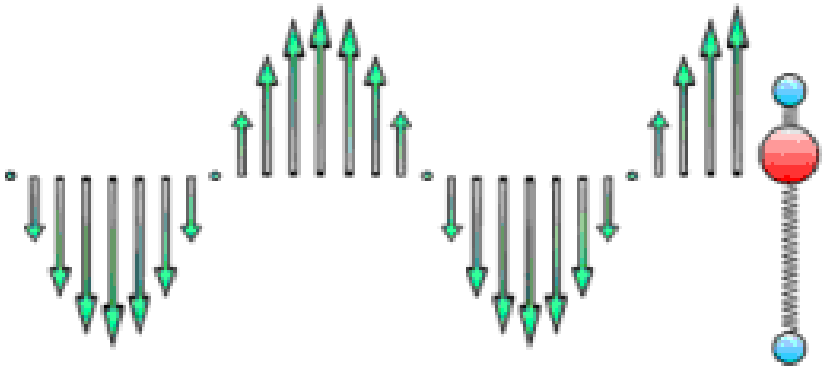
Molekulska spektroskopija
Vibracije molekula



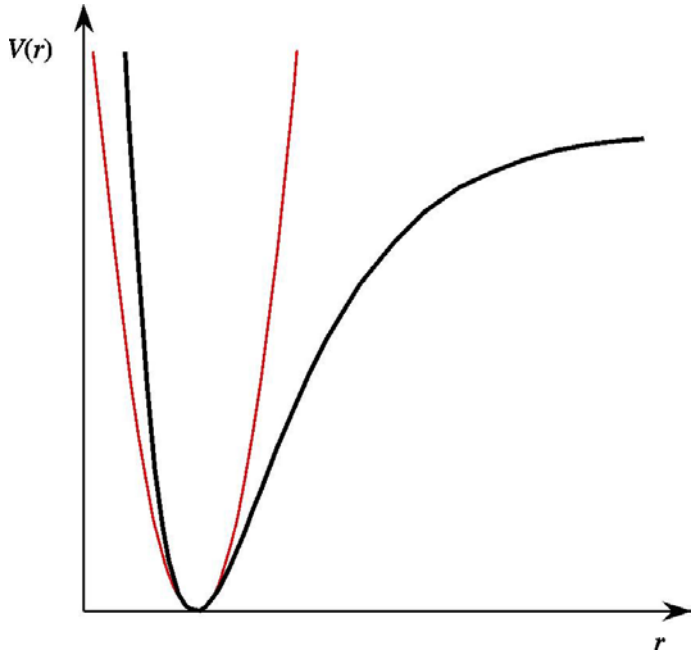
- IR – područje elektromagnetskog zračenja
  (≈ 400 cm^{-1} – 4000 cm^{-1})

Vibracije dvoatomnih molekula

- jedan stupanj slobode
- jezgre titraju oko ravnotežnih položaja
- ne dolazi do pomaka centra mase

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Gibanje dvaju čestica svodi se na gibanje jedne čestice reducirane mase μ.



Morse: potencijalna energija (za gibanje jezgara- vibraciju molekule)

$$V(x) = hcD_e \left\{1 - e^{-\beta(r-r_e)}\right\}^2$$

$$V(x) \approx \frac{1}{2}kx^2$$

(u blizini ravnotežnog položaja tj minimuma potencijalne energije)

Harmonijski oscilator

I. Klasični hamiltonijan $$H = T + V = \frac{p^2}{2\mu} + \frac{kx^2}{2}$$

II. Kvantnomehanički hamiltonijan $$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{kx^2}{2}$$

III. Schrödingerova jednadžba $$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\Psi_\mathrm{v}}{\mathrm{d}x^2} + \frac{kx^2}{2}\Psi_\mathrm{v} = E_\mathrm{v}\Psi_\mathrm{v}$$

IV. Rješenje Schrödingerove jednadžbe za Harmonijski oscilator

Energija $E_v = h\nu_e\left(v+\frac{1}{2}\right) \qquad v = 0,1,2,\ldots$

Klasična frekvencija titrala $\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Klasični valni broj HO $\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

Vibracijski term $G(v) = \frac{E_v}{hc} = \omega_e\left(v+\frac{1}{2}\right) \qquad v = 0,1,2,\ldots$

Harmonijski oscilator –vibracijski spektar

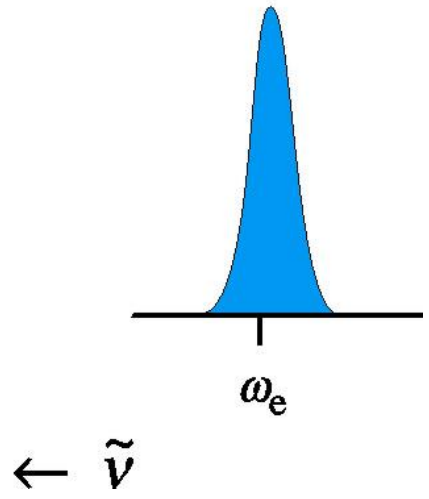
Uvjet: dipolni moment tijekom vibracije mora se mijenjati (molekula posjeduje stalni dipolni moment)

Izborno pravilo:

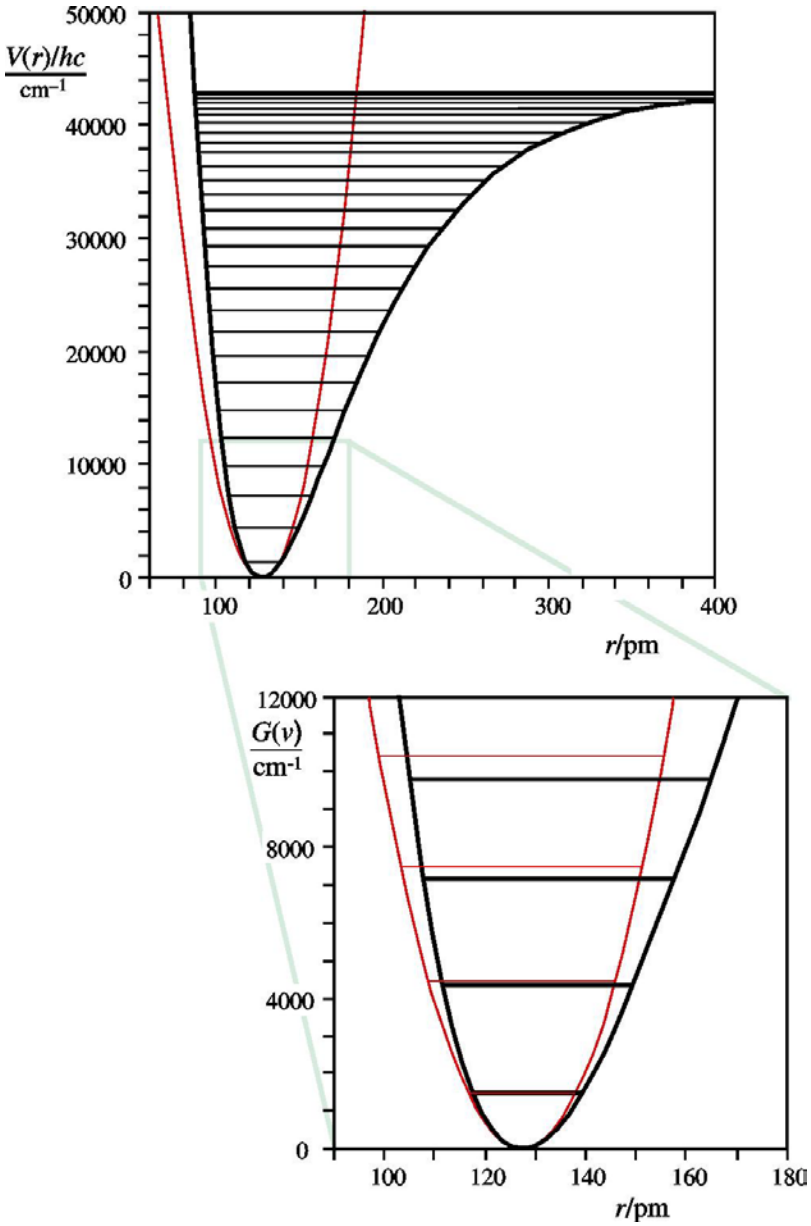
$\Delta v = 1$

Valni broj apsorbiranog zračenja:

$$\tilde{\nu} = G(v+1) - G(v) = \omega_e$$



Harmonijski i anharmonijski oscilator



Harmonijski oscilator:

jednaka razlika u energiji između dvaju susjednih stanja

Anharmonijski oscilator:

razlika u energiji između dvaju susjednih stanja smanjuje se s porastom vibracijskog kvantnog broja

Anharmonijski oscilator

Morseov potencijal $V(x) = hcD_e \left\{1 - e^{-\beta(r-r_e)}\right\}^2$

Vibracijski term $G(v) = \frac{E_v}{hc} = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 \qquad v = 0, 1, 2, \ldots$

Razlika susjednih termova

$$G(v+1) - G(v)$$

$$= \omega_e \left(v + 1 + \frac{1}{2}\right) - \omega_e x_e \left(v + 1 + \frac{1}{2}\right)^2 - \left[\omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2\right]$$

$$= \omega_e \left(v + 1 + \frac{1}{2} - v - \frac{1}{2}\right) - \omega_e x_e \left(v^2 + 3v + \frac{9}{4} - v^2 + v - \frac{1}{4}\right)$$

$$= \omega_e - 2\omega_e x_e (v+1)$$

Intenziteti linija

- ovisi o prmijeni dipolnog momenta molekule
- ovisi o napučenosti energetskih nivoa

$$N_i \propto g_i \exp\left[-\frac{E_i}{kT}\right]$$

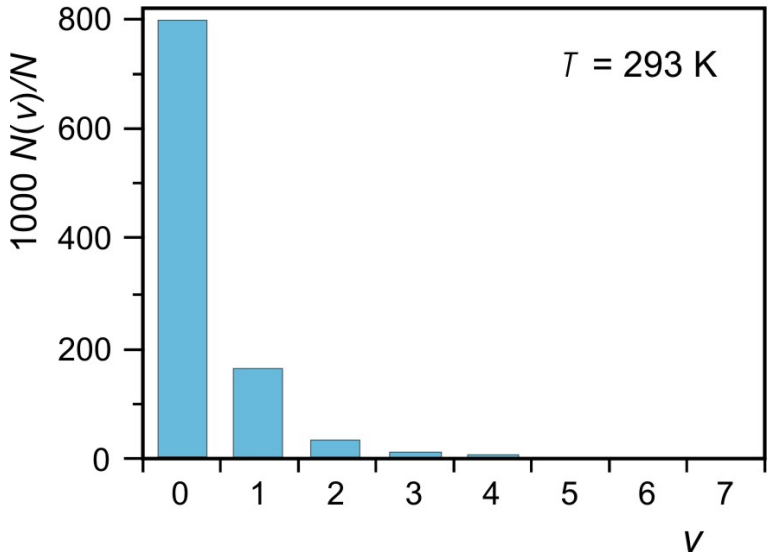
$$N_J \propto \exp\left[\frac{-E_{\text{vib}}}{kT}\right]$$

NAPUČENOST (VIBRACIJE)

$$\frac{N(v')}{N(v'')} = \frac{g(v')}{g(v'')} \exp\left(-\frac{\varepsilon(v') - \varepsilon(v'')}{kT}\right)$$

$g(v')$ $g(v'')$ Degeneracija vibracijskih stanja v' i v''

$\varepsilon(v') - \varepsilon(v'')$ Razlika u energiji vibracijskih stanja v' i v''

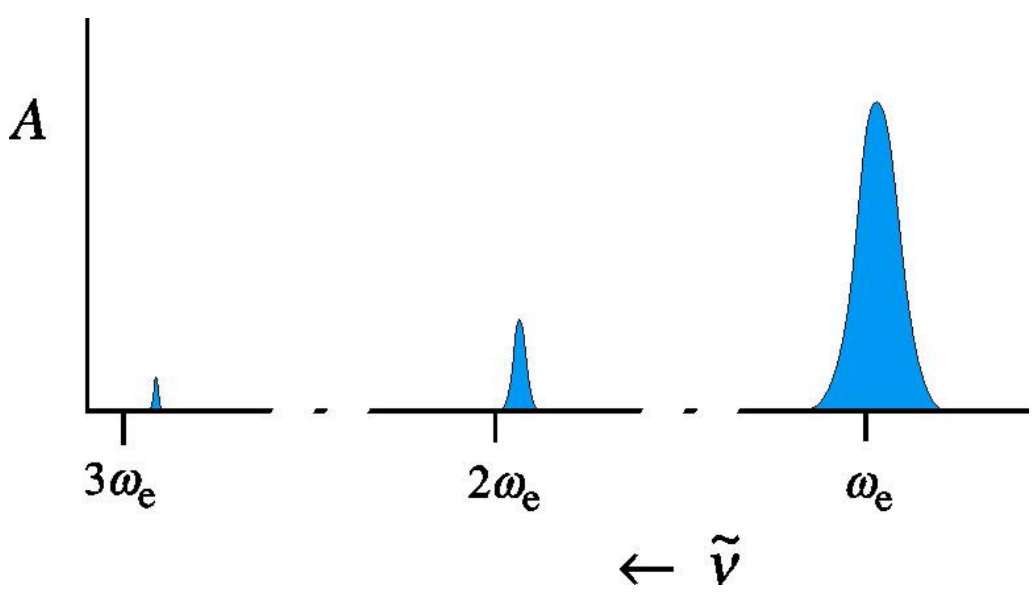


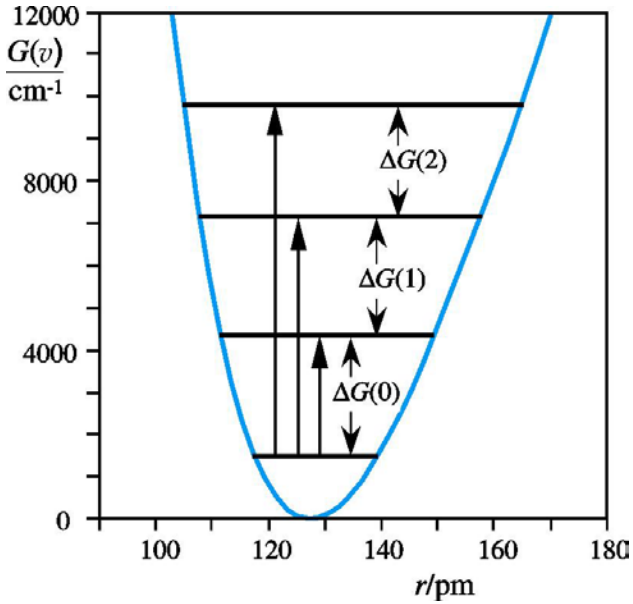
Br_2

Vibracijski spektar anharmonijskog oscilatora

Uvjet: dipolni moment tijekom vibracije mora se mijenjati (molekula posjeduje stalni dipolni moment)

– izborno pravilo: $\Delta v = 1, 2, 3, \ldots$





U vibracijskom spektru nalazimo više VRPCI:
-osnovna vrpca
-gornji ili viši tonovi
-vruće vrpce

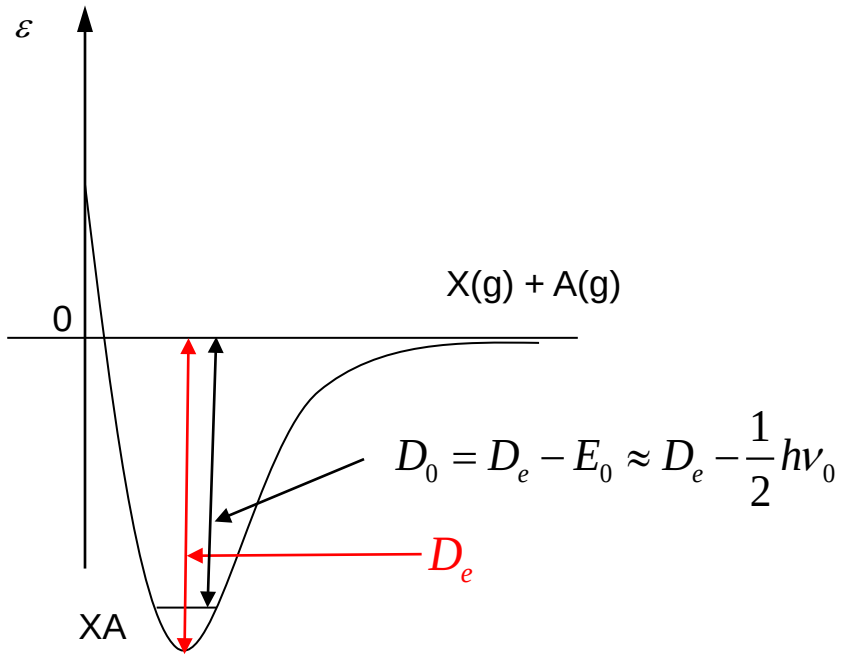
Vibracije dvoatomnih molekula –energija disocijacije

$$\Delta G(v) = G(v+1) - G(v) = \omega_e - 2\omega_e x_e (v+1) = 0$$

$$2\omega_e x_e (v_{max} + 1) = \omega_e$$

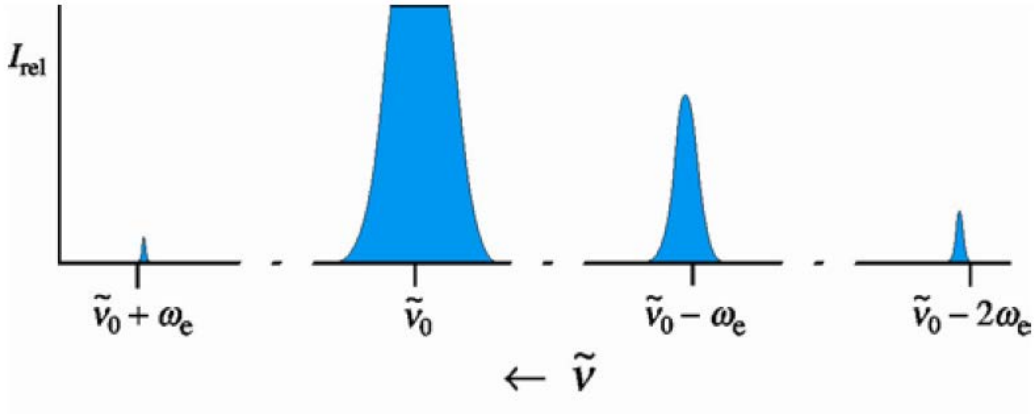
$$v_{max} = \frac{1}{2x_e} - 1$$

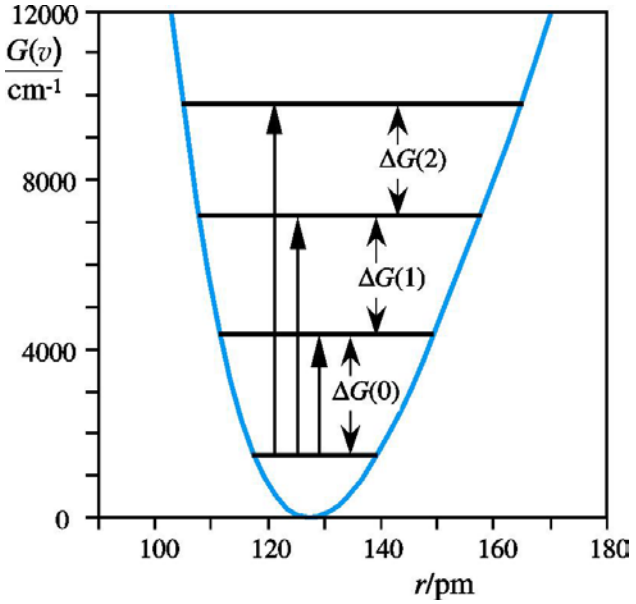
$$D_e = hcG(v_{max}) \approx hc\frac{\omega_e}{4x_e}$$



Vibracijski Ramanov spektar anharmonijskog oscilatora

izborno pravilo: $\Delta v = 1, 2, 3, \ldots$



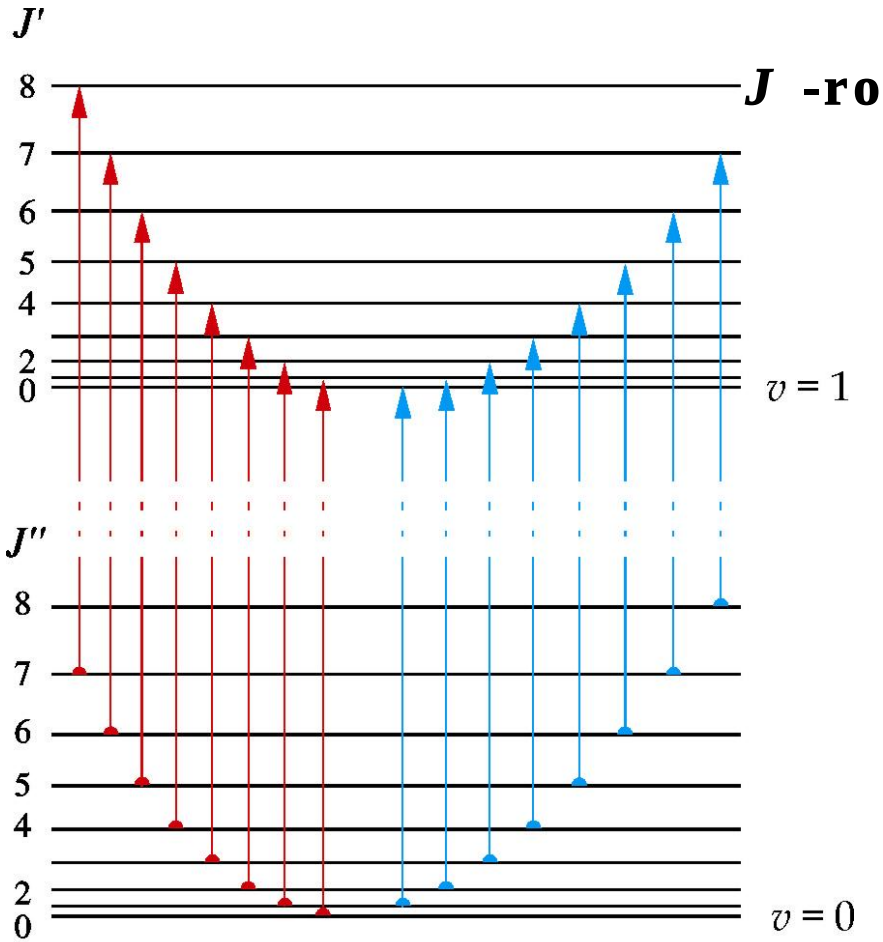


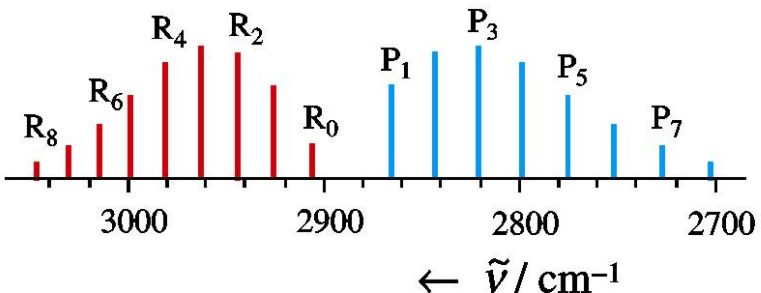
U vibracijskom spektru nalazimo više VRPCI:
-osnovna vrpca
-gornji ili viši tonovi
-vruće vrpce

Rotacijska struktura vibracijskih vrpci

$$\tilde{\nu} = \left[G'\left(v'\right) + F'\left(J'\right) \right] - \left[G''\left(v''\right) + F''\left(J''\right) \right]$$

Rotacijska struktura vibracijskih vrpci





J **-rotacijski broj u nižem vib stanju (*J*")**

$\tilde{\nu}_0$ **-valni broj za *J*' = 0 i *J*" =0**

R-grana, Δ*J* = +1

$$\tilde{\nu}_{\mathrm{R}} = \tilde{\nu}_0 + \left[F'(J') - F''(J'')\right]$$

$$\tilde{\nu}_{\mathrm{R}} = \tilde{\nu}_0 + \left[F'(J+1) - F''(J)\right]$$

$$\tilde{\nu}_{\mathrm{R}} \approx \tilde{\nu}_0 + \left[B(J+1+1)(J+1) - BJ(J+1)\right]$$

$$\tilde{\nu}_{\mathrm{R}} = \tilde{\nu}_0 + 2B(J+1); \quad J = 0,1,2,3\ldots$$

P-grana, Δ*J* = –1

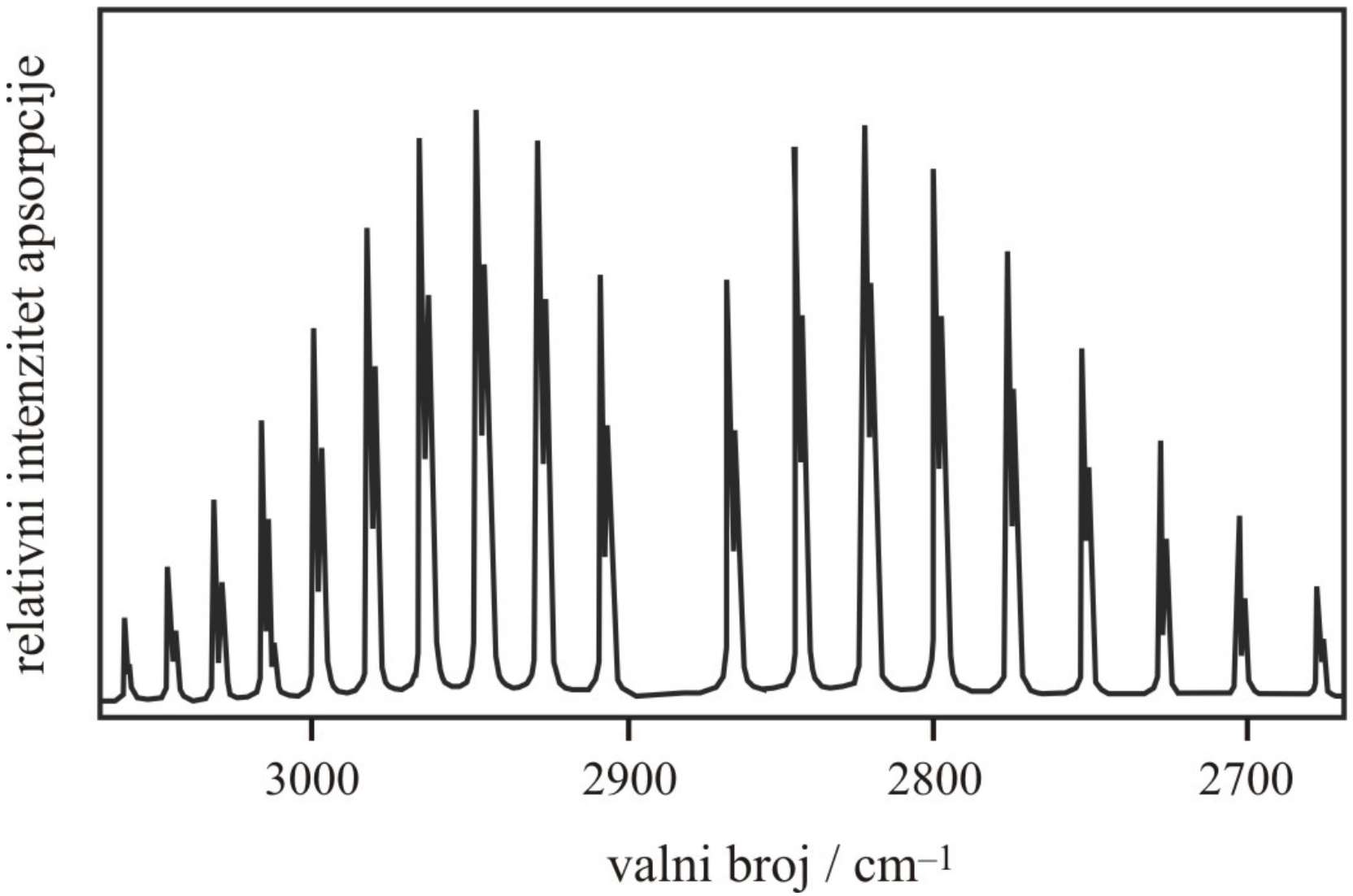
$$\tilde{\nu}_{\mathrm{P}} = \tilde{\nu}_0 + \left[F'(J') - F''(J'')\right]$$

$$\tilde{\nu}_{\mathrm{P}} = \tilde{\nu}_0 + \left[F'(J-1) - F''(J)\right]$$

$$\tilde{\nu}_{\mathrm{P}} \approx \tilde{\nu}_0 + \left[B(J-1)J - BJ(J+1)\right]$$

$$\tilde{\nu}_{\mathrm{P}} = \tilde{\nu}_0 - 2BJ, \quad J = 1,2,3,4$$

HCl



Osnovna vibracijska vrpca HCl

Informacije koje se mogu dobiti iz vibracijskih spektara dvoatomnih molekula:

- geometrija molekule
- konstanta sile
- energije disocijacije
- kemijska analiza
- Izotopni efekt $\Delta\omega_e = \omega_{e,1} - \omega_{e,2}$ $\frac{\omega_{e,1}}{\omega_{e,2}} = \sqrt{\frac{\mu_2}{\mu_1}}$

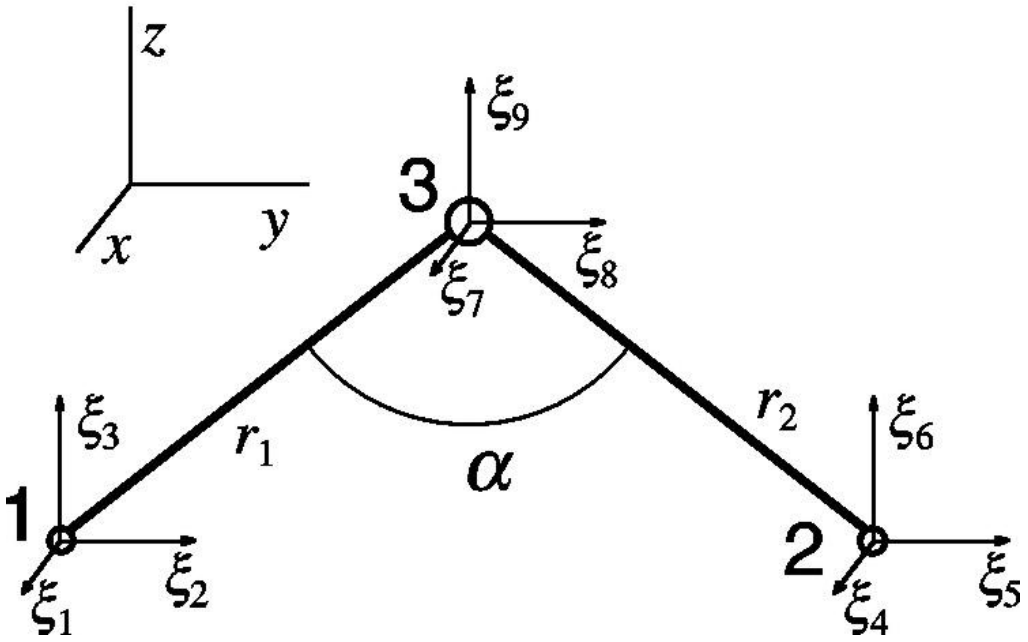
Npr. pomak linija $^{1}H^{35}Cl$ u odnosu na $^{2}H^{35}Cl$.

- rotacijska struktura (rotacijska konstanta, odnosno konstante)

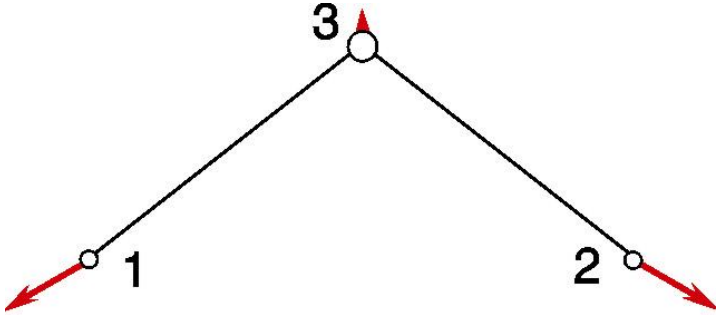
Vibracije višeatomnih molekula

- Nelinearne molekule: $3N$ - 6 načina vibriranja

- Linearne molekule: $3N$ - 5 načina vibriranja



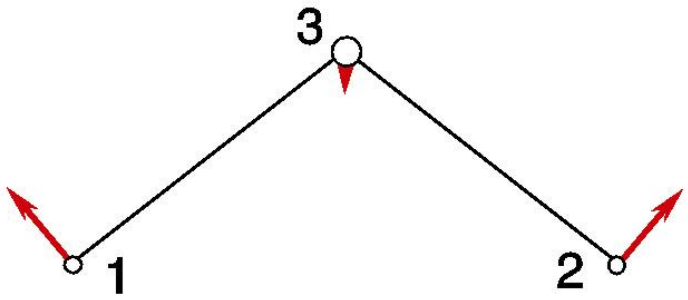
H_2O



n_1 $\tilde{\nu}_1 = 3585\ \text{cm}^{-1}$

simetrično istezanje

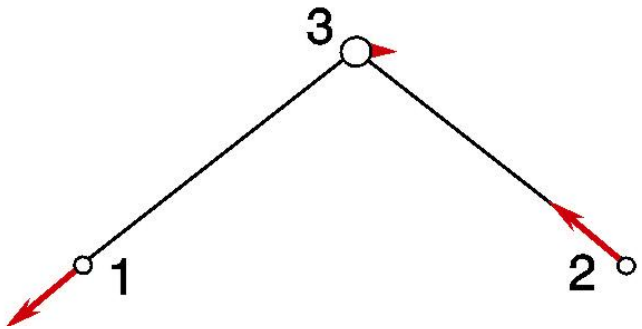
$$Q_1 = 0,719\ \delta r_1 + 0,719\ \delta r_2 + 0,009\ r_e \delta\alpha$$



n_2 $\tilde{\nu}_2 = 1885\ \text{cm}^{-1}$

deformacija kuta

$$Q_2 = -0,046\ \delta r_1 - 0,046\ \delta r_2 + 1,463\ r_e \delta\alpha$$

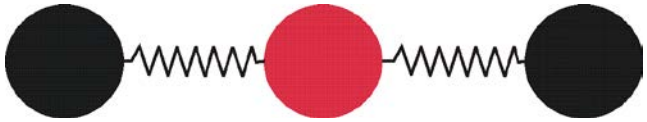


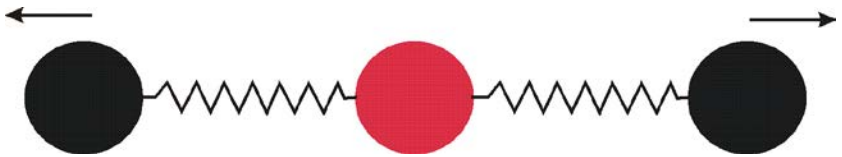
n_3 $\tilde{\nu}_3 = 3506\ \text{cm}^{-1}$

antisimetrično istezanje

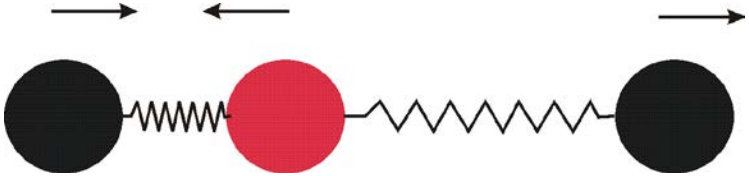
$$Q_3 = 0,732\ \delta r_1 - 0,732\ \delta r_2$$

CO_2

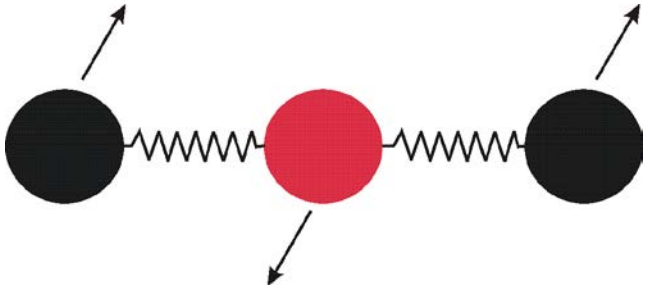




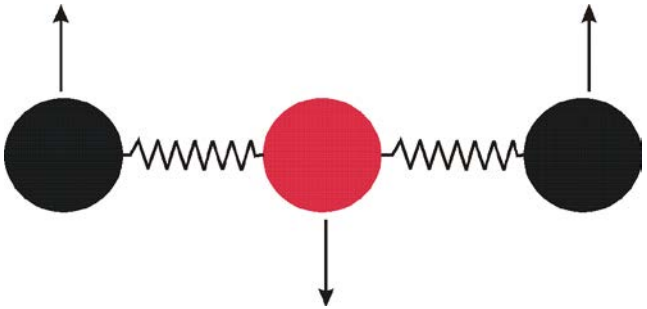
$\tilde{\nu}_1 = 1480\ \text{cm}^{-1}$



$\tilde{\nu}_2 = 2565\ \text{cm}^{-1}$



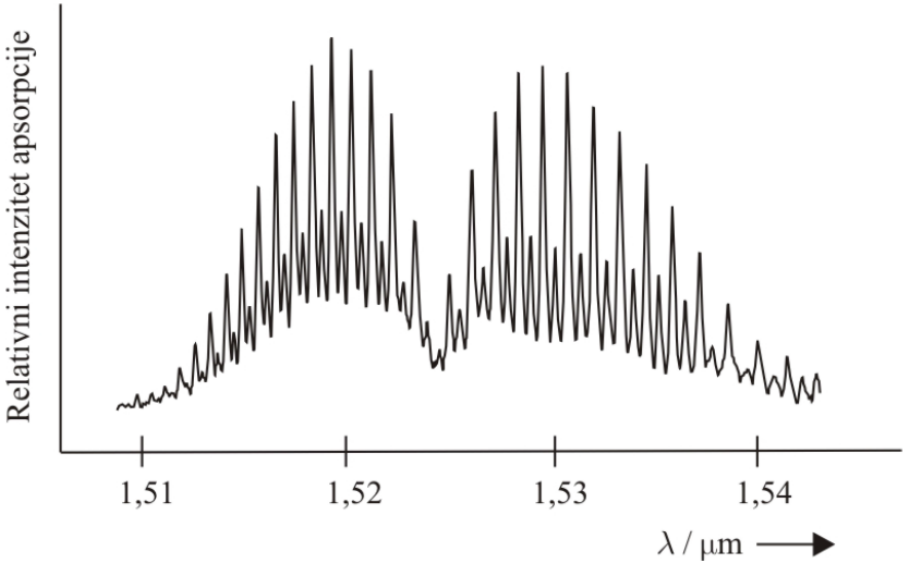
$\tilde{\nu}_3 = 526\ \text{cm}^{-1}$

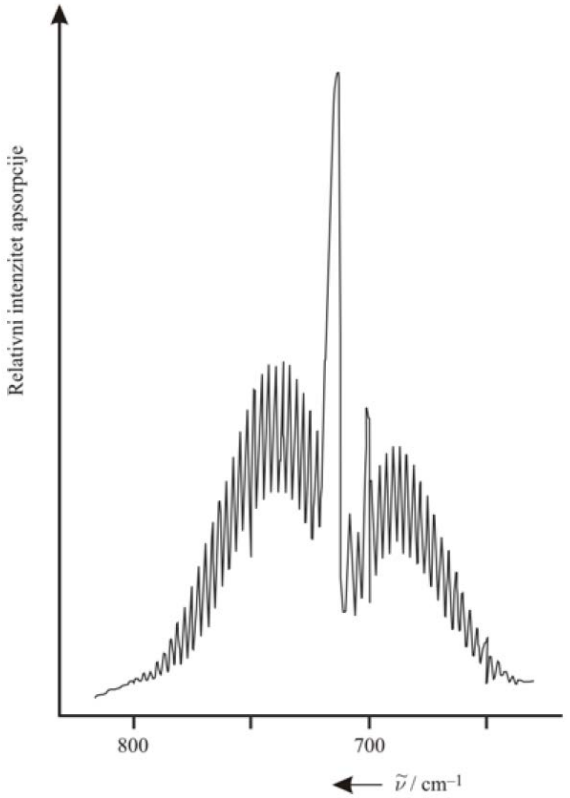


$\tilde{\nu}_4 = 526\ \text{cm}^{-1}$

Rotacijska struktura vibracijskih vrpci –višeatomne molekule

Etin (paralelna vrpca)

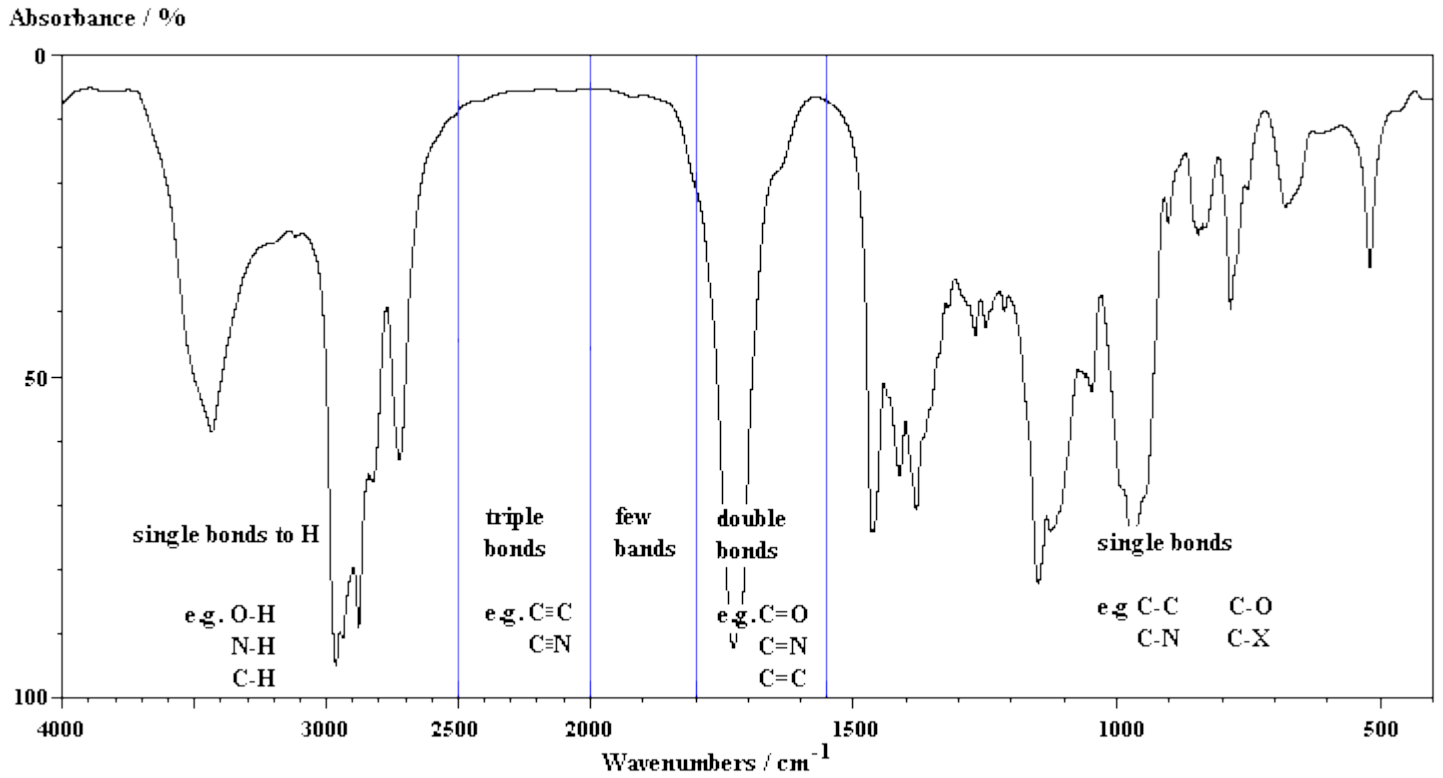




Cijanovodik (okomita vrpca)

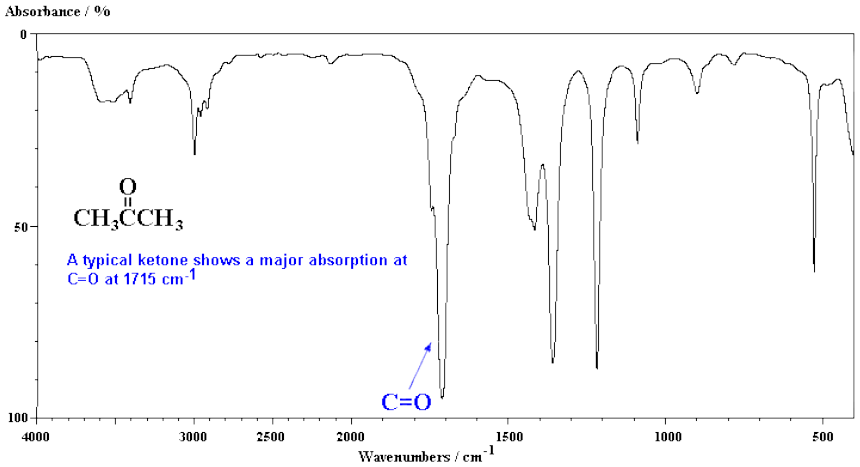
krutine – molekule ne rotiraju, međusobno interagiraju

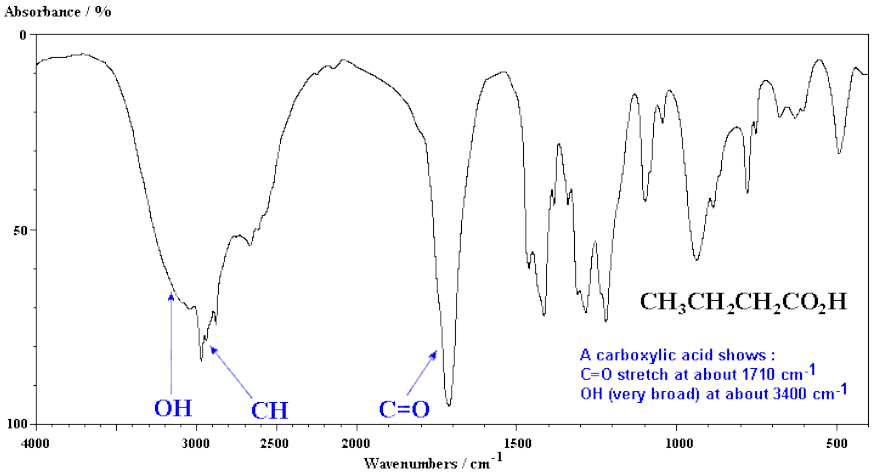
tekućine- neprekidni sudari molekula, interakcije između molekula

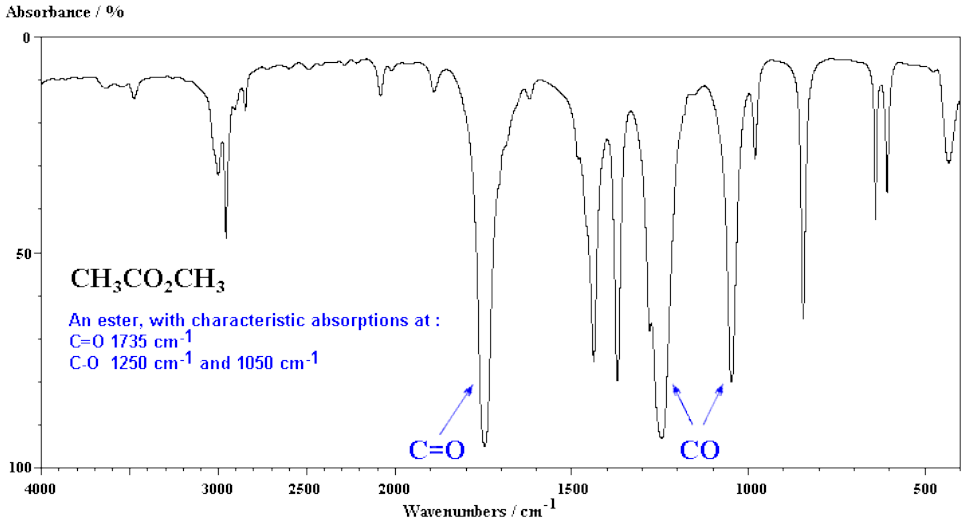


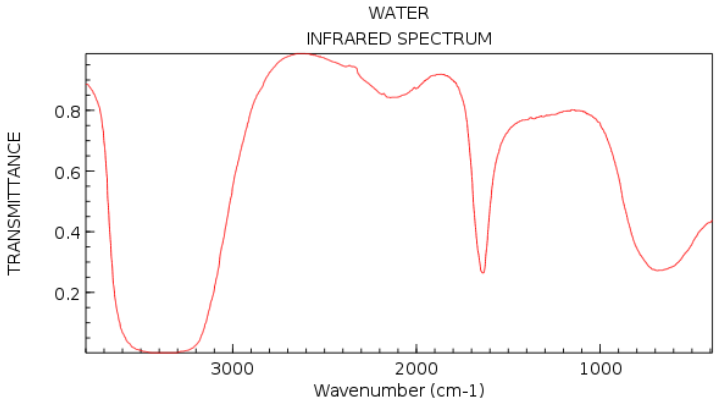
Skupina	Vibracija*	ω / cm^{-1}	Skupina	Vibracija*	ω / cm^{-1}
-CH_3	ν(CH)	2960(10)s	>CH_2	ν(CH)	2929(15)s
	ν(CH)	2870(10)s		ν(CH)	2855(10)s
	δ(HCH)	1450(20)m		δ(HCH)	1465(20)m
	δ(HCH)	1375(10)s			
=CH_2	ν(CH)	3080(10)m	RCCH	ν(CH)	3300(10)s
	ν(CC)	1650(30)v		ν(CC)	2120(20)v
	δ(HCH)i	1415(5)s			
	δ(HCH)o	900(15)s			
=CH-	ν(CH)	3025(15)m	ArH	ν(CH)	3030(10)wm
	δ(CH)o	990(5)s		δ(CH)o	730 ... 900s
>NH	ν(NH)	3400(100)	-OH	ν(OH)	3620(30)v+
	δ(NH)	m			
		1600(50)v+			
-CN	ν(CN)	2245(30)s	-CO_2H	ν(OH)	3525(25)m
				ν(CO)	1710(30)s
				ν(CO)	1420(20)w
				δ(OH)i	1260(50)s
				δ(OH)o	920(20)v
RCHO	ν(CO)	1730(10)s	>C=O	ν(CO)	1720(150)s
	δ(HCO)	780(100)w			
-N=O	ν(NO)	1550(100)s	-SH	ν(SH)	2575(25)w
-NO_2	ν(NO)	1550(60)s	-S=O	ν(SO)	1050(10)s
	ν(NO)	1330(70)s			
>SiH	ν(SiH)	2200(100)s	>C=S	ν(CS)	1120(80)s

* ν stoji za istezanje, δ za deformaciju kuta (i - u ravnini, o - izvan ravnine) Intenziteti: s = jaki; m = srednji; v = varijabilni; w = slabi; + označuje da vodikove veze mogu uzrokovati velike pomake.


Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1
CH3CCH3
O
A typical ketone shows a major absorption at
C=O at 1715 cm-1
C=O


Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1
CH3CH2CH2CO2H
A carboxylic acid shows :
C=O stretch at about 1710 cm-1
OH (very broad) at about 3400 cm-1
OH
CH
C=O

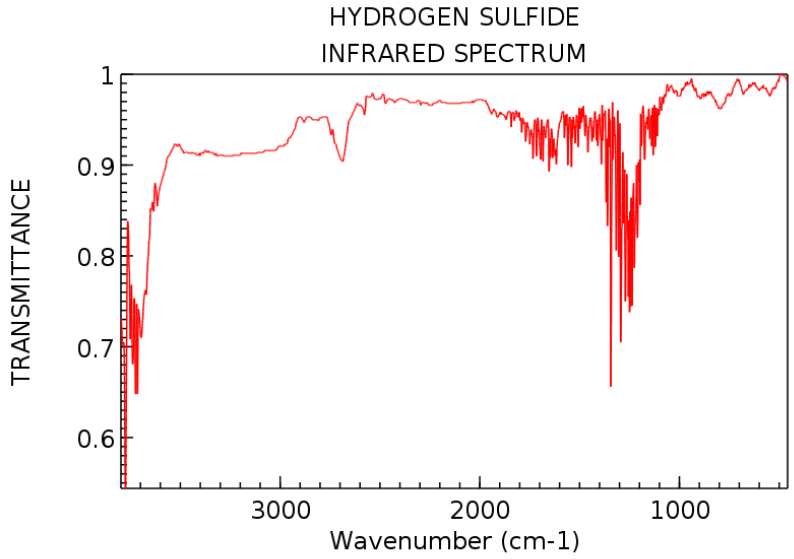

Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1
CH3CO2CH3
An ester, with characteristic absorptions at :
C=O 1735 cm-1
C-O 1250 cm-1 and 1050 cm-1
C=O
CO



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Molecule: Water H_2O No. 4
Symmetry C_{2v} Symmetry number $\sigma = 2$

Sym. species	No.	Approximate type of mode	Selected value of frequency	Infrared	Raman	Comments
				cm^{-1} (Gas)	cm^{-1} (Gas)	
a_1	ν_1	Sym. stretch	3657 A	3656.65	3654	
	ν_2	Bend	1595 A	1594.59		
b_1	ν_3	Antisym. stretch	3756 A	3755.79		



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Molecule: Hydrogen sulfide H_2S No. 9
Symmetry C_{2v} Symmetry number $\sigma = 2$

Sym. species	No.	Approximate type of mode	Selected value of frequency	Infrared	Raman	Comments
				cm^{-1} (Gas)	cm^{-1}	
a_1	ν_1	Sym. stretch	2615 A	2614.6		
	ν_2	Bend	1183 A	1182.7		
b_1	ν_3	Antisym. stretch	2626 B	2626		

Pitanja za ponavljanje

1. Koliko vibracijskih stupnjeva slobode ima linearna molekula?
2. Koliko vibracijskih stupnjeva slobode ima nelinearna molekula
3. Koji su uvjeti da bi došlo da apsorpcije u IR području?
4. Napišite izraz za vibracijski term harmonijskog oscilatora?
5. O čemu ovisi klasični valni broj?
6. Koja su izborna pravila za harmonijski oscilator?
7. Napišite izraz za vibracijske termove anharmonijskog oscilatora?
8. Koja su izborna pravila za anharmonijski oscilator?
9. Kako se iz IR spektara može procijeniti energija disocijacije?
10. Kako se određuje konstanta anharmoničnosti iz spektra?
11. Što je osnovna vrpca?
12. Što su gornji tonovi?
13. O čemu ovisi intenzitet vrpce?
14. Koje se informacije mogu dobiti iz IR spektara?