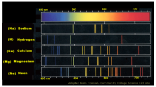

Atomic spectroscopy

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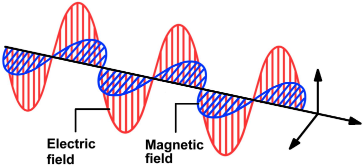
Facultad de Química

PHYSICAL CHEMISTRY I

Index

Electromagnetic waves



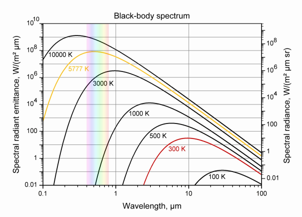
- Electric and magnetic fields

$$\mathrm{E} = \mathrm{i}\, E_x = \mathrm{i}\, E_{0x} \cos\left(\omega\, t - k\, z\right)$$
$$\mathrm{B} = \mathrm{j}\, B_y = \mathrm{j}\, B_{0y} \cos\left(\omega\, t - k\, z\right)$$

- Periodicity
  - Space $\Rightarrow E(z) = E(z+\lambda) \Rightarrow k = 2\pi/\lambda$
  - Time $\Rightarrow E(t) = E(t+\tau) \Rightarrow \omega = 2\pi/\tau = 2\pi\nu$
- Velocity $\Rightarrow c = \frac{1}{\sqrt{\epsilon_0 \mu_0}} = 2.9979\, 10^8$ m/s

Photons

- Plank (1900) $\Rightarrow$ EM radiation
  $\Rightarrow$ Photons $\Rightarrow$ Einstein (1905)



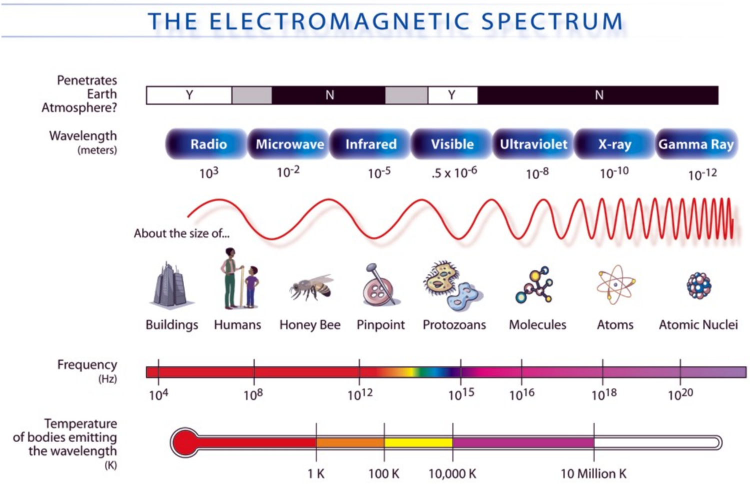
- Energy $\Rightarrow E = h\nu \Rightarrow E = h\frac{c}{\lambda} = \hbar\omega \;\; (\hbar = \frac{h}{2\pi})$
- Momentum

$$E = \sqrt{m_0^2 c^4 + p^2 c^2}$$

$$\Downarrow \; m_0 = 0$$

$$E = pc \rightarrow p = \frac{E}{c} = \frac{h}{\lambda}$$

EM spectrum


THE ELECTROMAGNETIC SPECTRUM
Penetrates Earth Atmosphere?
Y
N
Y
N
Wavelength (meters)
Radio
Microwave
Infrared
Visible
Ultraviolet
X-ray
Gamma Ray
10^3
10^-2
10^-5
.5 x 10^-6
10^-8
10^-10
10^-12
About the size of...
Buildings
Humans
Honey Bee
Pinpoint
Protozoans
Molecules
Atoms
Atomic Nuclei
Frequency (Hz)
10^4
10^8
10^12
10^15
10^16
10^18
10^20
Temperature of bodies emitting the wavelength (K)
1 K
100 K
10,000 K
10 Million K

EM spectrum

EM radiation	λ (nm)	E (eV)	Molecular transitions
Radio	3×10^{8} -	4×10^{-6} -	
Microwaves	3×10^{8} - 10^{6}	4×10^{-6} - 1.2×10^{-3}	rotation
Infrared (IR)	3.84×10^{14} - 10^{6}	1.2×10^{-3} - 1.7	vibration
Visible	780 - 390	1.7 - 3.2	electronic
Ultraviolet (UV)	390 - 10	3.2 - 120	electronic
X Rays	10 - 0.006	120 - 2.4×10^{5}	ionization
Gamma Rays	0.1 - 1×10^{-5}	10^{4} - 10^{8}	

Time-dependent Schrödinger's equation

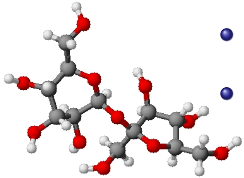
- Postulate 5. The time evolution of the system is governed by the time-dependent Schrödinger's equation

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}(x,t)\Psi(x,t)$$

- Stationary state

$$\Psi(x,t) = \psi(x) e^{-iE\,t/\hbar} \rightarrow \begin{cases} |\Psi(x,t)|^2 = |\psi(x)|^2 \\ \hat{H}\psi = E\psi \end{cases}$$

Transition probability



- Isolated system $\Rightarrow \hat{H}^{(0)}(x)\psi_n^{(0)}(x) = E_n^{(0)}\psi_n^{(0)}(x)$
- Stationary state

$$\psi(x,t) = \Psi_n^{(0)}(x)e^{-iE^{(0)}t/\hbar} \rightarrow |\Psi(x,t)|^2 = |\psi_n^{(0)}(x)|^2$$

- Perturbation (EM) $\Rightarrow \hat{H}(x,t) = \hat{H}^{(0)}(x) + \hat{H}'(x,t)$

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \hat{H}(x,t)\Psi(x,t) \longrightarrow \Psi(x,t) = \sum_j c_j(t)\psi_j^{(0)}(x)e^{-iE_j^{(0)}t/\hbar}$$

$$i\hbar\sum_j \frac{dc_j(t)}{dt}\psi_j^{(0)}(x)e^{-iE_j^{(0)}t/\hbar} = \sum_j c_j(t)\hat{H}'(x,t)\psi_j^{(0)}(x)e^{-iE_j^{(0)}t/\hbar}$$

$$\int_{\forall x}(\psi_j^{(0)}(x))^*\psi_m^{(0)}(x)dx = \left\langle \psi_j^{(0)} | \psi_m^{(0)} \right\rangle = \delta_{j,m}\begin{cases} = 1 & m = j \\ = 0 & m \neq j \end{cases}$$

Transition probability

$$i\hbar\frac{dc_m(t)}{dt}=\sum_j c_j(t)H'_{mj}(t)e^{i\omega_{mj}t} \qquad m=1,2,3,\ldots \begin{cases} H'_{mj}(t)=\langle\psi_m^{(0)}|\hat{H}'(x,t)|\psi_j^{(0)}\rangle \\ \omega_{mj}=\dfrac{E_m^{(0)}-E_j^{(0)}}{\hbar} \end{cases}$$

$$\Downarrow$$

$$\Psi(x,0)=\psi_n^{(0)}(x)\rightarrow c_j(0)=\delta_{n,j}$$

- If $H' \ll E_m^{(0)} - E_n^{(0)} \Rightarrow i\hbar\frac{dc_m(t)}{dt} \simeq H'_{mn}(t)e^{i\omega_{mn}t}$

$$c_m(t)=\frac{1}{i\hbar}\int_0^t H'_{mn}(t')e^{i\omega_{mn}t'}dt'$$

$$P_{n\rightarrow m}(t)=|c_m(t)|^2=\frac{1}{\hbar^2}\left|\int_0^t H'_{mn}(t')e^{i\omega_{mn}t'}dt'\right|^2$$

Transition probability

- Force

$$\mathbf{F} = q\,\mathbf{E} + \frac{q}{c}\,\mathbf{v}\times\mathbf{B}$$

$$\Downarrow \quad \langle v^2\rangle_{1s}^{1/2} \sim \frac{c}{137}$$

$$\mathbf{F} \simeq q\,\mathbf{E}$$

- Potential energy

$$\mathbf{F} = -\nabla V \rightarrow V = -\int \mathbf{F}\,d\mathbf{r}$$

$$\Downarrow \quad \text{discrete charges}$$

$$V = -\underbrace{\sum_i q_i\,\mathbf{r}_i}_{\boldsymbol{\mu}}\cdot\mathbf{E} = -\boldsymbol{\mu}\cdot\mathbf{E}$$

$\boldsymbol{\mu} \longrightarrow$ electric dipole moment

Transition probability

- Dipolar approximation $\Rightarrow$ molecular size $\ll \lambda$

$$\mathrm{E} \simeq \mathrm{i}\, E_{0x} \cos(\omega\, t) \Rightarrow H' = -\boldsymbol{\mu}\cdot\mathrm{E} = -\mu_x E_{0x} \cos(\omega\, t)$$

$$\downarrow$$

$$H'_{mn}(t) = -E_{0x} \underbrace{\langle m|\mu_x|n\rangle}_{\text{transition dipole moment}} \cos(\omega\, t) \leftarrow \mu_x = \sum_i q_i x_i$$

$$P_{n\to m}(t) = \frac{|E_{0x}|^2 |\langle m|\mu_x|n\rangle|^2}{\hbar^2} \left| \int_0^t \cos\omega\, t' e^{i\omega_{mn} t'} dt' \right|^2$$

Transition probability

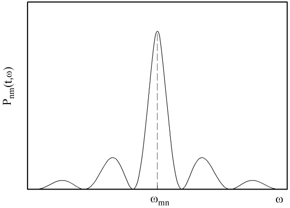
$$P_{n\to m}(t) = \frac{|E_{0x}|^2|\langle m|\mu_x|n\rangle|^2}{4\hbar^2}\left|\frac{e^{i(\omega_{mn}+\omega)t}-1}{\omega_{mn}+\omega}+\frac{e^{i(\omega_{mn}-\omega)t}-1}{\omega_{mn}-\omega}\right|^2$$

- $E_{0x} \neq 0$
- $\langle m|\mu_x|n\rangle \neq 0 \Rightarrow$ Selection rules
- If $\omega_{mn}-\omega \ll \omega_{mn}+\omega$

$$P_{n\to m}(t) = \frac{|E_{0x}|^2|\langle m|\mu_x|n\rangle|^2}{4\hbar^2}\left|\frac{e^{i(\omega_{mn}-\omega)t}-1}{\omega_{mn}-\omega}\right|^2$$

$$P_{n\to m}(t) = \frac{|E_{0x}|^2|\langle m|\mu_x|n\rangle|^2}{\hbar^2}\frac{\text{sen}^2(\omega_{mn}-\omega)t/2}{(\omega_{mn}-\omega)^2}$$

Transition probability



- Maximun

$$\omega = \omega_{mn} \rightarrow E_m - E_n = h\nu$$

- Absorption

$$\nu > 0 \Rightarrow E_m > E_n$$

- If $\omega_{mn} + \omega \ll \omega_{mn} - \omega$

$$P_{n\rightarrow m}(t) = \frac{|E_{0x}|^2 |\langle m|\mu_x|n\rangle|^2}{\hbar^2} \frac{\text{sen}^2(\omega_{mn}+\omega)t/2}{(\omega_{mn}+\omega)^2}$$

  - Maximun $\omega = -\omega_{mn} \rightarrow E_n - E_m = h\nu$
  - Emission $\nu > 0 \Rightarrow E_n > E_m$

Hydrogen atom

- Transition dipole moment $\Rightarrow \langle\psi_i|\boldsymbol{\mu}|\psi_j\rangle$

$$\begin{cases} \boldsymbol{\mu} = -e\,\boldsymbol{r} \\ \boldsymbol{r} = x\boldsymbol{i} + y\boldsymbol{j} + z\boldsymbol{k} = r\ \mathrm{sen}\,\theta\ \cos\phi\,\boldsymbol{i} + r\ \mathrm{sen}\,\theta\ \mathrm{sen}\,\phi\,\boldsymbol{j} + r\ \cos\theta\,\boldsymbol{k} \\ \langle\psi_i|\boldsymbol{\mu}|\psi_j\rangle = \langle\psi_{n',l',m',m'_s}|\boldsymbol{\mu}|\psi_{n,l,m,m_s}\rangle \end{cases}$$

$$\langle\psi_{n',l',m',m'_s}|\boldsymbol{\mu}|\psi_{n,l,m,m_s}\rangle = -e\int_0^\infty R^*_{n',l'}(r)\,r^3\,R_{n,l}(r)\,dr \cdot \int_0^{2\pi}\int_0^{\pi}\Theta^*_{l',m'}(\theta)\,\Phi^*_{m'}(\phi)[\mathrm{sen}\,\theta\ \cos\phi\,\boldsymbol{i} + \mathrm{sen}\,\theta\ \mathrm{sen}\,\phi\,\boldsymbol{j} + \cos\theta\,\boldsymbol{k}]\Theta_{l,m}(\theta)\,\Phi_m(\phi)\ \mathrm{sen}\,\theta\,d\theta\,d\phi\,\langle m_{s'}|m_s\rangle \neq 0$$

- $\langle m_{s'}|m_s\rangle \neq 0 \Rightarrow m_s = m'_s \Rightarrow \Delta m_s = 0$

Hydrogen atom

- $\langle \Phi^*_{m'} | \Phi_m \rangle = \int_0^{2\pi} e^{-im'\phi} e^{im\phi} d\phi \neq 0 \Rightarrow m = m' \Rightarrow \Delta m = 0$
- $\langle \Phi^*_{m'} | \operatorname{sen}\phi | \Phi_m \rangle = \int_0^{2\pi} e^{-im'\phi} \operatorname{sen}\phi\, e^{im\phi} d\phi \neq 0 \Rightarrow m' = m+1 \Rightarrow \Delta m = +1$
- $\langle \Phi^*_{m'} | \cos\phi | \Phi_m \rangle = \int_0^{2\pi} e^{-im'\phi} \cos\phi\, e^{im\phi} d\phi \neq 0 \Rightarrow m' = m-1 \Rightarrow \Delta m = -1$
- $\left\{ \begin{array}{l} \langle \Theta_{l'm'} | \cos\theta | \Theta_{lm} \rangle = \int_0^{2\pi} \Theta^*_{l'm'}(\theta) \cos\theta\, \Theta_{lm}(\theta) \operatorname{sen}\theta d\theta \neq 0 \\ \langle \Theta_{l'm'} | \operatorname{sen}\theta | \Theta_{lm} \rangle = \int_0^{2\pi} \Theta^*_{l'm'}(\theta) \operatorname{sen}\theta\, \Theta_{lm}(\theta) \operatorname{sen}\theta d\theta \neq 0 \end{array} \right\} \Rightarrow \Delta l = \pm 1$
- $\langle R_{n',l'} | r | R_{n,l} \rangle = \int_0^{\infty} R^*_{n',l'}(r)\, r^3\, R_{n,l}(r)\, dr \neq 0 \Rightarrow \Delta n = 0, \pm 1, \pm 2, \ldots$

Hydrogen atom

- Energy differences (excitation $\Rightarrow n_2 > n_1$)

$$\Delta E_{n_1 \to n_2} = E_{n_2} - E_{n_1} = -\frac{\mu Z^2 k^2 e^4}{2\hbar^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

- Lyman series $\Rightarrow n_1 = 1 \Rightarrow$ transitions from the $1s$ state
  - $1s \to 2s \Rightarrow \Delta l = 0 \Rightarrow$ Forbidden
  - $1s \to 2p \Rightarrow \Delta l = 1 \Rightarrow$ Allowed
  - $1s \to 3s \Rightarrow \Delta l = 0 \Rightarrow$ Forbidden
  - $1s \to 3p \Rightarrow \Delta l = 1 \Rightarrow$ Allowed
  - $1s \to 3d \Rightarrow \Delta l = 2 \Rightarrow$ Forbidden
  - $\vdots$
  - Transitions $1s \to np$

Hydrogen atom

- Balmer series $\Rightarrow n_1 = 2 \Rightarrow$ transitions from the $2s$ or $2p$ states
  - $2s \rightarrow 3s \Rightarrow \Delta l = 0 \Rightarrow$ Forbidden
  - $2s \rightarrow 3p \Rightarrow \Delta l = 1 \Rightarrow$ Allowed
  - $2s \rightarrow 3d \Rightarrow \Delta l = 2 \Rightarrow$ Forbidden
  - $2p \rightarrow 3s \Rightarrow \Delta l = -1 \Rightarrow$ Allowed
  - $2p \rightarrow 3p \Rightarrow \Delta l = 0 \Rightarrow$ Forbidden
  - $2p \rightarrow 3d \Rightarrow \Delta l = 1 \Rightarrow$ Allowed
  - $\vdots$
  - Degenerated transitions $2s \rightarrow np$, $2p \rightarrow ns$, $2p \rightarrow nd$

Hydrogen atom

- Initial state $2s \Rightarrow$ Relaxation into $1s \Rightarrow \Delta l = 0 \Rightarrow$ Forbidden $\Rightarrow$ Metastable state
- Spin-orbit coupling $\Rightarrow \propto \boldsymbol{L} \cdot \boldsymbol{S}$