# Infrared spectroscopy

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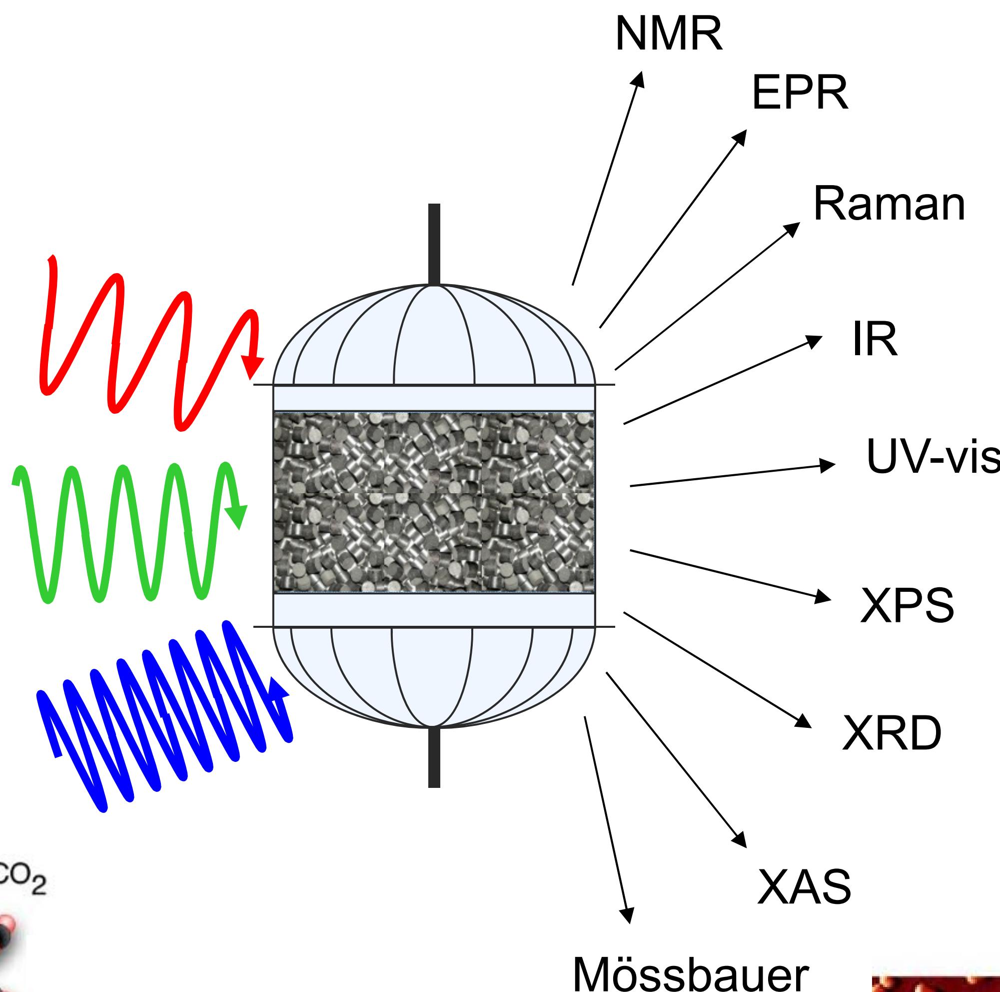
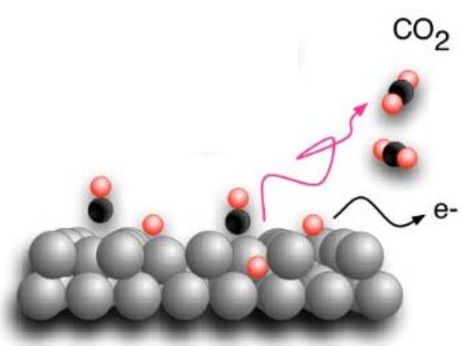
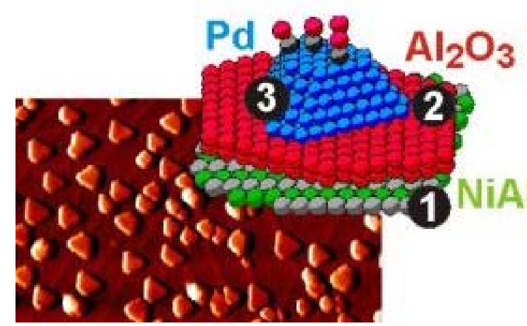
# Why characterization?

photons
electrons
neutrons
protons
…



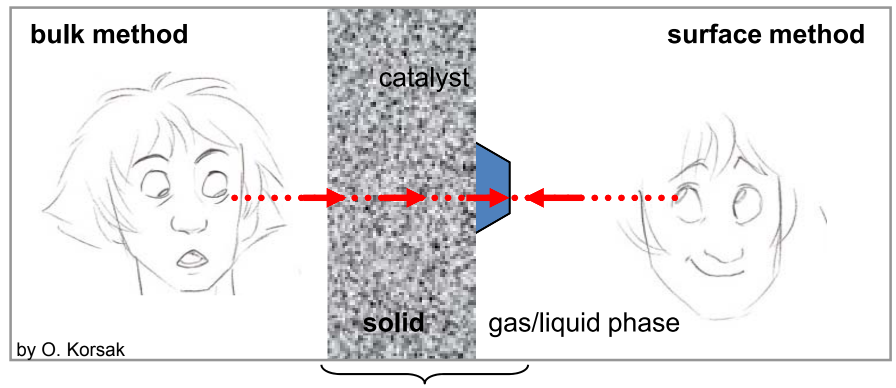



# Why characterization?

Boiling coffee with a mokka
A movie made with neutron images that shows the coffee making process.
Movie by A. Kaestner, Neutron imaging and activation group, PSI, Switzerland. The movie is four times faster than in real time.

# Why characterization?

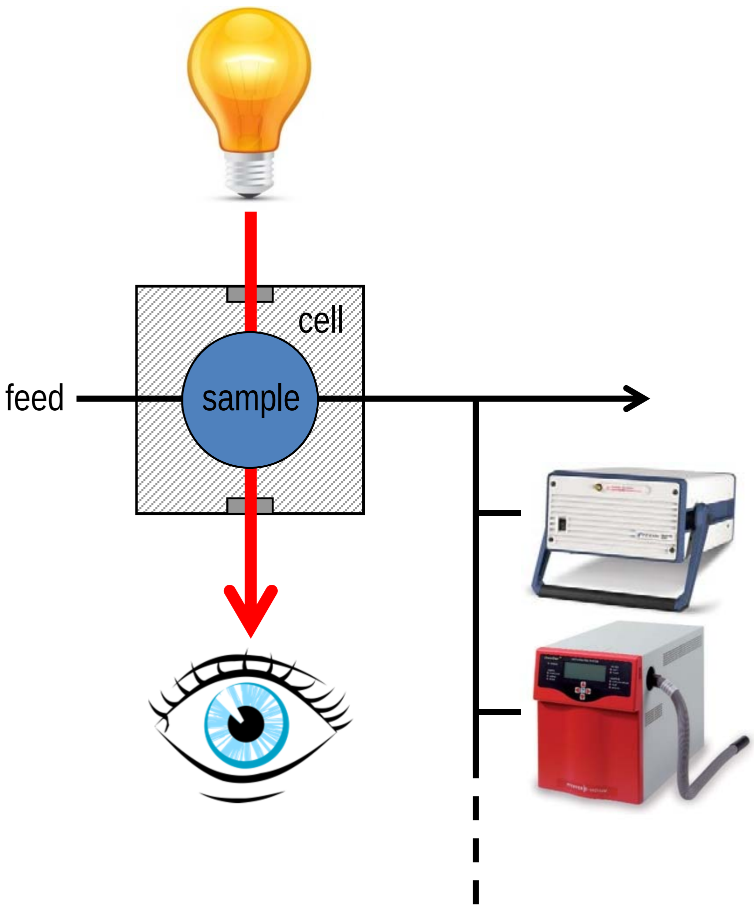




which method to use?

- advantages
- disadvantages
- combination of methods

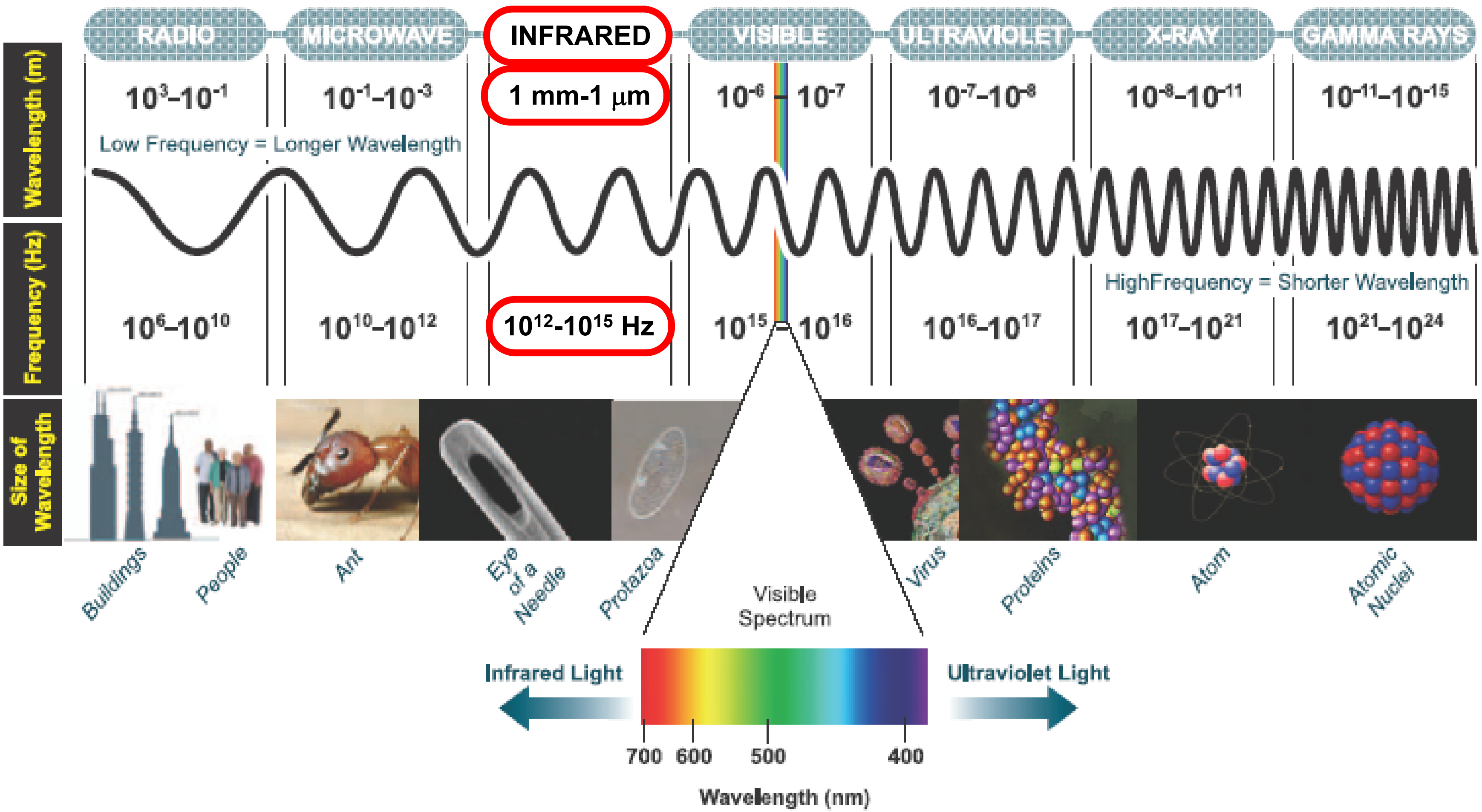
# Definitions

- ***Ex situ*** spectroscopy
  - *pre-natal/post-mortem* structure of material as is
  - away from sorption/reaction conditions
  - typically, room temperature/pressure
- ***In situ*** spectroscopy
  - defined sample environment
  - sorption/reaction in presence of reactants
  - relevant reaction conditions (T/P)
  - time-resolved
- ***Operando*** spectroscopy
  - synchronous measurement of activity/selectivity
  - structure-activity relationship
  - time-resolved
  - strict definition: cell design comparable to real reactor




Weckhuysen, *Chem. Commun.* (2002) 97; Banares, *Catal. Today* 100 (2005) 71; Banares et al., *Catal. Today* 113 (2006) 48
*In situ spectroscopy of catalysts*, Weckhuysen (Ed).; Am. Scientific Publishers, Stevenson Ranch, 2004

# The electromagnetic spectrum




source: Andor.com

# Infrared spectroscopy

- Use of infrared radiation
- Excitation of vibrational and rotational modes (vibrational transitions)
- Identifies functional groups ($-(C=C)_n-$, -C=O, -C=N, etc.)
- Access to molecular structure, interactions and lattice vibrations of solids (e.g. O-H, M-O)
- Use of probe molecules to characterize solid surfaces

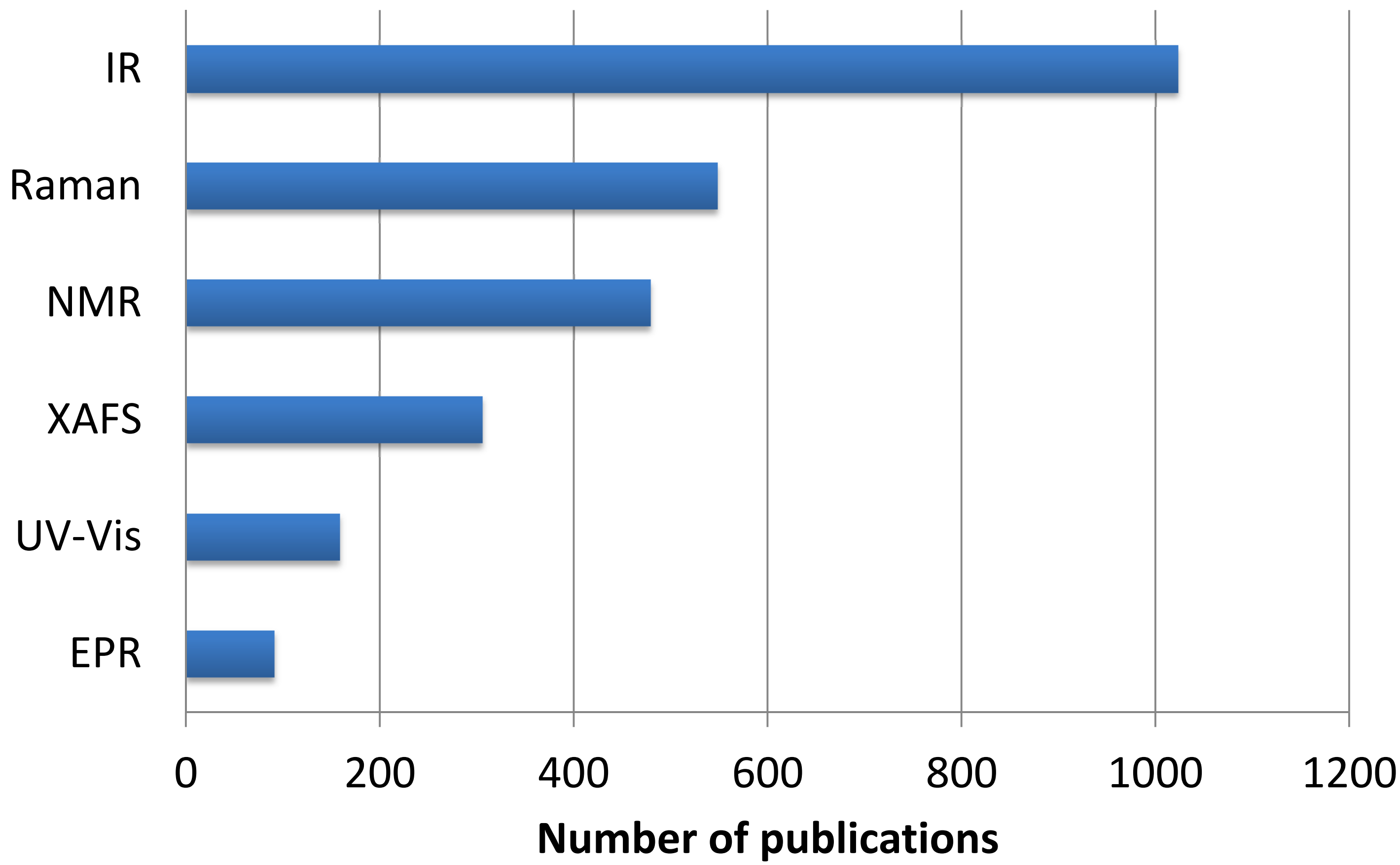
**pros**

- economic
- non-invasive
- versatile (e.g. solid, liquid, gas and interfaces)
- very sensitive (concentration)
- fast acquisition (down to ns!)

**cons**

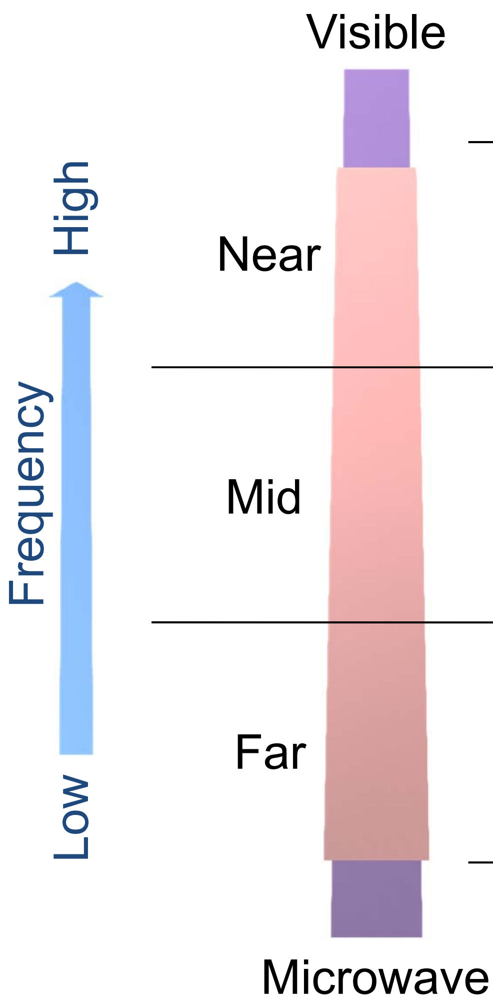
- no atomic resolution

# Importance of IR spectroscopy in catalysis



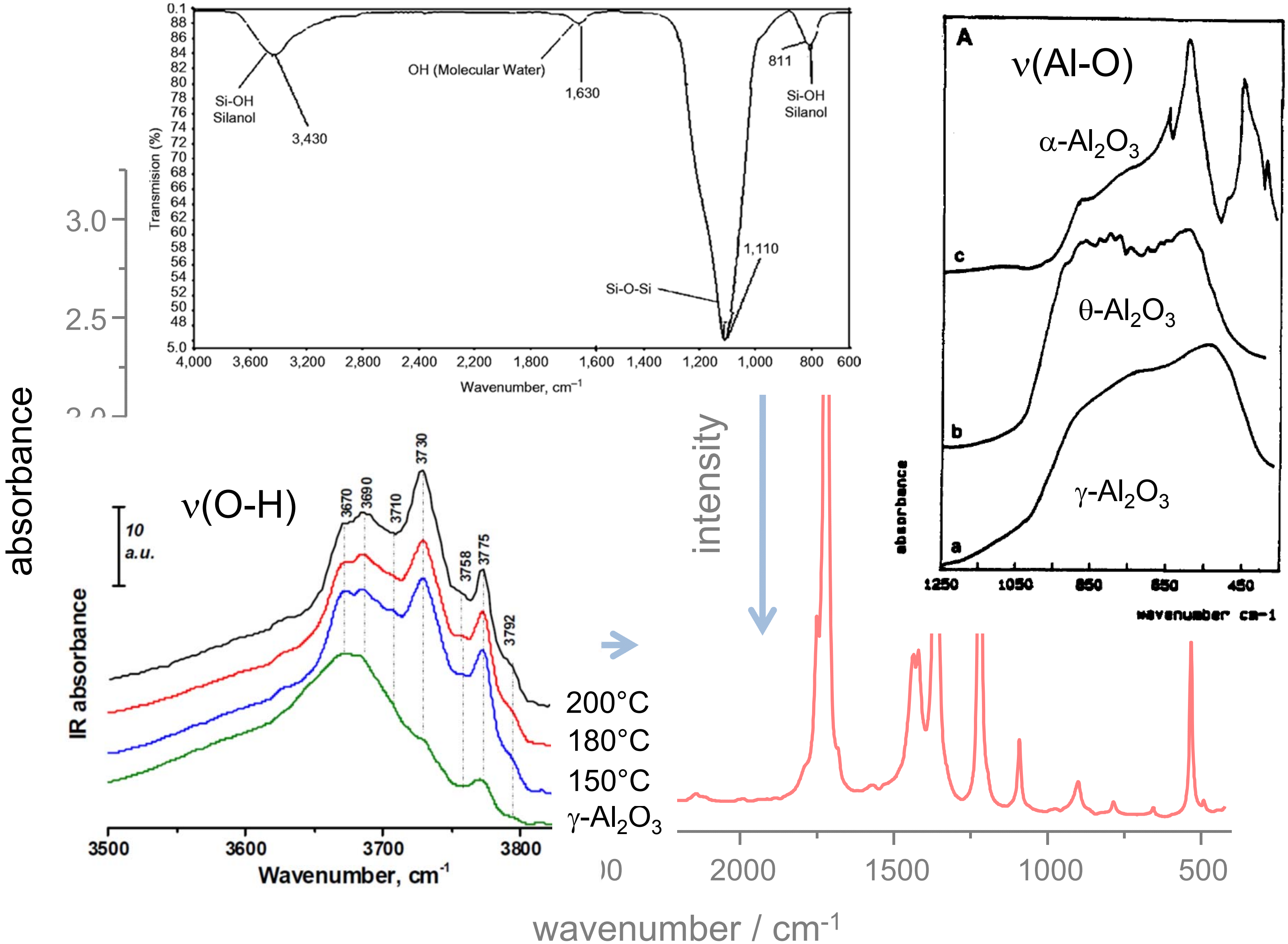

Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

# The IR region



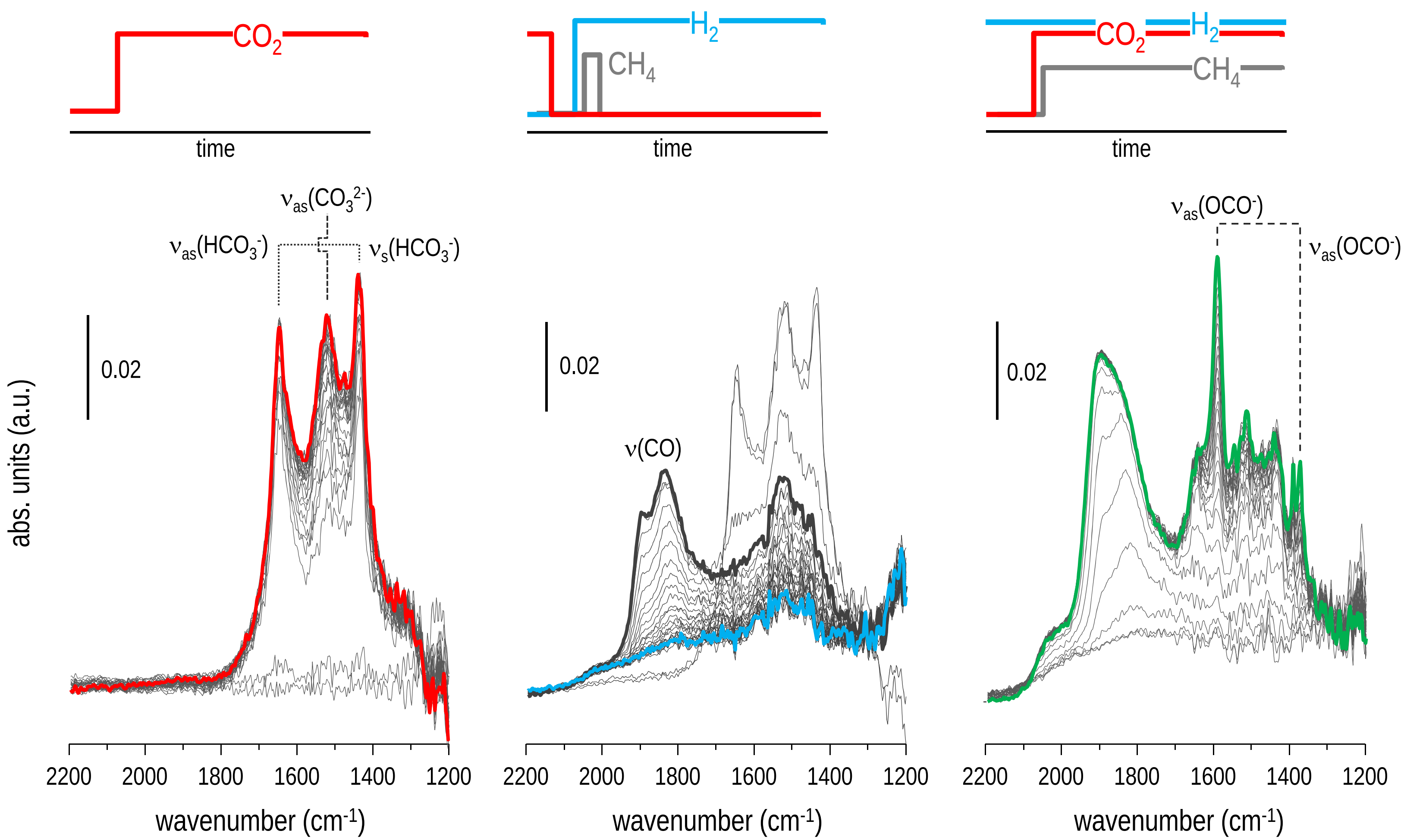

| | $\lambda$ [μm]õ | $\tilde{\nu}$ [cm$^{-1}$] | E [kJ/mol] | |
|---|---|---|---|---|
| Near | 0.78-2.5 | 12800-4000 | 150-50 | overtone, combination vibrations |
| Mid | 2.5-25 | 4000-400 | 50-5 | fundamental vibrations |
| Far | 25-1000 | 400-10 | 5-0.1 | fundamental vibrations of heavy elements, lattice vibrations |

# The mid-IR spectrum



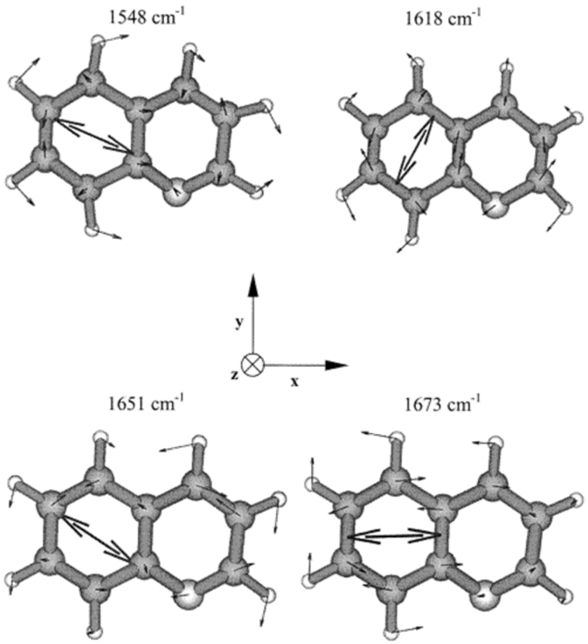

Morterra, Catal. Today 27 (1996) 497

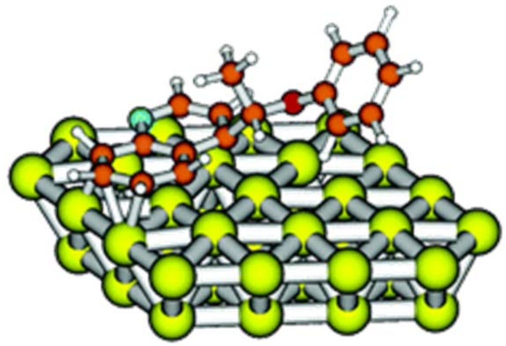
# Adsorbates by IR spectroscopy

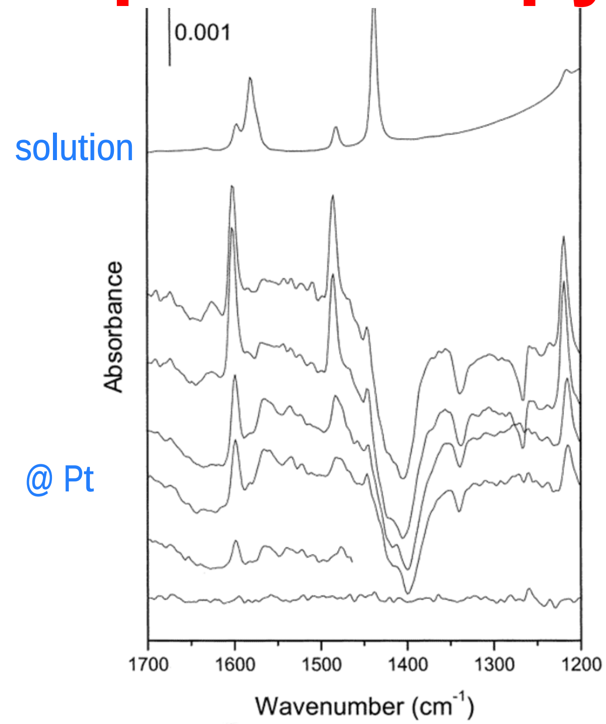


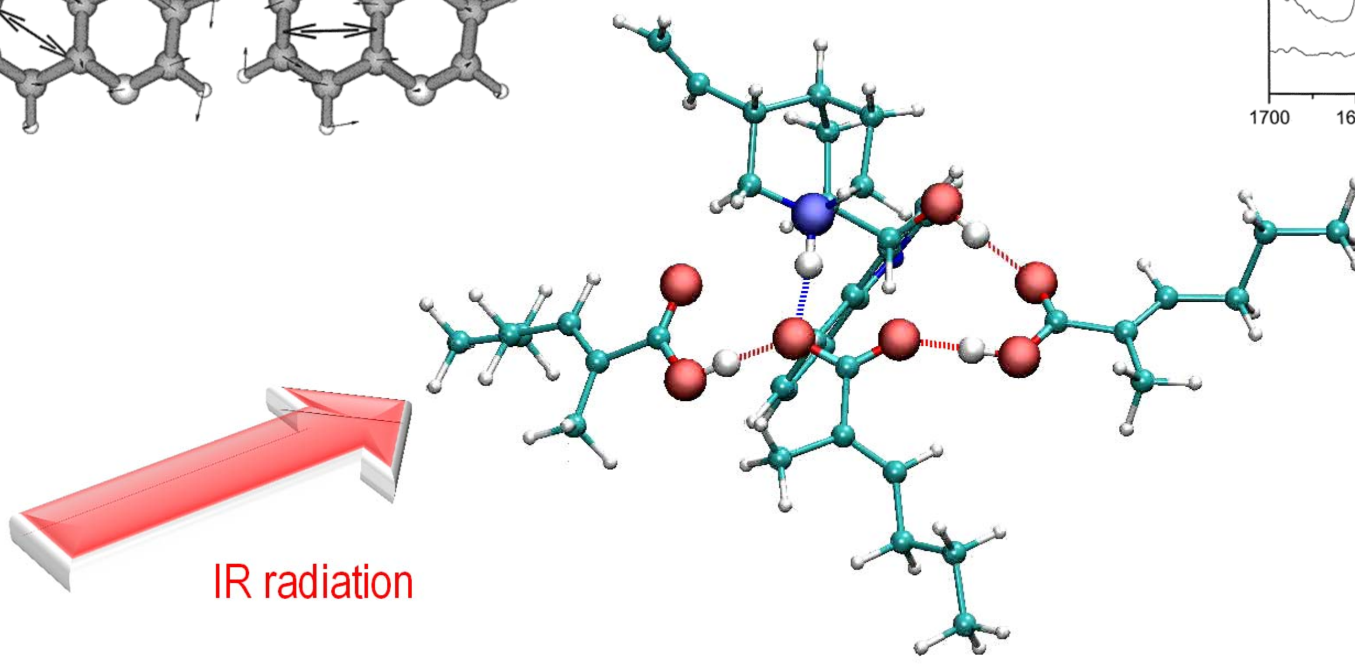

1.6. wt% $Pd/Al_2O_3$; red. 573 K, 30 min; 548 K

# IR spectroscopy is vibrational spectroscopy





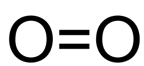




Ferri et al., *JACS* 123 (2001) 12074; Bonalumi et al., *JACS* 127 (2005) 8467

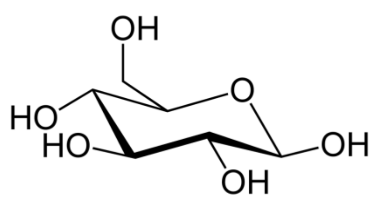
# How many vibrations in a molecule?

| molecule | number of vibrations |
|---|---|
| linear | **3N-5** |
| non-linear | **3N-6** |

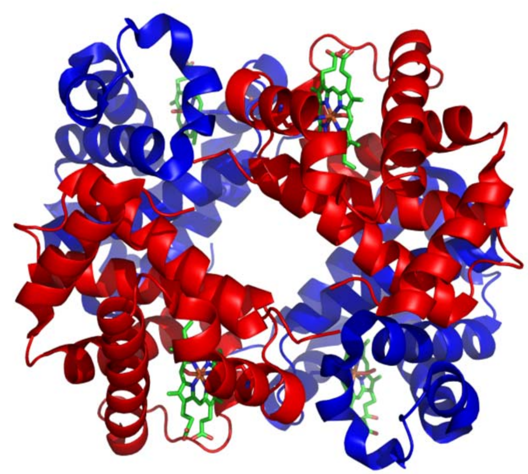
vibrational normal modes




Oxygen molecule (N=2)
1 fundamental mode



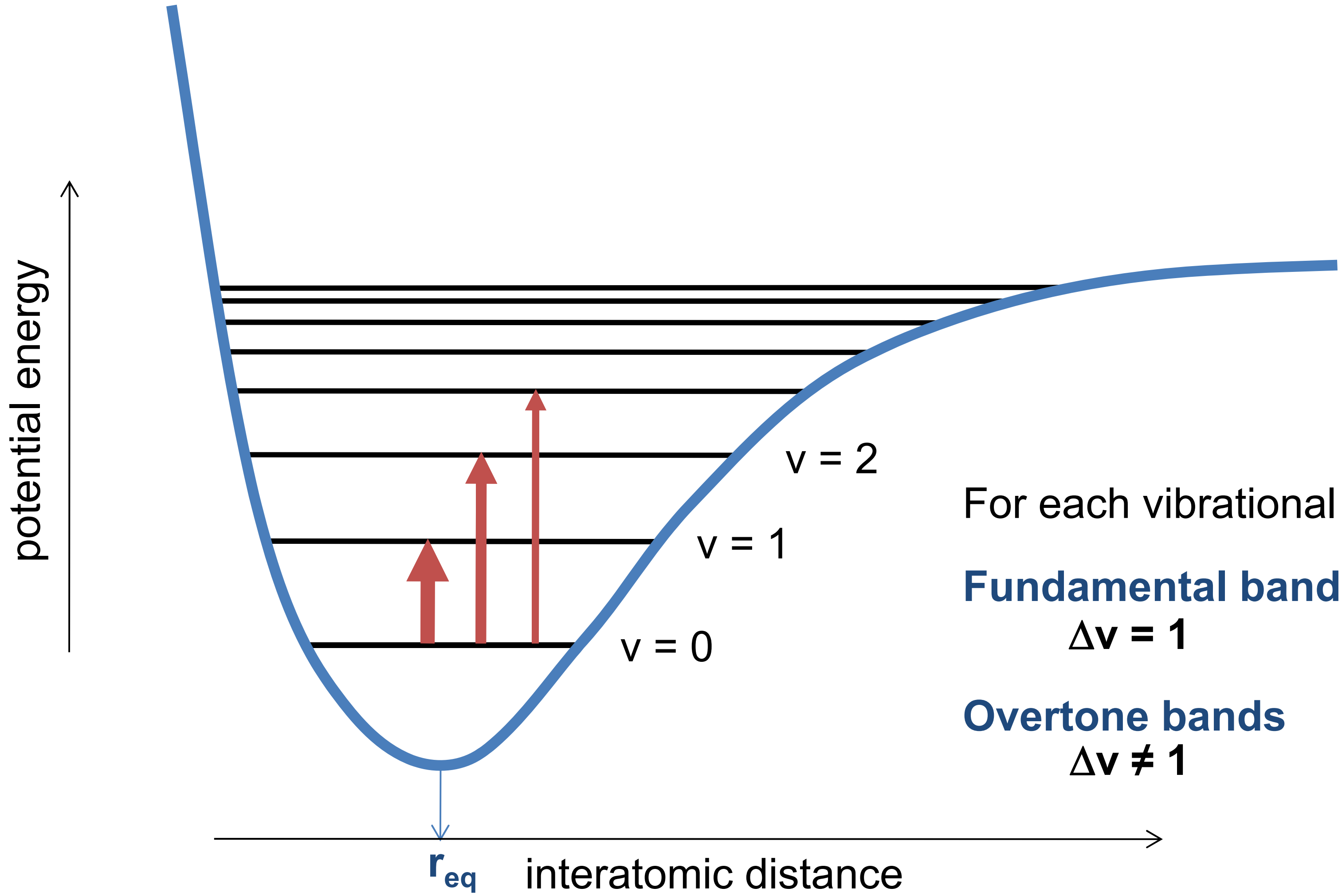

Glucose (N=24)
66 fundamental modes



Proteins (hemoglobin)
N typically 10'000...

# Vibrational transition

- **Real potential**




For each vibrational mode

**Fundamental band**
**Δv = 1**

**Overtone bands**
**Δv ≠ 1**

v= vibrational number

# Which vibrations do appear in a spectrum?

Selection rule

$$\left(\frac{\partial \mu}{\partial Q}\right) \neq 0$$

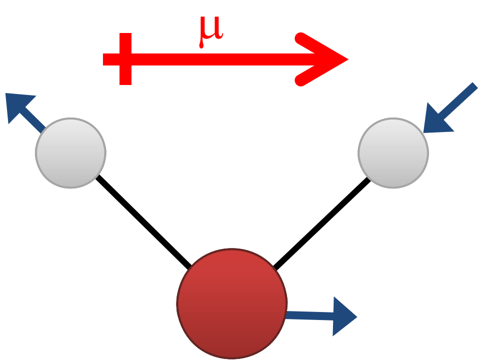
Molecular dipole moment $\mu$ must change due to vibration or rotation along its coordinate (so called, normal mode or normal coordinate, ***Q***)

**Q** Are these molecules infrared active or inactive?

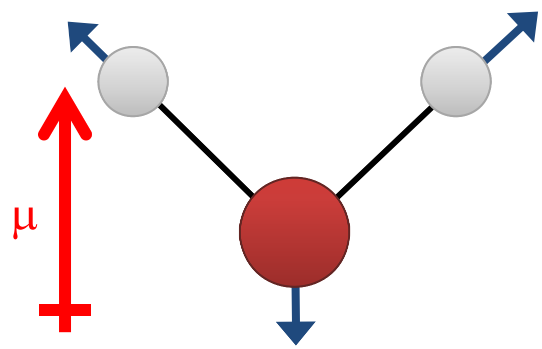
O=O H-Cl Ar

# The $H_2O$ molecule

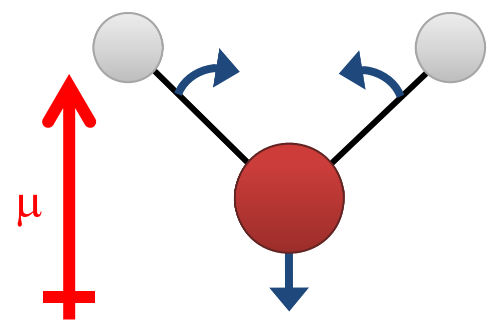
N=3, non-linear, 3 fundamental modes




**3756 cm$^{-1}$**
asymmetric stretching



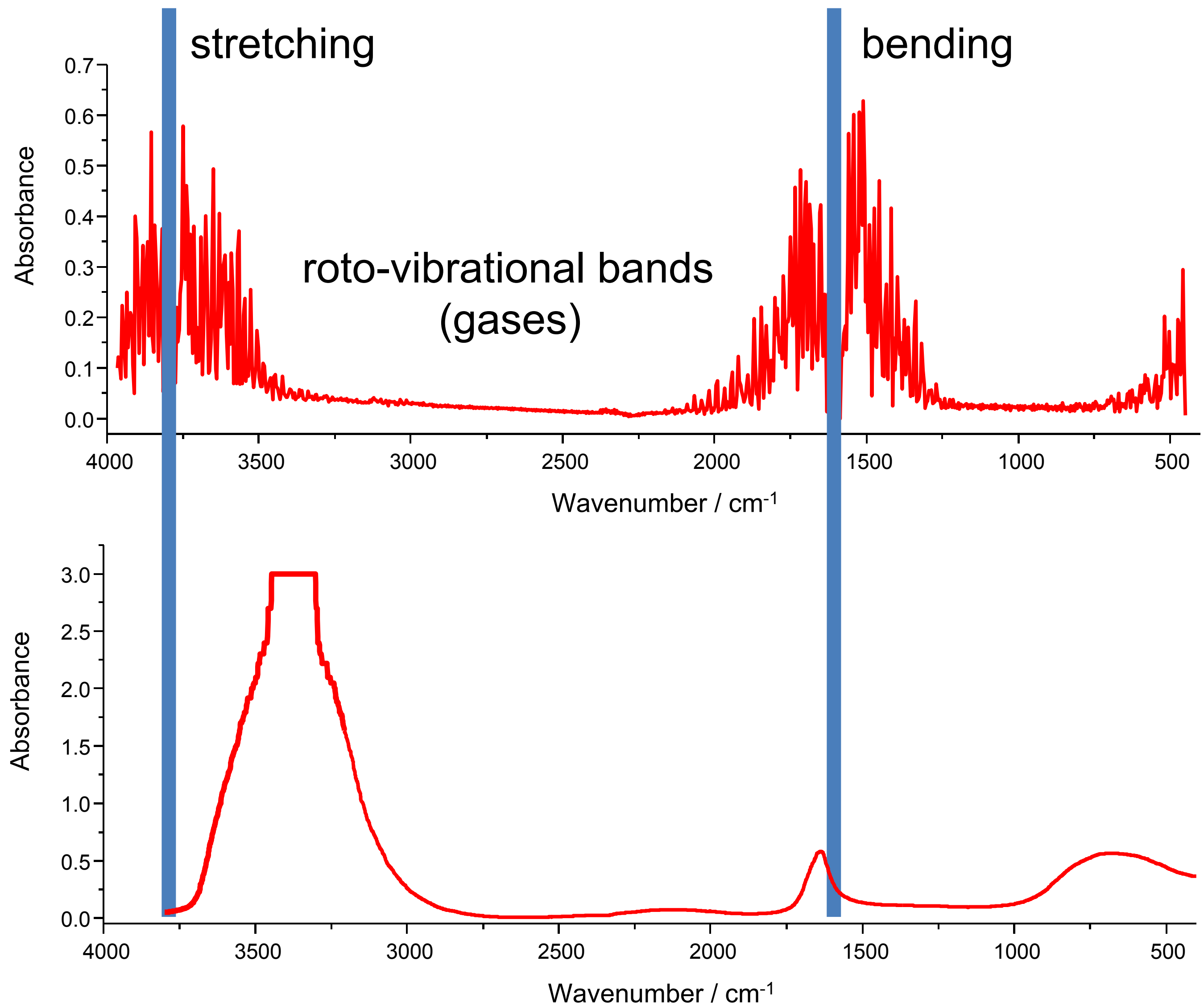

**3657 cm$^{-1}$**
symmetric stretching




**1595 cm$^{-1}$**
scissoring (bending)

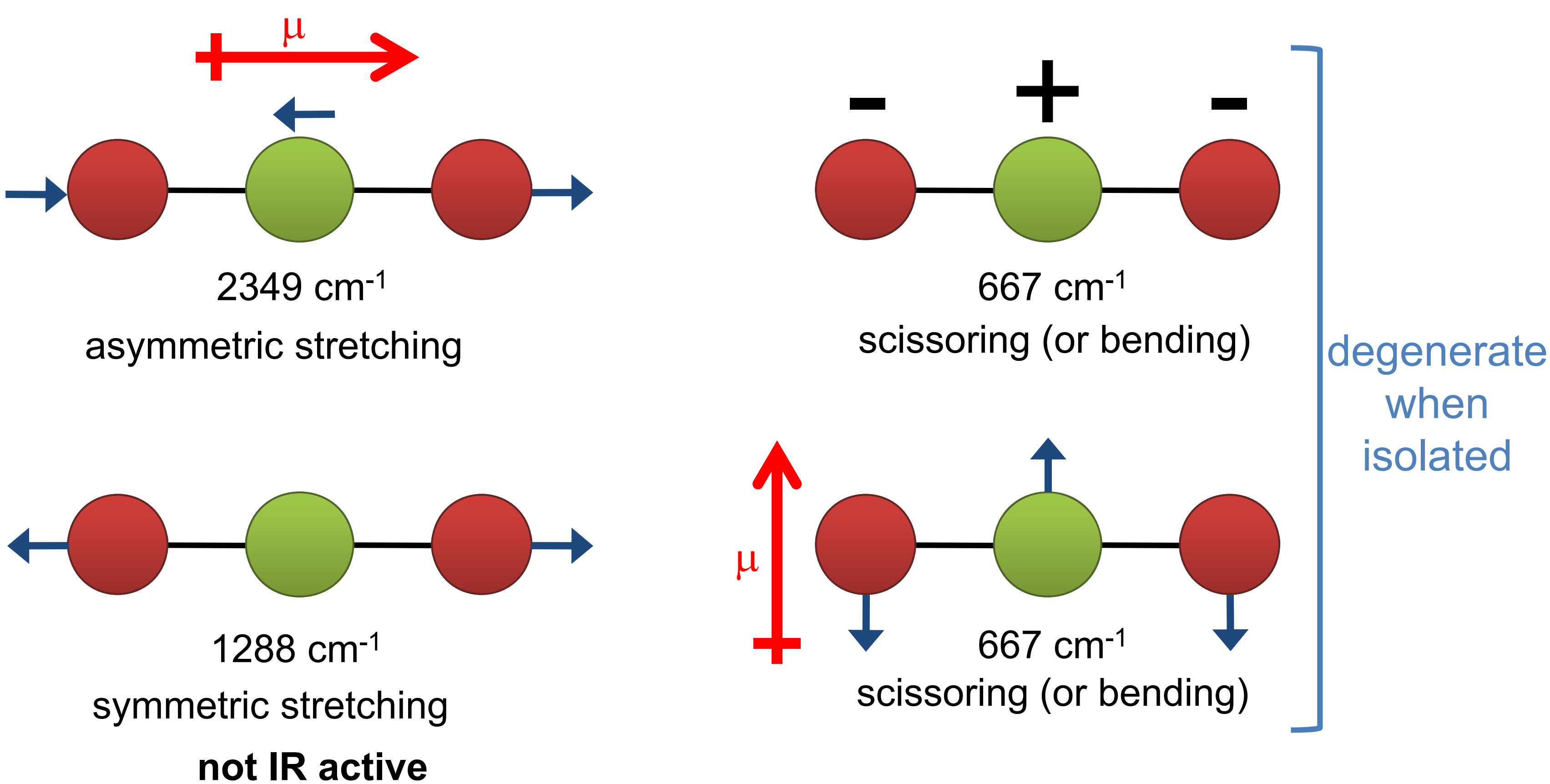
**All modes IR active**

# Gas and liquid phase $H_2O$

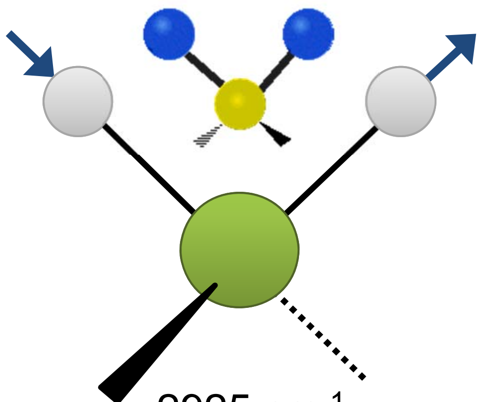


# The $CO_2$ molecule

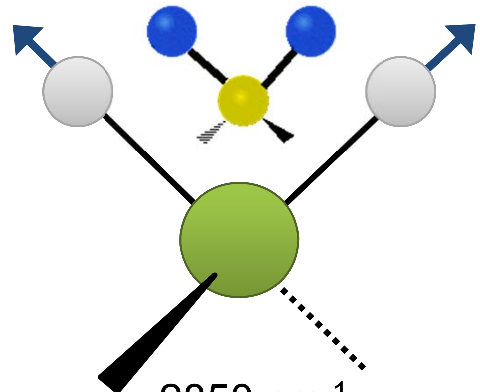
## N=3, linear, 4 fundamental modes



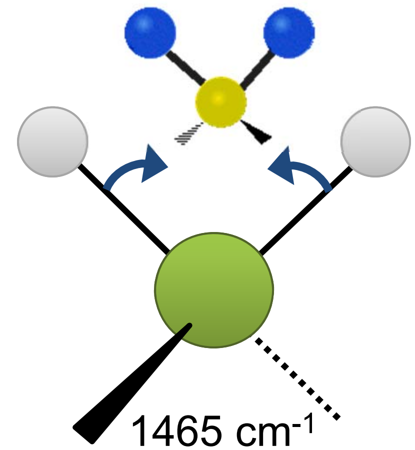
# The $-CH_2$ group



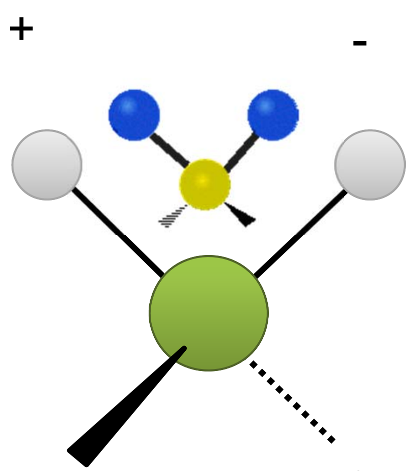
2925 $cm^{-1}$
asymmetric stretching



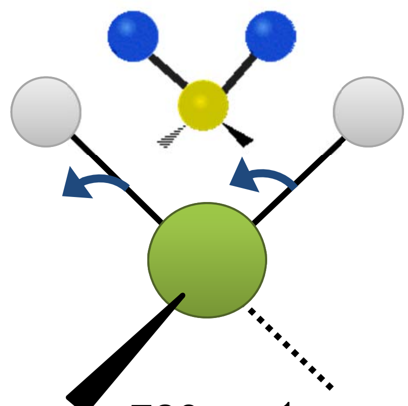
2850 $cm^{-1}$
symmetric stretching



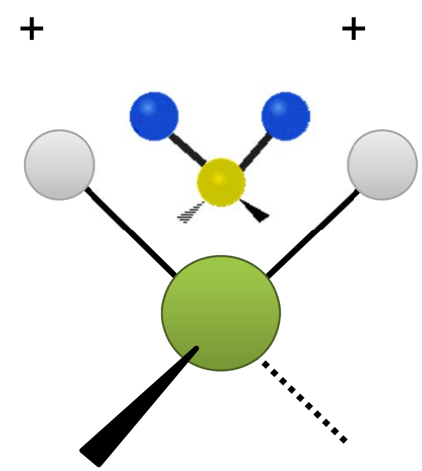
1465 $cm^{-1}$
scissoring /
bending in-plane




1350-1150 $cm^{-1}$
twisting /
bending out-of-plane

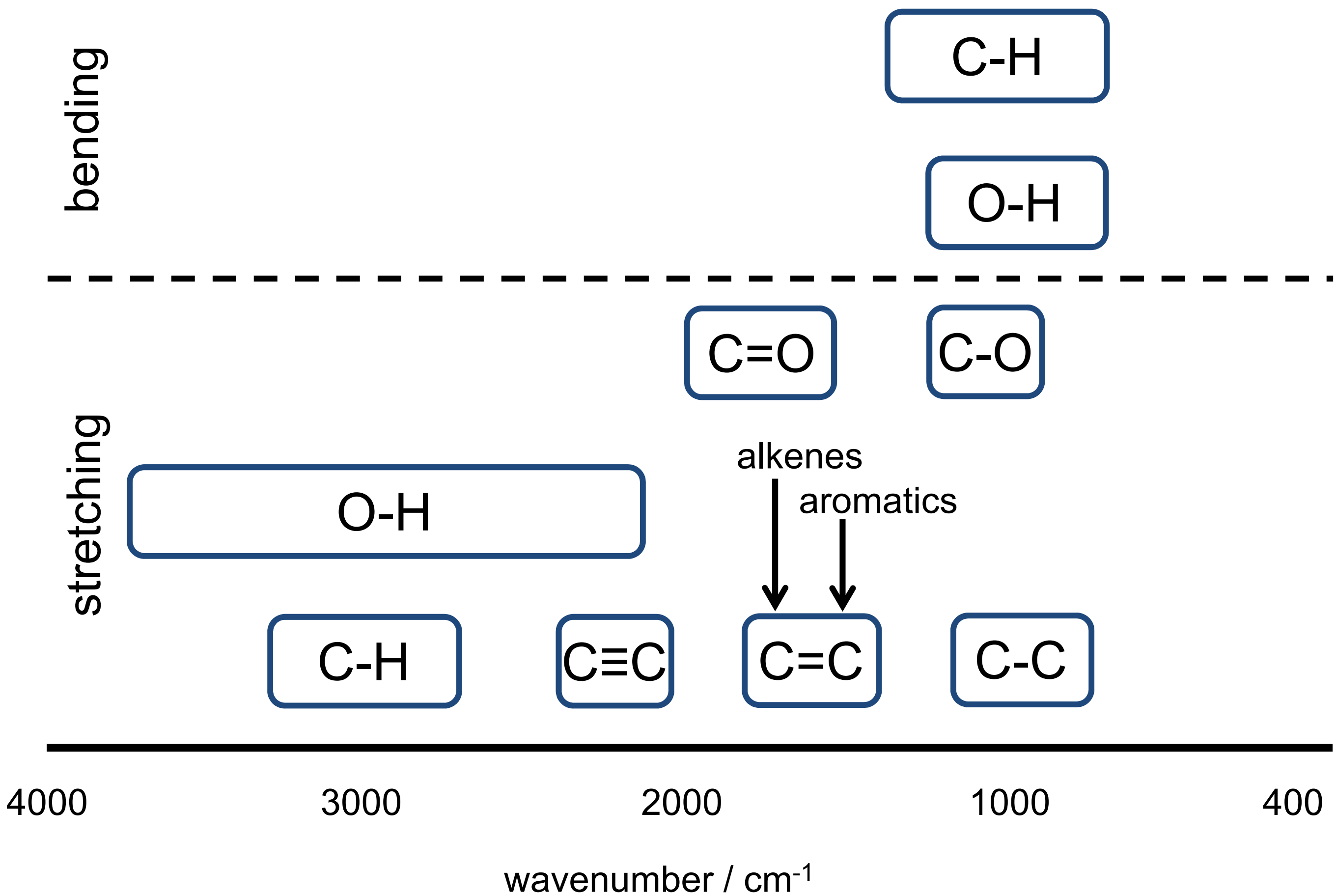


720 $cm^{-1}$
rocking /
bending in-plane



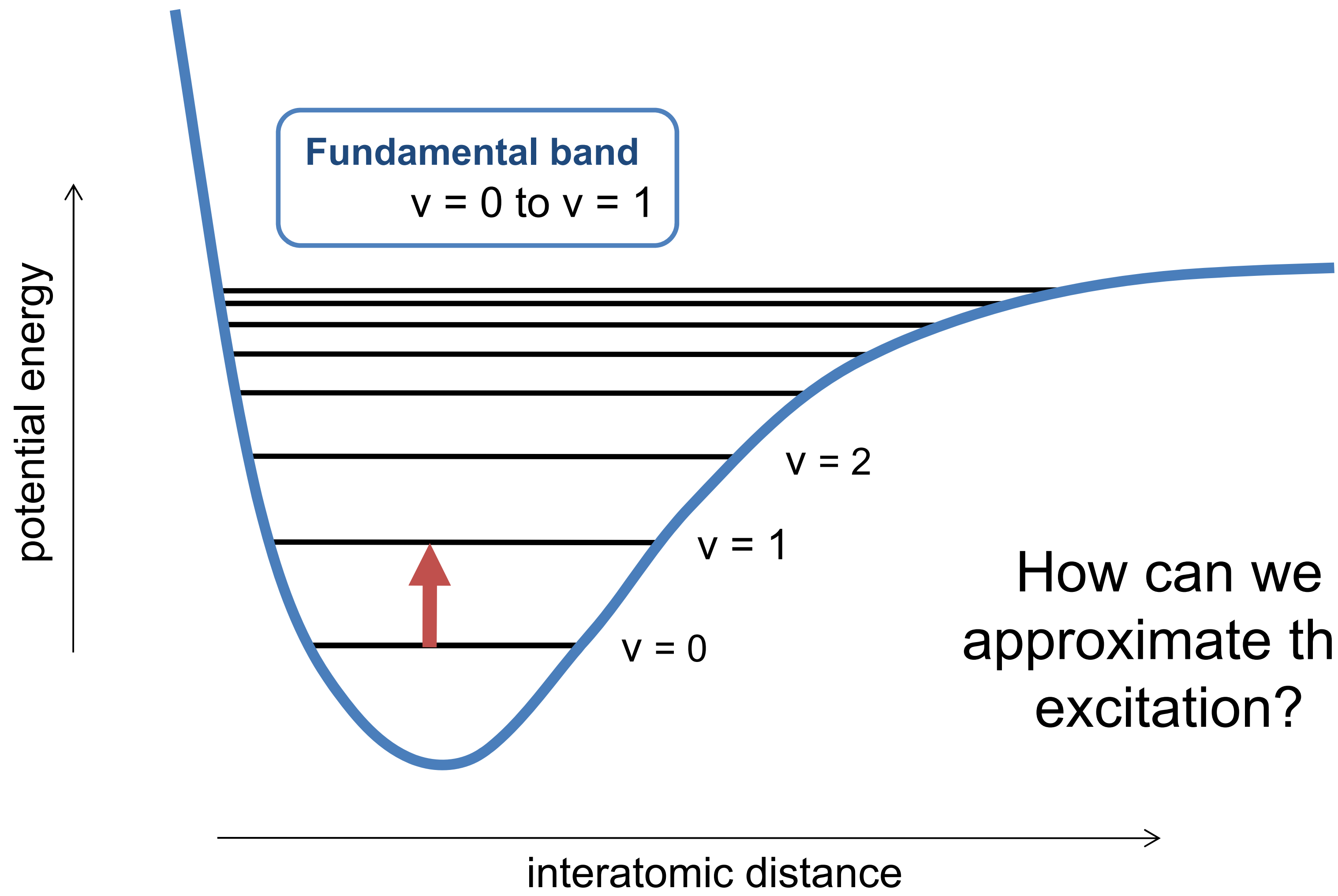

1350-1150 $cm^{-1}$
wagging /
bending out-of-plane

# Basic functional groups



# Frequency

- **Real potential**

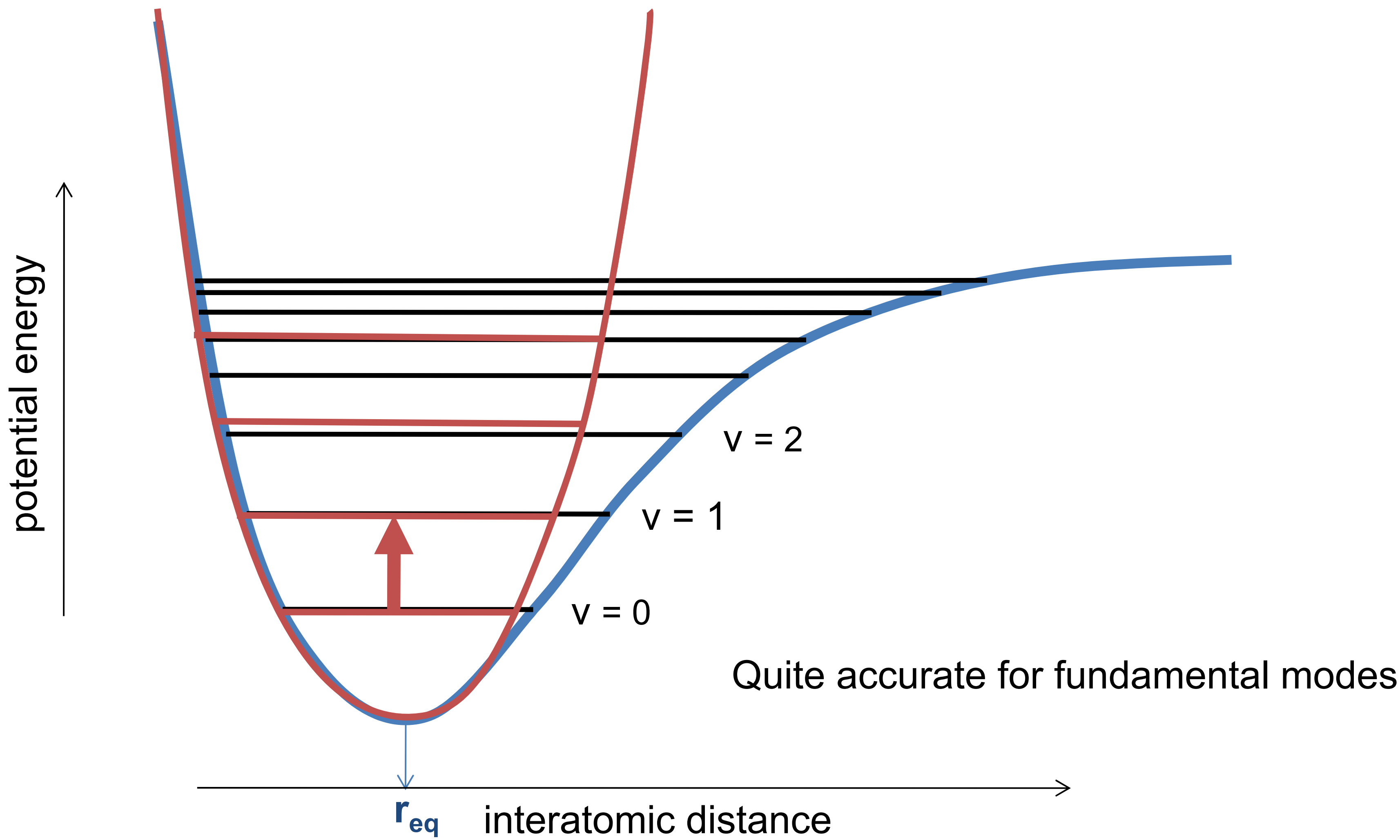



How can we approximate this excitation?

v= vibrational number

# Frequency

- **Approximation: harmonic oscillator**

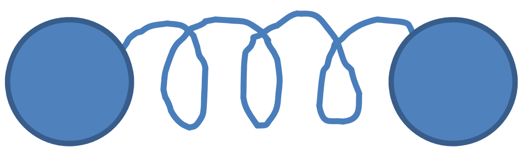



v= vibrational number

# Frequency

- **Approximation: harmonic oscillator**

The stretching frequency of a bond can be approximated by Hooke's law. Two atoms and the connecting bond are treated as a harmonic oscillator composed of two masses (atoms) joined by a spring.

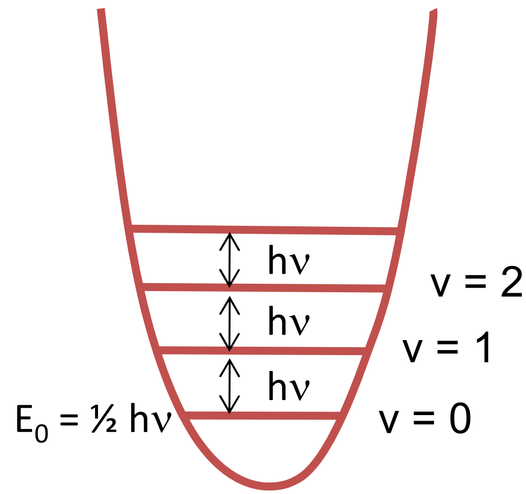


$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k: force constant

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

μ: reduced mass




v= vibrational number

# Stretching modes

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

| C-C | C=C | C≡C |
|---|---|---|
| 1200 $cm^{-1}$ | 1650 $cm^{-1}$ | 2200 $cm^{-1}$ |

→ larger k

| C-H | C-D | C-C | C-O | C-Cl |
|---|---|---|---|---|
| 3000 $cm^{-1}$ | 2100 $cm^{-1}$ | 1200 $cm^{-1}$ | 1100 $cm^{-1}$ | 800 $cm^{-1}$ |

→ larger $\mu$