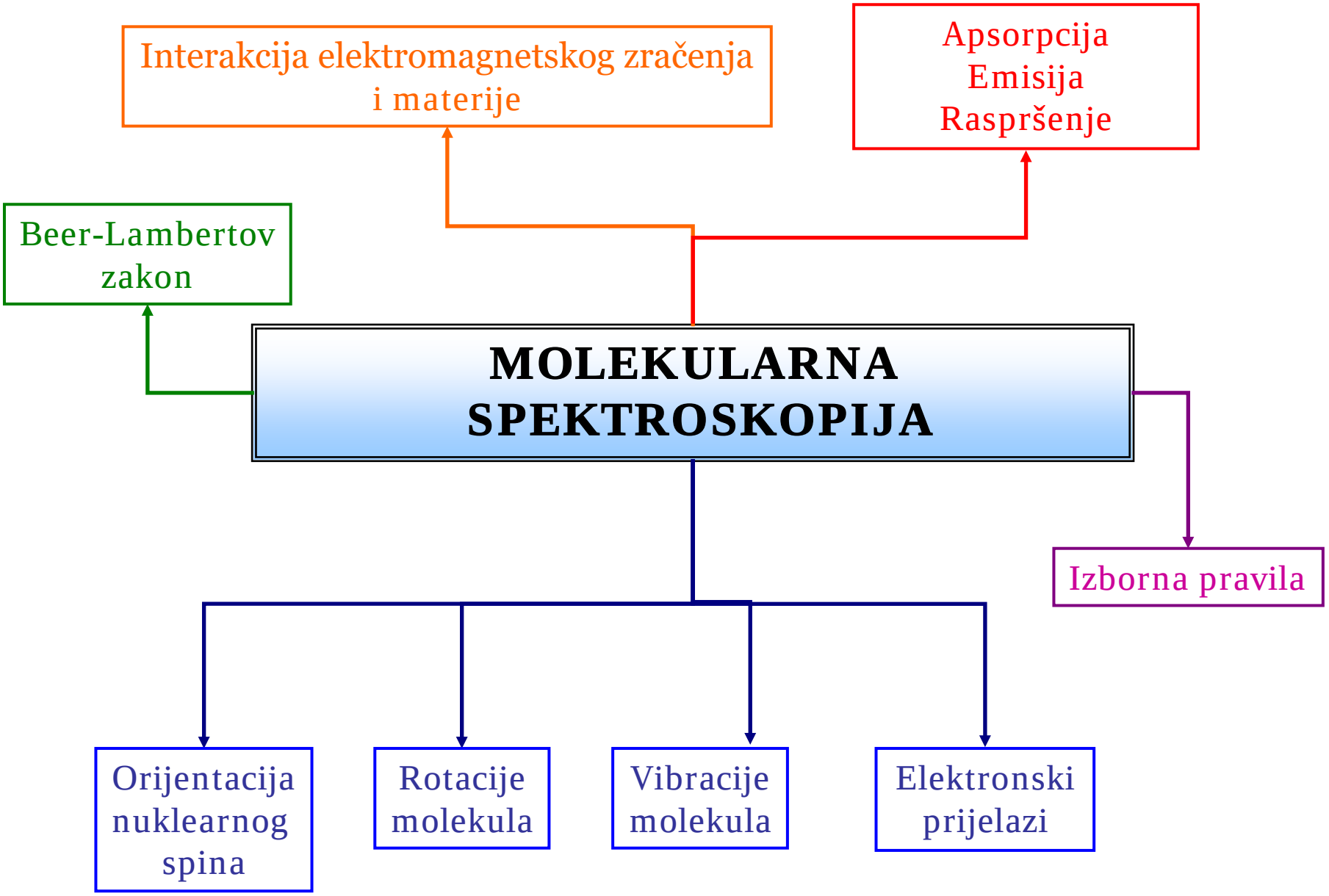
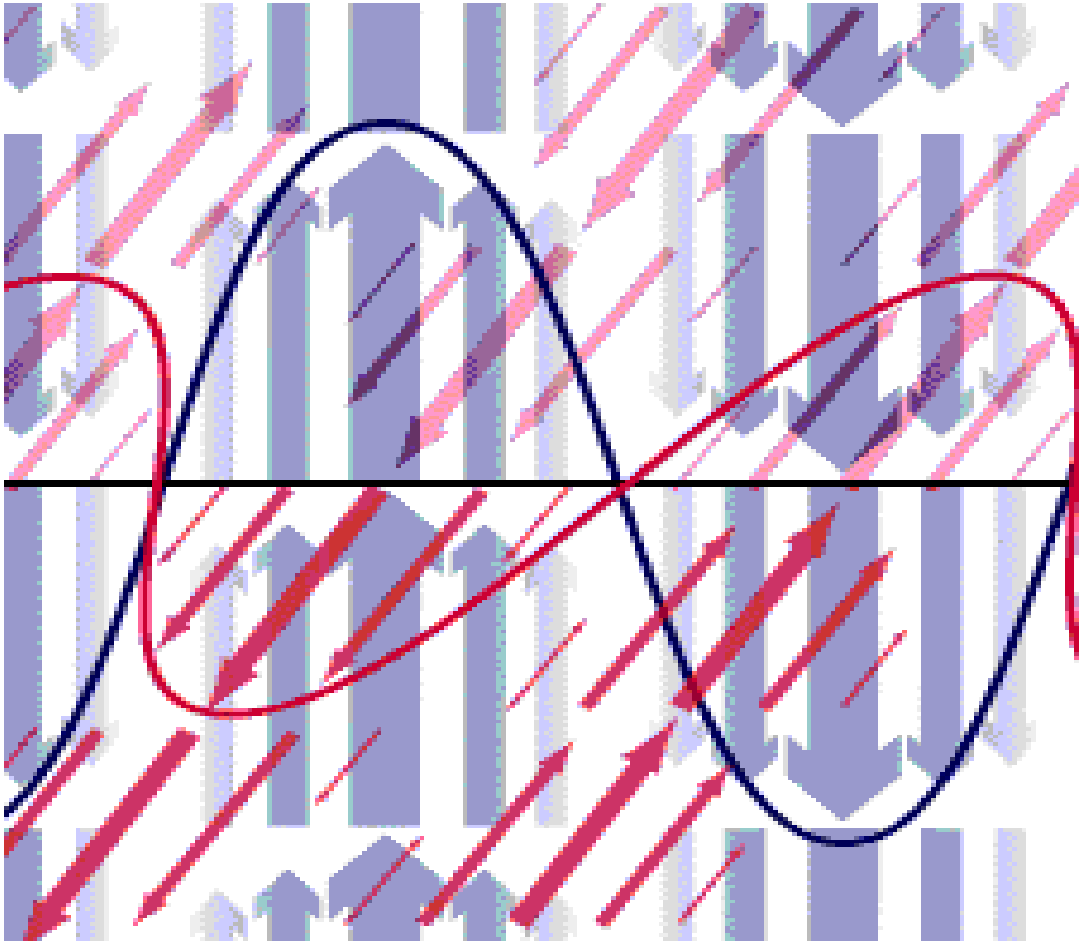

Interakcija elektromagnetskog zračenja i materije
Apsorpcija
Emisija
Raspršenje
Beer-Lambertov zakon
MOLEKULARNA SPEKTROSKOPIJA
Izborna pravila
Orijentacija nuklearnog spina
Rotacije molekula
Vibracije molekula
Elektronski prijelazi



$\lambda, \quad \nu, \quad \tilde{\nu}$

EMZ: valna duljina, frekvencija, valni broj, energija

Snaga EMZ $\Phi = \frac{\mathrm{d}E}{\mathrm{d}t}$ **odaslana energija/vrijeme**

Egzitancija izvora $M = \frac{\mathrm{d}\Phi}{\mathrm{d}A_{\text{izvor}}}$ **snaga/ploština**

Intenzitet izvora $I = \frac{\mathrm{d}\Phi}{\mathrm{d}\Omega}$ **snaga/prostorni kut**

Ozračenost tijela, iradijancija, intenzitet (ozračenosti), gustoća, fluks zračenja $E = I = \frac{\mathrm{d}\Phi}{\mathrm{d}A_{\text{uzorak}}}$ **snaga/ploština**

Interakcija EMZ s materijom

- odbijanje, **refleksija**
- prolaz kroz tijelo, **transmisija**
- upijanje, **apsorbcija**

$$I_0 = I_{\text{refl}} + I_{\text{aps}} + I_{\text{trans}}$$

$$1 = \frac{I_{\text{refl}}}{I_0} + \frac{I_{\text{aps}}}{I_0} + \frac{I_{\text{trans}}}{I_0}$$

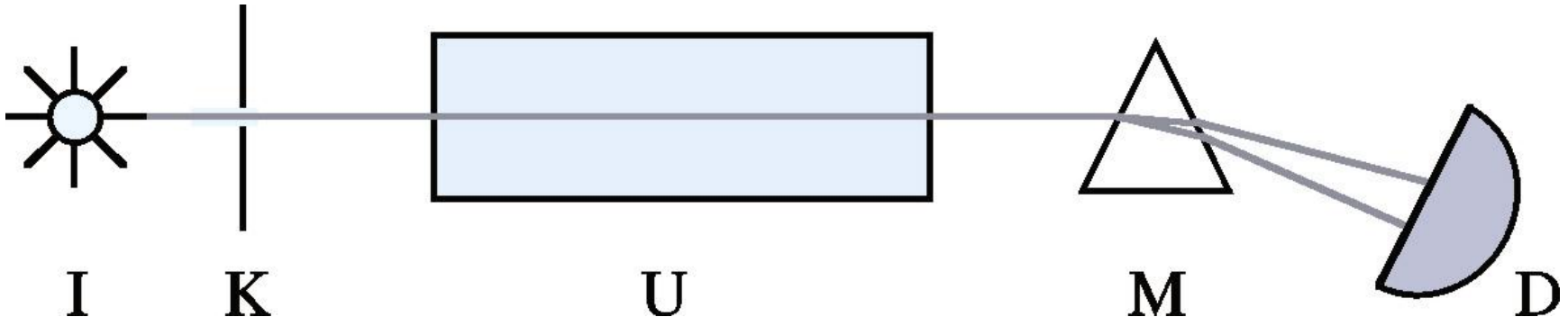
$$1 = \rho + \alpha + \tau$$

reflektancija apsorptancija transmitancija

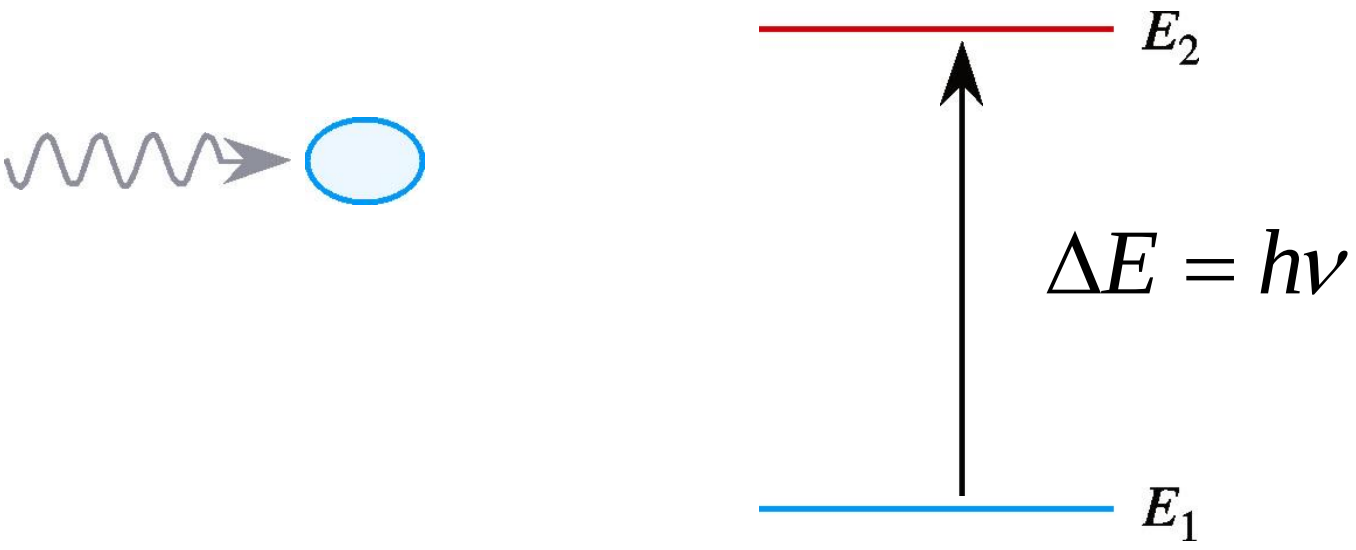
Apsorbancija

$$A = \log\frac{I_0}{I_t} = -\log\tau$$

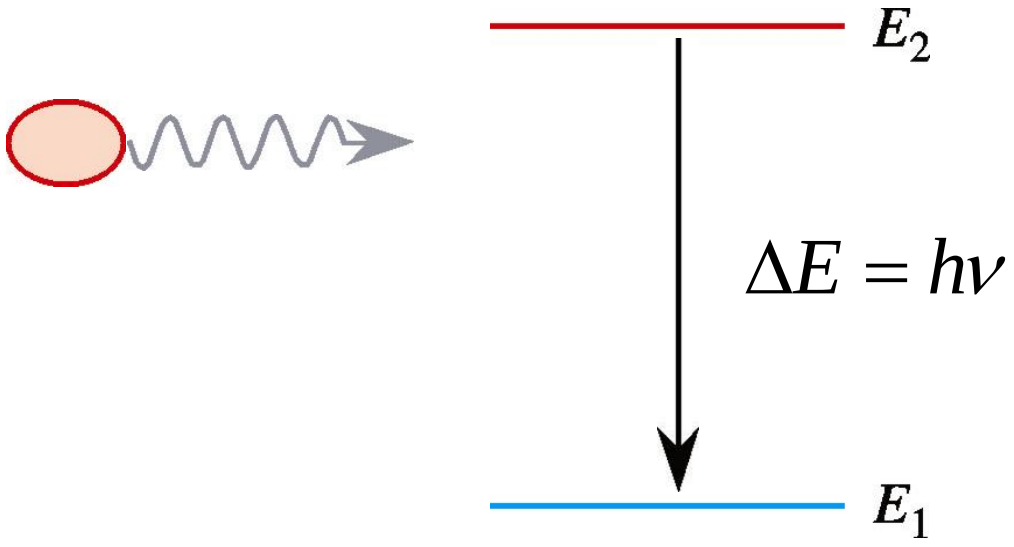
Uređaj za ispitivanje apsorpcije EMZ



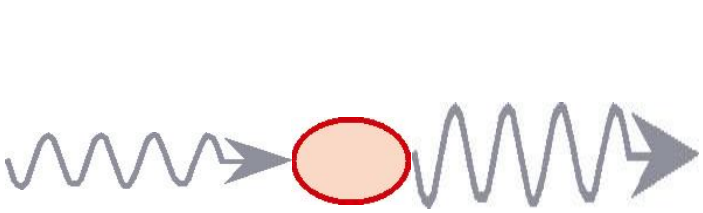
Apsorpcija

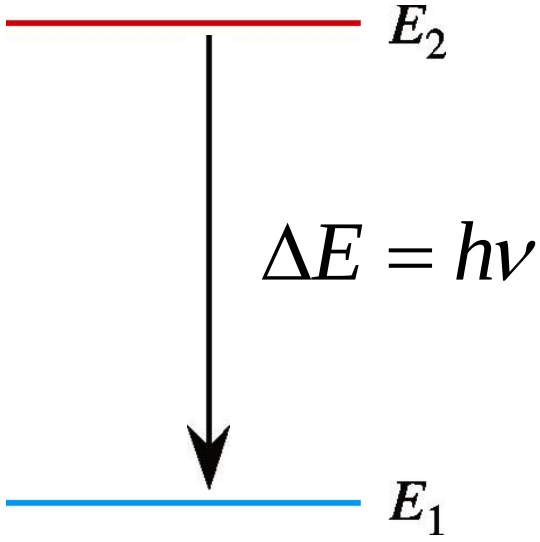


Spontana emisija

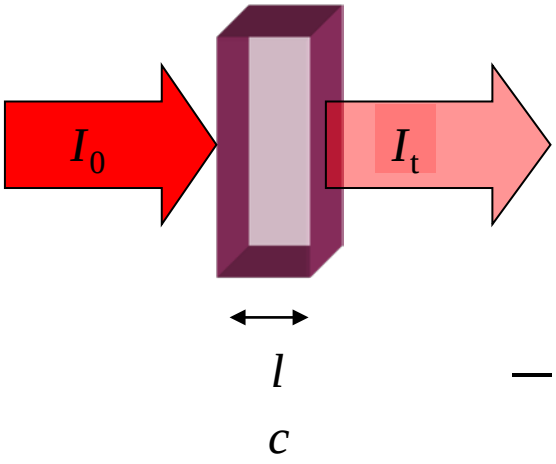


Inducirana (stimulirana) emisija





Lambert- Beerov zakon



$$-\frac{\mathrm{d}I}{\mathrm{d}l} = \kappa c I$$

$$-\frac{\mathrm{d}I}{I} = \kappa c \mathrm{d}l$$

$$-\int_{I_0}^{I} \frac{\mathrm{d}I}{I} = \kappa c \int_{0}^{l} \mathrm{d}l$$

$$-\ln(I)\,]_{I_0}^{I_t} = \kappa c l\,]_0^l$$

$$\ln\left(\frac{I_0}{I_t}\right) = \kappa c l$$

$$I = I_0 \exp\left[-\kappa c l\right]$$

(indeks t se izostavlja, podrazumijeva se)

$$e^x = y \rightarrow x = \ln y$$

$$\log(e^x) = \log(y)$$

$$x\log(e) = \log(y)$$

$$\ln y \log(e) = \log(y)$$

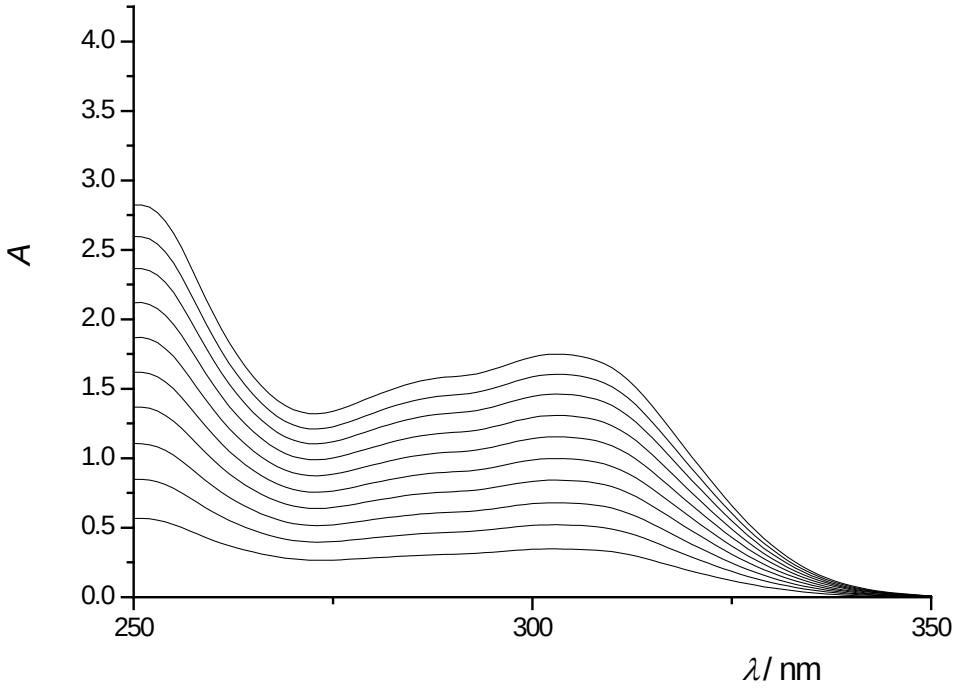
$$\ln y = \frac{\log(y)}{\log(e)}$$

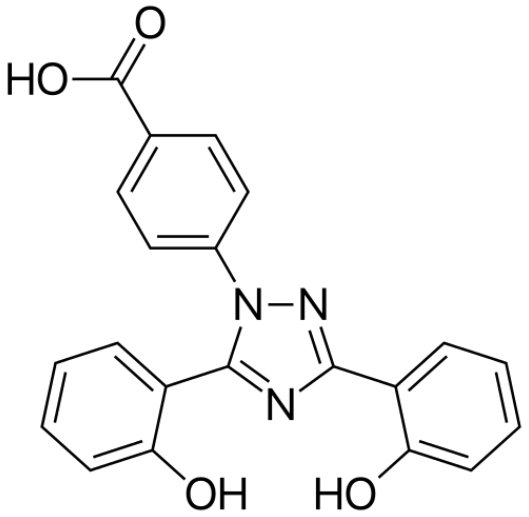
$$\log\left(\frac{I_0}{I_t}\right) = \log(e)\kappa c l$$

$$\log\left(\frac{I_0}{I_t}\right) = \varepsilon c l$$

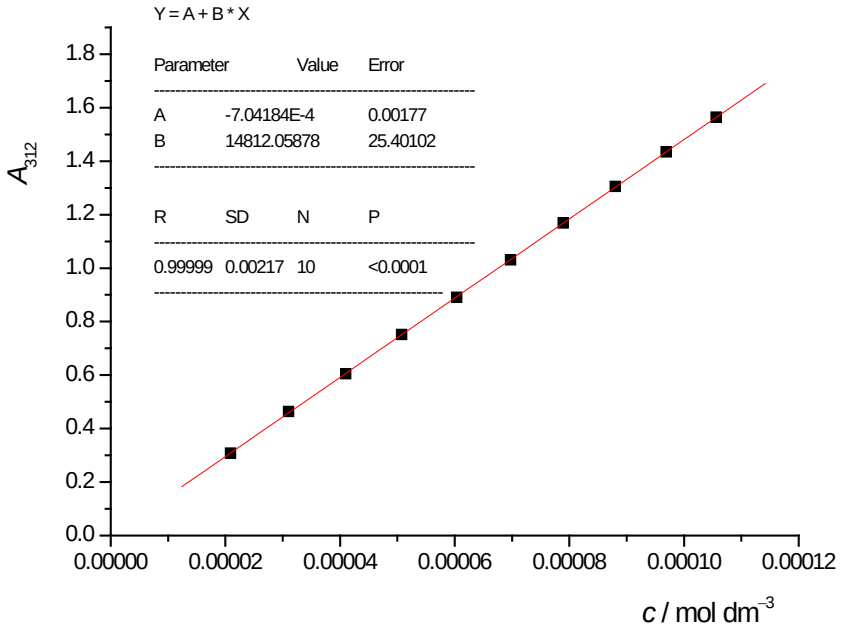
$$A = \log\frac{I_0}{I} = -\log\tau$$

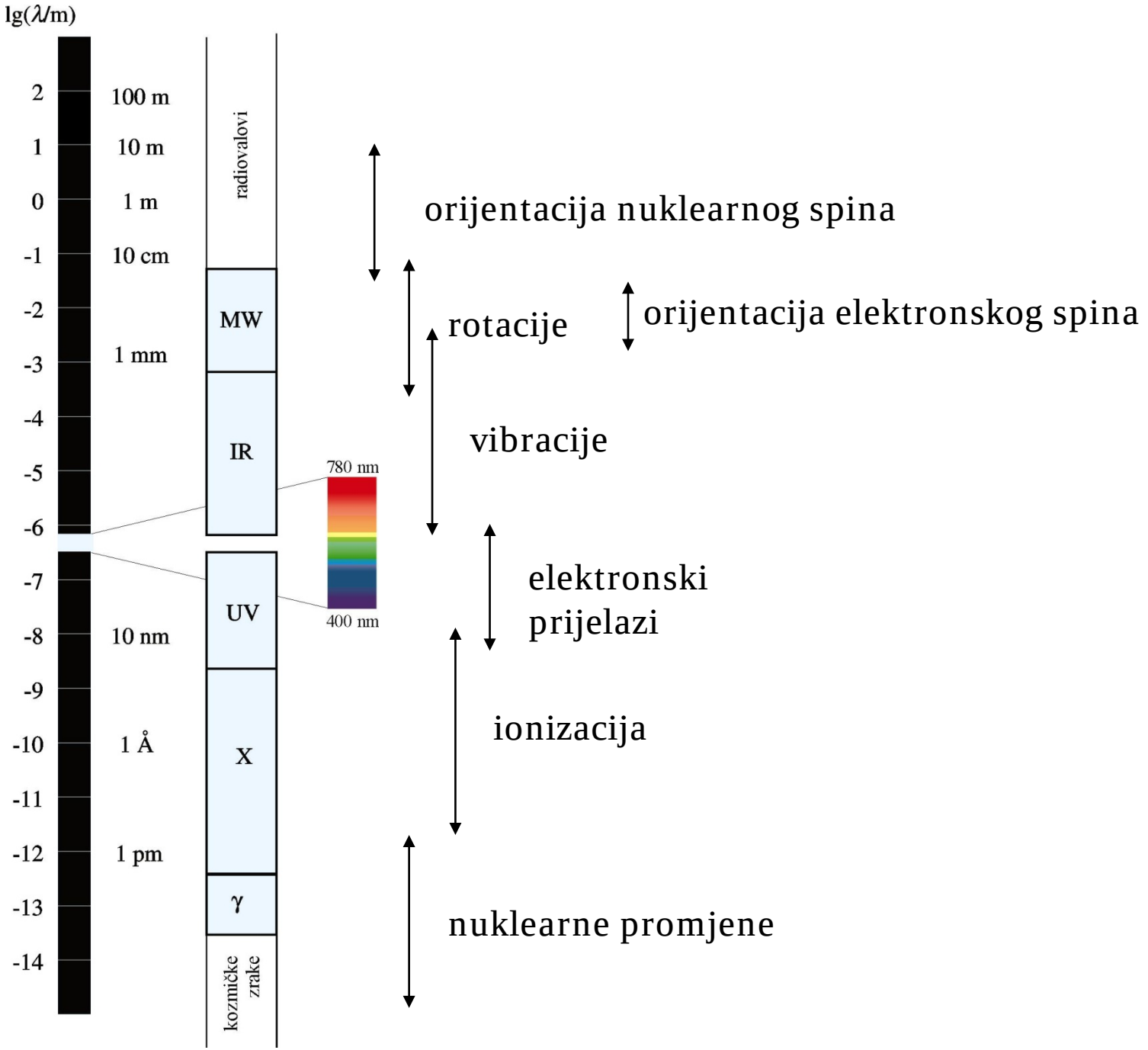
http://www.chm.davidson.edu/vce/Spectrophotometry/EffectOfConcentration.html





$$A = \varepsilon c l$$




lg(λ/m)
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
100 m
10 m
1 m
10 cm
1 mm
10 nm
1 Å
1 pm
radiovalovi
MW
IR
UV
X
γ
kozmičke zrake
780 nm
400 nm
orijentacija nuklearnog spina
rotacije
orijentacija elektronskog spina
vibracije
elektronski prijelazi
ionizacija
nuklearne promjene

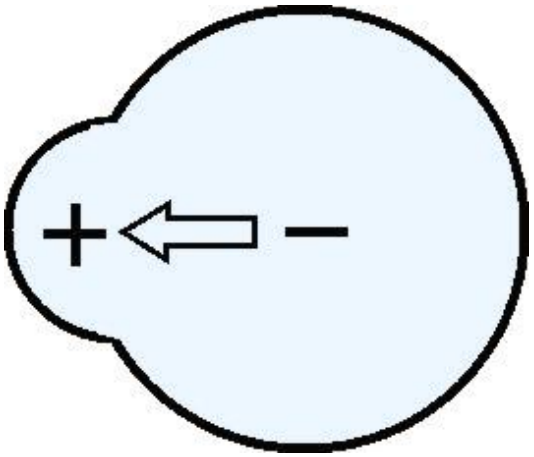
Interakcija EMZ i molekula

- interakcija električnog polja zračenja i električnog dipolnog momenta

- interakcija zračenja i magnetskog dipolnog momenta

- interakcija zračenja i električnog kvadrupolnog momenta

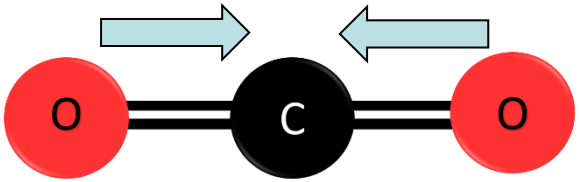
Električni dipolni moment



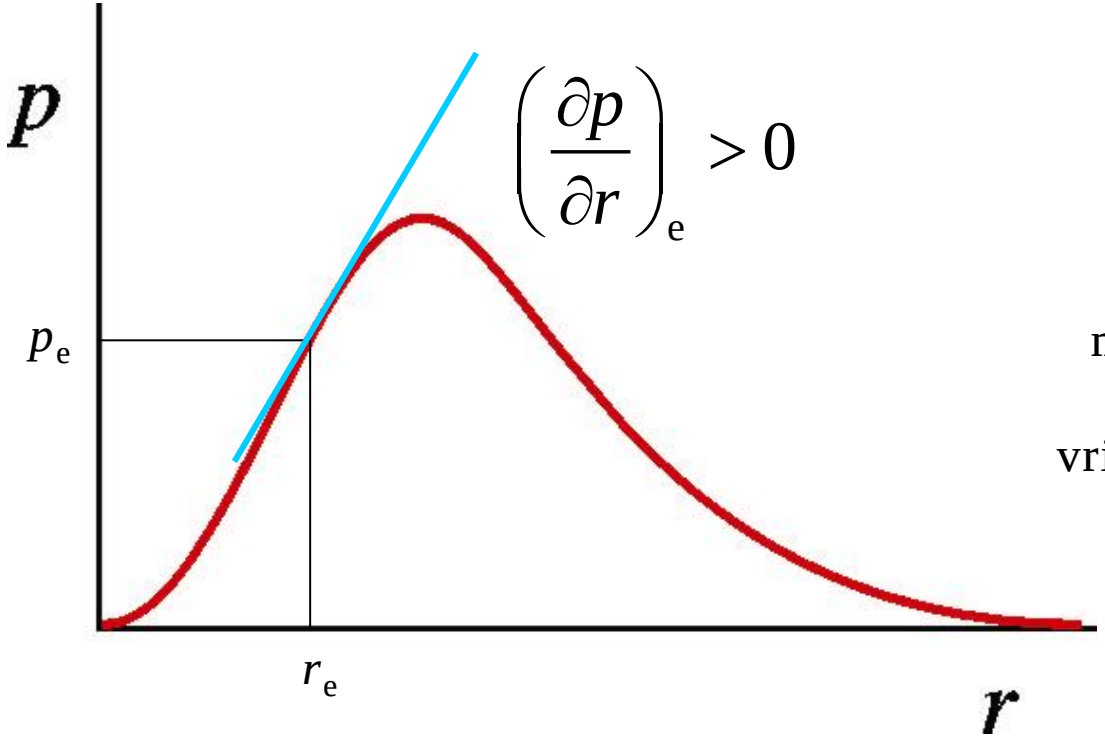
HCl

$$\vec{p} = \sum_i Q_i \vec{r}_i$$

Električni dipolni moment
je vektor iznosa
$p = Qr$
usmjeren od
težišta negativnog prema
težištu pozitivnog naboja



CO2



Električni dipolni moment heteronuklearne dvoatomne molekule ovisi o internuklearnoj udaljenosti a pri ekstremnim vrijednostima ($r = 0$ i $r = \infty$) jednak je nuli.

Herzov oscilator – klasični model izvora EMZ

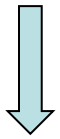
EMZ se odašilje u prostor jednakom frekvencijom kojom titraju električni naboji, a intenzitet zračenja ovisi o promjeni dipolnog momenta.

- prijelazni moment R_{12}

$$R_{12} = \int_{\tau} \psi_2 \hat{p} \psi_1 \mathrm{d}\tau$$

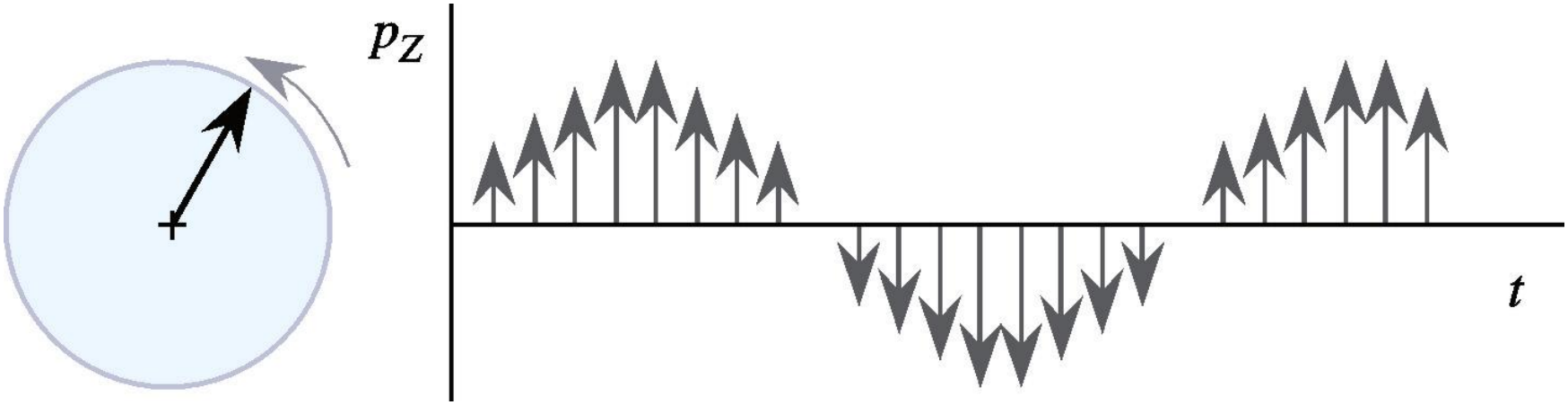
ψ_2, ψ_1 - rješenja vremenski ovisne Schrödingerove jednadžbe

zabranjeni prijelaz $1 \rightarrow 2$ $R_{12} = 0$
dozvoljeni prijelaz $1 \rightarrow 2$ $R_{12} \neq 0$



IZBORNA PRAVILA (razlika kvantnih brojeva dvaju stanja za koje prijelazni dipolni moment nije nula)

Rotacija molekula



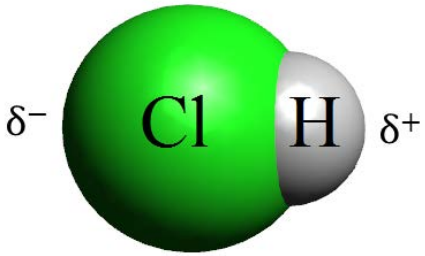
-Molekule koje imaju stalni dipolni moment

- rotacijom dolazi do interakcije s EMZ koja dovodi do apsorpcije ili emisije

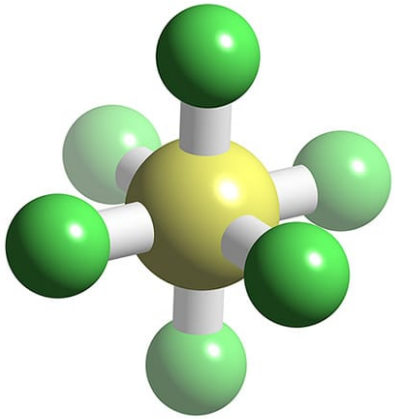
- rotacijski spektri- **molekule moraju imati stalni dipolni moment!**

Rotacija molekula

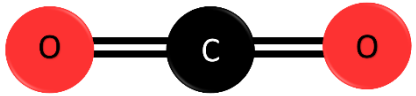
H–Cl



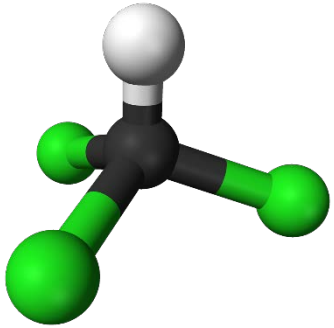
SF_6



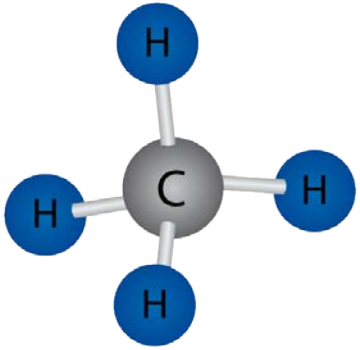
O=C=O



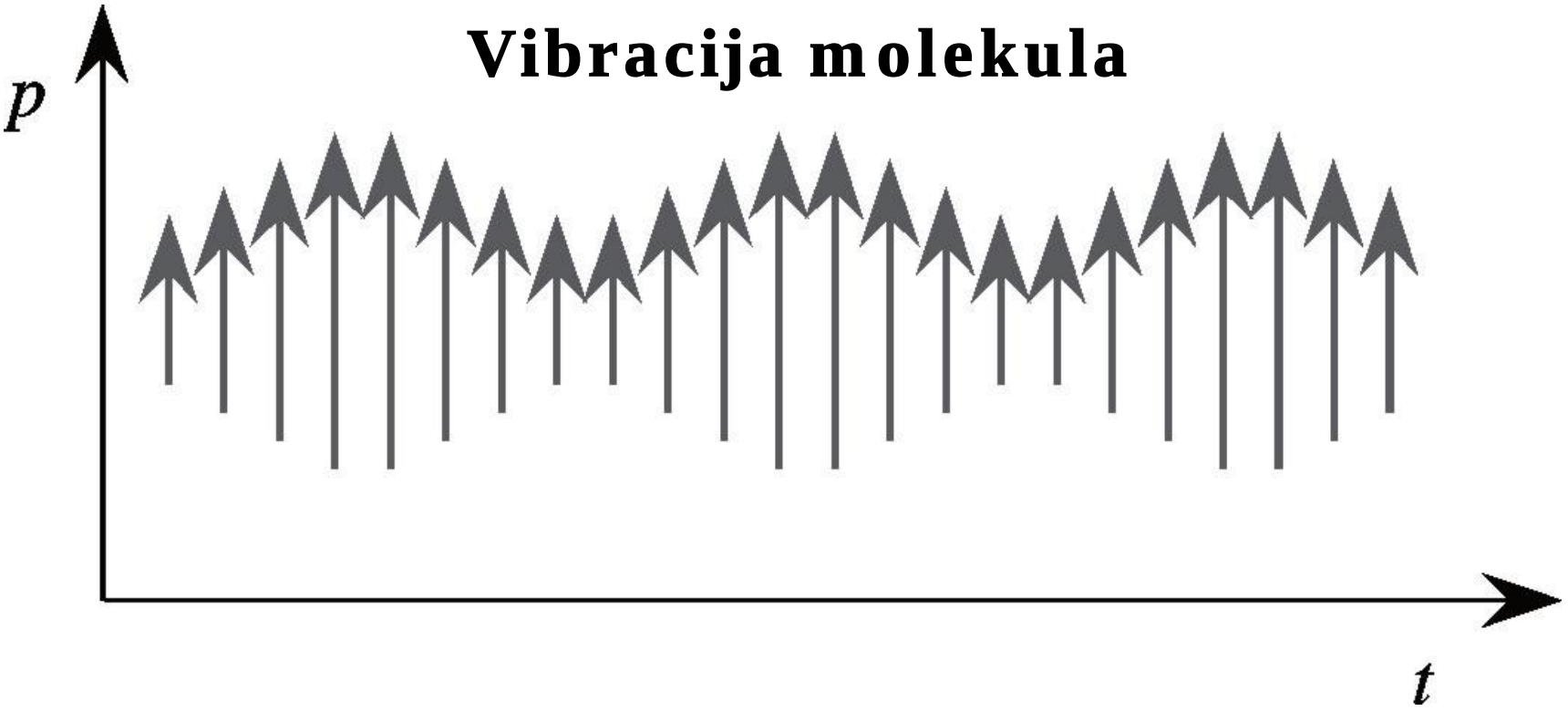
$CHCl_3$



CH_4



Vibracija molekula



-vibracija (gibanje jezgara u molekuli) uzrokuje promjenu internulkearne udaljenosti i dipolnog momenta

- dolazi do interakcije s EMZ koja dovodi do apsorpcije ili emisije

- vibracijski spektri – **tijekom vibracije mora se mijenjati dipolni moment molekule!**

Energije molekula

Molekula s *N* atoma - $3N$ koordinata

NELINEARNE MOLEKULE

3*N* načina gibanja
3 koordinate za translaciju
3 koordinate za rotaciju

3N-6 koordinate za vibracije

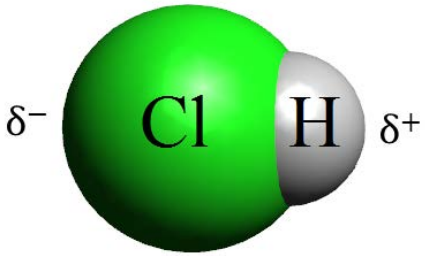
LINEARNE MOLEKULE

3*N* načina gibanja
3 koordinate za translaciju
2 koordinate za rotaciju

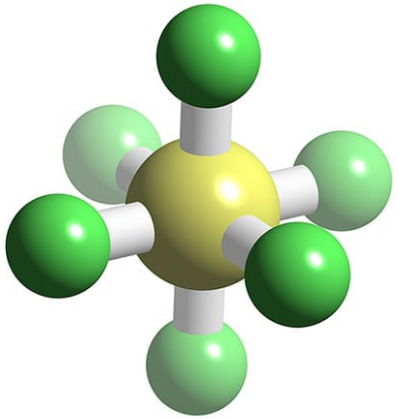
3N-5 koordinate za vibracije

Vibracija molekula

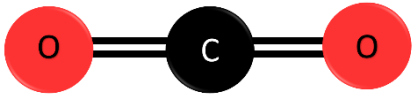
H–Cl



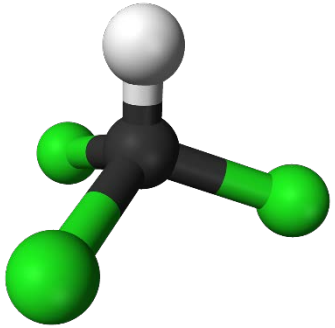
SF_6



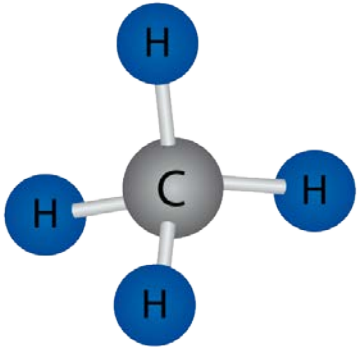
O=C=O



$CHCl_3$



CH_4

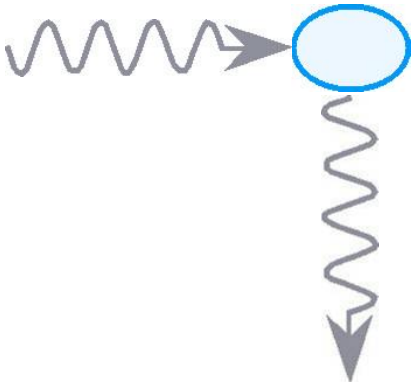


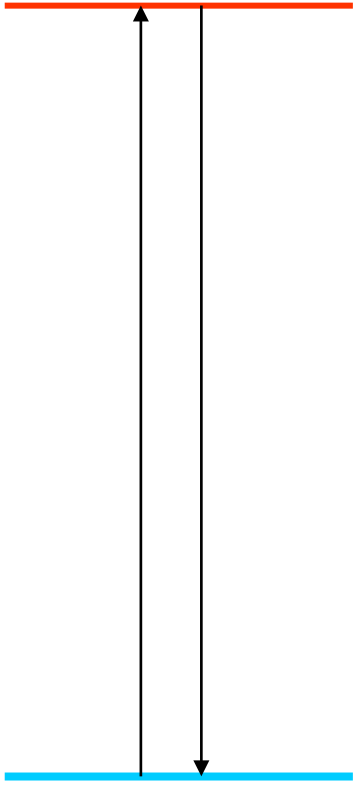
Elektronski spektri

- vjerojatnost prijelaza iz jednog elektronskog stacionarnog stanja u drugo
- prijelazni moment $R_{12} \neq 0$

(vrijedi za neka elektronska stanja a za druga ne, ne postoje jednostavna izborna pravila)

Raspršenje (Rayleighovo-elastično)

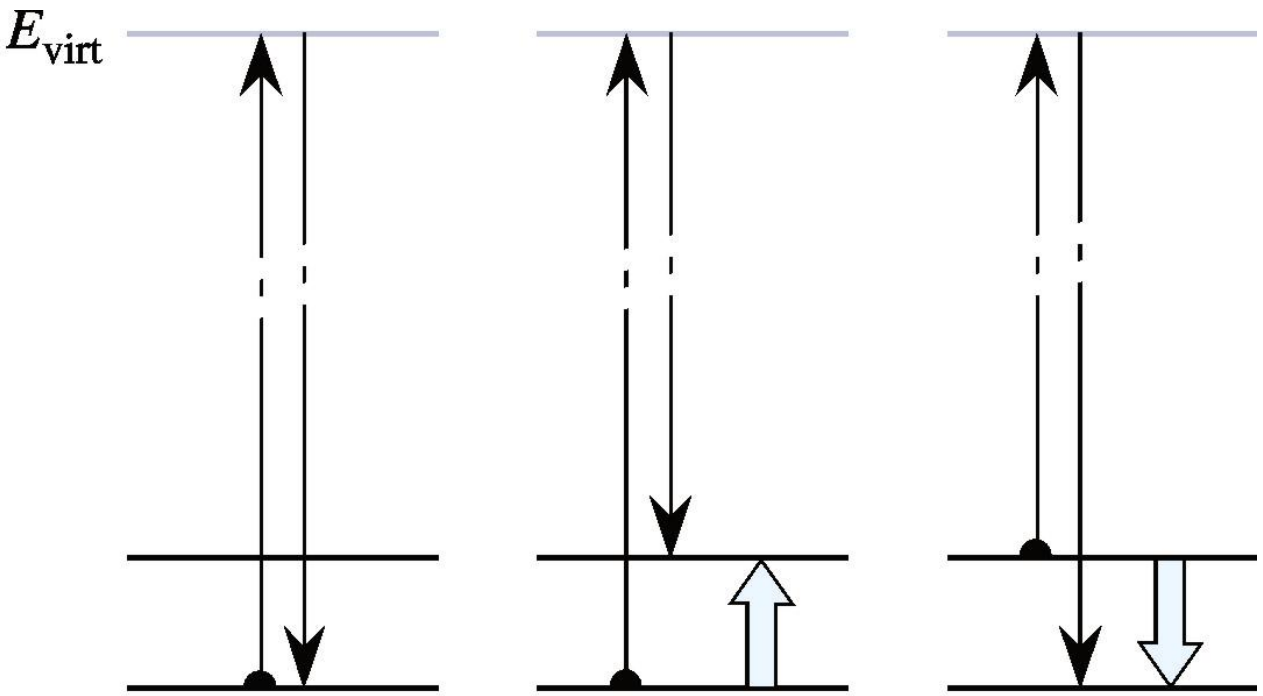




RASPRŠENJE ZRAČENJA NA MOLEKULAMA

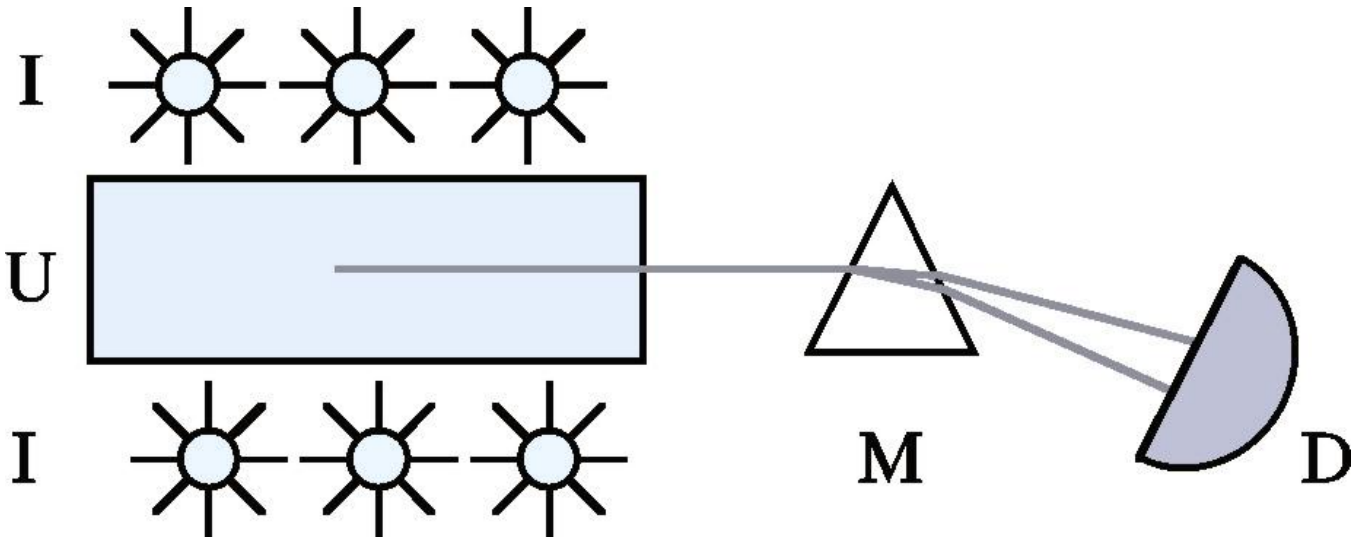
Rayleigh **Raman**

Stokes anti-Stokes

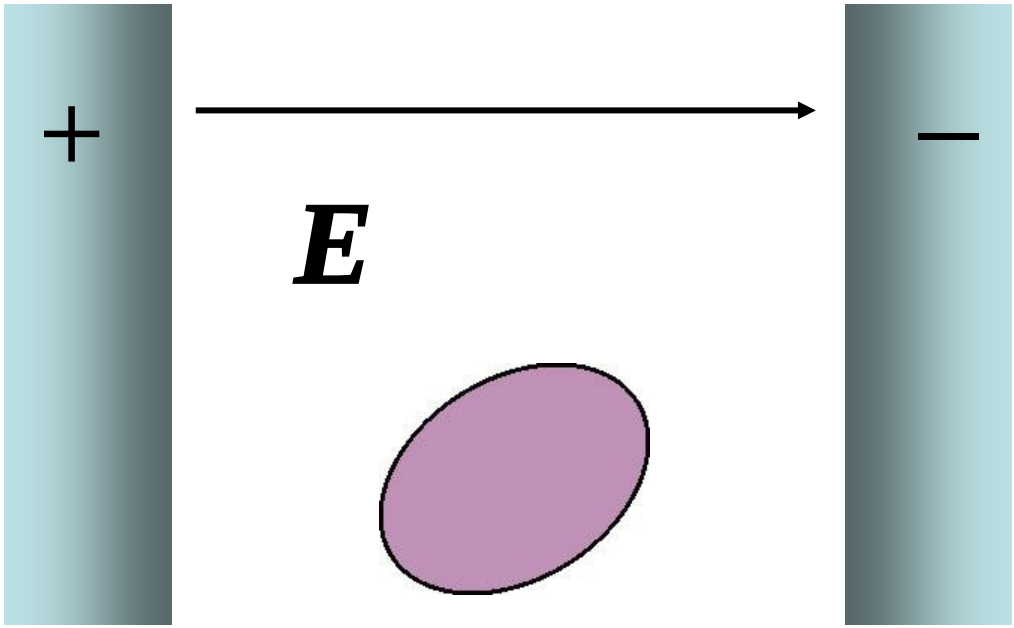


molekula:	$E_{\text{kon}} = E_{\text{poč}}$	$E_{\text{kon}} > E_{\text{poč}}$	$E_{\text{kon}} < E_{\text{poč}}$
foton:	$\nu_r = \nu_0$	$\nu_r < \nu_0$	$\nu_r > \nu_0$

Uređaj za ispitivanje raspršenja EMZ

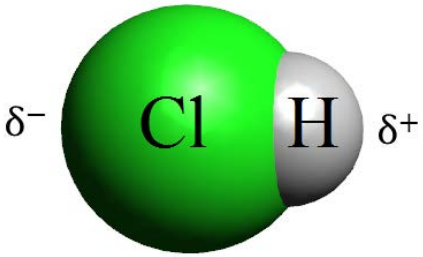


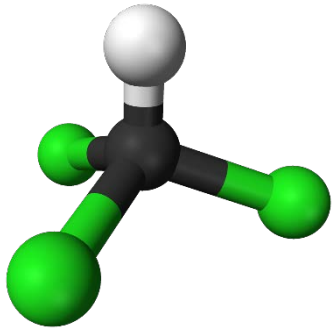
Polarizabilnost

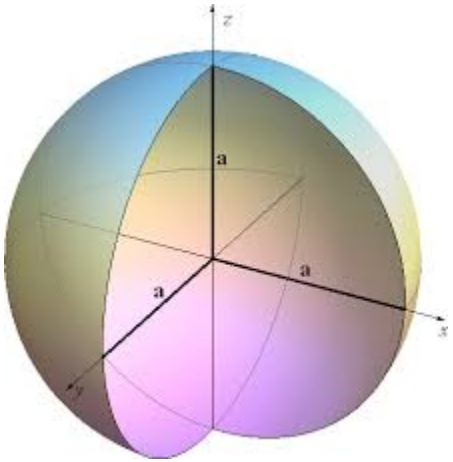


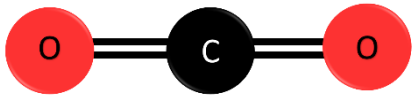
$$\boldsymbol{p}_{\mathrm{i}} = \boldsymbol{\alpha E}$$

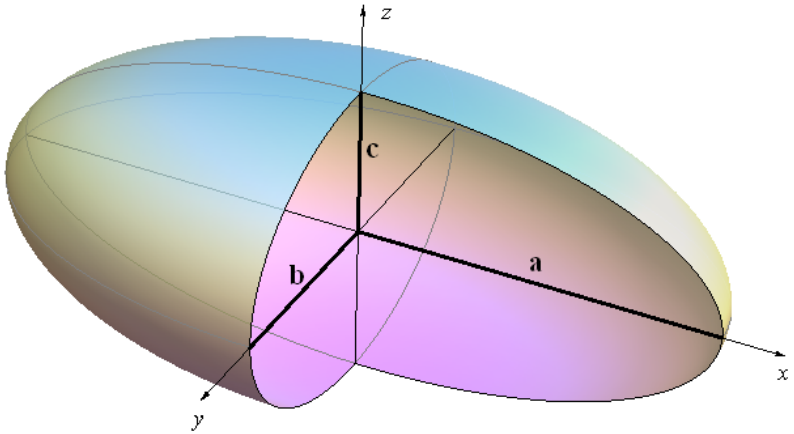
$$P_{12} = \int_{\tau} \psi_2 \hat{a} \psi_1 \mathbf{d}\tau$$

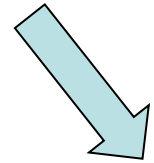


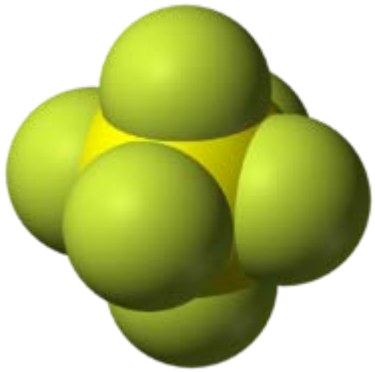


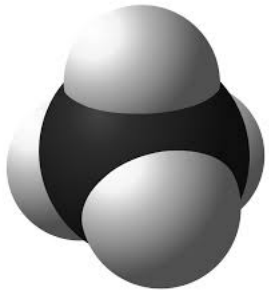












Rotacijski RAMAN- molekule moraju biti anizotropno polarizabilne
Vibracijski RAMAN- polarizabilnost se tijekom vibracije mora mijenjati

Pitanja za ponavljanje

1. Što je elektromagnetsko zračenje?
2. Što je valni broj?
3. Nabrojite područja elektromagnetskog zračenja.
4. Koje se promjene zbivaju kod molekula u tim područjima energije?
5. Kako glasi Lambert-Beerov zakon?
6. Što je apsorpcija, spontana i inducirana emisija?
7. Koji je smjer dipolnog momenta?
8. Kako se mijenja dipolni moment s internuklearnom udaljenošću heteronuklearne dvoatomne molekule?
9. Zašto homonuklearne dvoatomne molekule ne apsorbiraju infracrveno zračenje?
10. Koje molekule nemaju apsorpcijske rotacijske spektre?
11. Koji je najčešći tip interakcije zračenja i molekula?
12. Što su izborna pravila?
13. Kako zapažamo raspršenje zračenja?
14. Objasnite Raygleighevo i Ramanovo raspršenje kvalitativnim opisom zračenja.
15. Koji uvjet mora biti zadovoljen da dođe do Ramanova raspršenja?
16. Što je polarizabilnost molekule?