Universidade de São Paulo
Instituto de Química

VIBROS IV

LEM
Laboratório de Espectroscopia Molecular

CÁLCULOS TEÓRICOS DE ESPECTROS VIBRACIONAIS

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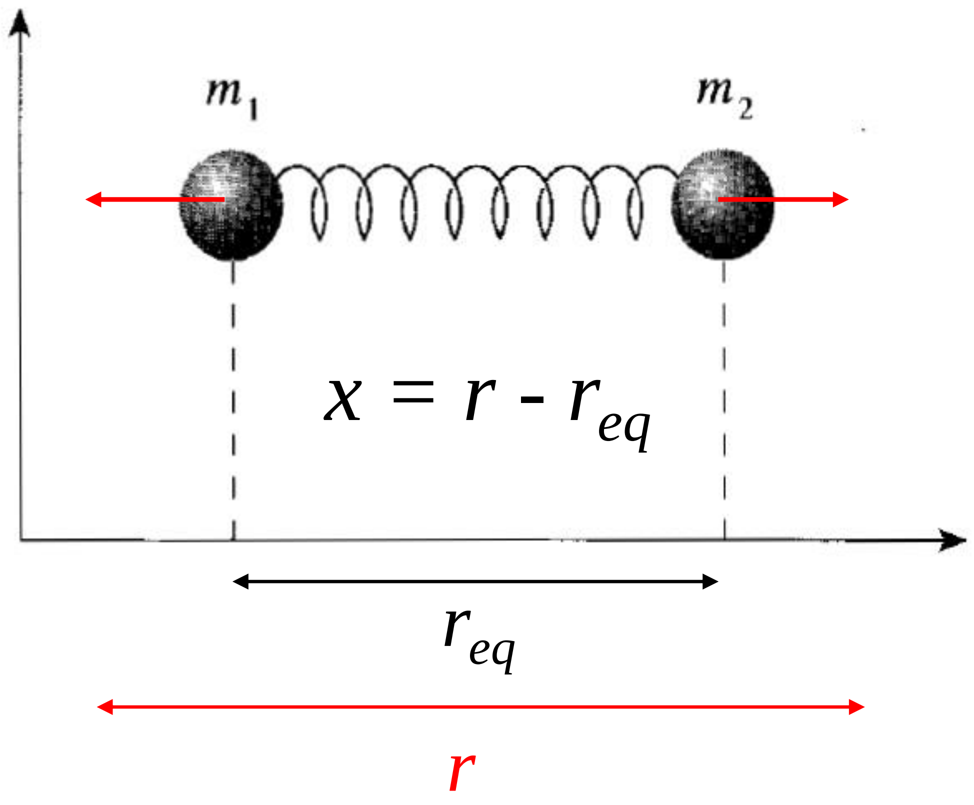
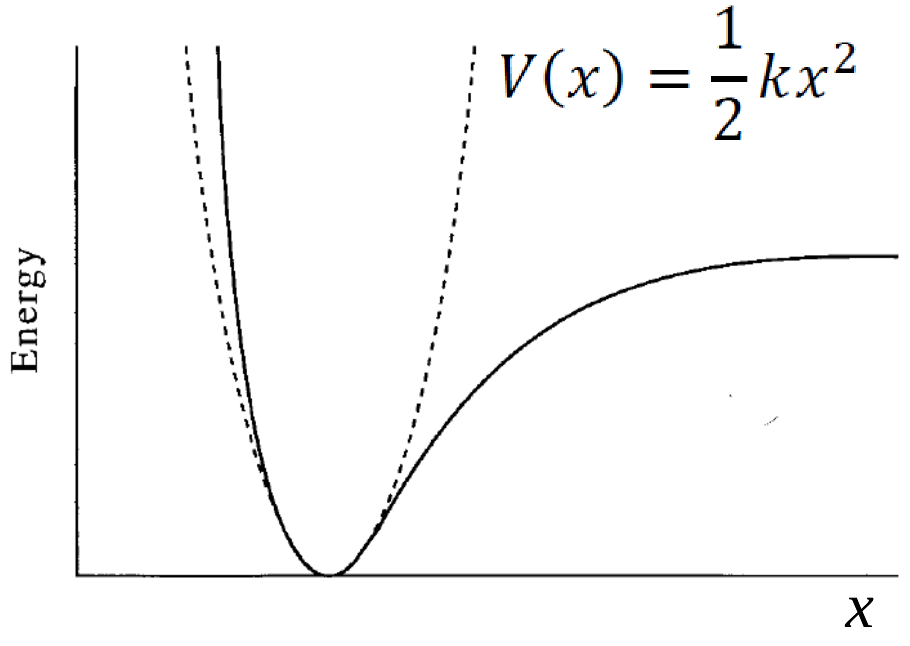
Prof. Dr. Vitor H. Paschoal

O Modelo do Oscilador Harmônico

$F = -kx$ (lei de Hooke)



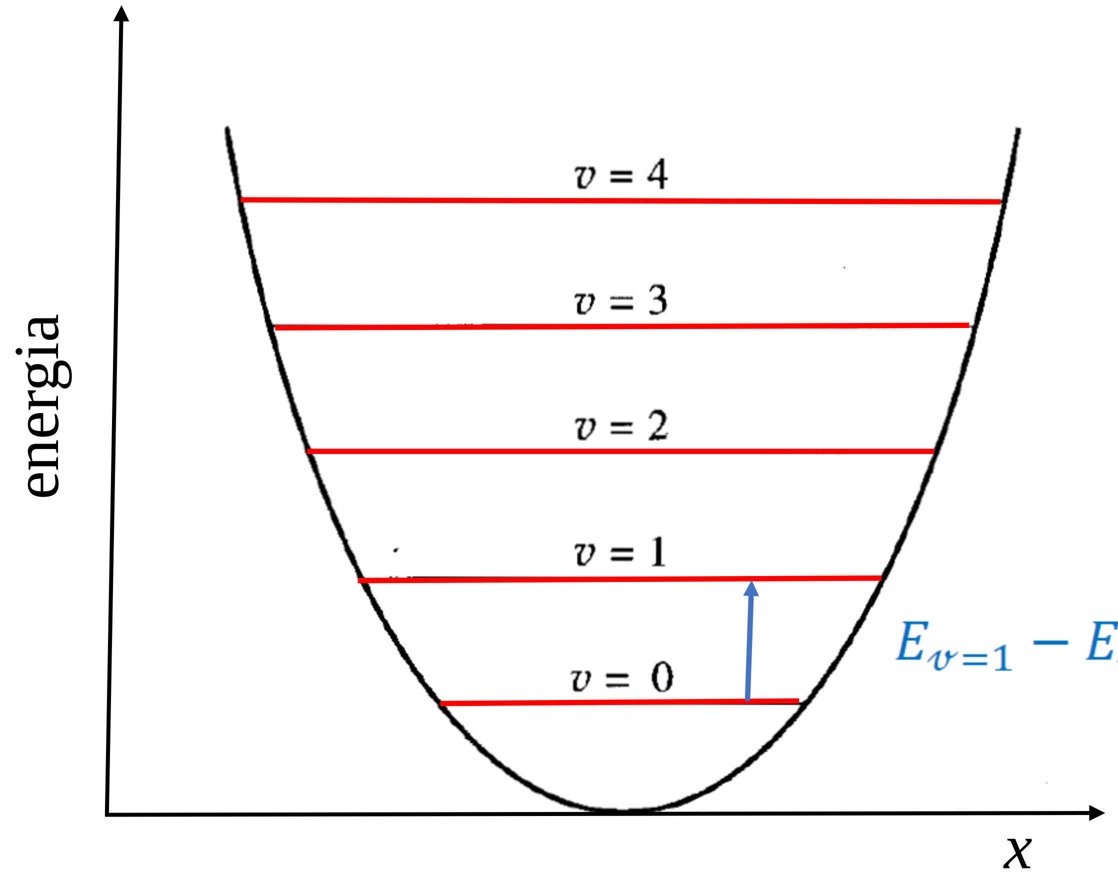


Frequência vibracional

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

massa reduzida $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Níveis de Energia do Oscilador Harmônico



$$E_v = h\nu\left(v + \frac{1}{2}\right), \quad v = 0, 1, 2, \ldots$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$E_{v=1} - E_{v=0} = \Delta E = h\nu$$

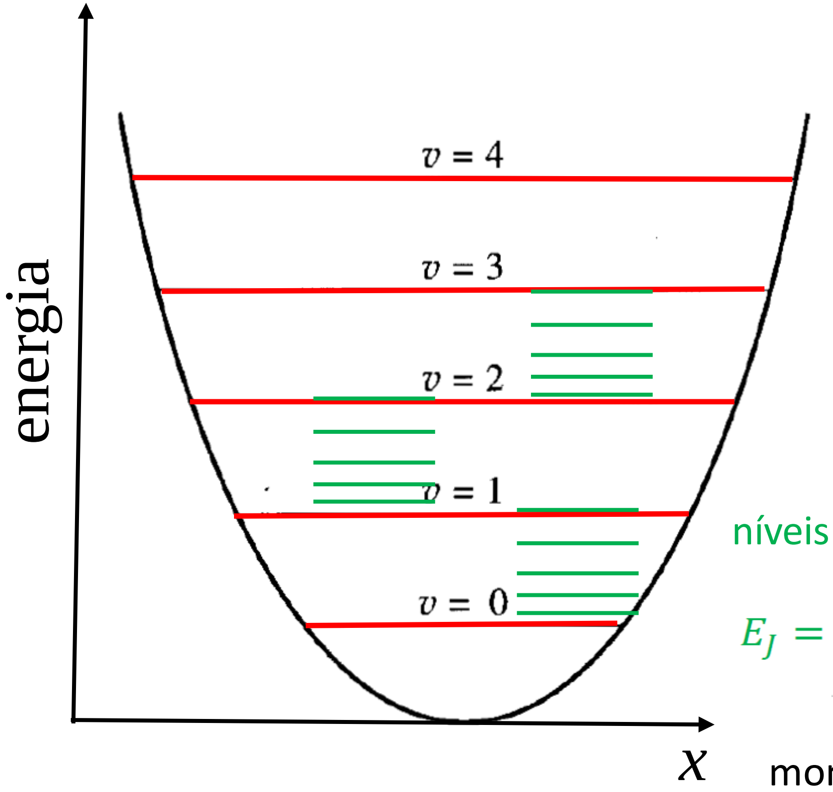
Radiação infravermelho absorvida

frequência: $12 < \nu < 120$ THz

comprimento de onda: $25 < \lambda < 2{,}5$ μm

número de onda (*wavenumber*): $400 < \tilde{\nu} < 4000$ cm^{-1}

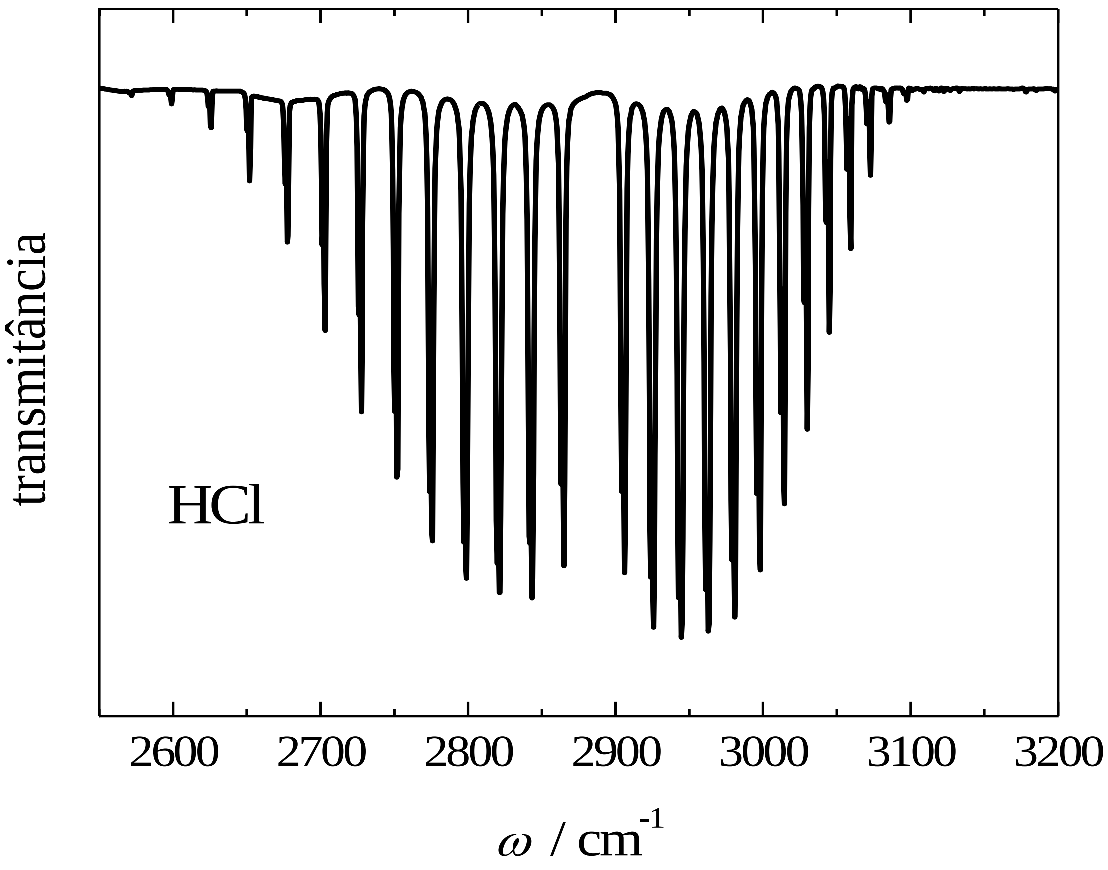
Espectroscopia Vibracional-Rotacional



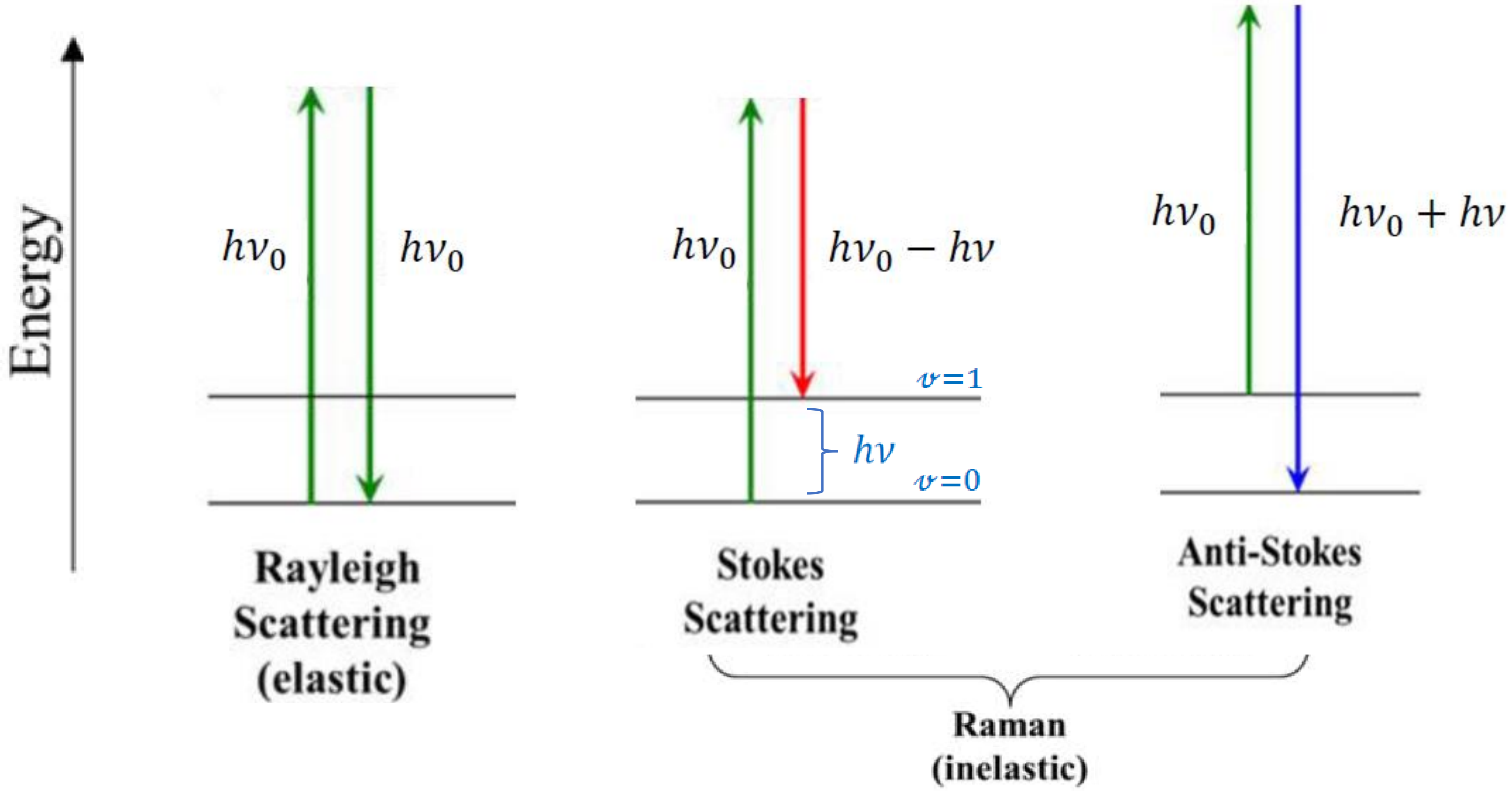
níveis de energia rotacional

$$E_J = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, 2,$$

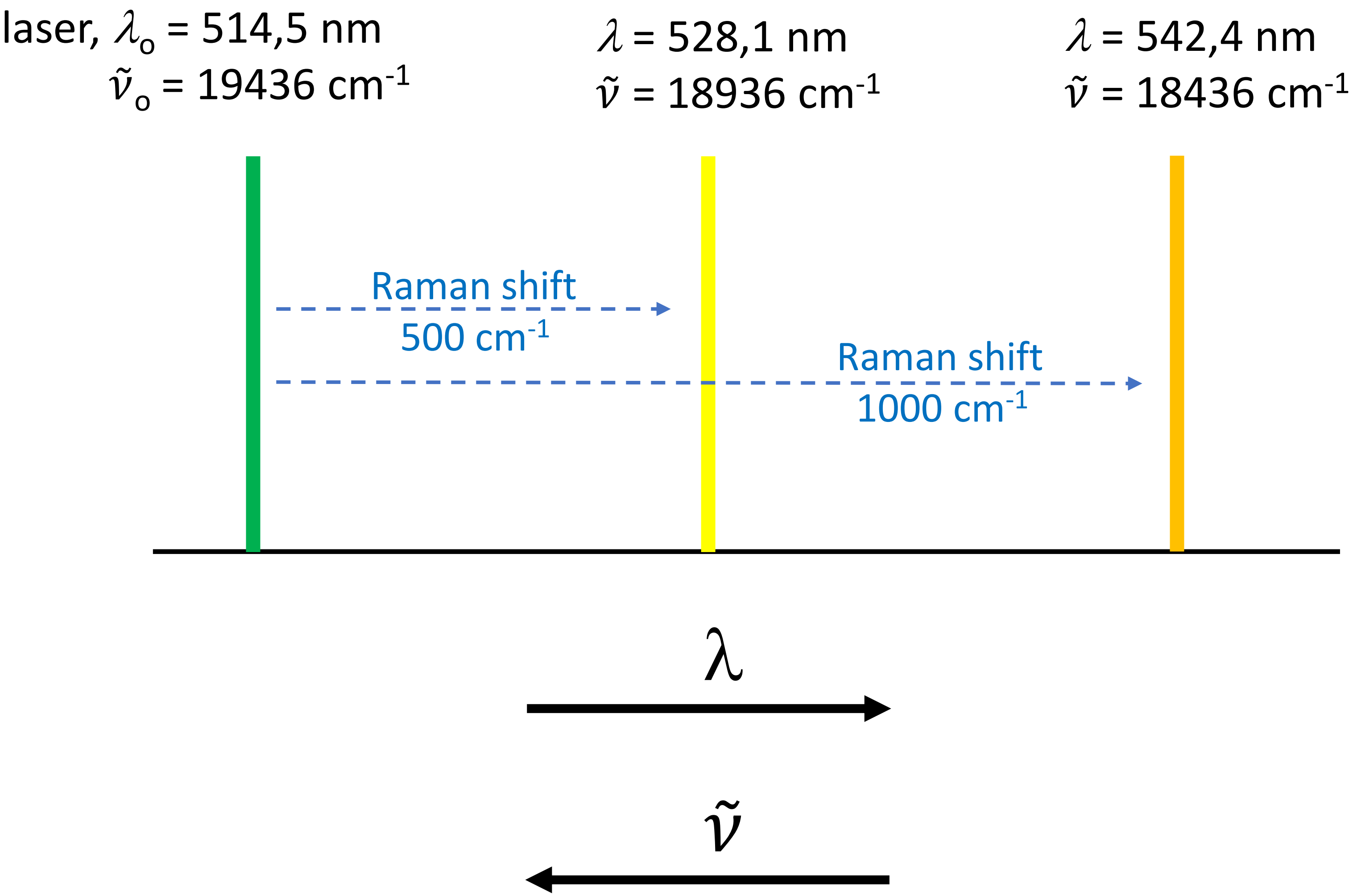
momento de inércia: $I = \mu r^2$



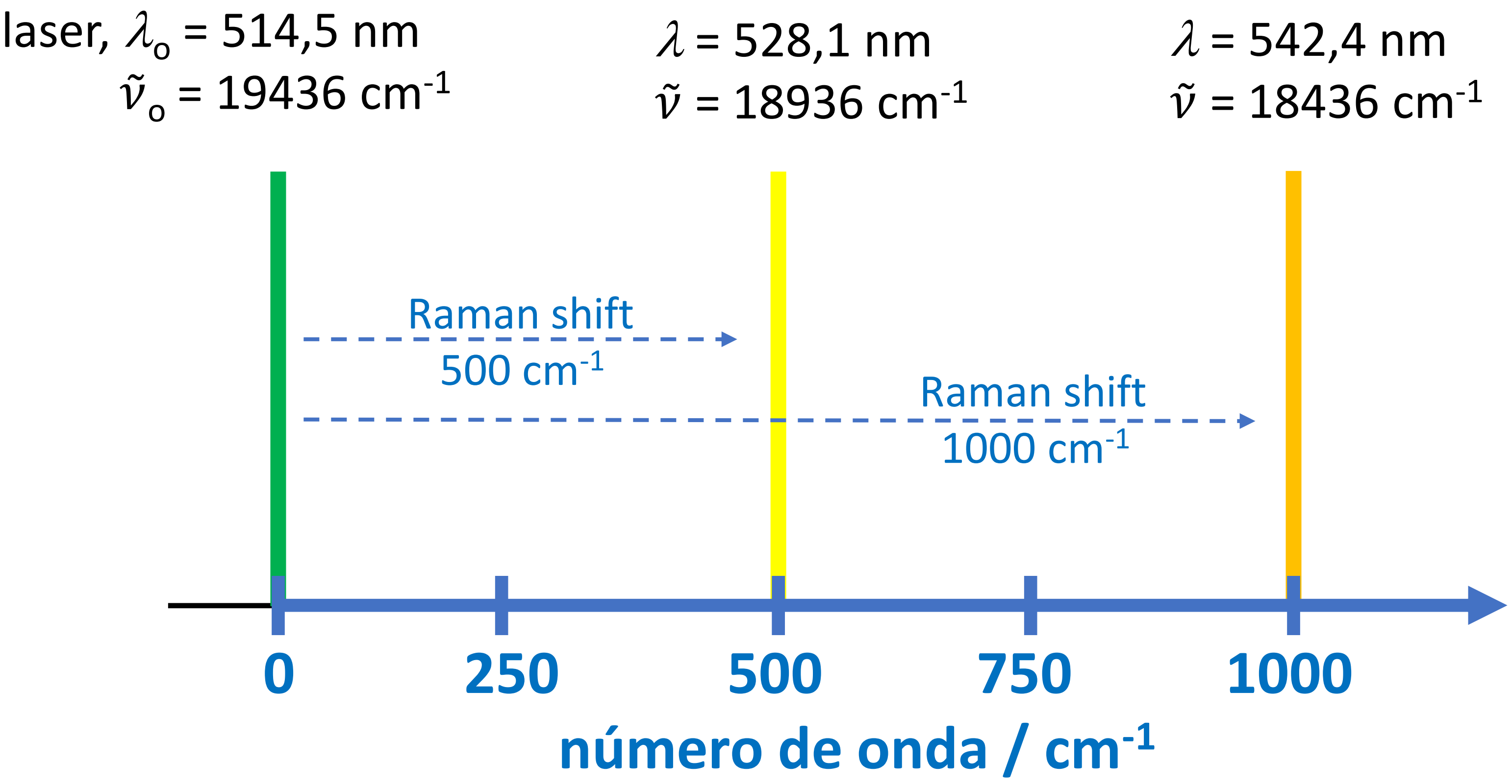
Espectroscopia Raman

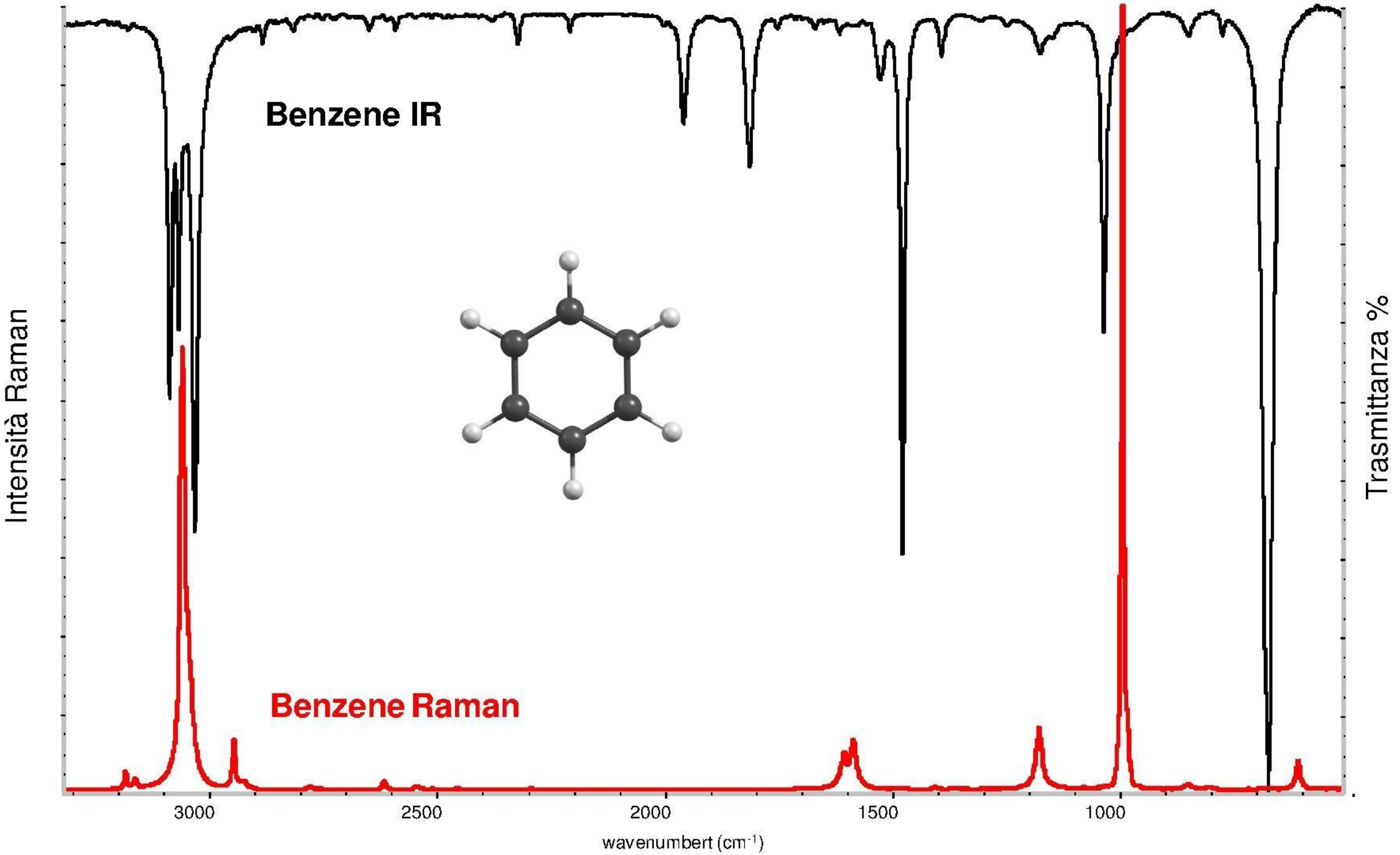


Espalhamento Stokes



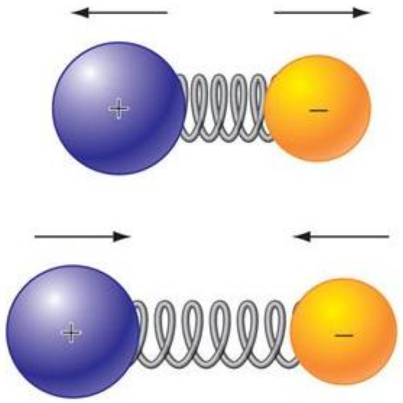
Espalhamento Stokes

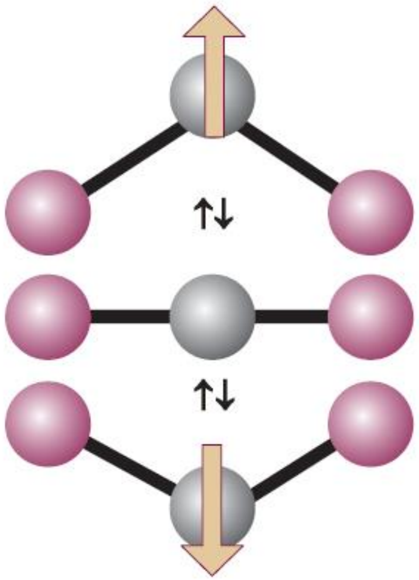




Benzene IR
Benzene Raman
Intensità Raman
Trasmittanza %
3000
2500
2000
1500
1000
wavenumbert (cm-1)

Atividade no infravermelho: dipolo oscilante

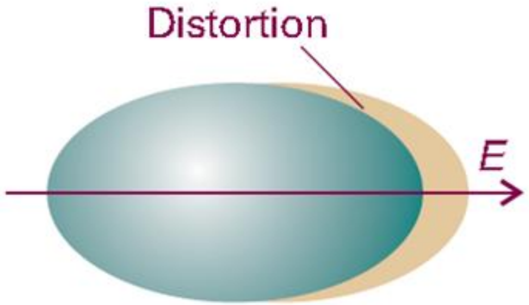




Variação do momento de dipolo elétrico com a vibração:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_e + \left(\frac{d\boldsymbol{\mu}}{dx}\right)_e x + \ldots$$

Atividade no Raman: polarizabilidade oscilante

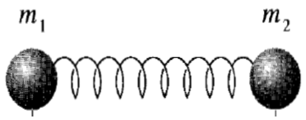


dipolo induzido → μ_{ind}

polarizabilidade → α

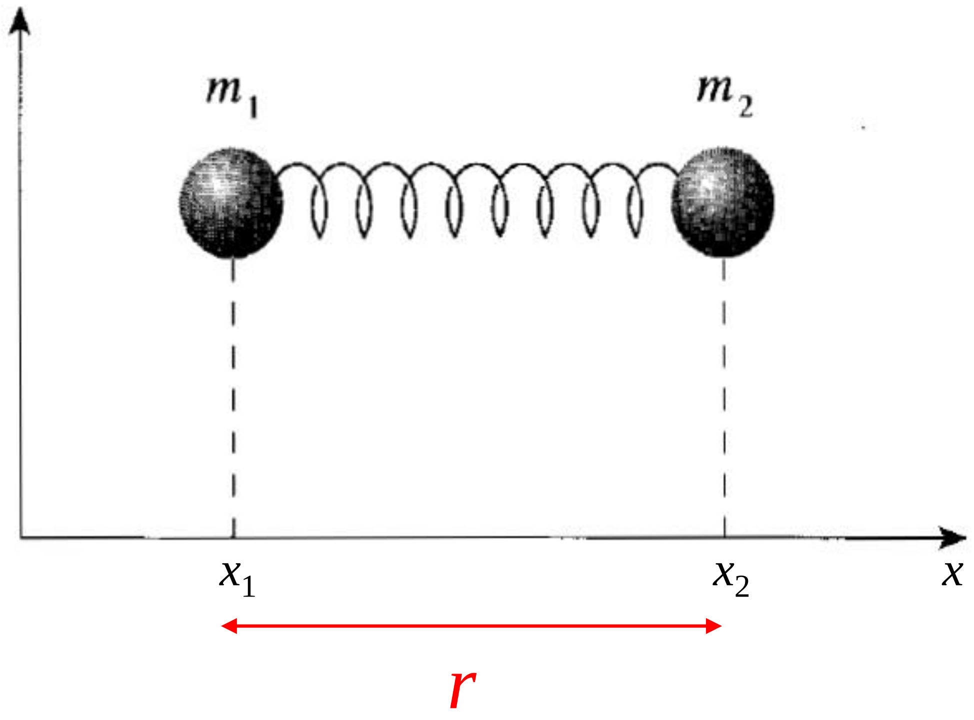
$$\mu_{ind} = \alpha . E$$

E → campo elétrico da radiação incidente $E_o.cos(2\pi\nu_o t)$



$$\mu_{ind} \propto cos[2\pi(\nu_o \pm \nu_{vib})t]$$

Modos Normais de Vibração



coordenada normal

$$Q = x_2 - x_1$$

coordenadas cartesianas

$$Q = r$$

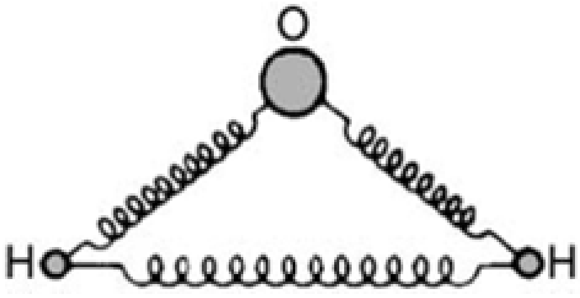
coordenada interna

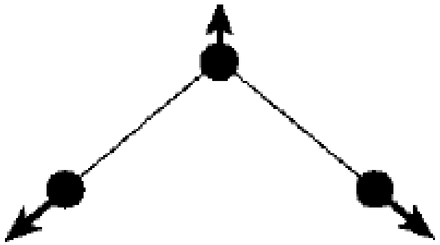
potencial harmônico

$$V(Q) = \frac{1}{2} k Q^2$$

$$(Q_{equil.} = 0)$$

Modos Normais de Moléculas Poliatômicas

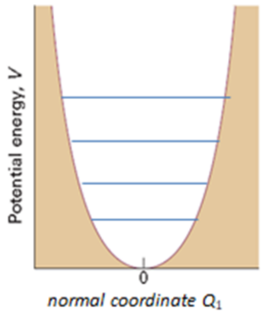


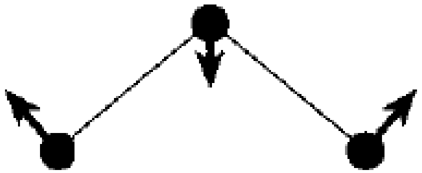


Symmetric stretch

ν_1

3650 cm^{-1}

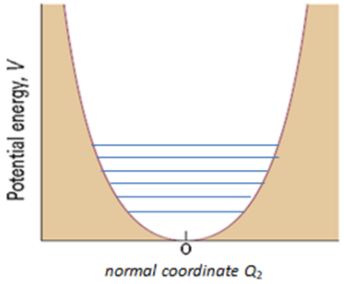


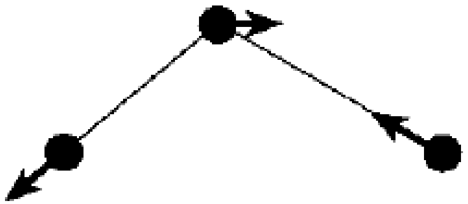


Bend

ν_2

1600 cm^{-1}

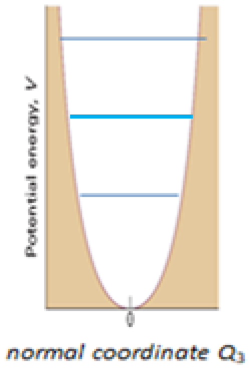




Asymmetric stretch

ν_3

3760 cm^{-1}



Modos Normais de Moléculas Poliatômicas

$$V(x) = \frac{1}{2} k x^2$$

$$k = \left(\frac{d^2V}{dx^2}\right)_{x_{eq}}$$

$$V = \frac{1}{2}\sum_{i=1}^{N}\left[\left(\frac{\partial^2 V}{\partial x_i^2}\right)_0 x_i^2 + \left(\frac{\partial^2 V}{\partial y_i^2}\right)_0 y_i^2 + \left(\frac{\partial^2 V}{\partial z_i^2}\right)_0 z_i^2\right]$$

$$+\frac{1}{2}\sum_{i<j}^{N}\left[\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 x_i x_j + \left(\frac{\partial^2 V}{\partial y_i \partial y_j}\right)_0 y_i y_j + \left(\frac{\partial^2 V}{\partial z_i \partial z_j}\right)_0 z_i z_j\right]$$

$$+\frac{1}{2}\sum_{i,j=1}^{N}\left[\left(\frac{\partial^2 V}{\partial x_i \partial y_j}\right)_0 x_i y_j + \left(\frac{\partial^2 V}{\partial y_i \partial z_j}\right)_0 y_i z_j + \left(\frac{\partial^2 V}{\partial x_i \partial z_j}\right)_0 x_i z_j\right]$$

Coordenada normal Q_α como combinação linear de coordenadas cartesianas X_i :

$$Q_\alpha = \sum_{i=1}^{N} \sum_{\mu=(x,y,z)} L_{\alpha,i\mu} X_{i\mu}$$

$$V(Q_1, Q_2, \dots Q_{3N-6}) = \frac{1}{2}\sum_{\alpha=1}^{3N-6} k_\alpha Q_\alpha^2$$

deslocamento da coordenada cartesiana $X_{i\mu}$ no modo normal Q_α

$$V = \tfrac{1}{2}\,\mathbf{X}^t \quad \mathbf{D} \quad \mathbf{X}$$

$$\begin{pmatrix} x_1 & y_1 & z_1 & x_2 & y_2 & \dots & z_N \end{pmatrix}$$

$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ \cdot \\ \cdot \\ \cdot \\ z_N \end{pmatrix}$$

Matriz Hessiana

$$\begin{pmatrix} \frac{\partial^2 V}{\partial x_1^2} & \frac{\partial^2 V}{\partial x_1 \partial y_1} & & \dots & \frac{\partial^2 V}{\partial x_1 \partial z_N} \\ . & \frac{\partial^2 V}{\partial y_1^2} & \frac{\partial^2 V}{\partial y_1 \partial z_1} & \dots. & \frac{\partial^2 V}{\partial y_1 \partial z_N} \\ . & & . & & \dots. \\ . & & . & & \frac{\partial^2 V}{\partial z_N^2} \end{pmatrix}$$

$$V = \tfrac{1}{2}\, \mathbf{X}^t\, \mathbf{L}^t\, \mathbf{L}\, \mathbf{D}\, \mathbf{L}^t\, \mathbf{L}\, \mathbf{X}$$

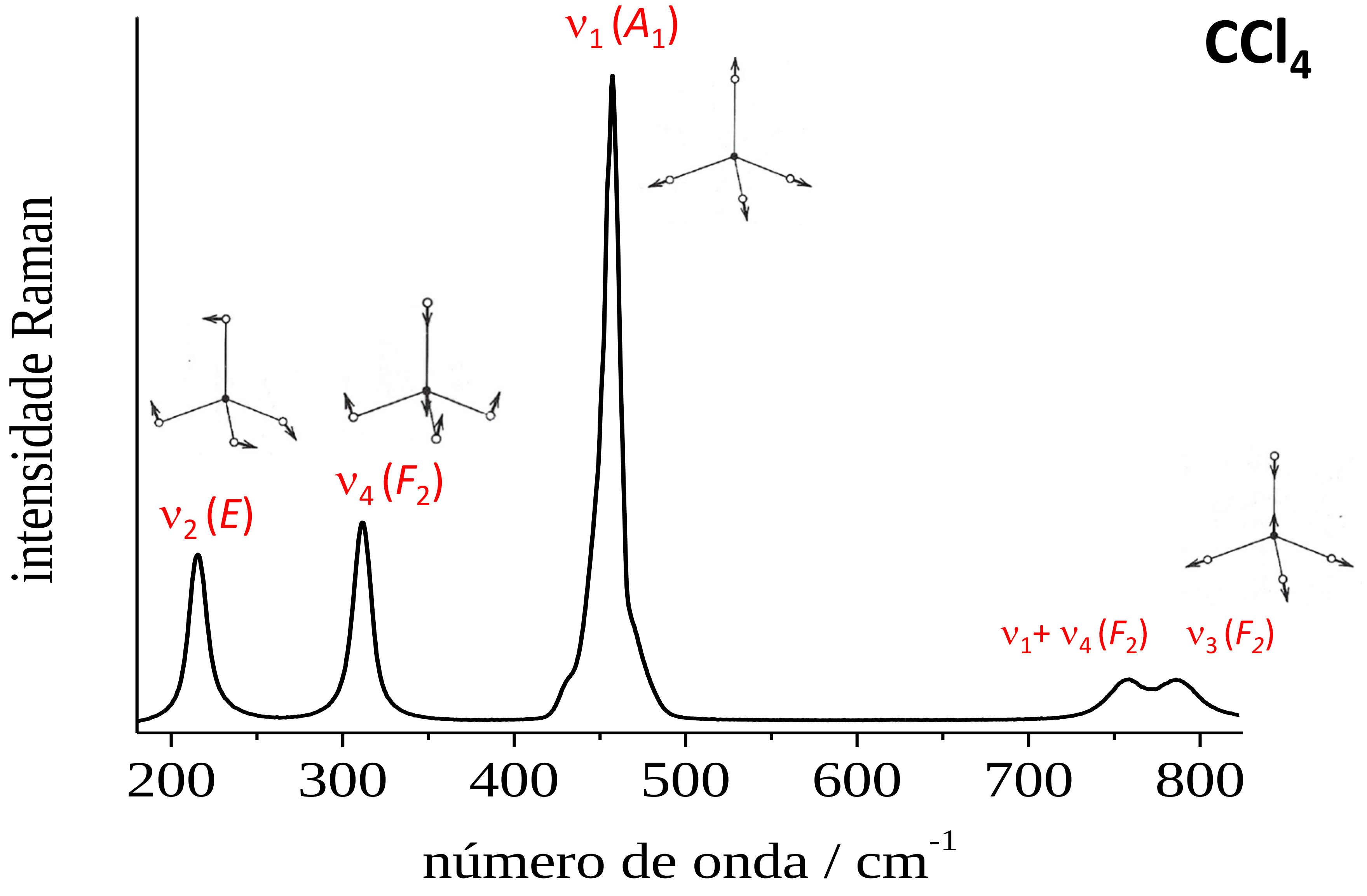
$$\mathbf{X}^t \mathbf{L}^t \rightarrow \mathbf{Q}^t \qquad \mathbf{L}\,\mathbf{X} \rightarrow \mathbf{Q}$$

Diagonalização da Hessiana

$$\omega_i^2 = [\mathbf{L}\,\mathbf{D}\,\mathbf{L}^t]_{ii}$$

$$V(Q_1, Q_2, \dots Q_{3N-6}) = \frac{1}{2} \sum_{\alpha=1}^{3N-6} k_\alpha Q_\alpha^2$$

$$Q_\alpha = \sum_{i=1}^{N} \sum_{\mu=(x,y,z)} L_{\alpha,i\mu} X_{i\mu}$$


CCl4
ν1 (A1)
ν2 (E)
ν4 (F2)
ν1+ ν4 (F2)
ν3 (F2)
intensidade Raman
200
300
400
500
600
700
800
número de onda / cm-1