

Infrared Spectroscopy (IR)

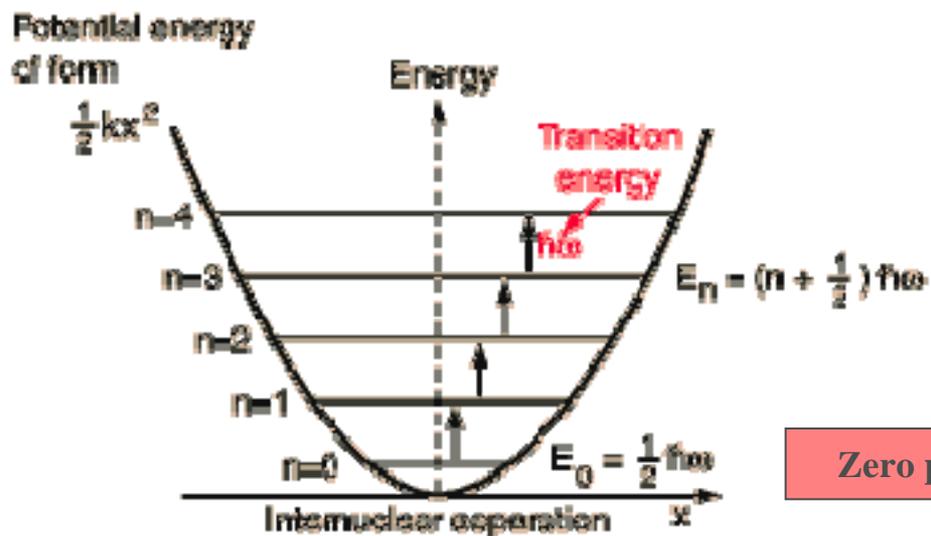
Vibrational spectroscopy is an energy sensitive method and is used to characterize compounds in terms of the strengths and number of the bonds present. One can get/detect:

- the presence of known compounds (finger print)
- the components of an unknown compound (functional groups)
- and thus a likely structure of a compound
- changes in the concentration of a species during reaction
- the properties of bonds (bond strength, force constants)

Since a bond in a molecule behaves like a spring, the harmonic/anharmonic oscillator model is used to describe the $3N-6$ or $3N-5$ different ways a non-linear or linear molecule, respectively, consisting of N atoms can vibrate.

These vibrational modes (normal modes) give rise to absorption bands of characteristic energies/frequencies/wave numbers, intensities, and widths (change of dipole moment required), which are detected and analyzed.

Vibrational energy levels in harmonic approximation



Zero point vibration/energy!



$x=0$ represents the equilibrium separation between the nuclei.

Please note that vibrations normally are more or less anharmonic

Vibrational levels in harmonic/anharmonic approximation

$$E_{\text{VIB}} = h \nu_{\text{osc}} \left(n + \frac{1}{2} \right) = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right)$$

$$n = 0, 1, 2, \dots \quad \Delta n = \pm 1$$

$$\Delta E_{\text{VIB}} = E_{n+1} - E_n = h \nu_{\text{osc}}$$

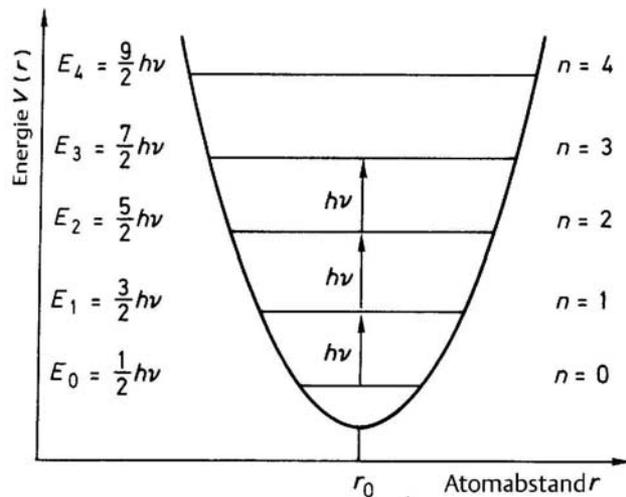
n Schwingungsquantenzahl

h Planck-Wirkungsquantum

E_{VIB} Schwingungsenergie (VIB von Vibration)

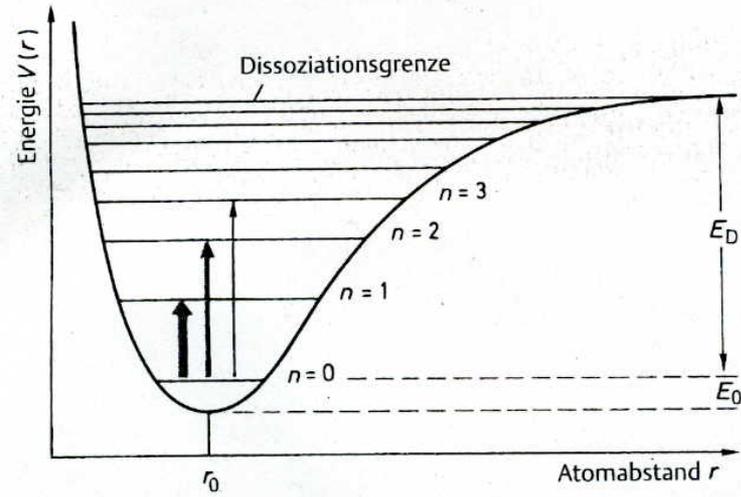
$$E_{\text{VIB}} = h \nu_{\text{osc}} \left(n + \frac{1}{2} \right) - \frac{h^2 \nu^2}{4E_D} \cdot \left(n + \frac{1}{2} \right)^2 \quad (\Delta n = \pm 1, \pm 2, \dots)$$

In case of an anharmonic vibration, the distances of neighbouring levels become smaller with increasing n (the arrows symbolize transition probabilities and intensities).



Potential curve of an harmonic oscillator

(E_n : Vibrational levels, E_0 : Zero point energy)

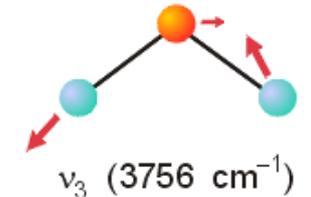
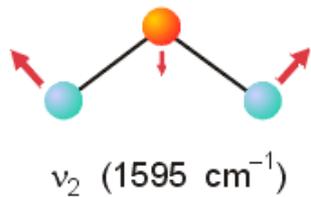
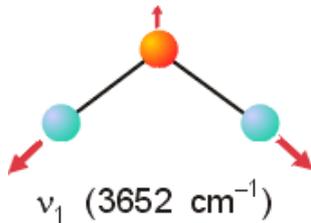


Potential curve of an anharmonic oscillator

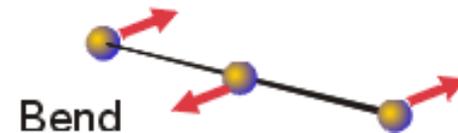
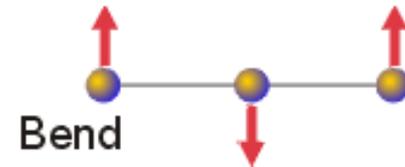
(E_0 : Zero point energy, E_D : Dissociation energy)

Normal modes of vibration

$3N - 6$ modes ($3N - 5$ if linear)



$$\tilde{\nu} \sim \sqrt{f / m}$$



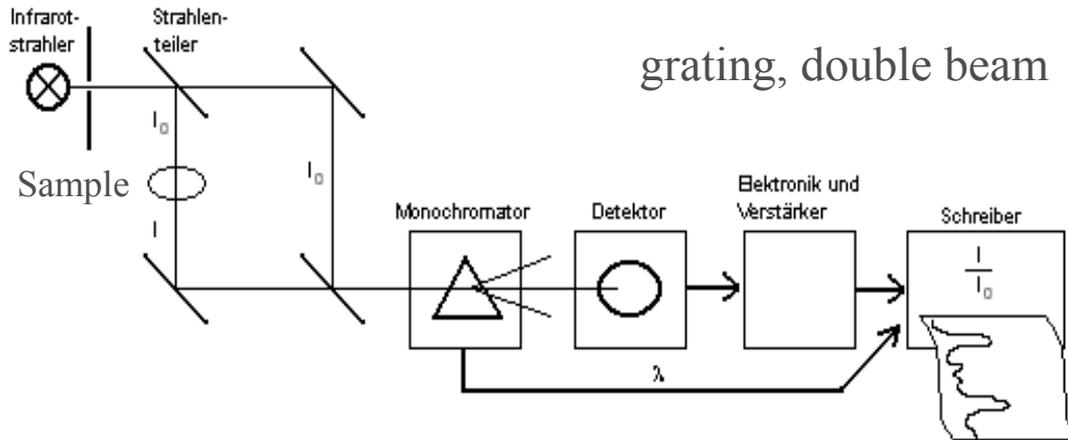
The three normal modes of H₂O
and their wavenumbers

The four normal modes of
(linear) CO₂

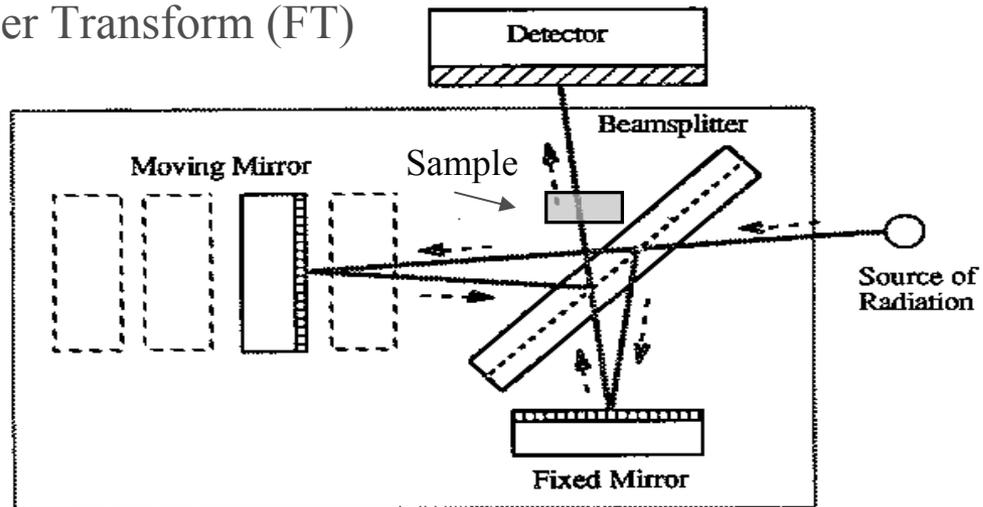
Typical wavenumbers of stretching/bending vibrations

“molecule“	stretching	bending
C - H	2800 - 3000	
N - N	3300 - 3500	
H ₂ O	3600 - 3000	1600
C = O	1700	
C = C	1600	
SO ₃ ²⁻	970 (ν _s)	620 (γ)
	930 (ν _{as})	470 (δ)

IR - Spectrometer



Fourier Transform (FT)



Examples

