

# Vibrational excitations of diatomic molecules

$$\left\{ \frac{d}{R^2 dR} \left( R^2 \frac{d}{dR} \right) + \frac{2M}{\hbar^2} \left[ E - E_{\text{pot}} - \frac{\cancel{J(J+1)\hbar^2}}{2M R^2} \right] \right\} S(R) = 0$$

$\uparrow$   
 $J = 0$

$\hat{=}$  "normal" SE particle in a box

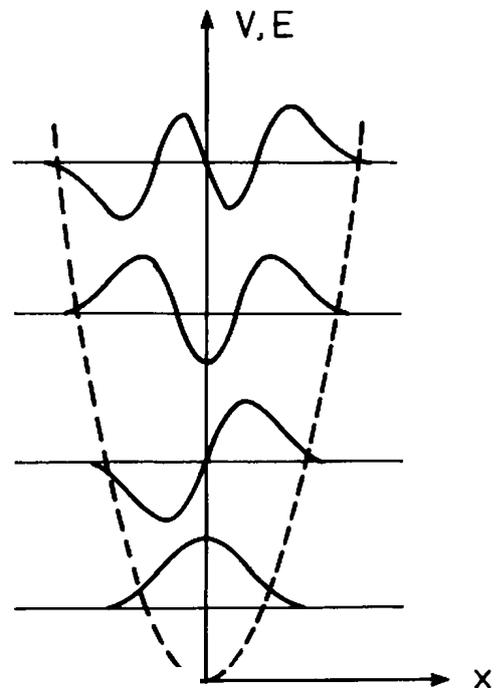
e.g. harmonic oscillator (parabolic potential)

→ Energy levels

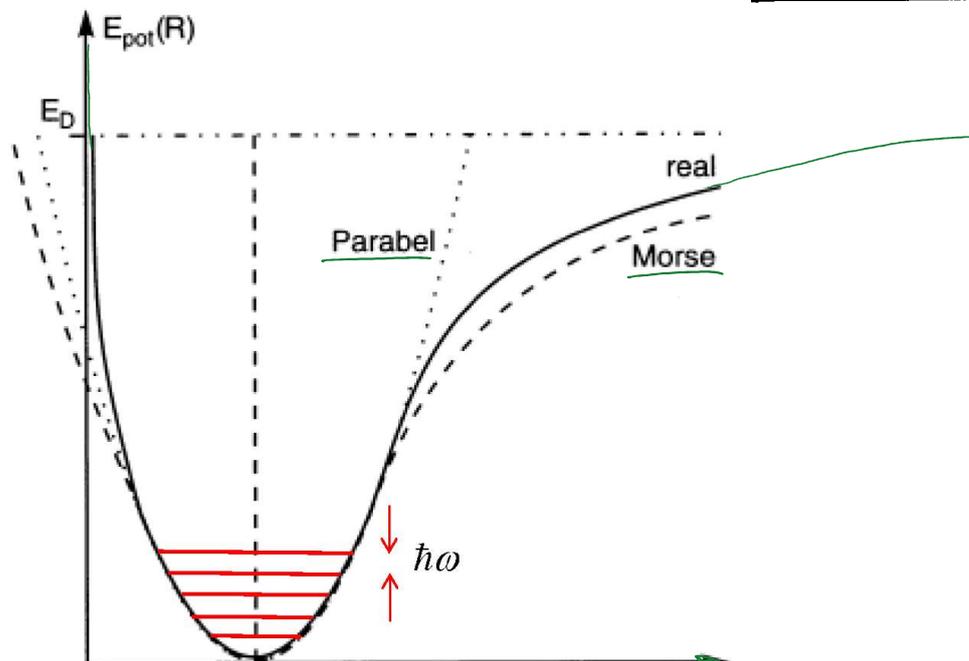
$$E(v) = \hbar \omega \left( v + \frac{1}{2} \right)$$

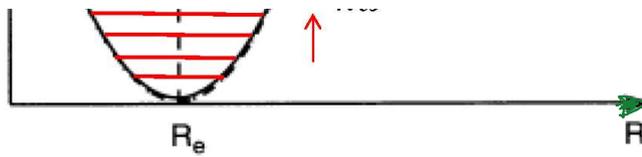
$$\omega = \sqrt{\frac{k}{\mu}}$$

$k =$  "spring" constant

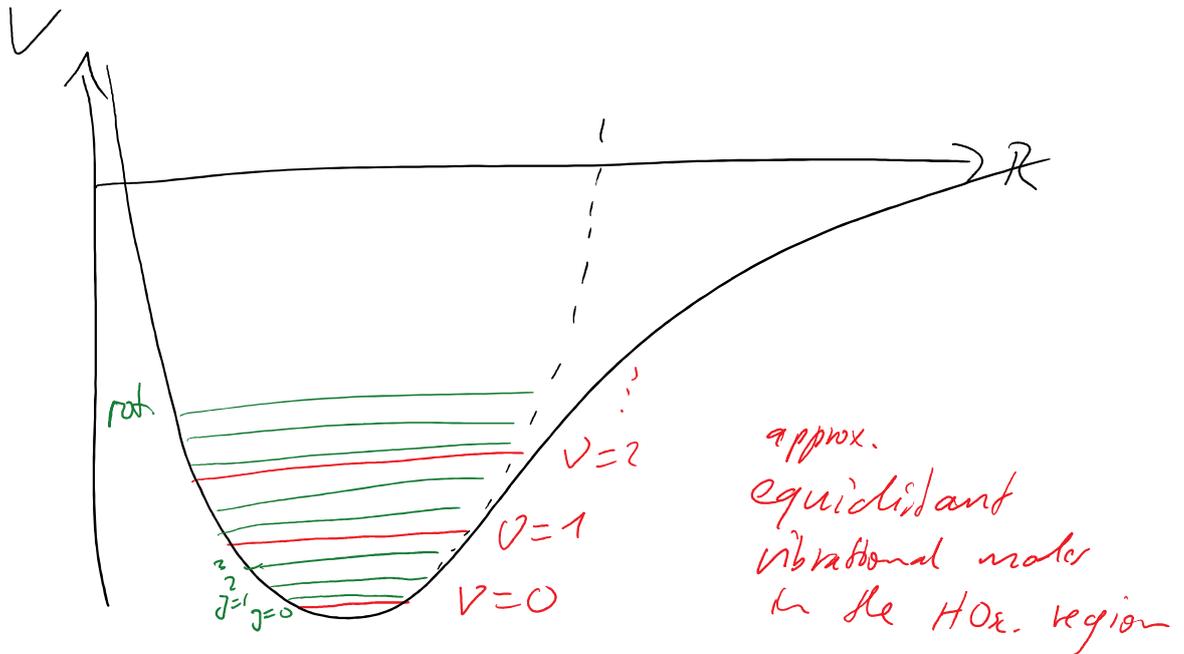


in reality





Of course molecules can do both  
 = rotate & vibrate at the same time



Schwingungskonstanten für zweiatomige Moleküle

Molekül	$\omega_e = \frac{\hbar\omega}{hc} [cm^{-1}]$	$\hbar\omega [eV]$
H <sub>2</sub>	4395	0.55
Li <sub>2</sub>	351	0.044
N <sub>2</sub>	2359	0.296
O <sub>2</sub>	1580	0.198
NO	1904	0.239
I <sub>2</sub>	214	0.027
ICI	384	0.048
HCl	2990	0.376

Rotationskonstanten

Molekül	$B_e [meV]$
H <sub>2</sub>	7,64
Li <sub>2</sub>	0,085
N <sub>2</sub>	0,253
O <sub>2</sub>	0,182
NO	0,22
I <sub>2</sub>	0,005
ICI	0,014
HCl	1,33

meV

vib. spacings (eV)  $\gg$  rotational spacings (meV)

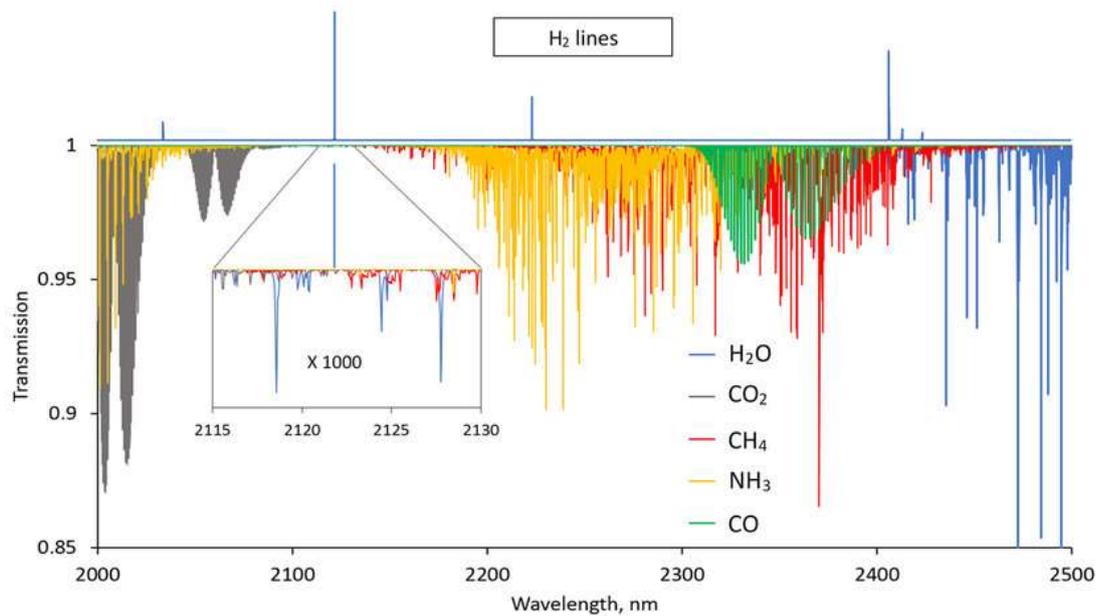
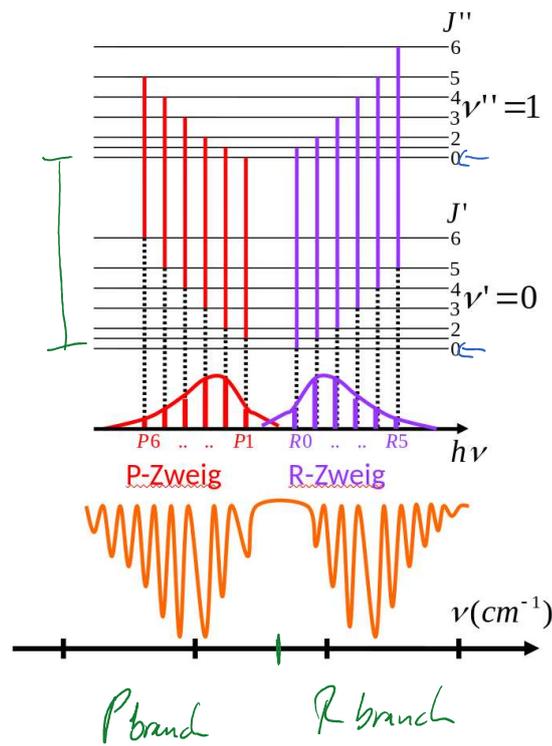
$$E_{\text{tot}} = E_{\text{rot}} + E_{\text{vib}} + E_{\text{pot}} = \text{constant (if no radiation)}$$

energy exchange between rotational & vibrational excitations

typical molecular spectrum: band spectra

absorption/  
emission  
bands

b/c rot. levels  
are  
not equidistant

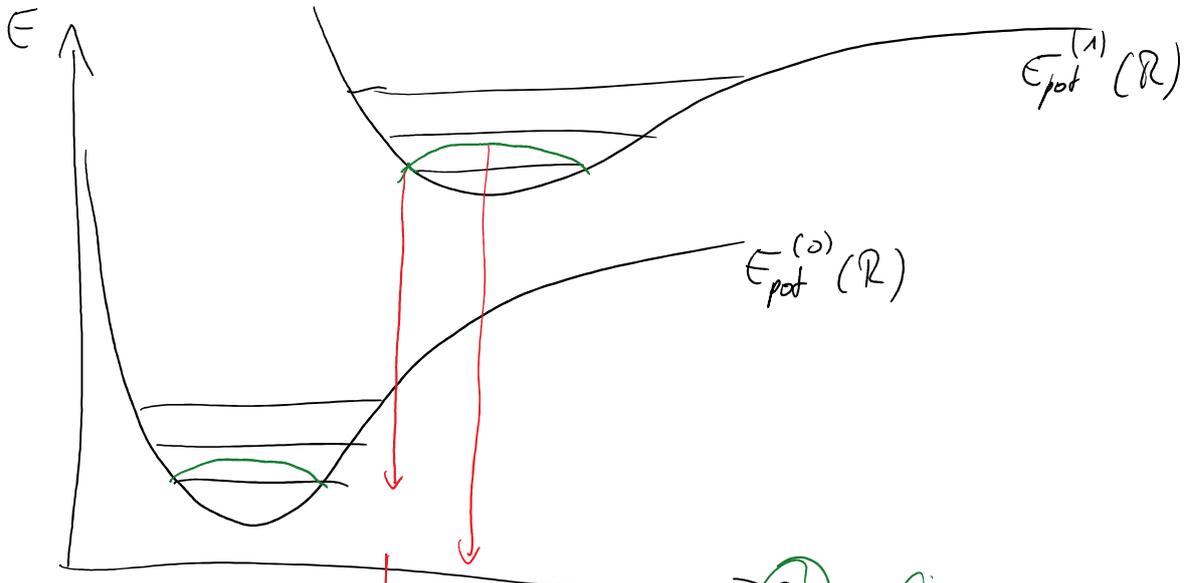


Frank Condon principle

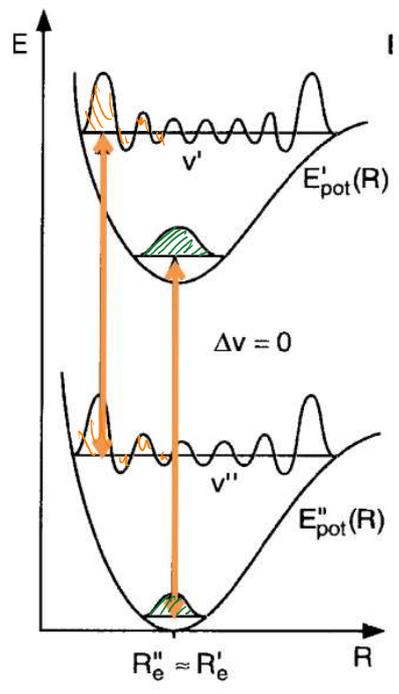
electronic (de) excitations between different  
vib-rotational states

↓  $v_0 - v_0$  rational ...

during the short time of an electronic transition the distance of the nuclei does not change

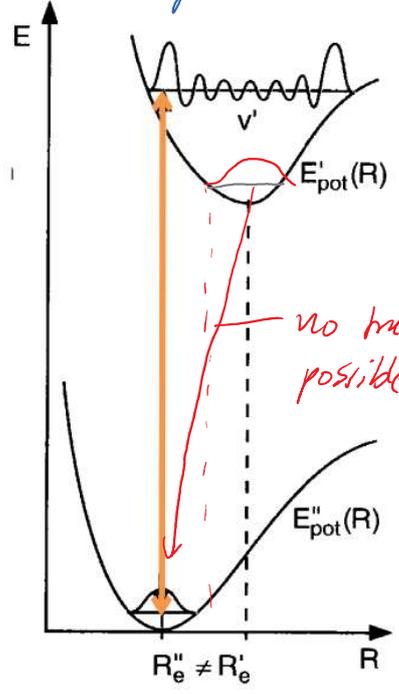


$R$  = fixed  
transitions are "vertical" in this plot



excited electronic state

e.g. g.s.



no transition possible

