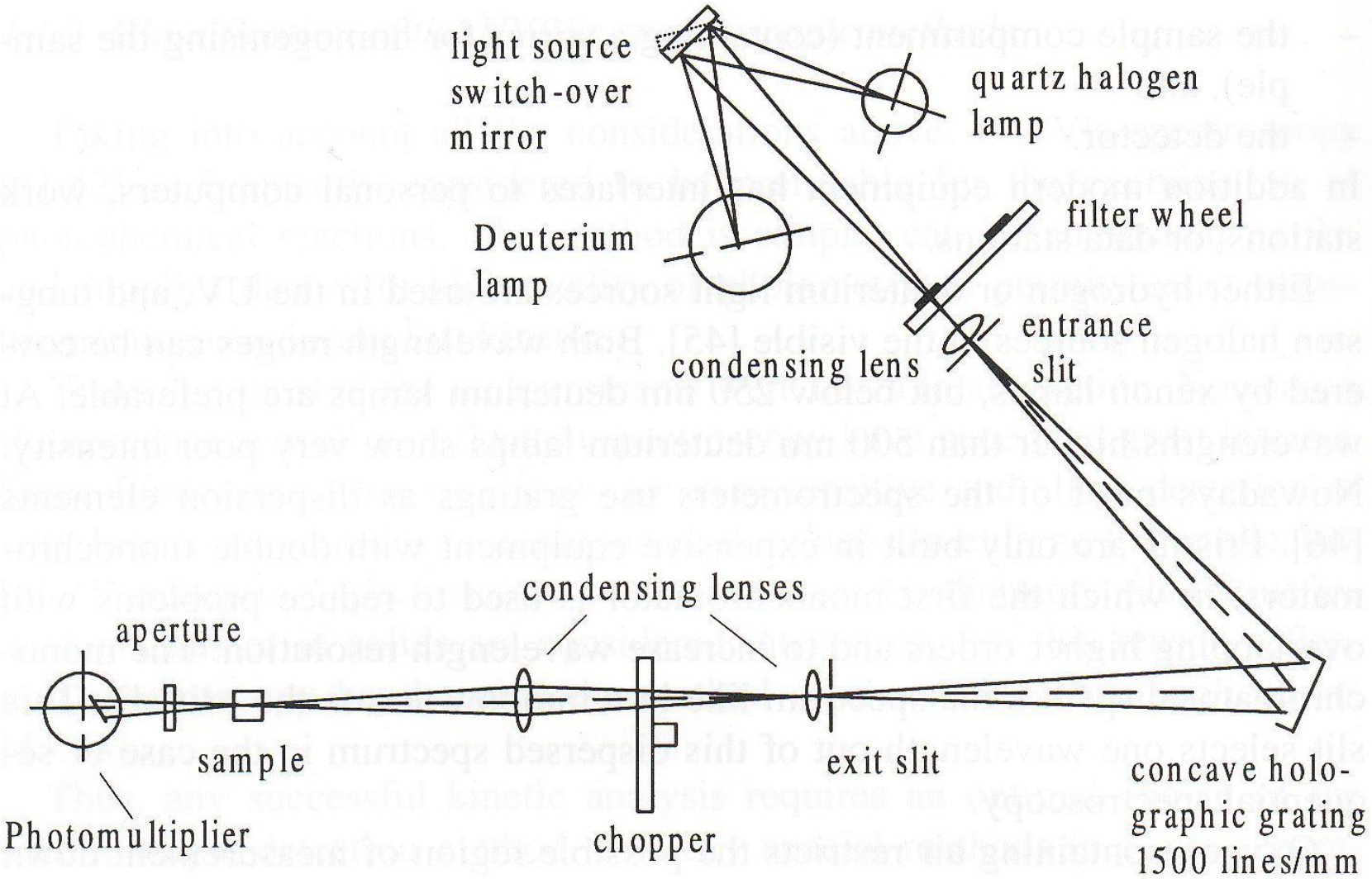


Fig. 4.1. Optical geometry of a single beam instrument, the Uvikon 710 by Kontron Instruments, Eching.

Double beam UV – VIS spectrophotometer

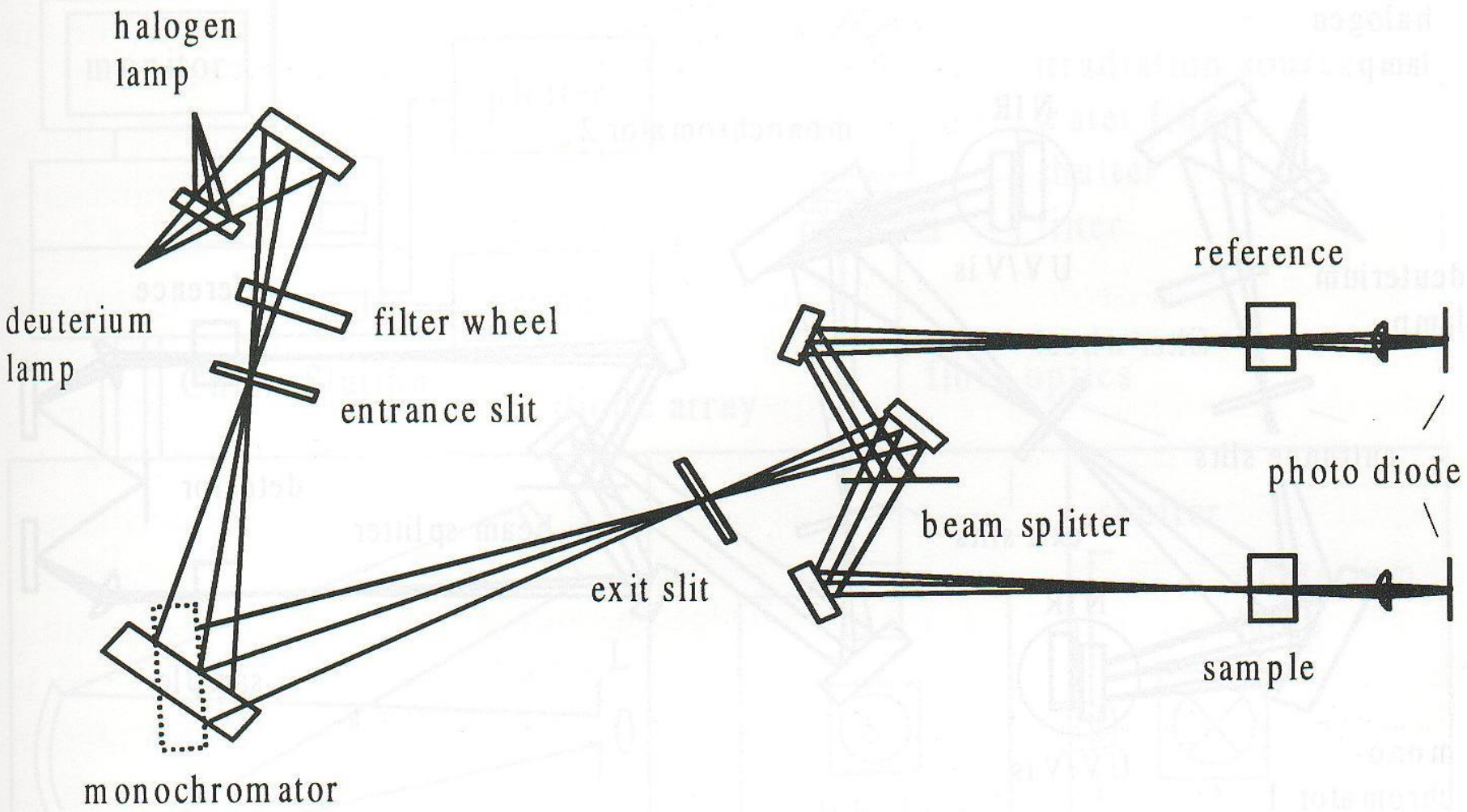


Fig. 4.2. Schematic diagram of the optical pathway in a double beam instrument Lambda 2, Perkin Elmer, Überlingen.

Double beam, double monochromators
UV – VIS spectrophotometer

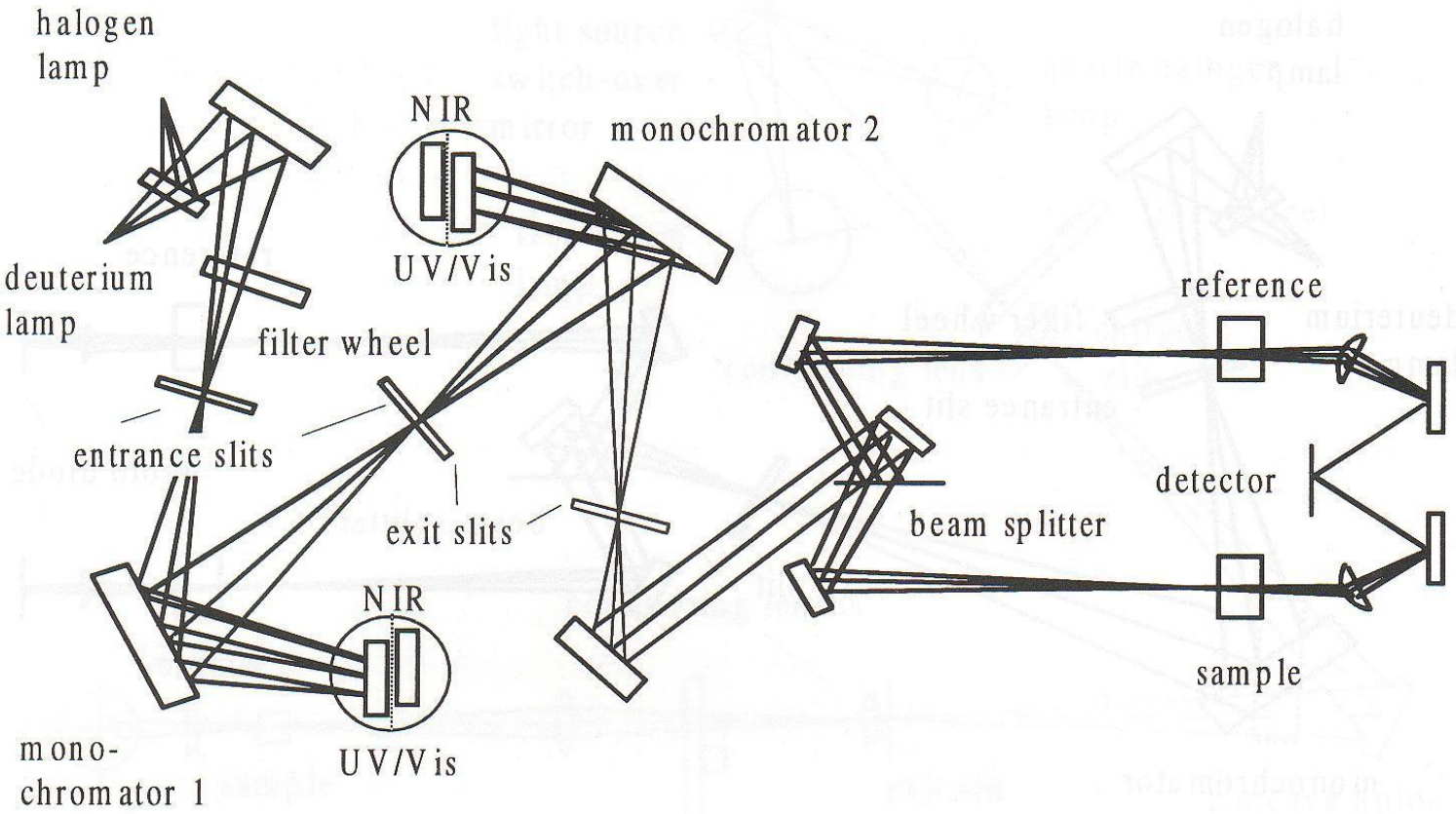


Fig. 4.3. Double beam set-up with a double monochromator for very precise photometric measurements and the possibility of taking high resolution spectra (Lambda 9, Perkin Elmer, Überlingen). This instrument covers the wavelength range from the UV until the near infrared (NIR).

UV – VIS spectrophotometer

Light source

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

Spectrometer

- Single beam × double beam
- Sequential × simultaneous

Detectors

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

Cuvettes

- shape
- volume
- material
- use of matched cells

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

Lamps

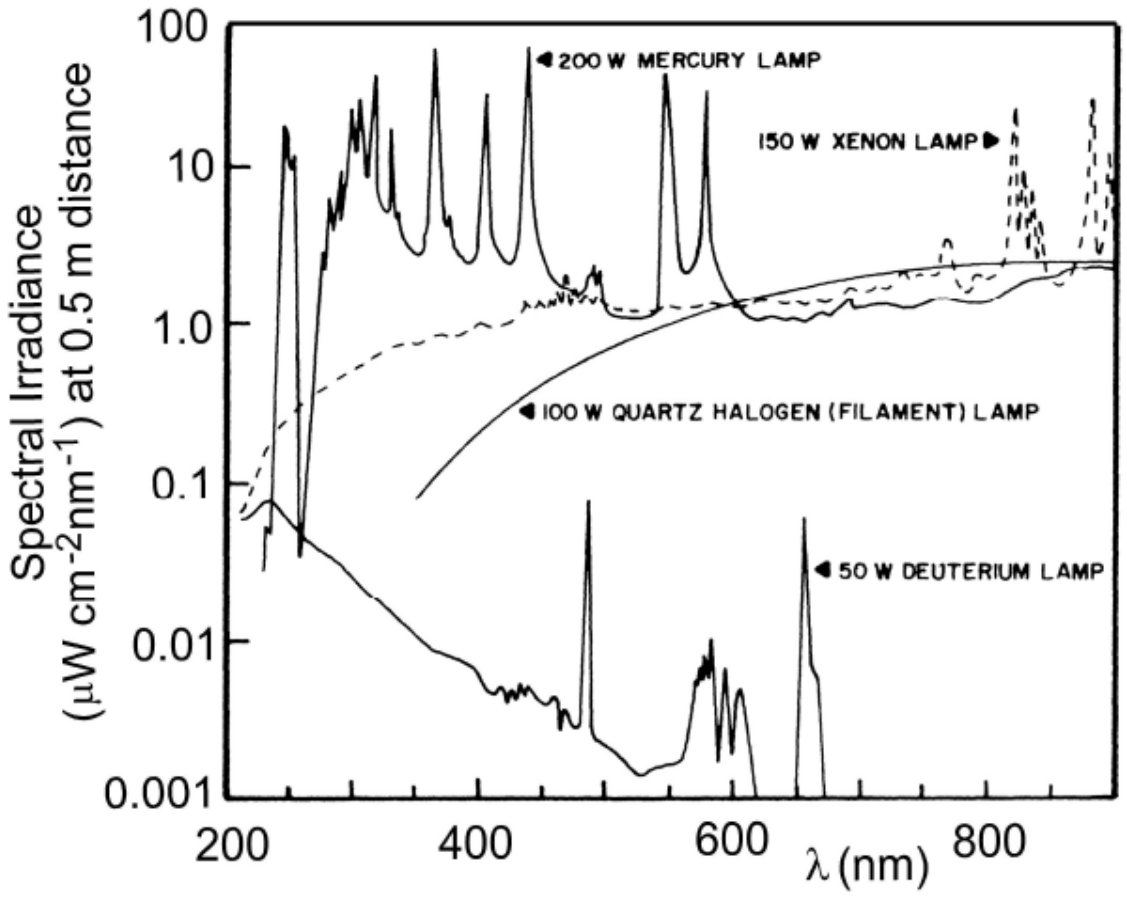
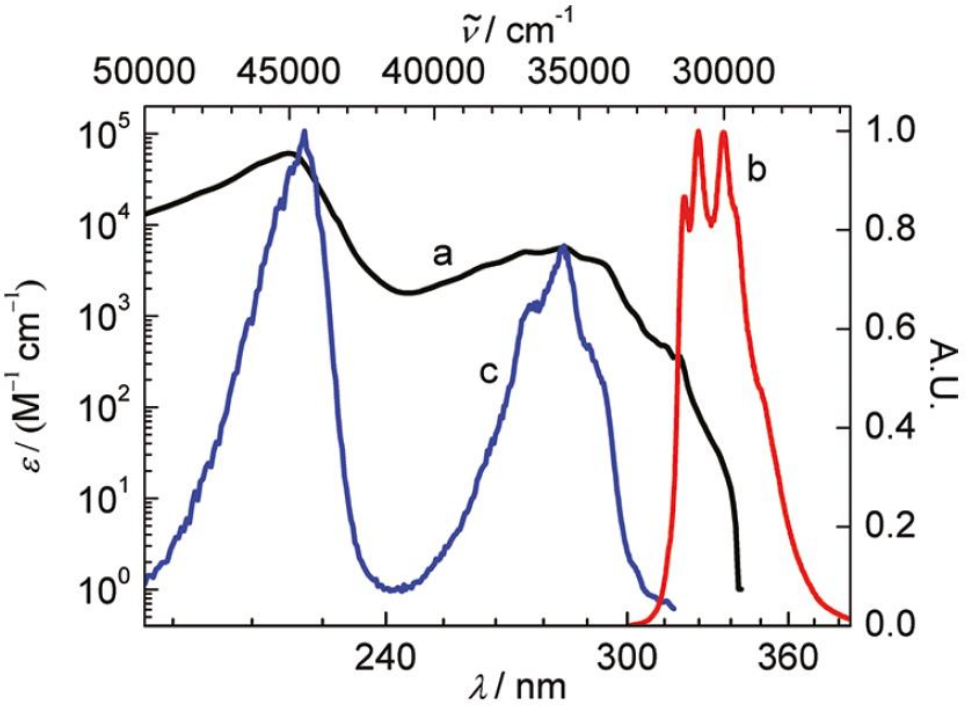


Fig. 11a-2. Spectral irradiance of some arc lamp sources. Reprinted by permission from LOT-Oriel catalogue.

Methyl-Naftalen



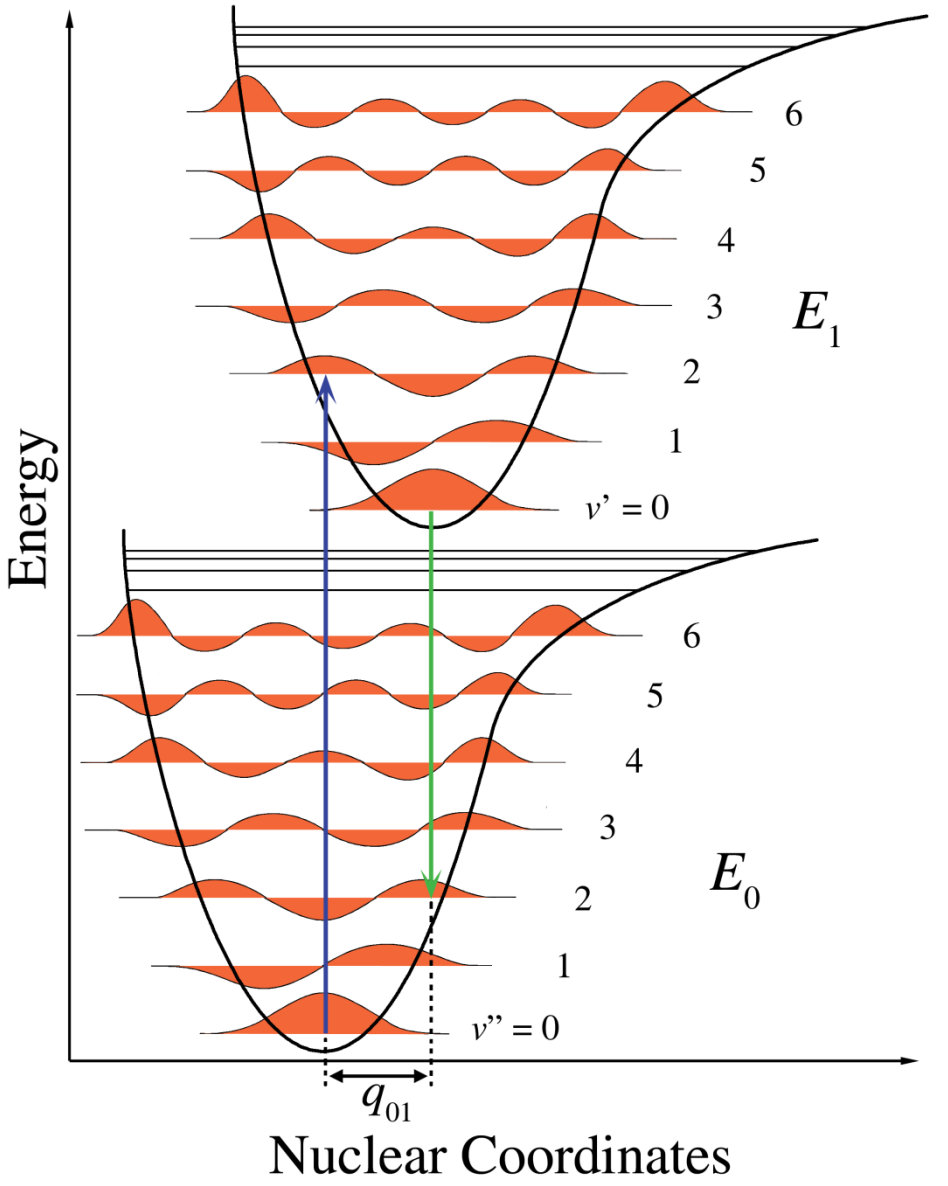
$$0.1 \leq A \leq 1.5$$

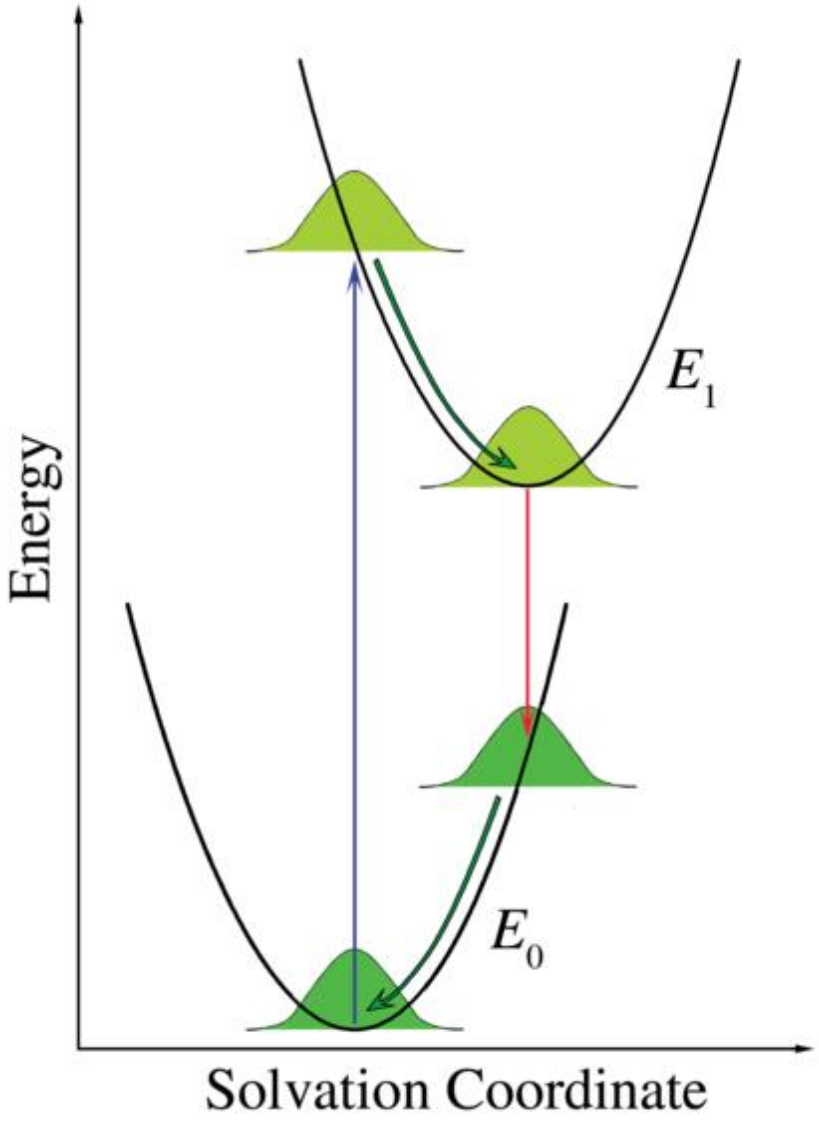
A	τ
0.001	0.998
0.010	0.977
0.046	0.900
0.100	0.794
0.430	0.370
0.500	0.316
1.000	0.100
1.500	0.032
2.000	0.010
3.000	0.001
4.0000	0.0001

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

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





Franck-Condon Principle

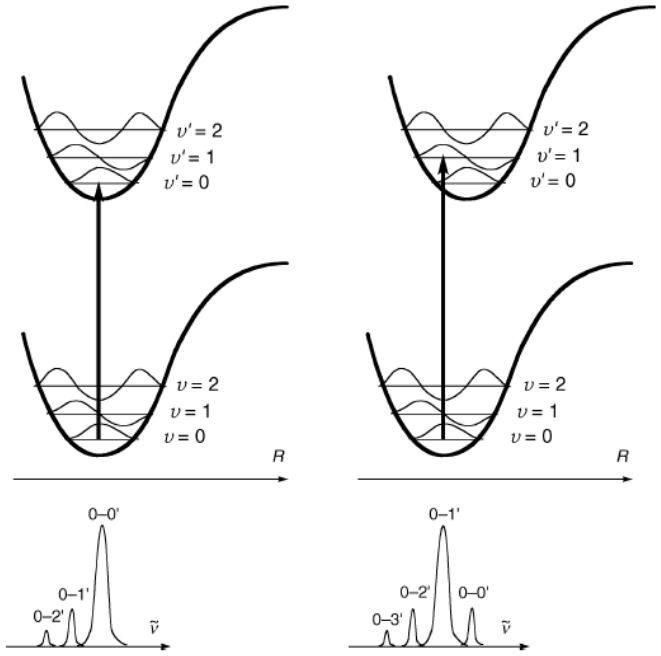
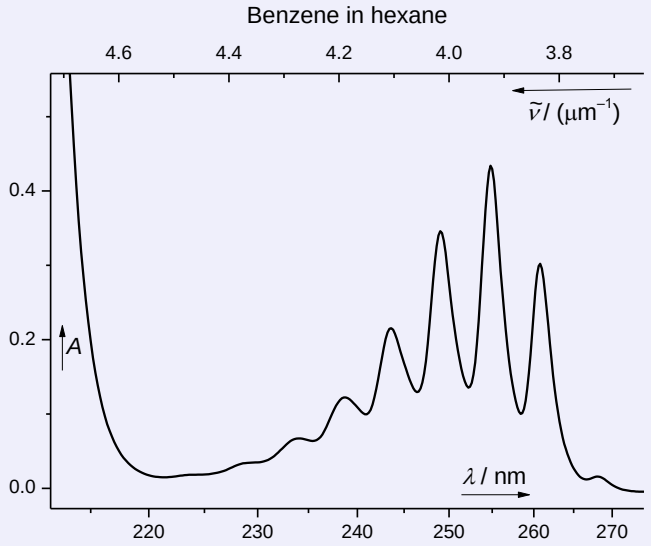
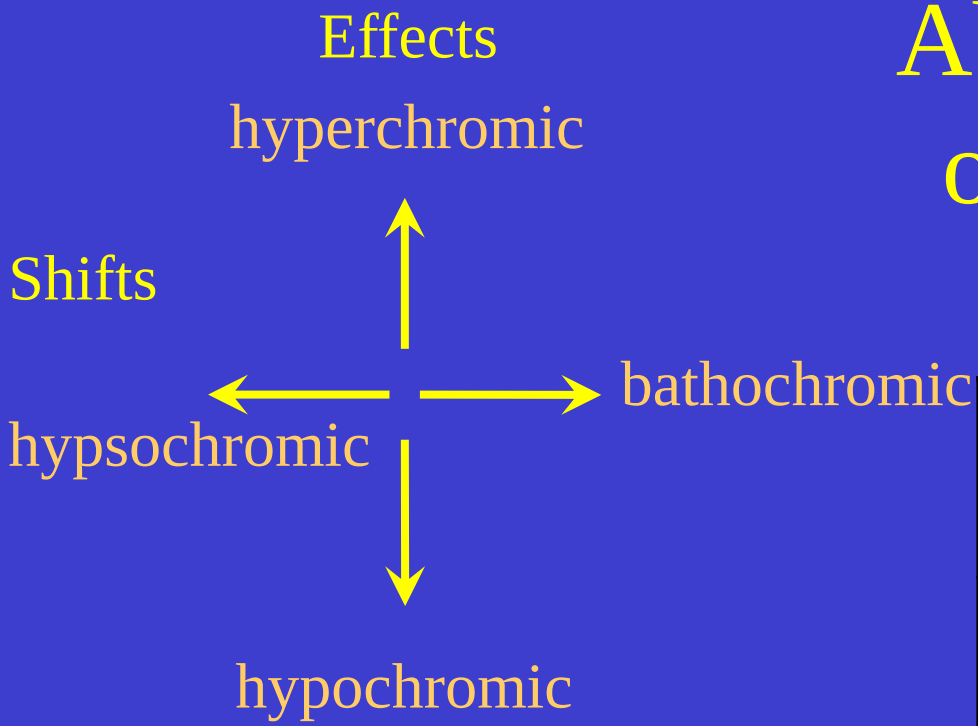


Figure 2.10 Illustration of the Franck–Condon principle. The bottom diagrams illustrate the vibrational structure of the absorption bands



0-0 band
Hot band

Absorption bands of organic molecules



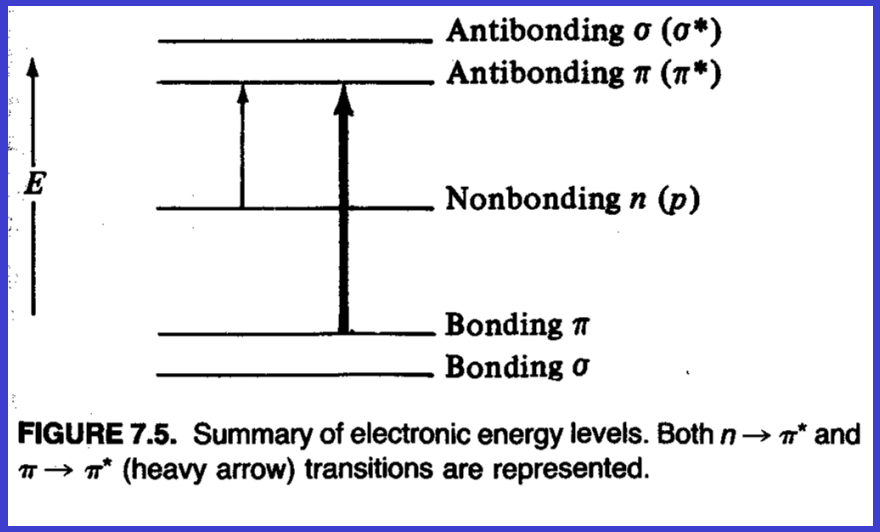


FIGURE 7.5. Summary of electronic energy levels. Both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (heavy arrow) transitions are represented.

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

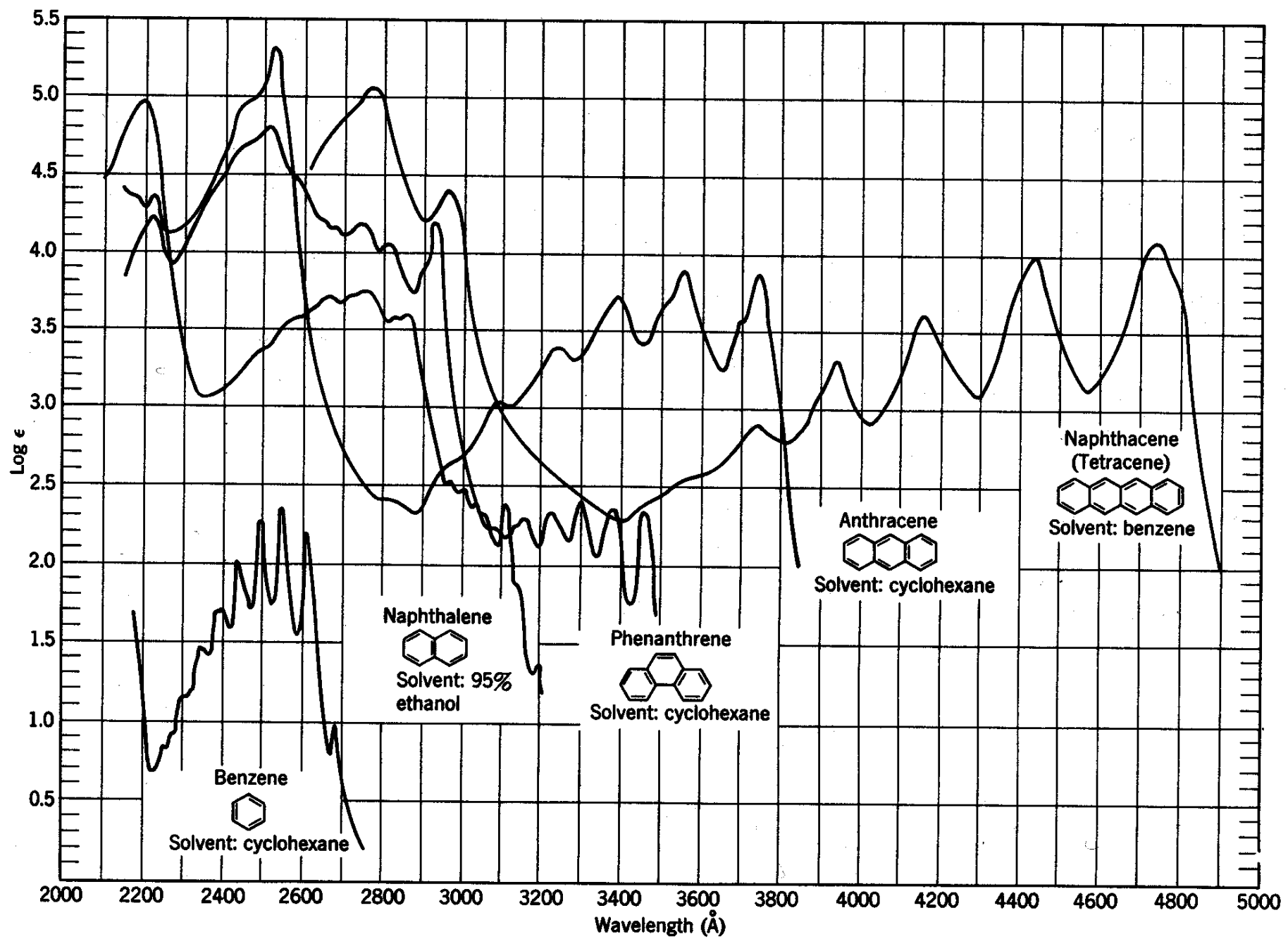

Log ε
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
4400
4600
4800
5000
Wavelength (Å)
Benzene
Solvent: cyclohexane
Naphthalene
Solvent: 95% ethanol
Phenanthrene
Solvent: cyclohexane
Anthracene
Solvent: cyclohexane
Naphthacene (Tetracene)
Solvent: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

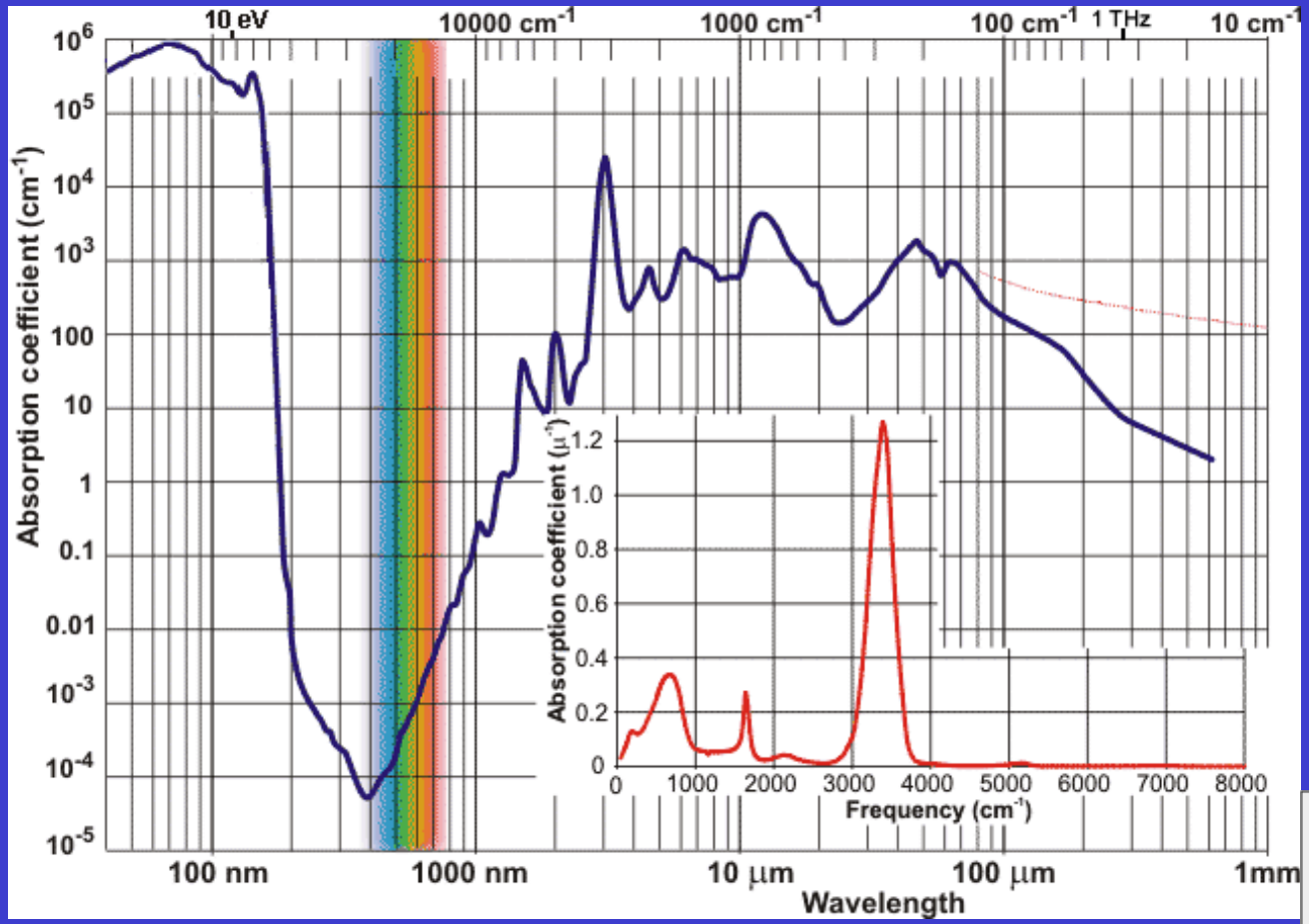
Table A-4. Ultraviolet "cut-off points"[a] of spectroquality solvents commonly used in UV/Vis-Spectroscopy, for 1 cm pathlengths (accuracy *ca.* ±5 nm)[b].

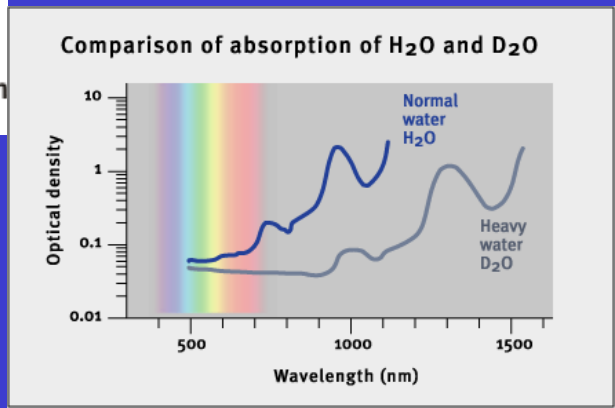
[a] The "cut-off point" in the ultraviolet region is the wavelength at which the absorbance approaches 1.0 using a 1-cm cell path with water as the reference. Solvents should not be used for measurements below the cut-off point, even though a compensating reference cell is employed. The cut-off points 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.

UV-VIS-NIR spekrum vody



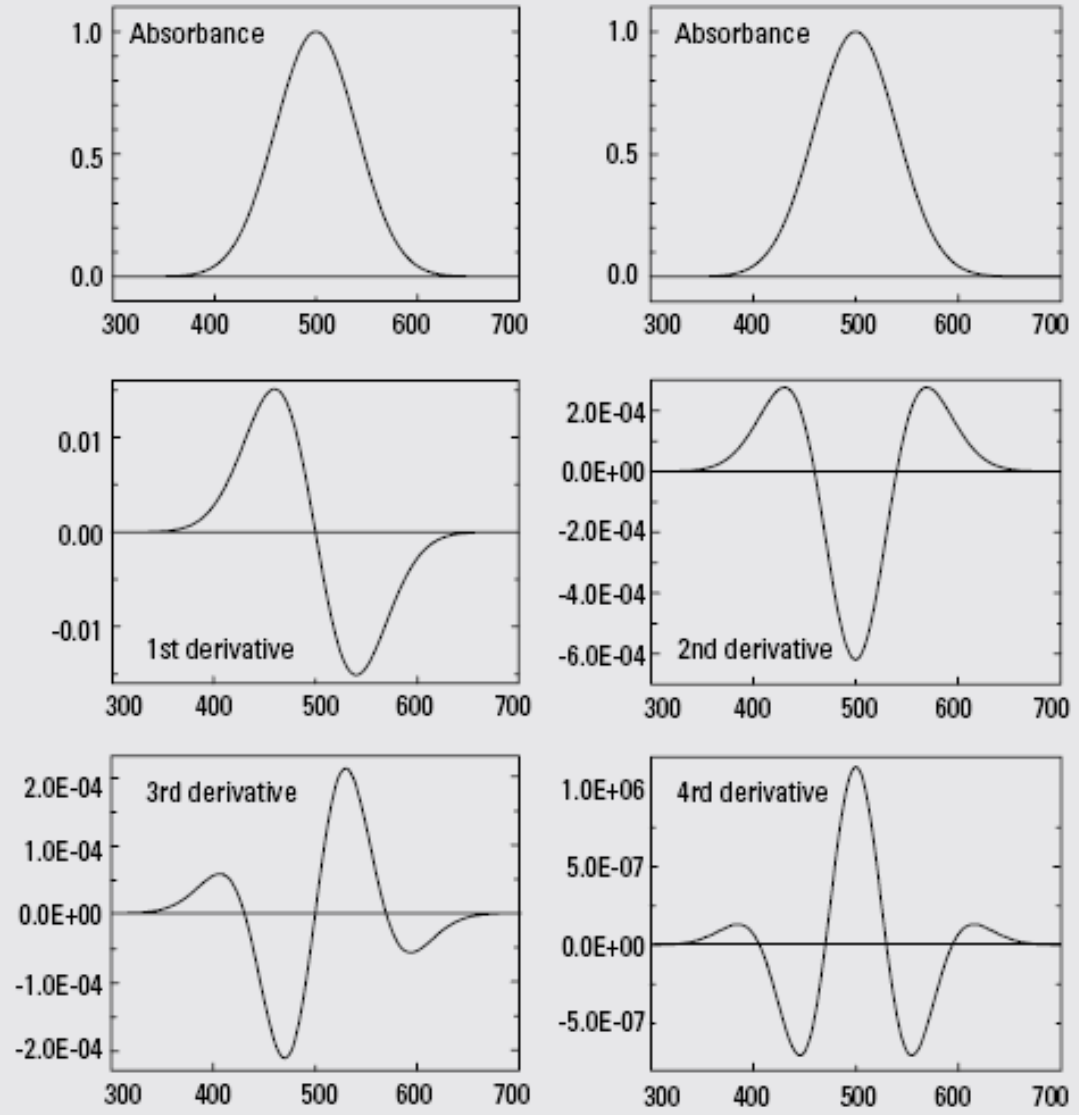


C8785_Photophysical_spectroscopic_methods

Measuring techniques

- Kvantitativní analýza
- Multicomponent analysis
- 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



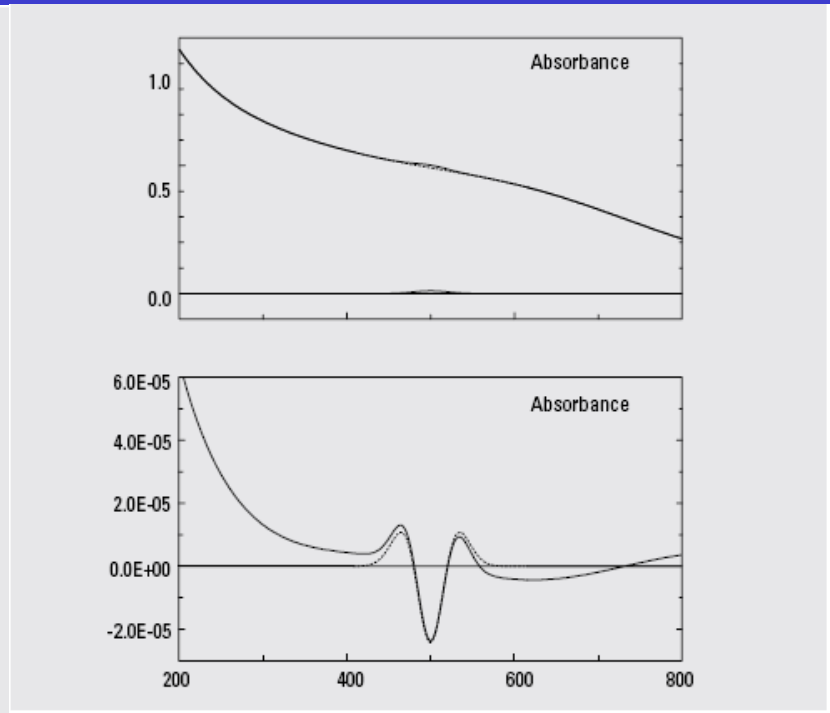


Figure 6
Matrix supression

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

Application of derivative spectroscopy to benzene

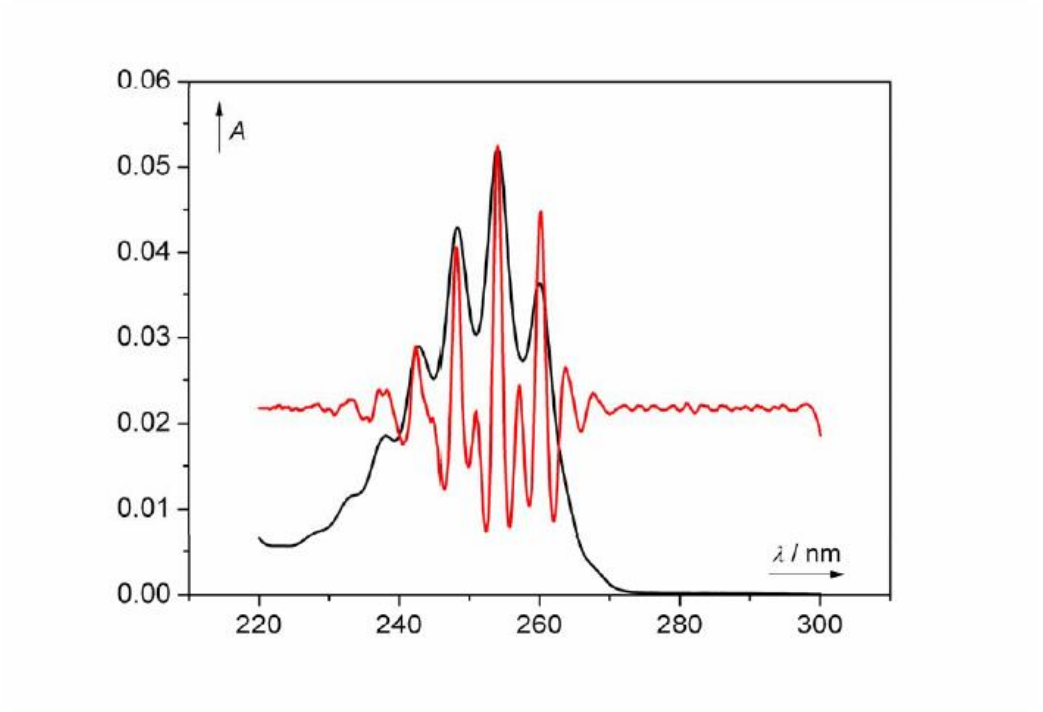
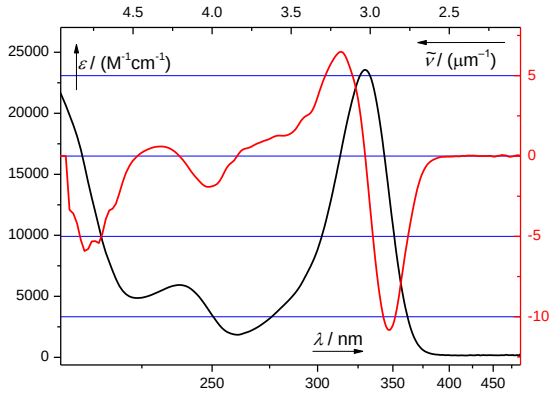


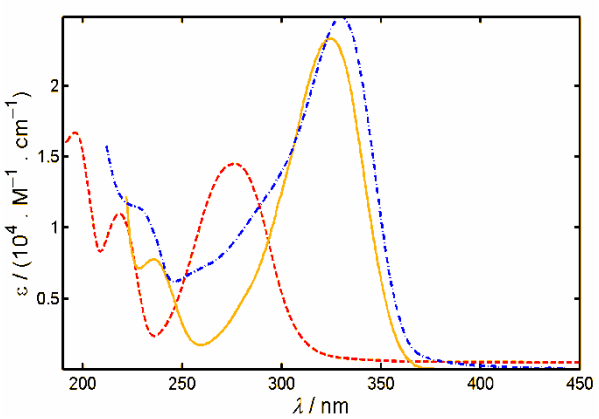
Figure S1. The absorption spectrum of benzene aq solution (black) with its 4th derivative (red).

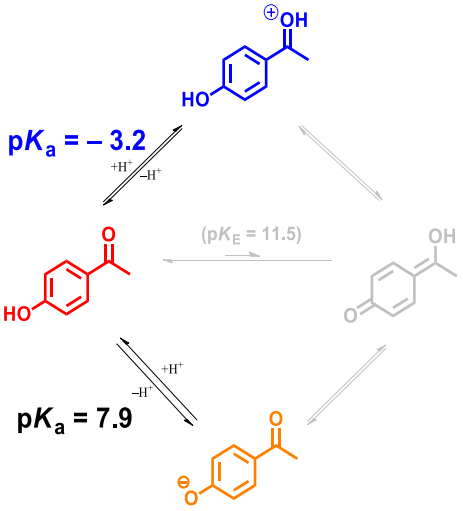
transition	band notation	λ_{max}^{abs}/nm (298 K)
6_1^0	B_0^0 (hot)	267.5
1_0^0	K_1 (0–0)	263.6
$6_0^1\ 1_0^0$	A_0^0	260.1
1_0^1	K_2	257.0
$6_0^1\ 1_0^1$	A_1^0	253.9
1_0^2	K_3	250.9
$6_0^1\ 1_0^2$	A_2^0	248.0
1_0^3	K_4	245.0
$6_0^1\ 1_0^3$	A_3^0	242.5
1_0^4	K_5	238.4
$6_0^1\ 1_0^4$	A_4^0	237.2
1_0^5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

Derivative spectroscopy

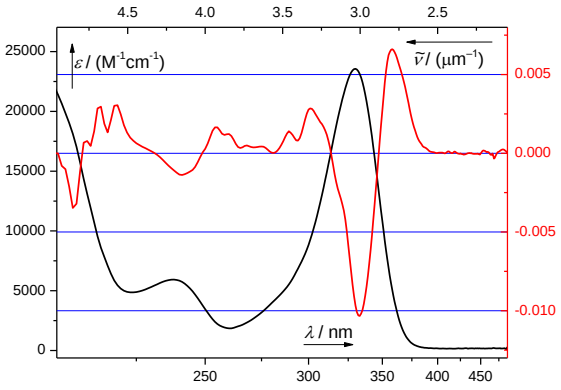
1st derivative



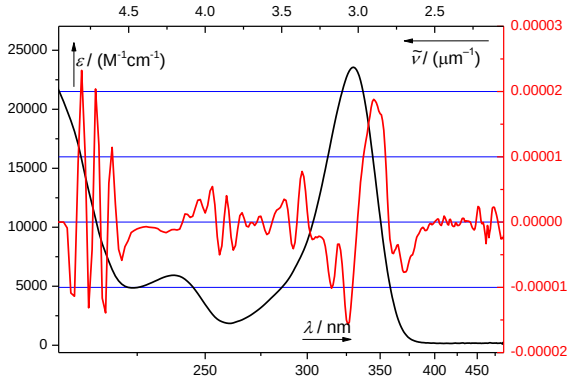




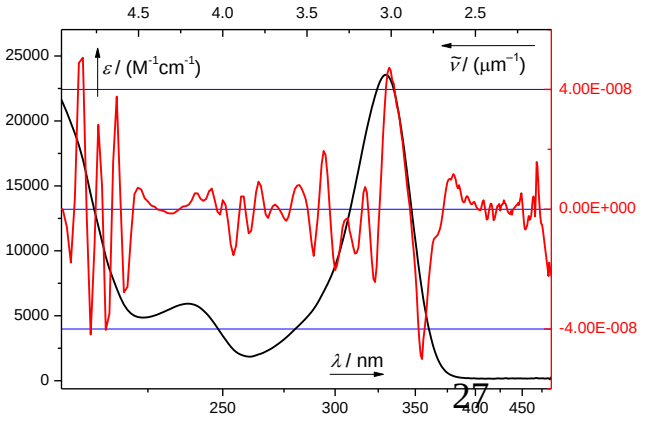
2nd derivative



3th derivative



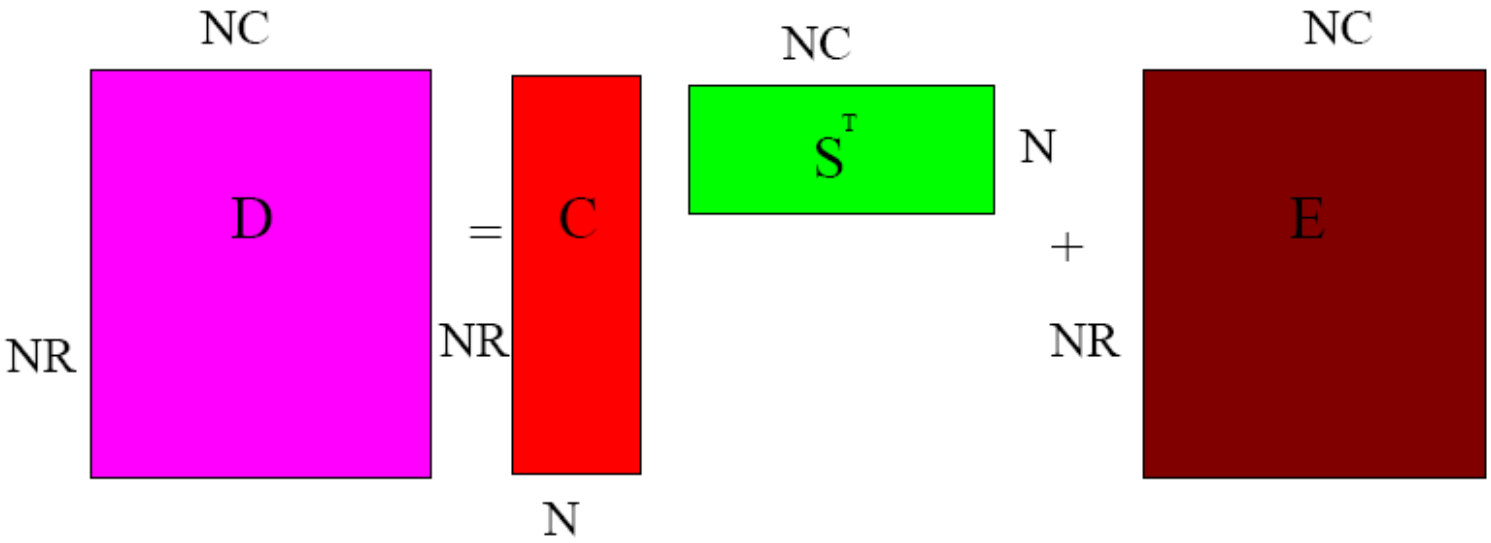
4th derivative



Multivariate Curve Resolution (MCR)

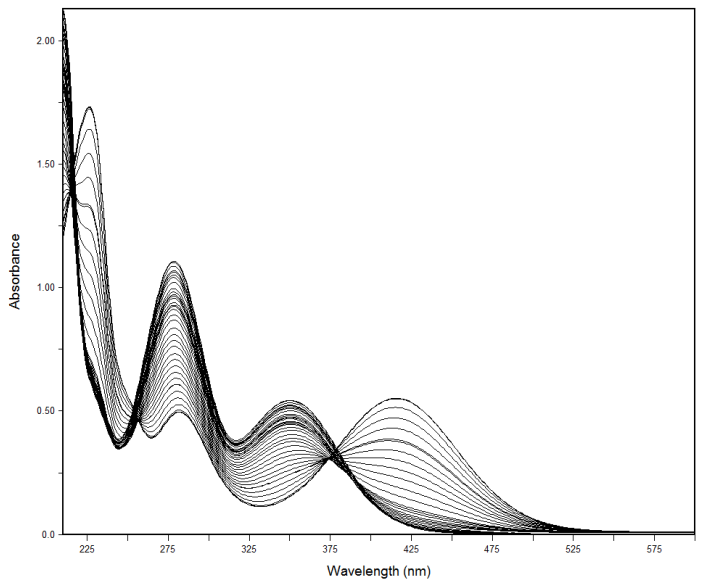
$$d_{ij} = \sum_{k=1}^{N} c_{ik} s_{kj} + e_{ij}$$

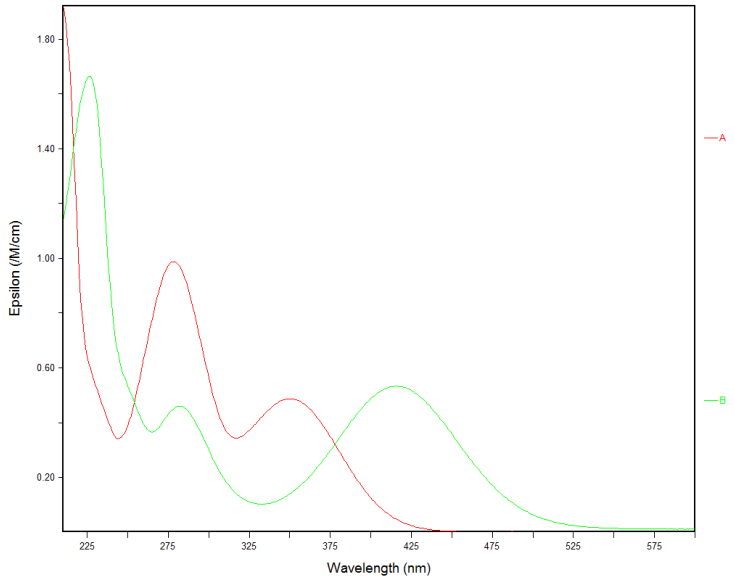
Bilinearity!



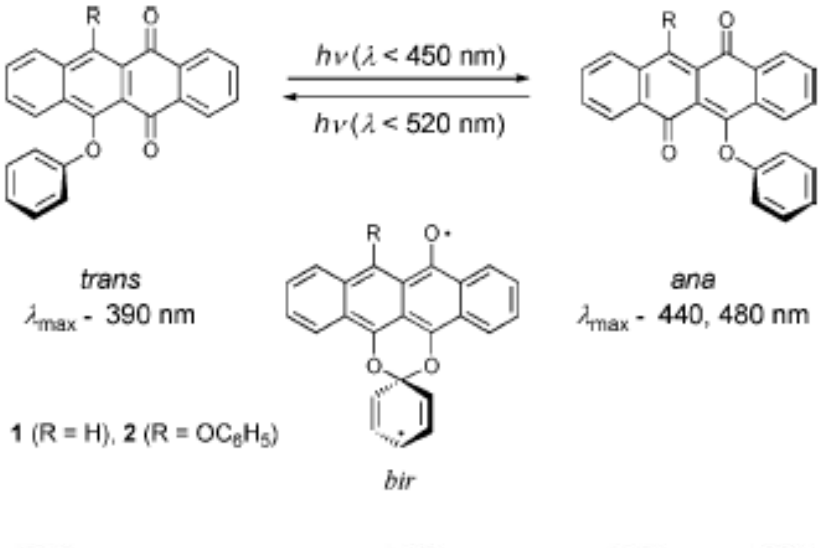
D(NR,NC) experimental data matrix
C(NR,N) row (concentration) profiles matrix
S(NC,N) column (spectra) profiles matrix
E(NR,NC) residual (noise, error) matrix

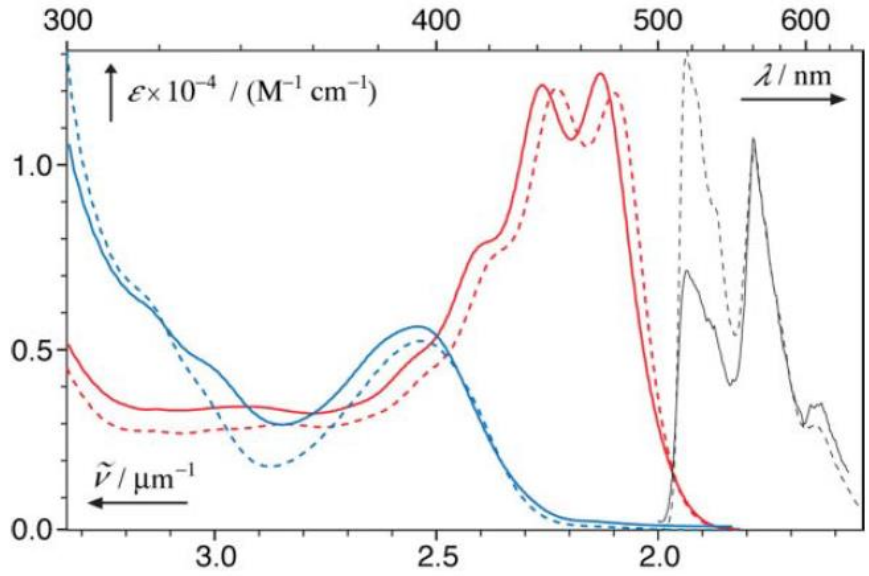
pH titration – *o*-nitrophenol



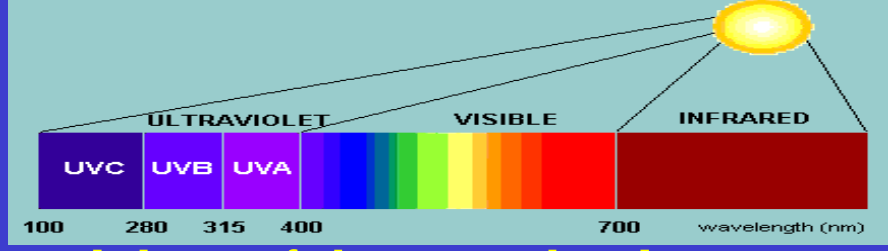


Photochromism





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



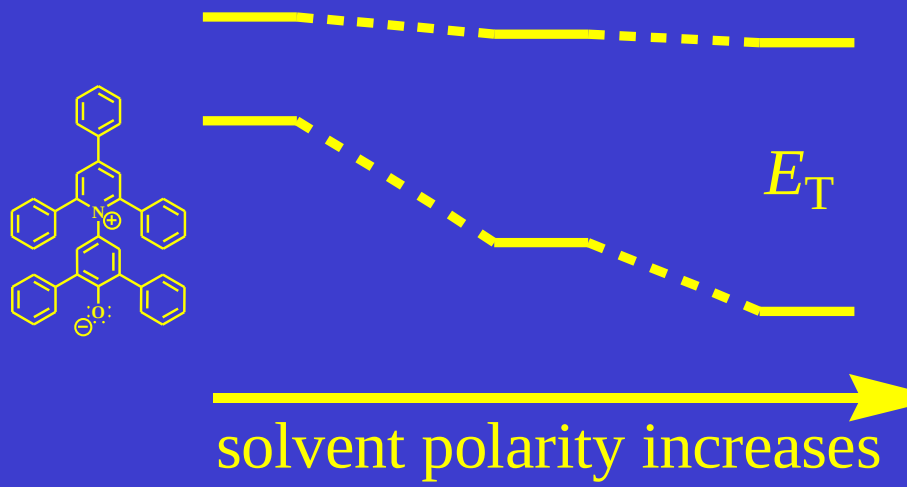
solvatochromism

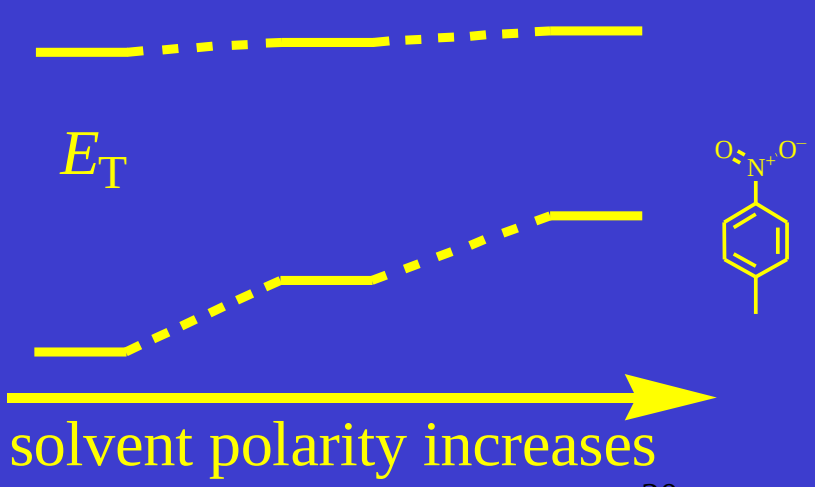
change in the position, intensity, and shape of absorption bands due to the surrounding medium

= perichromism (peri - around)

surrounding medium - liquids, solids, glasses, and surfaces

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



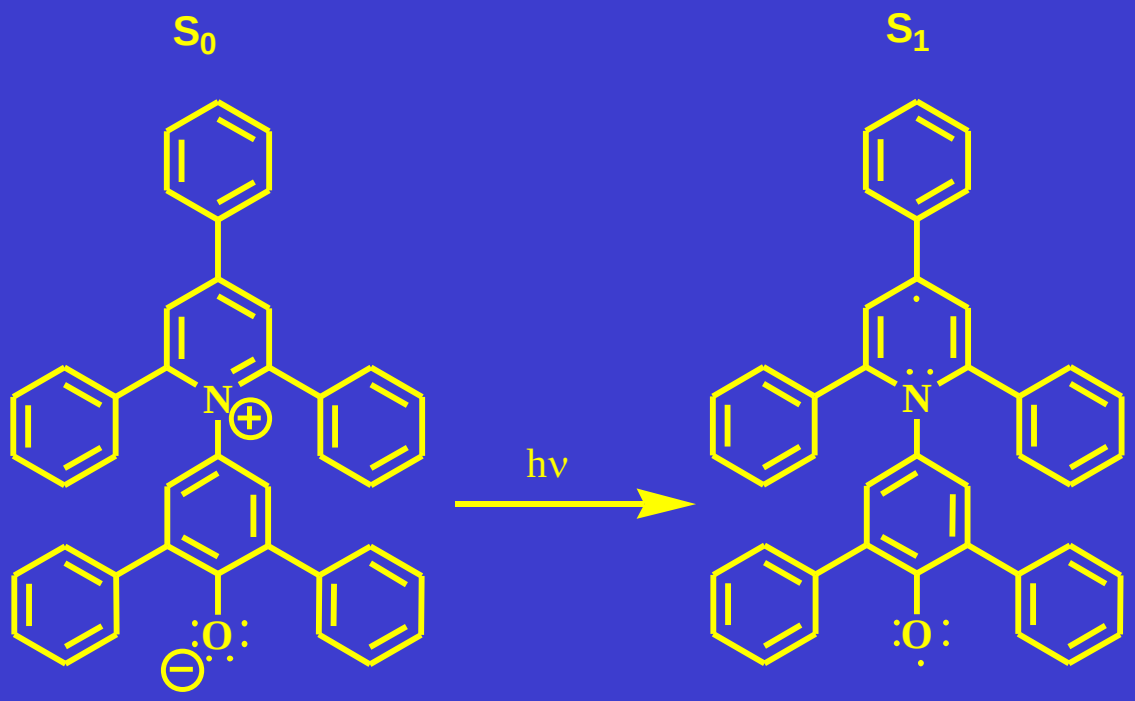


Reichardt's dye

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

Literature

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  - http://webbook.nist.gov/chemistry/name-ser.html
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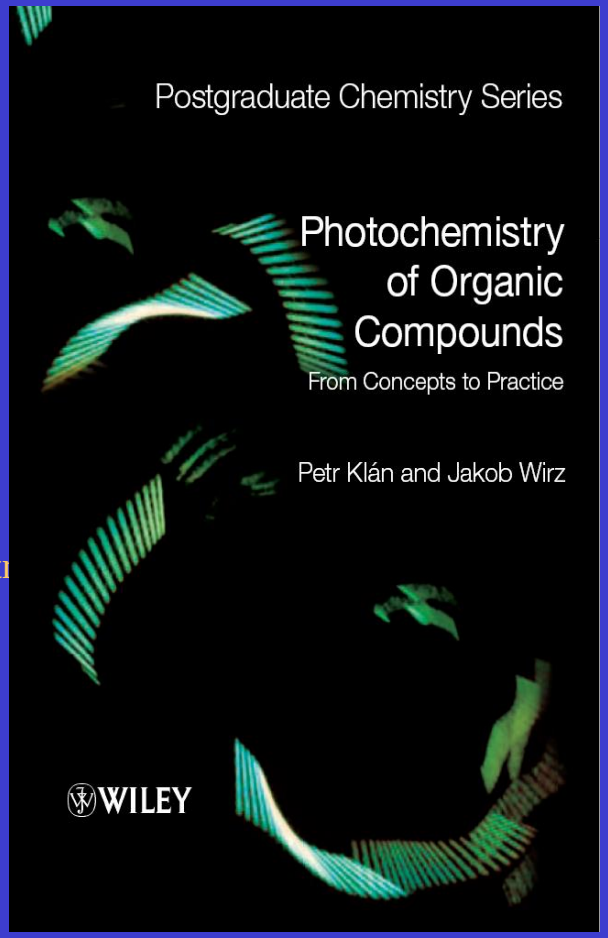


Diffuse Reflectance Spectroscopy

Diffuse (volume) reflection – phenomenon resulting from the reflection, refraction, diffraction and absorption

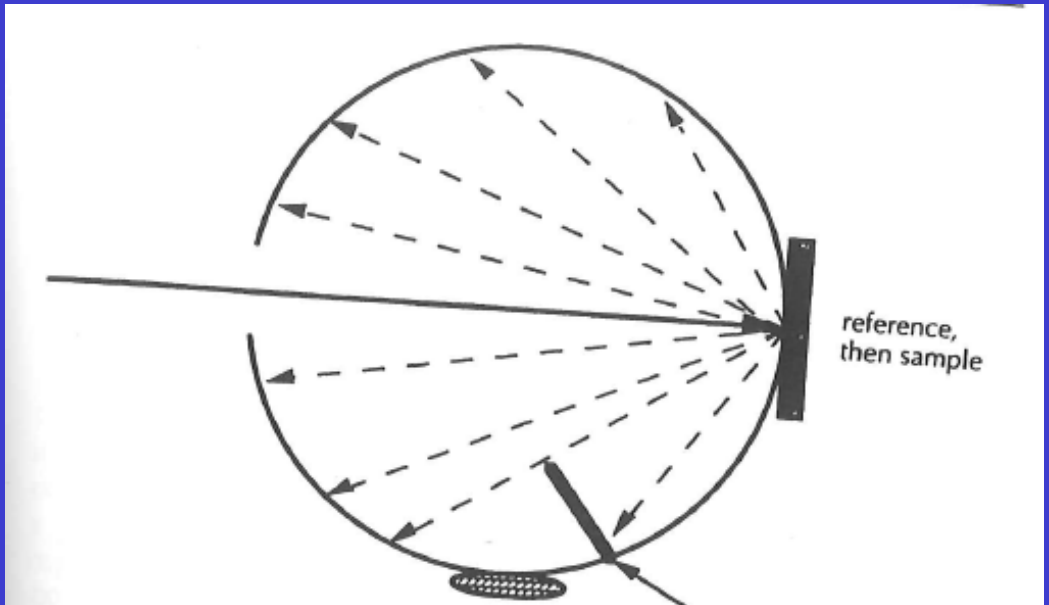


Fig. 5.5 Integrating sphere used to obtain a diffuse reflectance spectrum by the substitution method. Reprinted with permission from [16].

MgO
$BaSO_4$
PTFE – polytetrafluoroethylene = halon = Spectralon

Diffuse Reflectance Spectroscopy

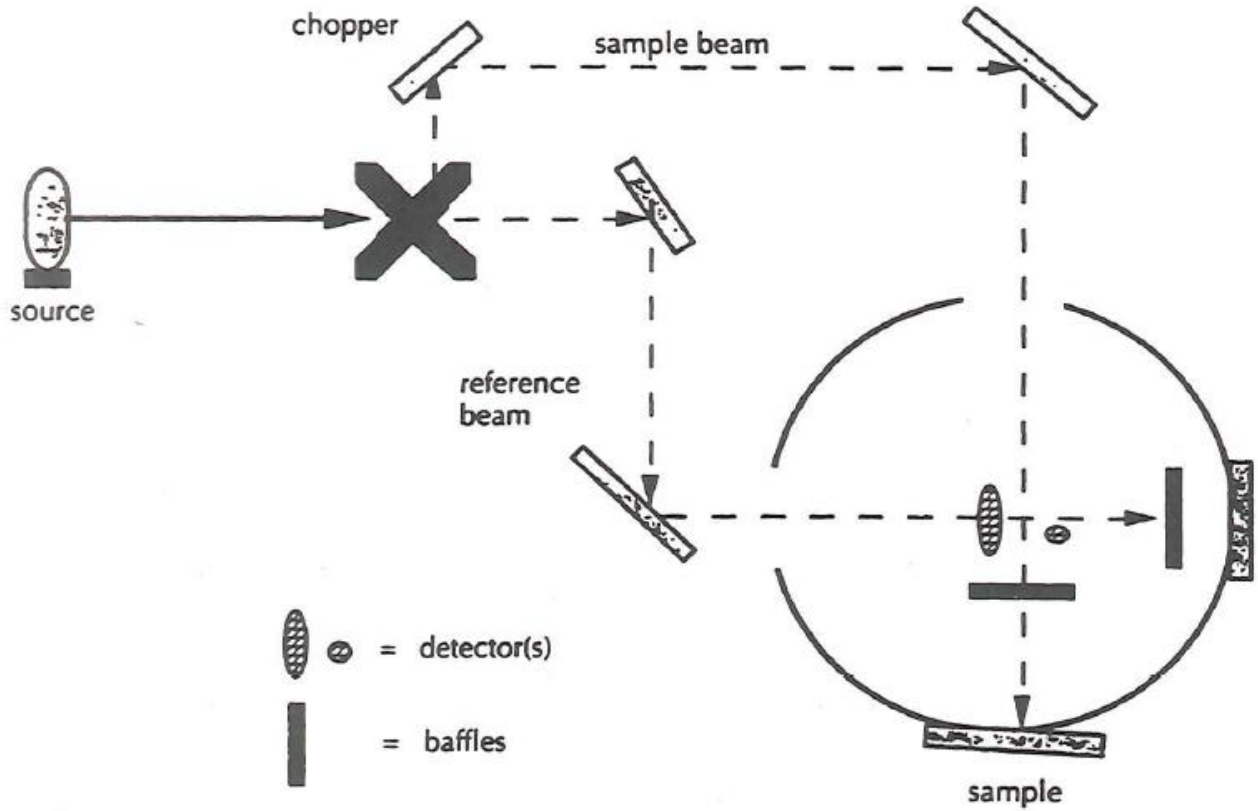


Fig. 5.7 Interesting sphere for a double-beam spectrophotometer. Reprinted with permission from [16].

Diffuse Reflectance Spectroscopy

TABLE 5.1 Comparison of Absorbance and Kubelka-Munk Units at Various % Reflectance Values

% Reflectance	Apparent Aborbance (log $1/R_\infty$)	Kubelka-Munk Units $[(1 - R_\infty)^2/2R_\infty]$
100	0	0
90	0.046	0.0056
80	0.097	0.025
70	0.15	0.064
60	0.22	0.13
50	0.30	0 25
40	0.40	0.45
30	0 52	0.82
20	0.70	1.6
10	1.0	4.0
1	2.0	49

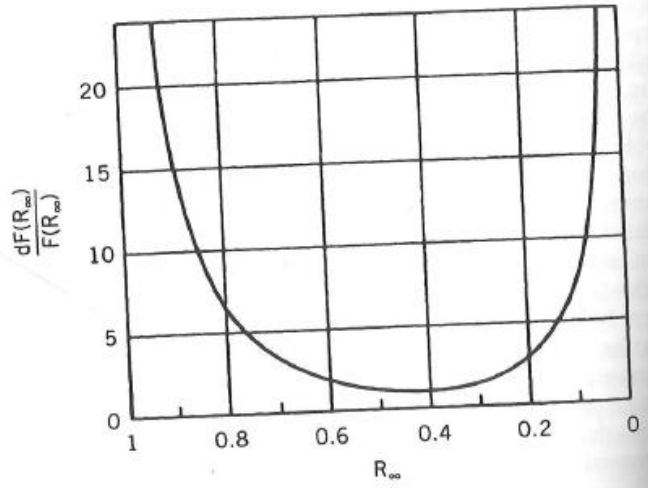
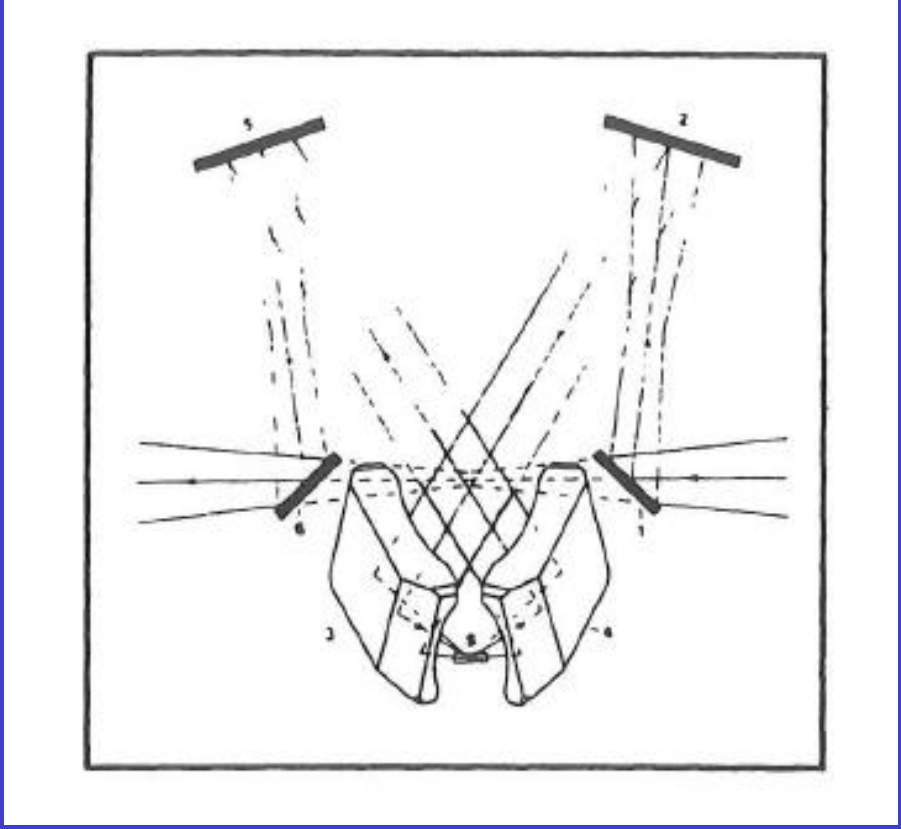


Fig. 5.3 Inherent error in the Kubelka-Munk function versus R_∞.

Diffuse Reflectance Spectroscopy



Harrick - Praying Mantis