Aspecte teoretice si experimentale privind cuantele si cuantificarea

Propagarea luminii: *Unda electromagnetica descrisa de ecuatiile Maxwell*

- ***interferenta;***
- ***difractia.***

Emisia si absorbtia luminii: *Lumina se comporta ca un corpuscul*

- ***radiatia termica de echilibru;***
- ***efect fotoelectric;***
- ***efect Compton.***

Relațiile Einstein-Planck

$$\varepsilon = h\nu = \frac{h}{2\pi}2\pi\nu = \hbar\omega$$

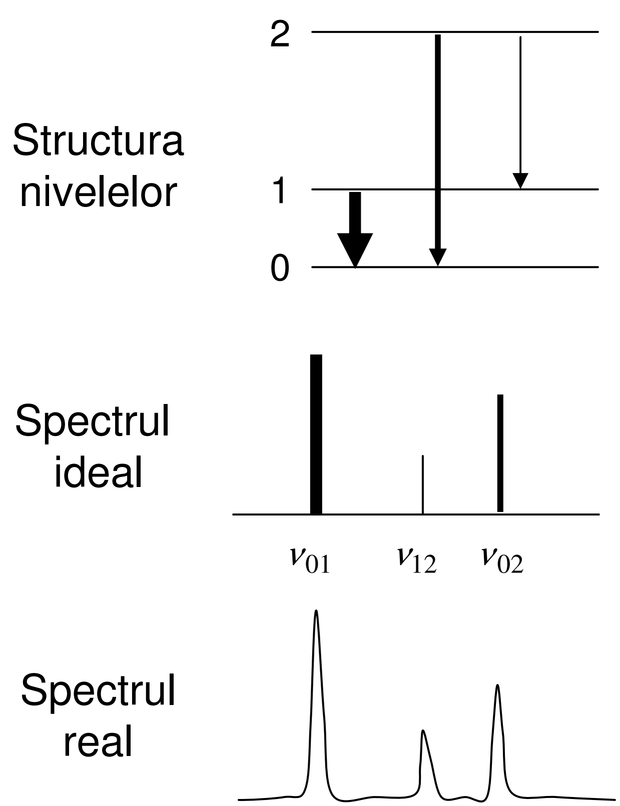
$$p = \frac{\varepsilon}{c} = \frac{h\nu}{c} = \frac{h}{2\pi}\frac{2\pi\nu}{c} = \hbar k$$

Cuantificarea sistemelor energetice:

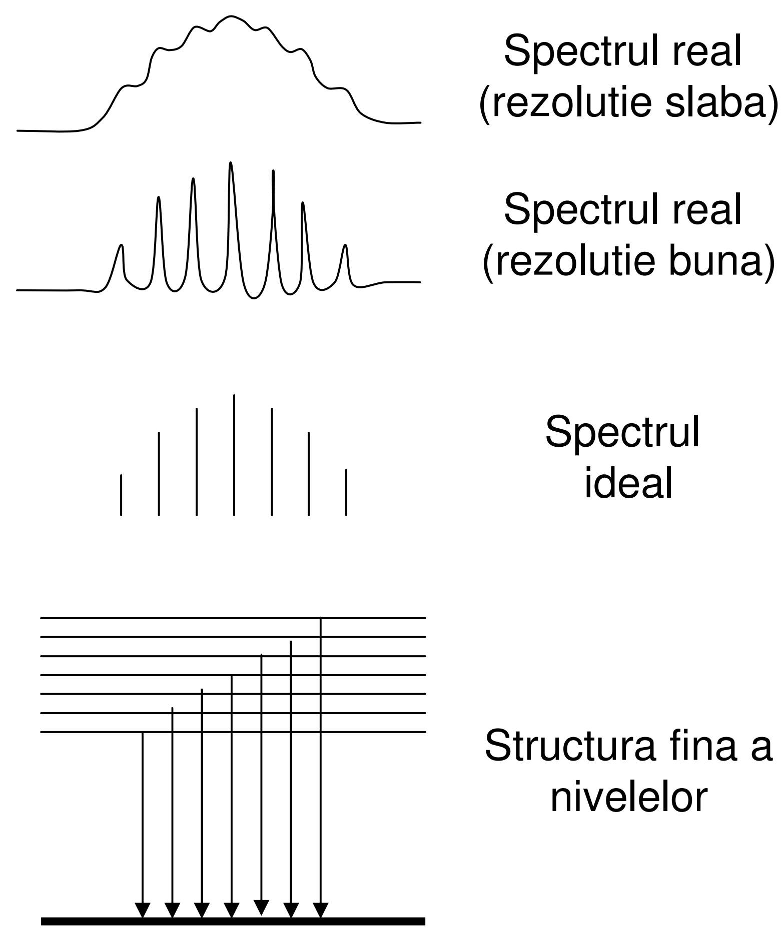
- Atomi: Spectre de linii
- Molecule: Spectre de banda

Tipuri de spectre

Spectru electronic



Spectru cu structura fina

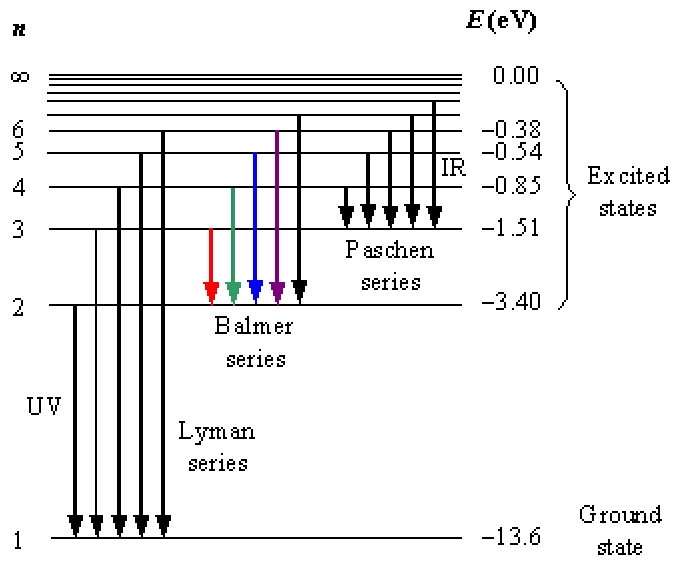


Spectrofotometria

Este o metoda bazata pe inregistrarea spectrelor de emisie si de absorbtie.

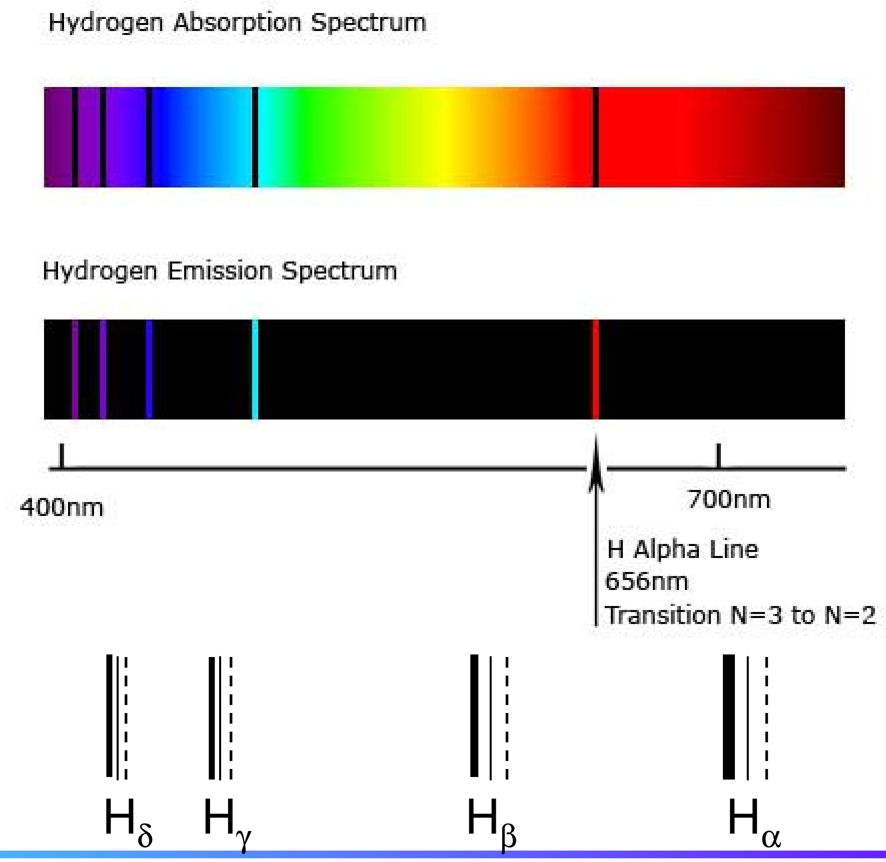
Metoda extrem de precisa mergand pana la punerea in evidenta a izotopilor extrem de putin abundenti

Ex: separarea spectrala izotopica



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.

Seria Balmer a hidrogenului



Descoperirea deuteriului si tritiului

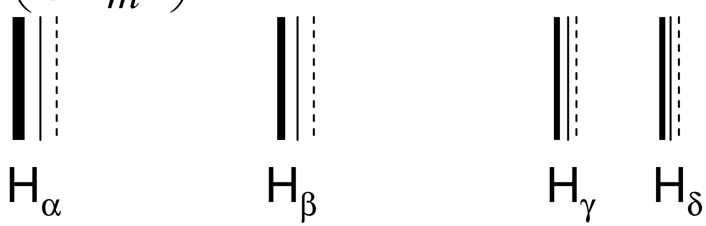
Teoria Bohr pentru nucleul hidrogenoid fix (cu masa infinita) conduce la cuantificarea energetica

$$E_n = -\frac{1}{n^2}\frac{Z^2 e_0^4 m}{2\hbar^2} = \frac{1}{n^2}E_1 \qquad h\nu_{mn} = E_1\left(\frac{1}{n^2}-\frac{1}{m^2}\right) \qquad \frac{1}{\lambda_{mn}} = R_\infty\left(\frac{1}{n^2}-\frac{1}{m^2}\right)$$

$$R_\infty = -E_1/hc = 2\pi^2 m e_0^4/(h^3 c) = 1.097373\times 10^7\ m^{-1}$$

Experimental

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4}-\frac{1}{m^2}\right),\ m = 3,4,5,6; \quad R_H = 10967776\ \mathrm{m}^{-1}$$



$$R_H = R_\infty \frac{1}{1+m/M} \cong R_\infty\left(1-\frac{m}{M}\right) \qquad R_D \cong R_\infty\left(1-\frac{m}{2M}\right) \qquad R_T \cong R_\infty\left(1-\frac{m}{3M}\right)$$

În 1932 a fost descoperită apa grea D_2O, foarte importantă în energetica nucleară. În natură, în apa oceanelor, există 1 atom de deuteriu la 6800 de atomi de hidrogen şi un atom de tritiu la 10^{18} atomi de hidrogen uşor.

Cuantificarea nivelelor energetice

Ecuatia Schrodinger temporala

$$-\frac{\hbar^2}{2m}\Delta\Psi(x,y,z;t)+U(x,y,z;t)\cdot\Psi(x,y,z;t)=i\hbar\frac{\partial}{\partial t}\Psi(x,y,z;t)$$

Este utila in studiul fenomenelor dependente de timp:
- -emisiade radiatie;
- - absorbtia de radiatie.

Ecuatia Schrodinger atemporala

$$\Psi(x,y,z;t)=\psi(x,y,z)\cdot T(t) \Rightarrow -\frac{\hbar^2}{2m}\Delta\psi(x,y,z)+U(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

Este utila indeterminarea nivelelor energetice ale sistemelor atomice si moleculare

- De comentat: $\rho(x,y,z;t)=\frac{\mathrm{d}P}{\mathrm{d}V}=\psi^*(x,y,z,t)\psi(x,y,z,t)=|\psi|^2$

Spectre. Reguli de selectie

Spectre electronice: $E_n = -\frac{1}{n^2}\frac{Z^2 e_0^4 m}{2\hbar^2} = \frac{1}{n^2}E_1$

Reguli de selectie: $\Delta l = \pm 1,$ $\Delta m = 0, \pm 1$

$\nu_{electronice} \sim 10^{14} - 10^{16} MHz(UV - VIS)$

$l = 0, ..., n-1;$ $m = -l, -l+1, \cdots, 0, \cdots, l-1, l$

Numar cuantic orbital — **Numar cuantic magnetic**

Spectre de vibratie: $E_{vib} = h\nu\left(v + \frac{1}{2}\right)$

Reguli de selectie: $\Delta v = 0, \pm 1$

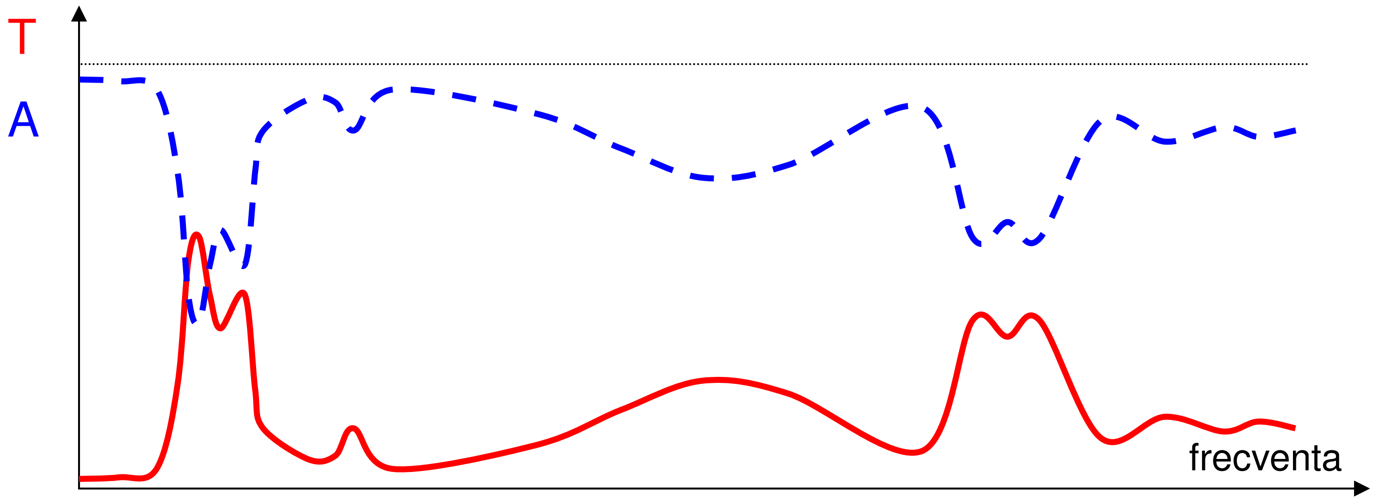
$\nu_{vibratie} \sim 10^{11} - 10^{14} MHz(IR)$

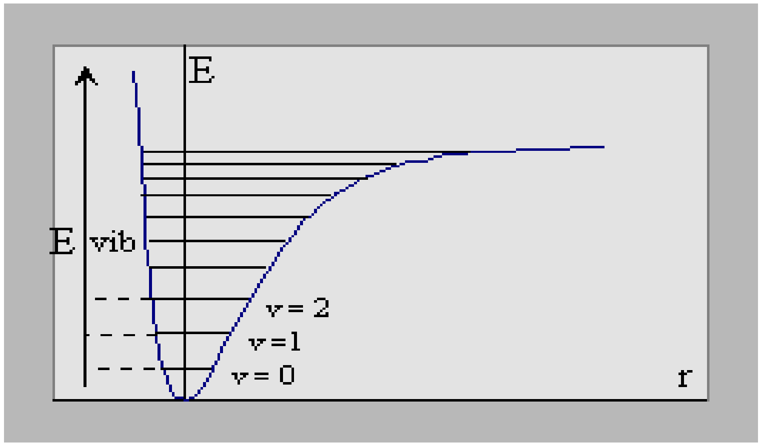
Spectre de rotatie: $E_{rot} = \frac{h^2}{8\pi I} J(J+1)$

Reguli de selectie: $\Delta J = 0, \pm 1$

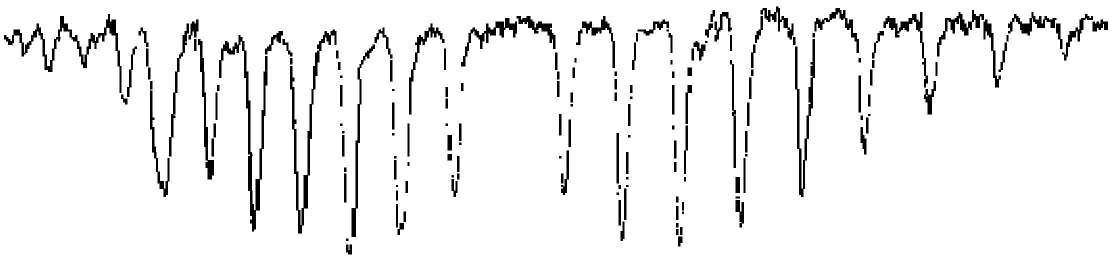
$\nu_{rotatie} \sim 10^{10} MHz(microunde)$

Spectre de emisie. Spectre de absorbtie





Spectru de vibratie de absorbtie



Tipuri de spectrometrii / spectroscopii

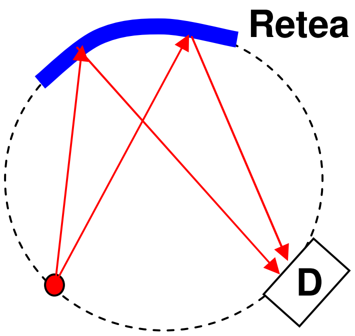
Spectroscopie cu raze X	→	fluorescenta, efect Auger, structura atomului
Spectroscopie radiatiilor X	→	studiul stelelor
Spectroscopie UV	→	spectre electronice
Spectroscopie in vizibil	→	spectre electronice
Spectroscopie in infrarosu si Raman	→	spectre de vibratie- rotatie
Spectroscopie de microunde	→	spectre de rotatie
Spectrometrie de masa		

Componentele unui spectrometru

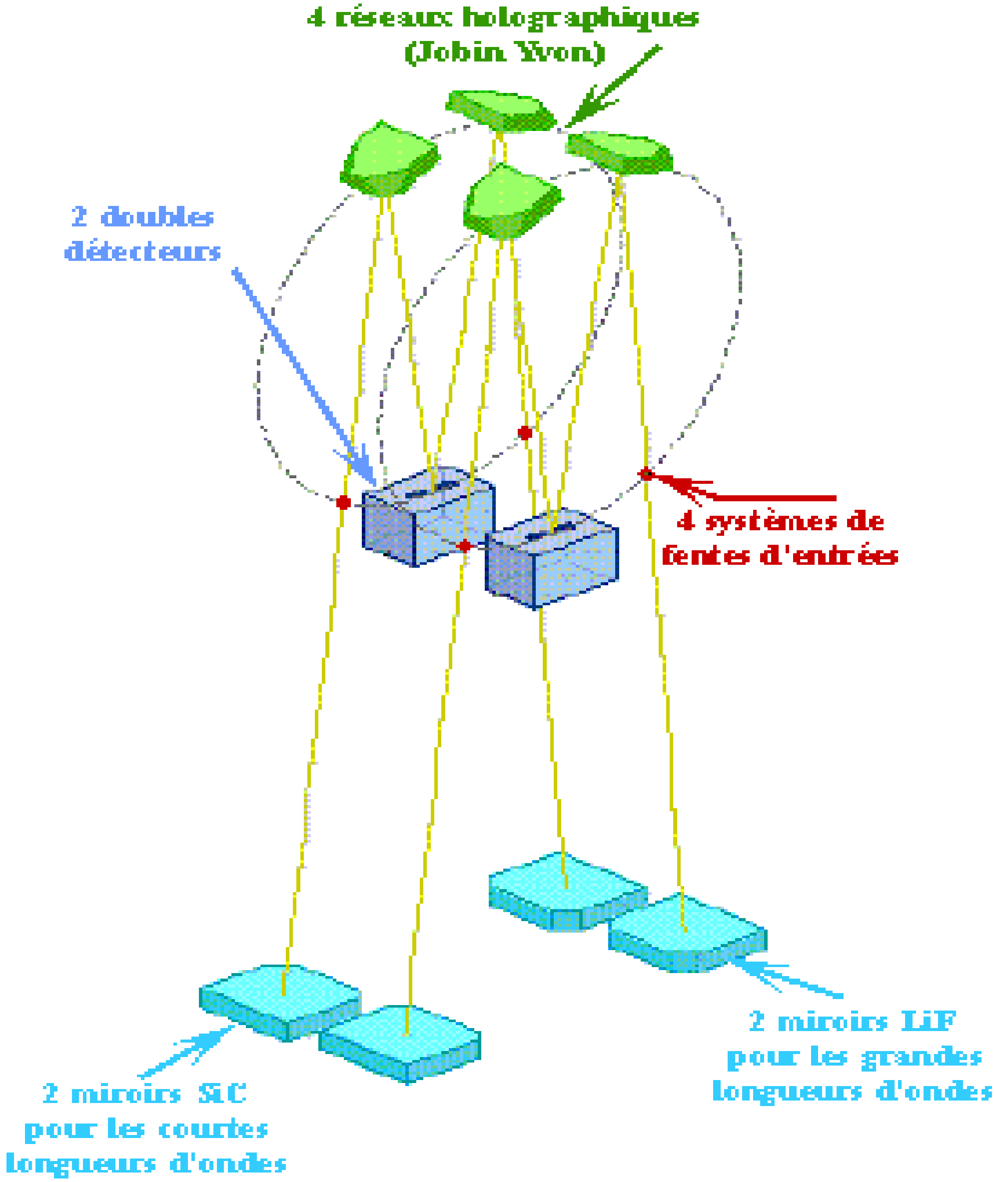
Spectrometru:
- sursa
- monocromatorul:
  - cu prisma
  - cu retea plana
  - cu retea curba
- Receptorul (detector)

Surse:
- pentru spectrometria de absorbtie:
  - *VIS (lampa cu W, lampa cu Na)*
  - *IR (bastonase de sticla incalzite electric)*
  - *UV (lampa cu H. lampa cu deuteriu)*
- pentru spectrometria de emisie:
  - *Flacara*
  - *Arcul electric*
  - *Scanteia electrica*
  - *Plasma de descarcare electrica*
  - *Descarcare corona*

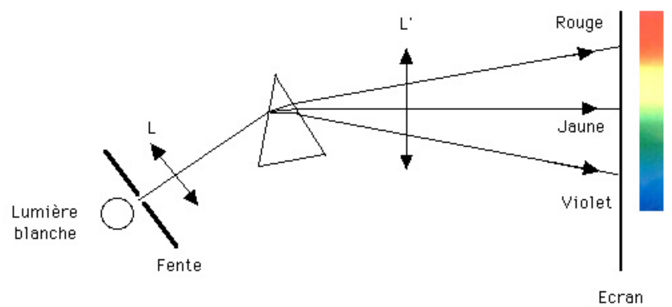
Crecul Rowland: Sursa, reteaua si detectorul se afla pe acelasi cerc

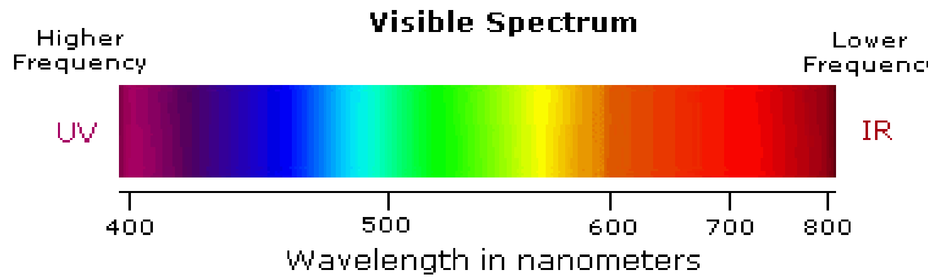


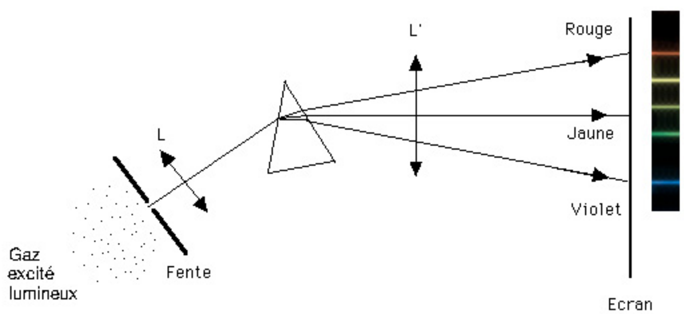
Cercul lui Rowland



Spectroscopul cu prisma

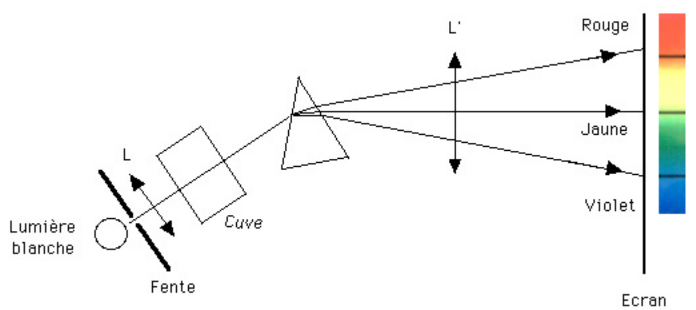






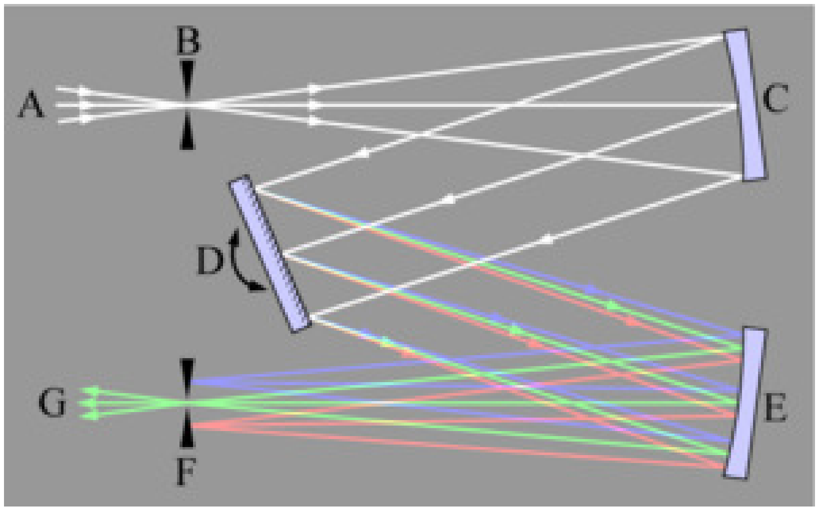
Spectru de emisie

Violet:	400 - 420 nm
Indigo:	420 - 440 nm
Blue:	440 - 490 nm
Green:	490 - 570 nm
Yellow:	570 - 585 nm
Orange:	585 - 620 nm
Red:	620 - 780 nm



Spectru de absorbtie

Monocromatorul Czerny-turner



Fanta B este situata in planul focal al oglinzii sferice C, actfel incat pe D cade un fascicol paralel de lumina

Elementul D poate fi o prisma,
o retea de difracatie sau un cristal

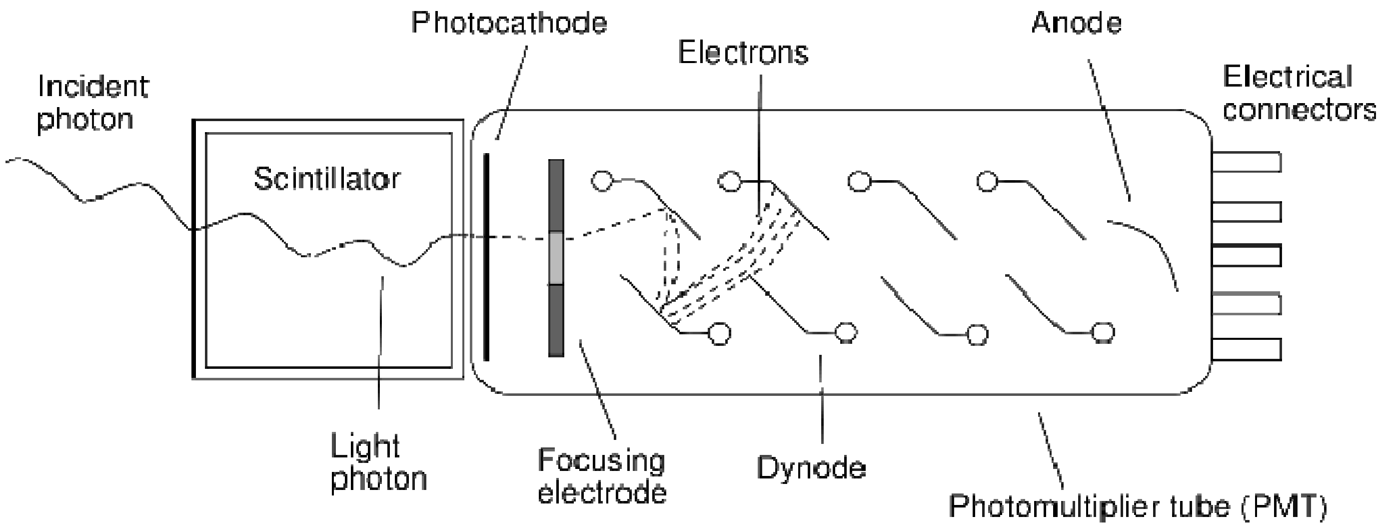
Oglinda E focalizeaza in planul fantei de iesire F o singura lungime de unda.

Observatie:

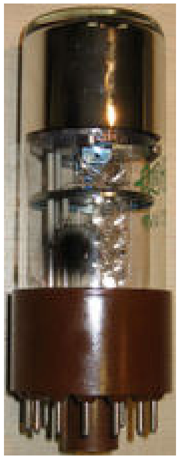
In cazul spectroscopiei UV elemntele dispersive trebuiesc facute din cuart (sticla absoarbe rad. UV)

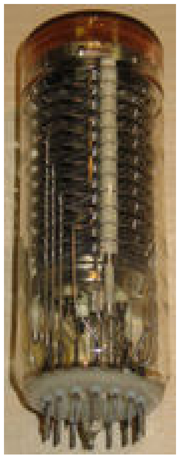
Receptori spectrali

Fotomultiplicatorul



Tipuri de fotomultiplicatori

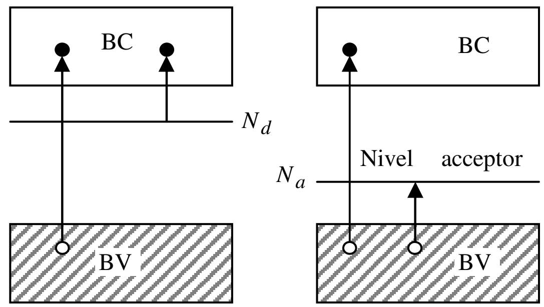




Dinode sub forma de semicilindru

Jonctiunea p - n

Structura de benzi a semiconductorilor

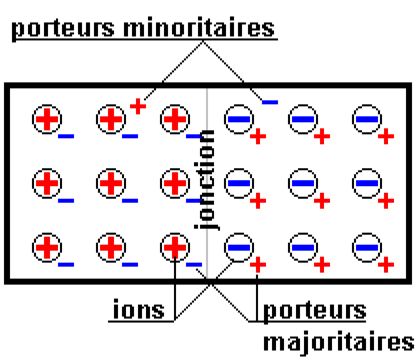


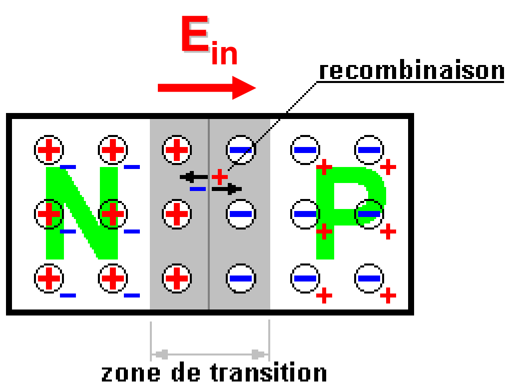
$$n = n_0 + N_d$$

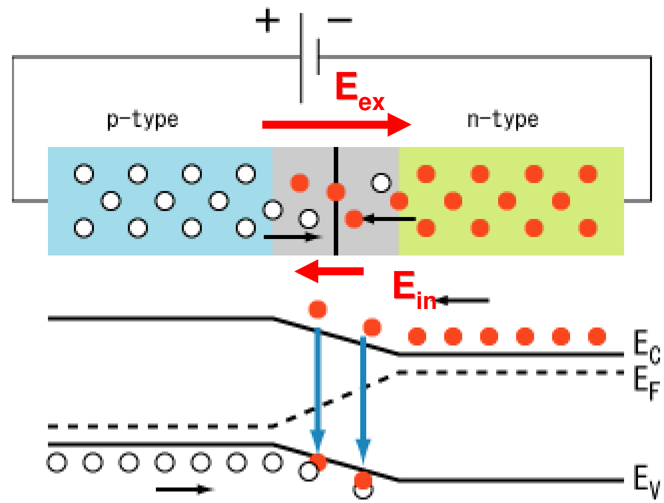
$$\sigma_n = e\left[(n_0 + N_d)\mu_n + p_0\mu_p\right] = \sigma_0^{intrinsec} + eN_d\mu_n$$

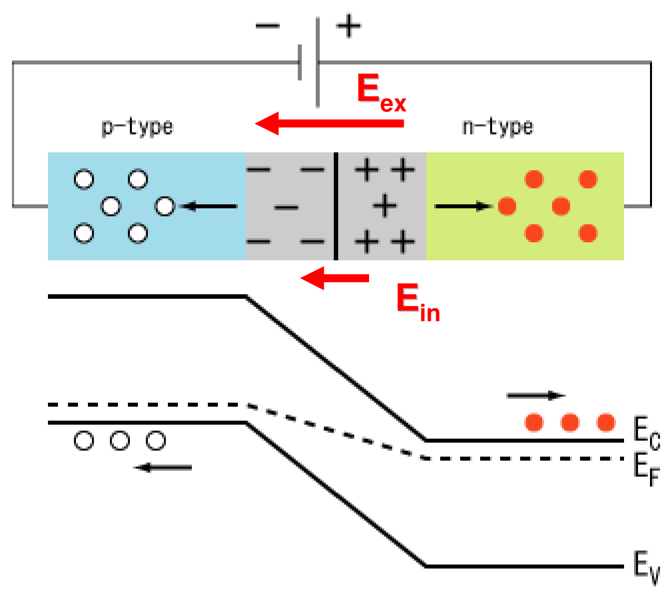
$$p = p_0 + N_a$$

$$\sigma_p = e\left[n_0\mu_n + (p_0 + N_a)\mu_p\right] = \sigma_0^{intrinsec} + eN_a\mu_p$$









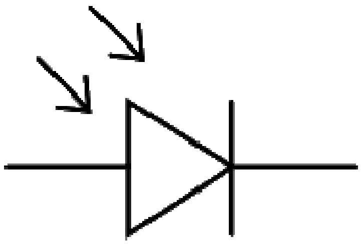
Receptori spectrali

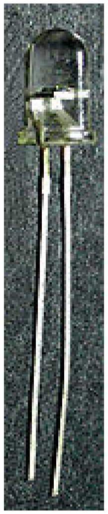
Fotodioda

Activare semiconductorilor :

- termic (electroni din BV primesc suficienta energie de agitatie termica pentru a trece in BC)
- optic (energia necesara trecerii electronilor in BC este primita prin absorbtia unui foton)

Fotodioda este un dispozitiv semiconductor a carei activare se face optic



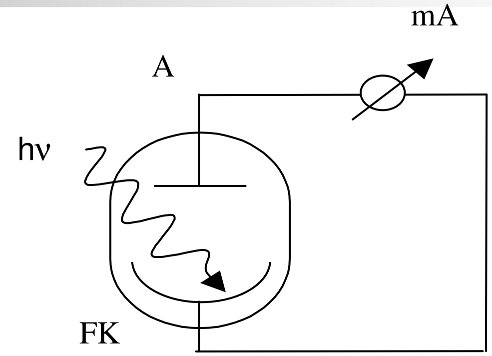


$$I_d = I_s\left[\exp\left(\frac{E_g}{k_B T}\right) - 1\right] - I_f$$

I_s – curent de saturatie
I_f – fotocurent
E_g – largimea benzii interzise

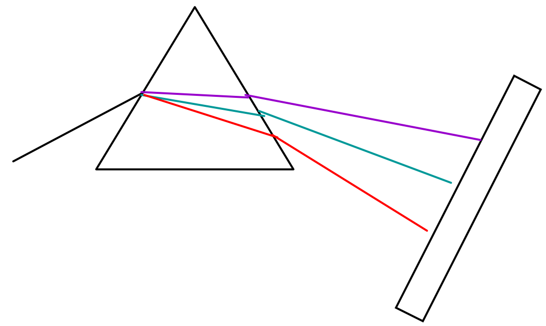
Receptori spectrali

Celula fotoelectrica



Placa fotografica

Holograma



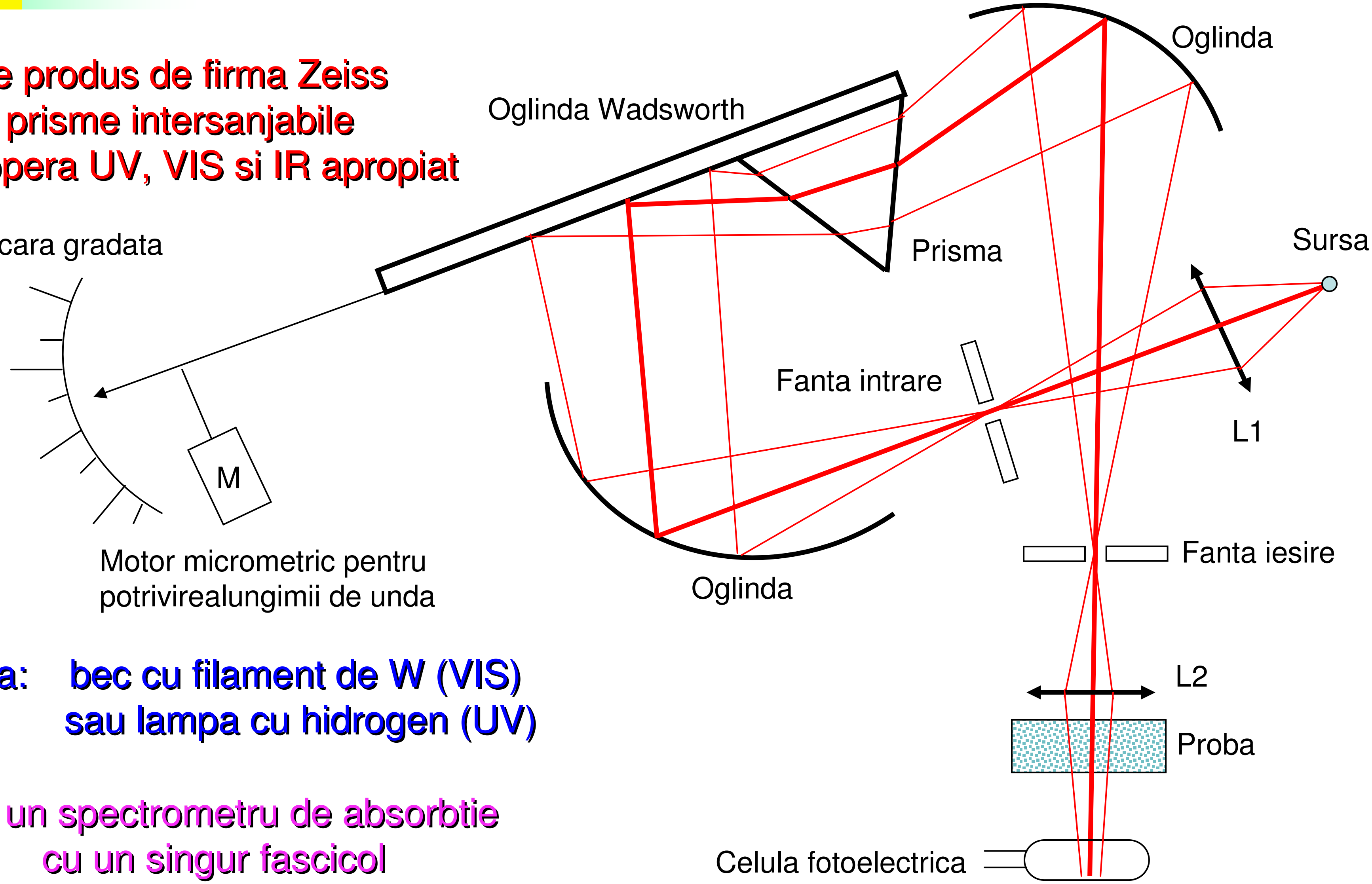
Camera CCD
(charge coupled device)

Photomètre et radiomètre CCD de capture d'image

Au soft incorporat:
LabView, Matlab,
VBA, VBScript,
Javascript, C sau C++.

Schema monocromatorului spectrometrului VSU1

Este produs de firma Zeiss
Are prisme intersanjabile
Acopera UV, VIS si IR apropiat



Sursa: bec cu filament de W (VIS)
sau lampa cu hidrogen (UV)

Este un spectrometru de absorbtie
cu un singur fascicol

Spectrometrul cu dublu fascicol

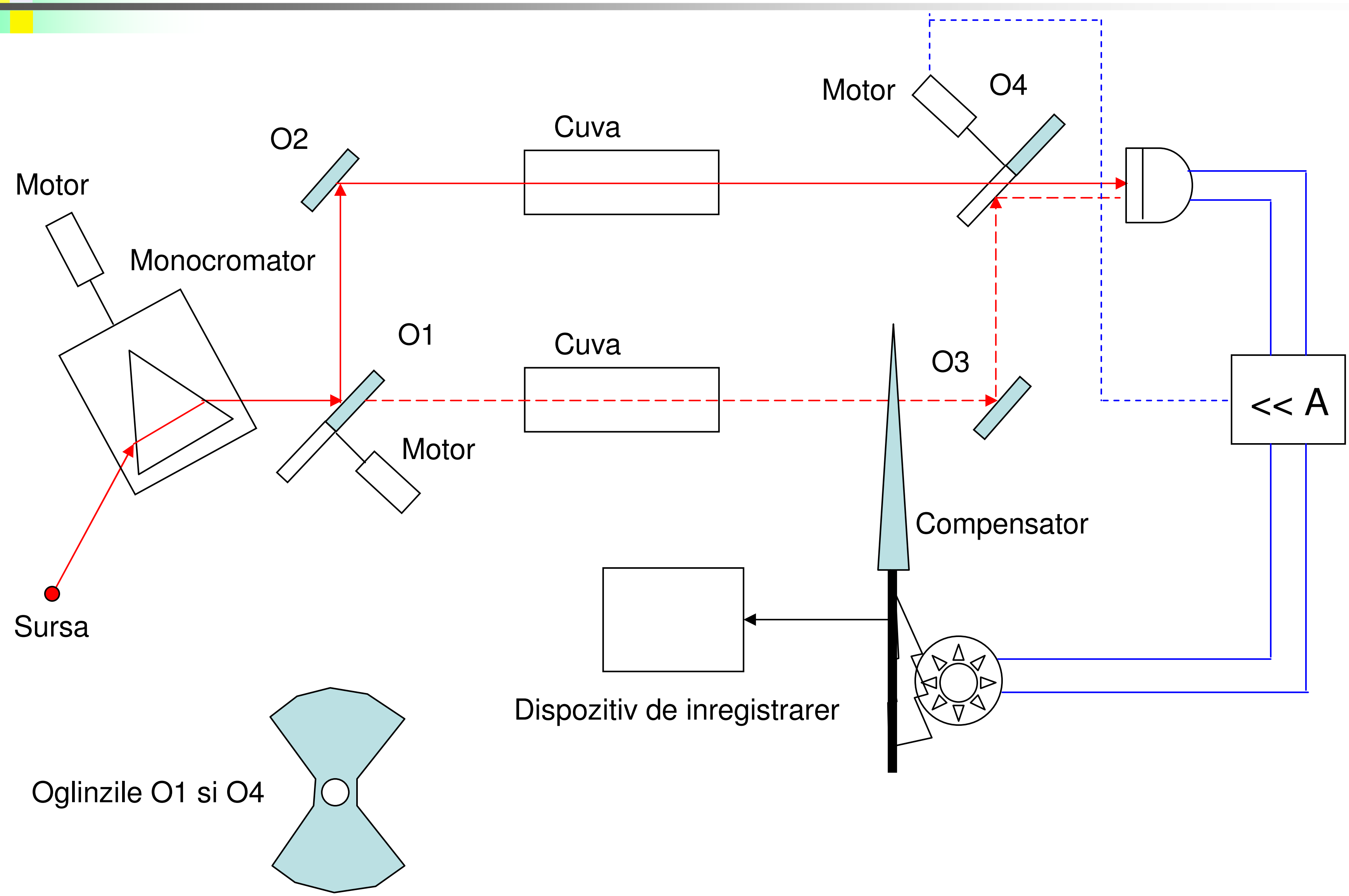
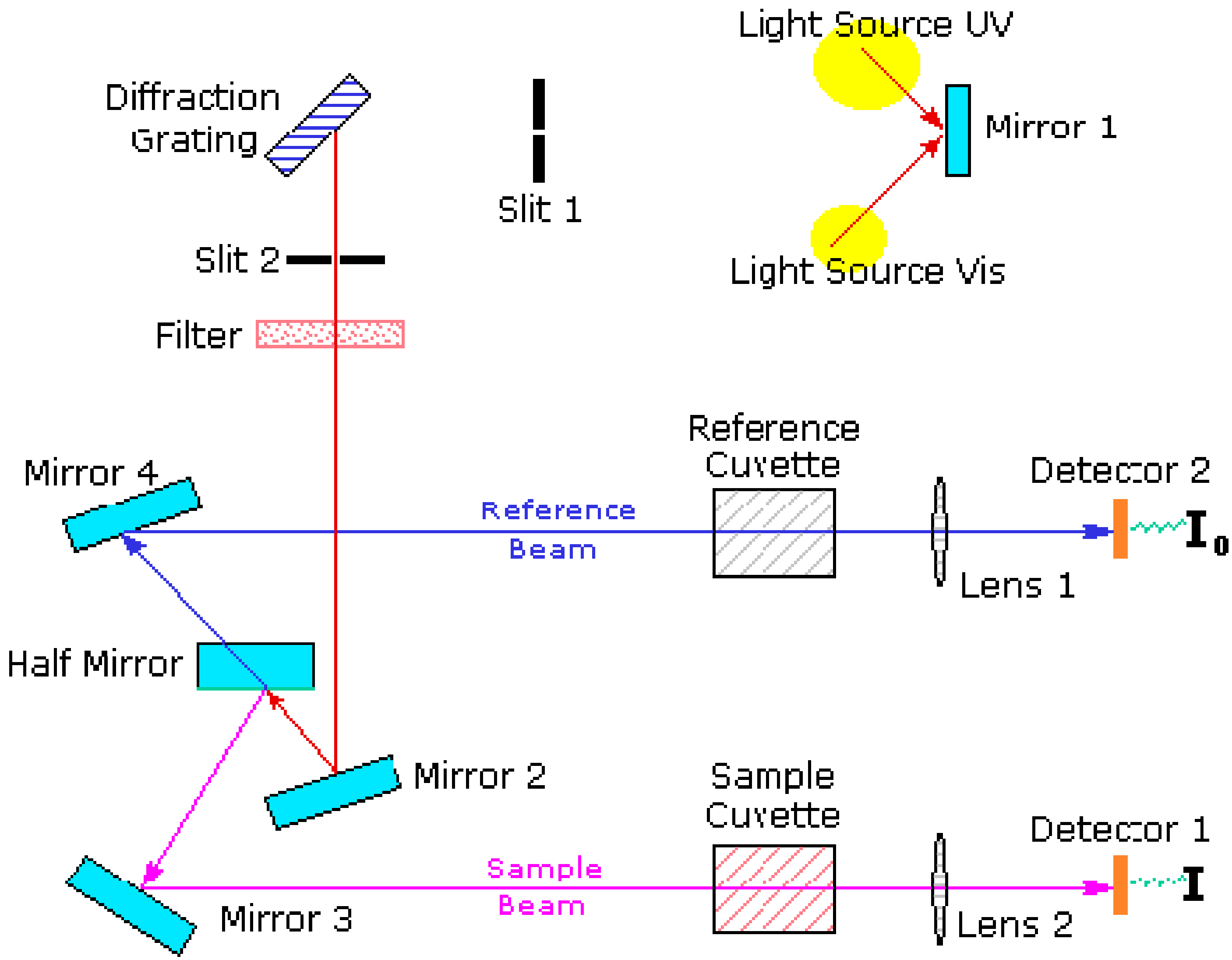
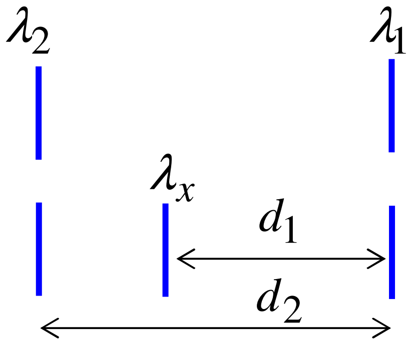


Diagrama componentelor unui spectrometru UV-VIS



Analize spectrale

Analiza spectrala calitativa



$$\frac{d_1}{d_2} = \frac{\lambda_x - \lambda_1}{\lambda_2 - \lambda_1}$$

$$\lambda_x = \lambda_1 + (\lambda_2 - \lambda_1)\frac{d_1}{d_2}$$

Analiza spectrala cantitativa

$I = n\hbar\omega$ $\quad$ $I = ac^b$ $\quad\Rightarrow\quad$ $\ln I = \ln a + b \ln c$ $\quad$ ***c* - concentratia emitatorului**

Exista un etalon intern $\quad$ $\ln I_{etalon} = \ln a_e + b_e \ln c_e$

$$\ln\left(\frac{I_x}{I_e}\right) = const + b\ln\left(\frac{c_x}{c_e}\right)$$