Infrared spectroscopy

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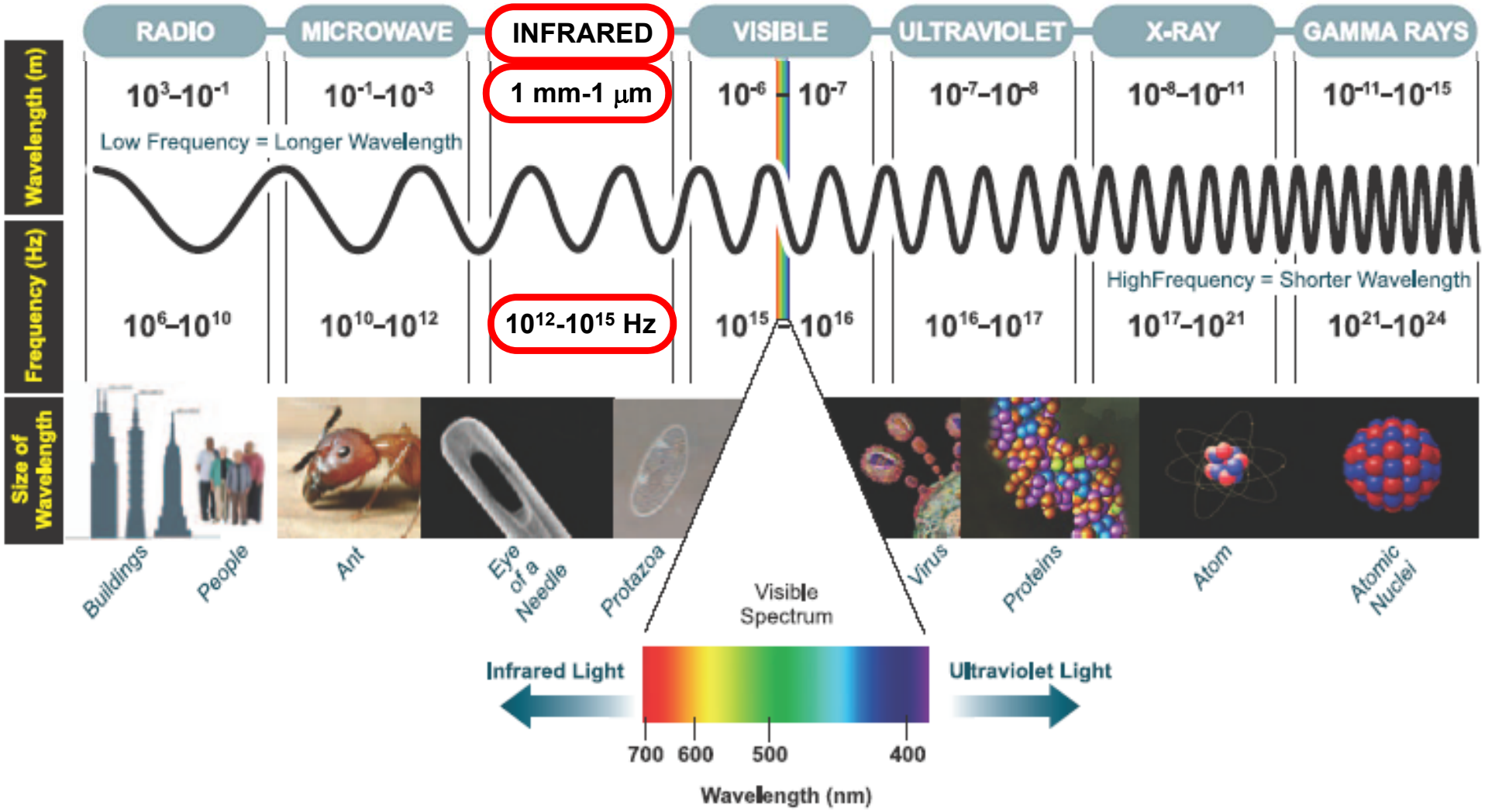
The electromagnetic spectrum



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

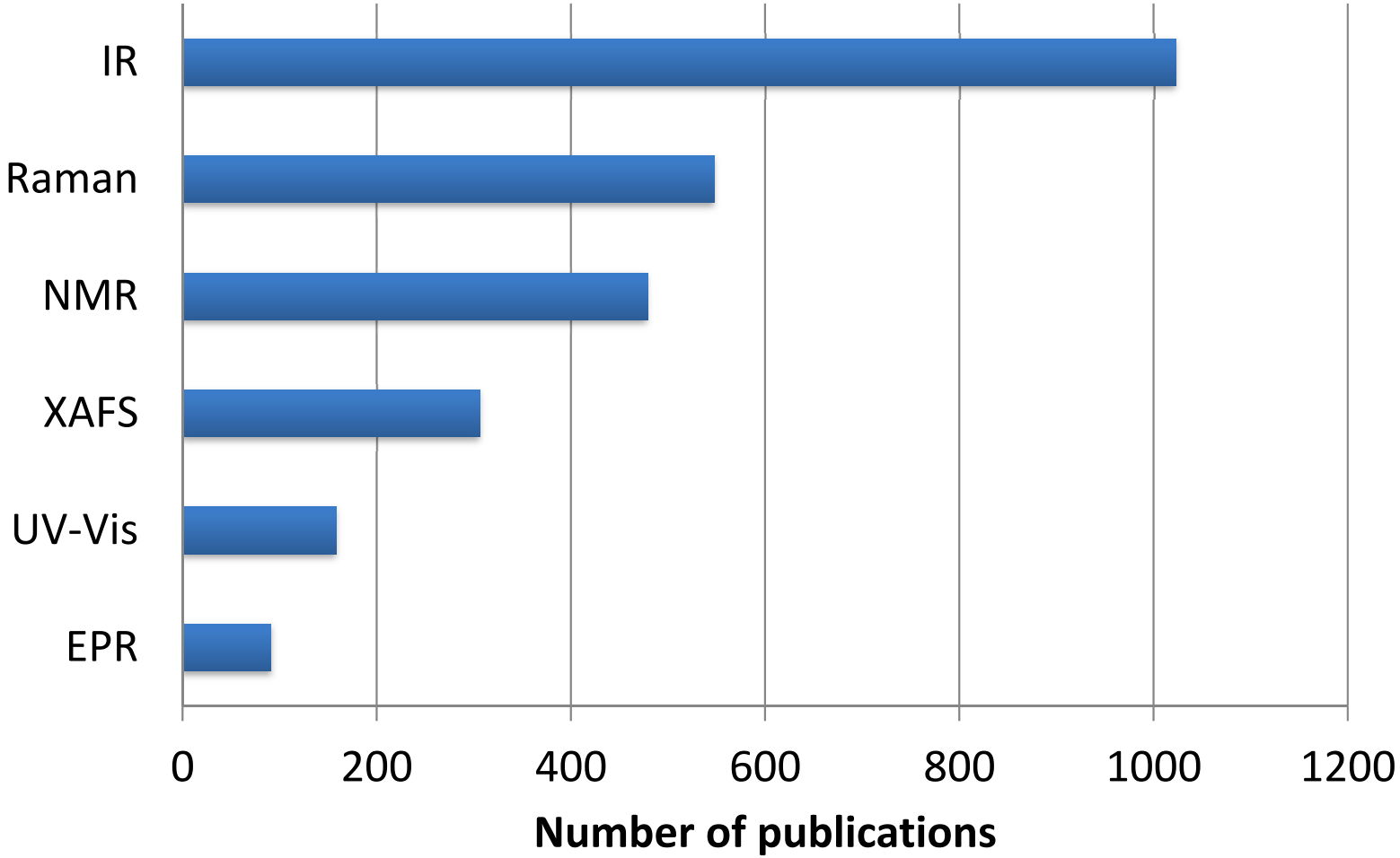
pros

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

cons

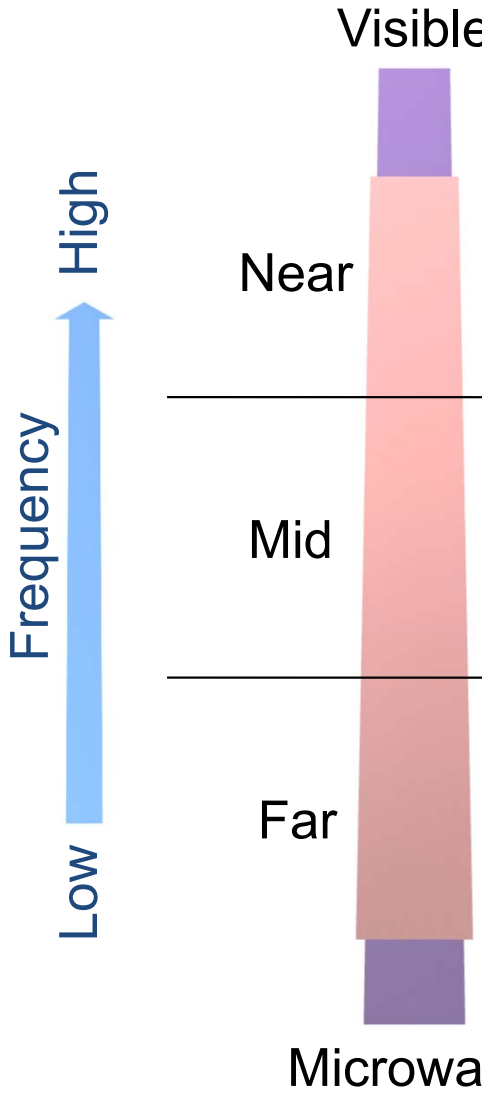
- no atomic resolution

Importance of IR spectroscopy in catalysis



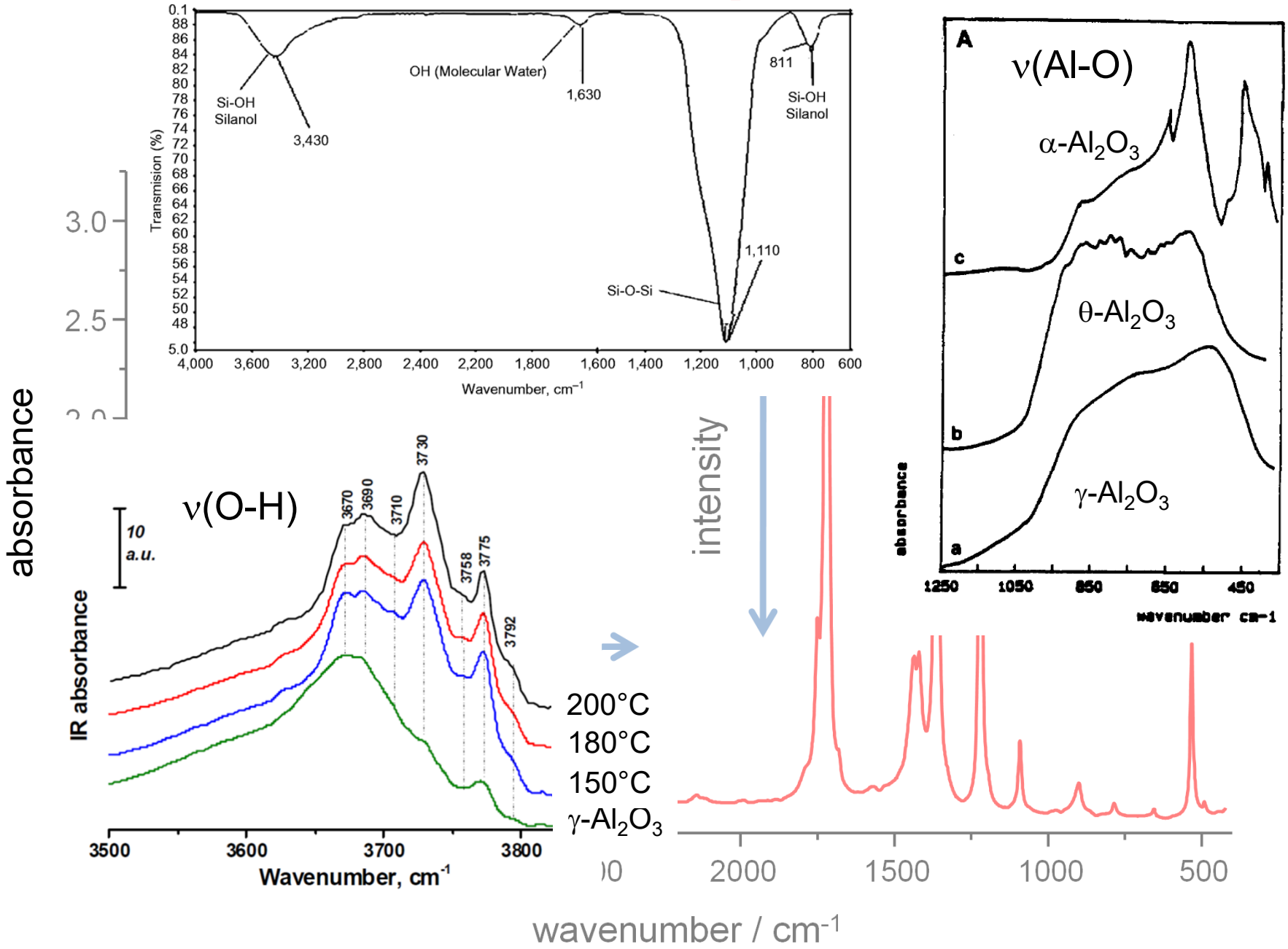
Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

The IR region



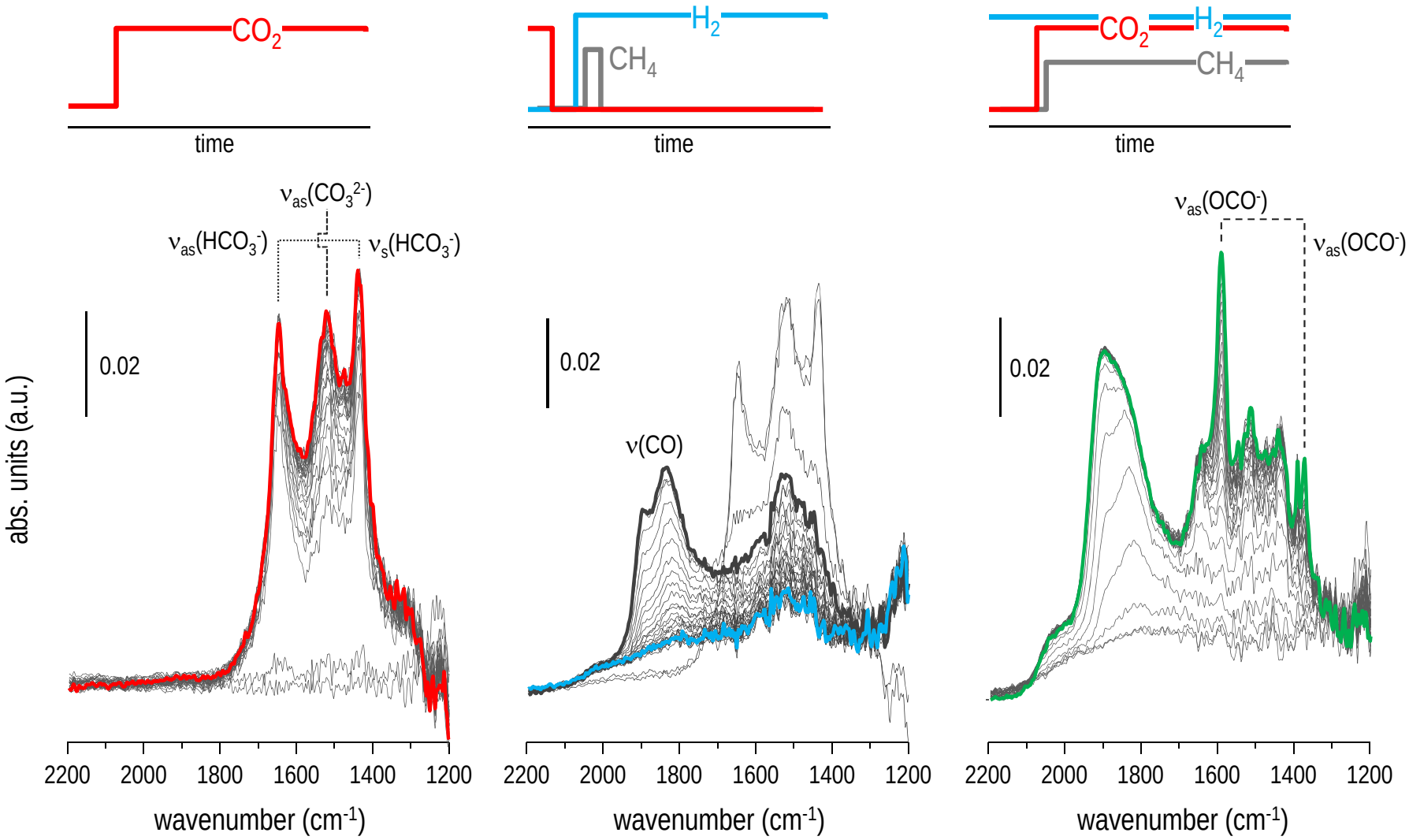
	λ [μm]õ	ν̃ [cm^{-1}]	E [kJ/mol]	
Near	0.78-2.5	12800-4000	150-50	overtone, combination vibrations
Mid	2.5-25	4000-400	50-5	fundamental vibrations
Far	25-1000	400-10	5-0.1	fundamental vibrations of heavy elements, lattice vibrations

The mid-IR spectrum



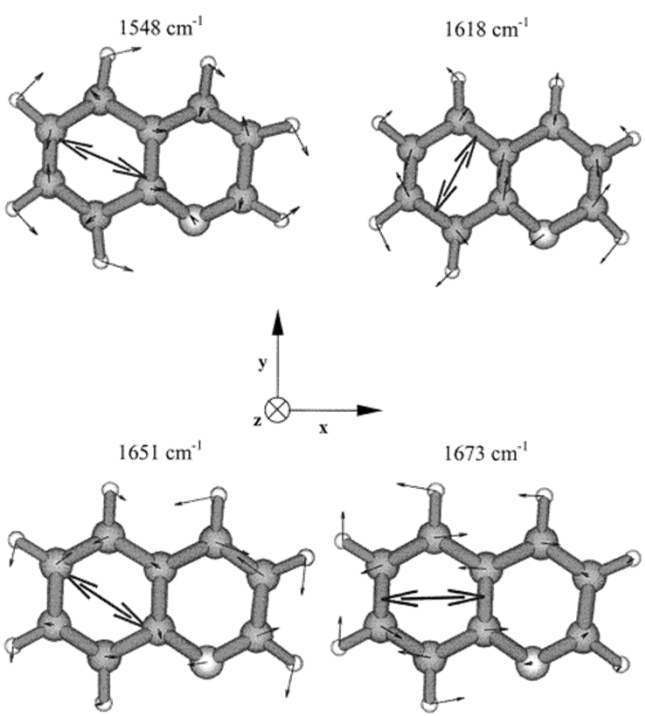
Morterra, Catal. Today 27 (1996) 497

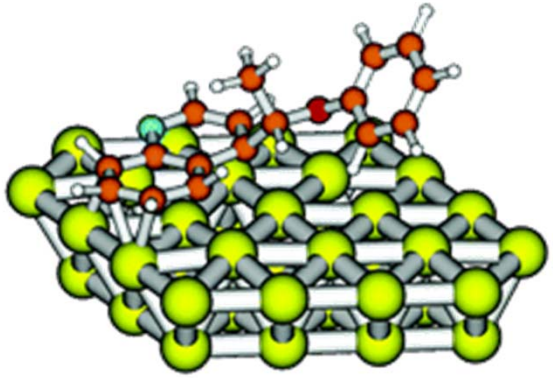
Adsorbates by IR spectroscopy

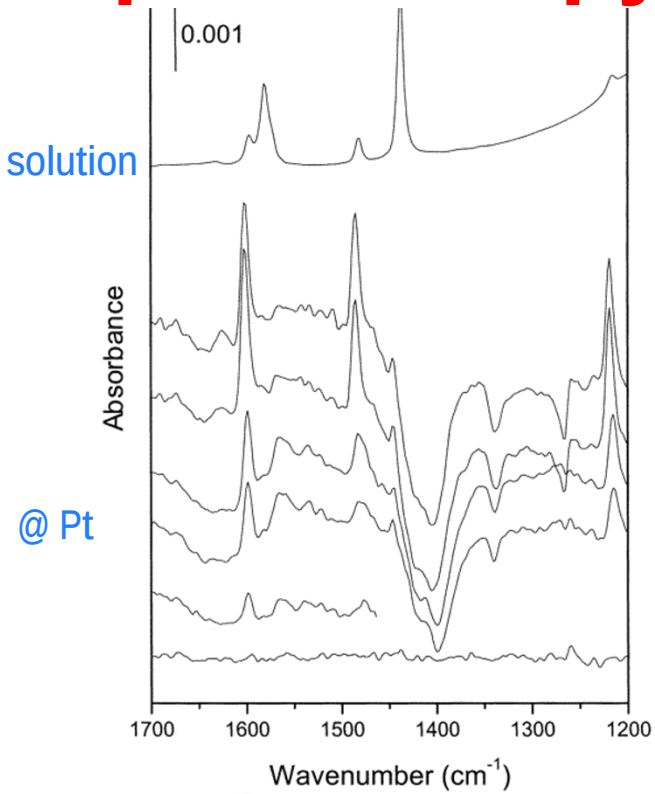


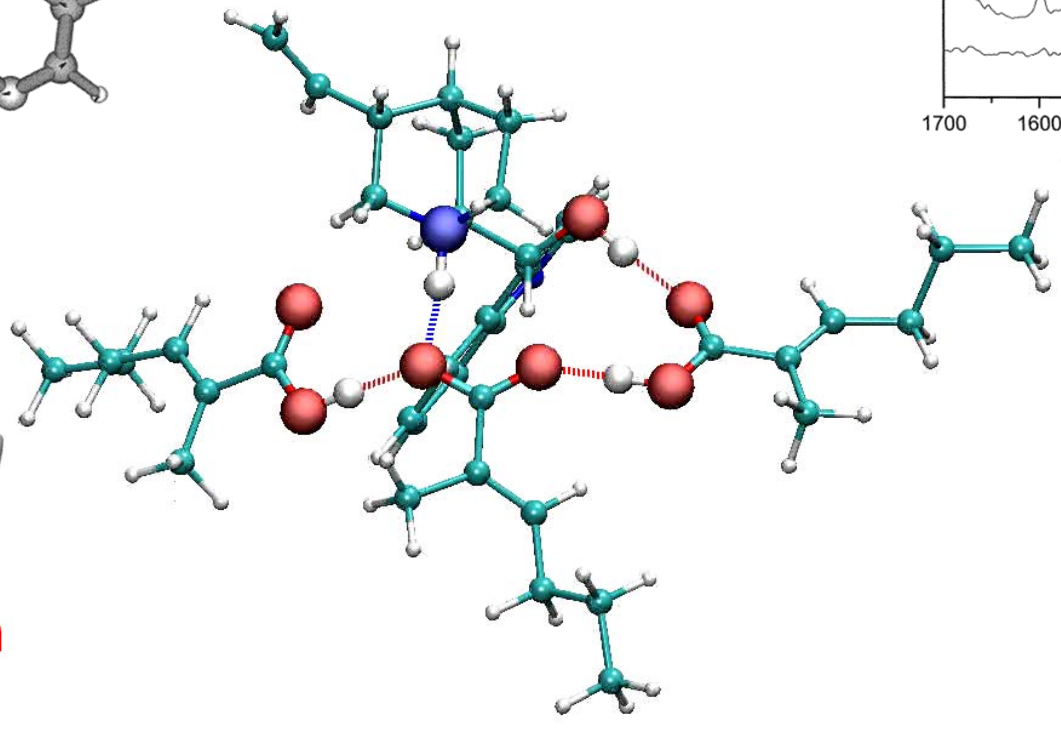
1.6. wt% Pd/Al_2O_3; red. 573 K, 30 min; 548 K

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?

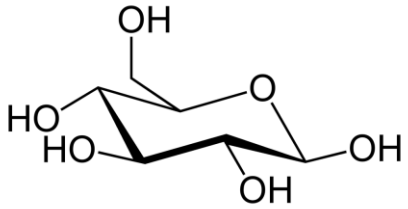
molecule	number of vibrations
linear	**3N-5**
non-linear	**3N-6**

vibrational normal modes

O=O

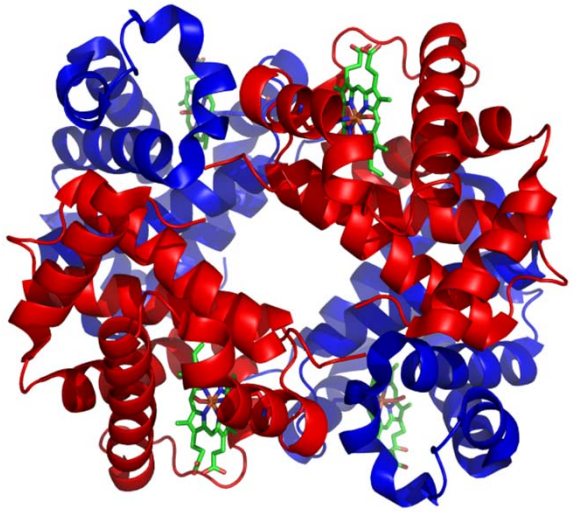
Oxygen molecule (N=2)

1 fundamental mode



Glucose (N=24)

66 fundamental modes

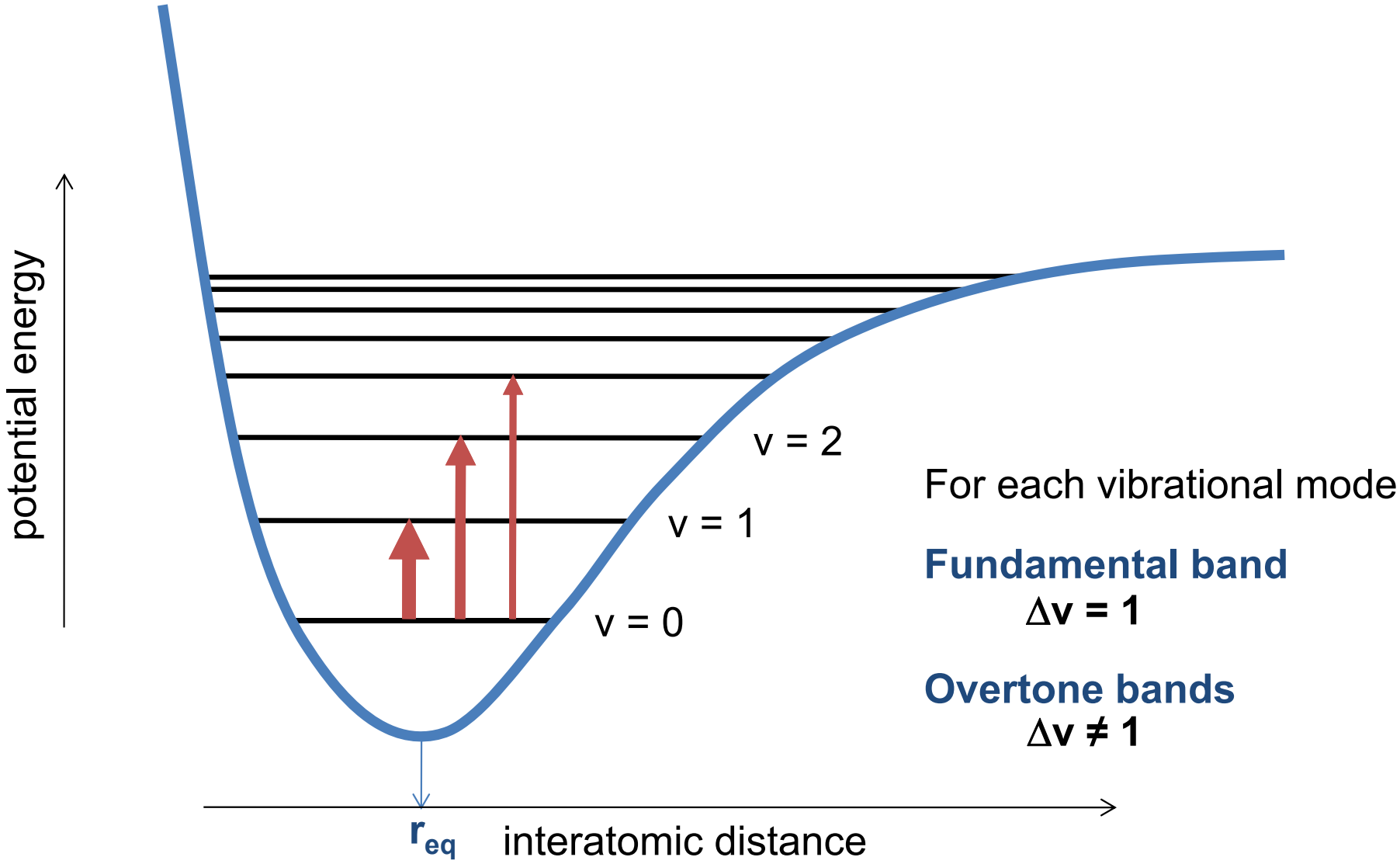


Proteins (hemoglobin)

N typically 10'000...

Vibrational transition

- **Real potential**



For each vibrational mode

Fundamental band
$\Delta v = 1$

Overtone bands
$\Delta v \neq 1$

v= vibrational number

Which vibrations do appear in a spectrum?

Selection rule

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

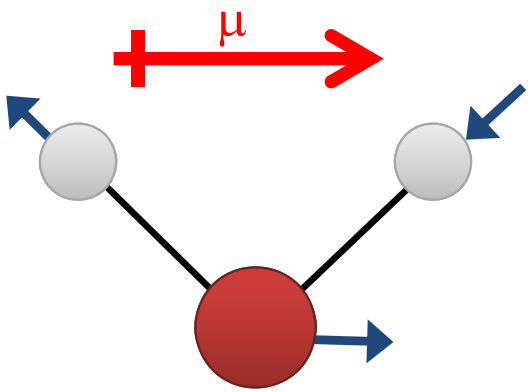
Molecular dipole moment μ must change due to vibration or rotation along its coordinate (so called, normal mode or normal coordinate, Q)

Q Are these molecules infrared active or inactive?

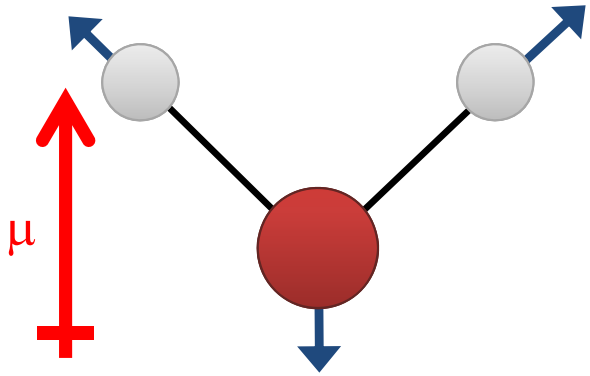
O=O H-Cl Ar

The H_2O molecule

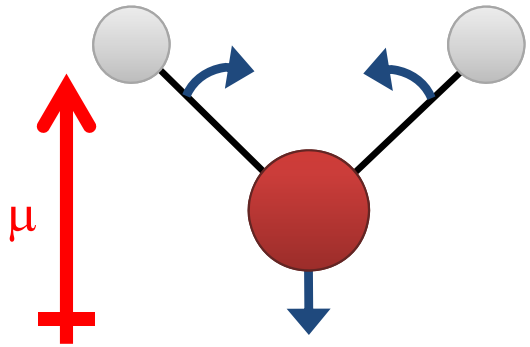
N=3, non-linear, 3 fundamental modes



3756 cm^{-1}
asymmetric stretching



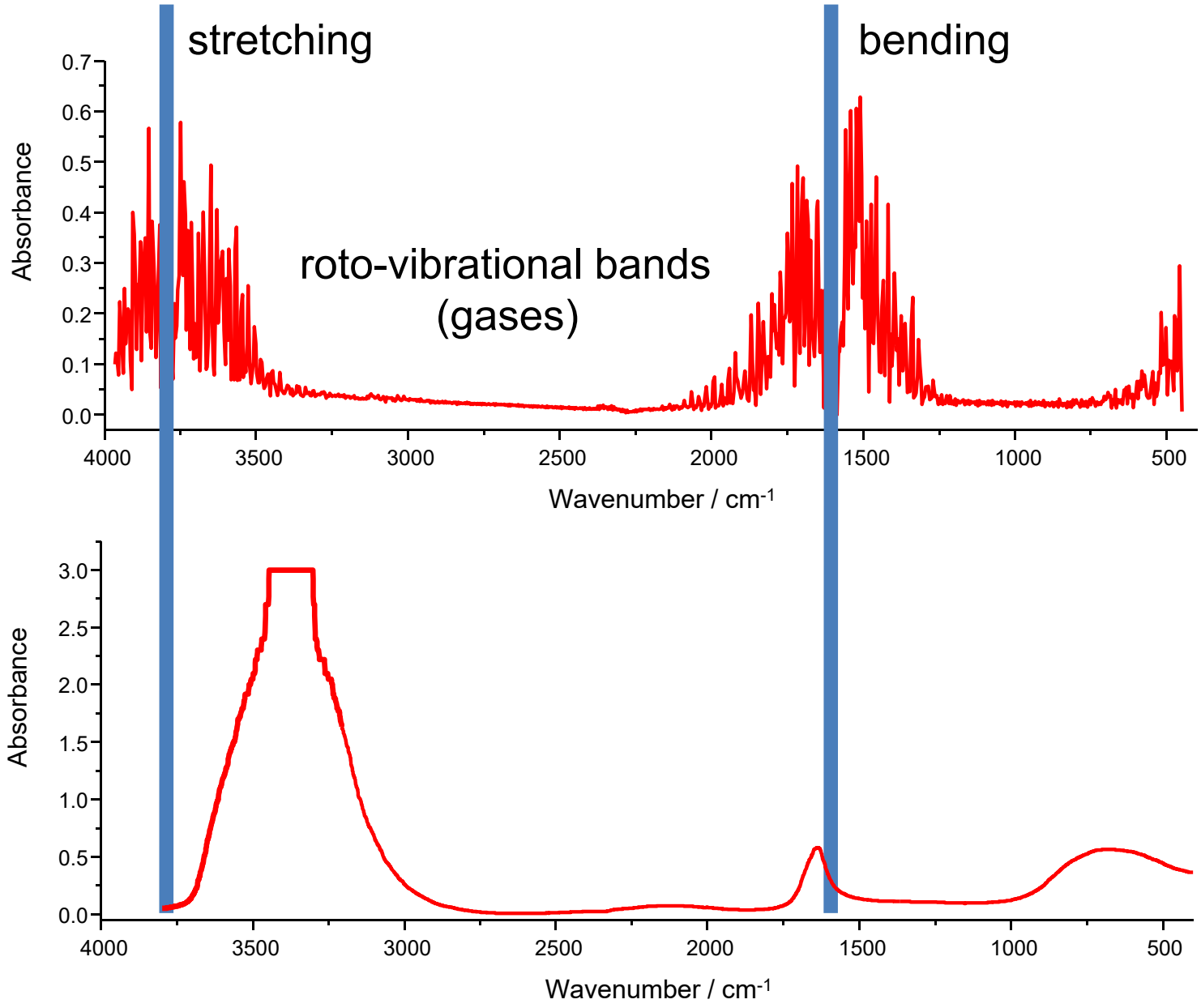
3657 cm^{-1}
symmetric stretching



1595 cm^{-1}
scissoring (bending)

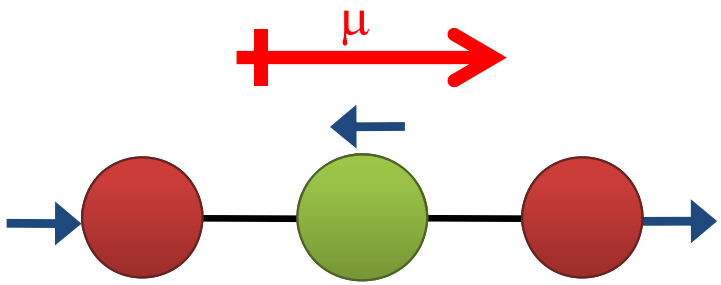
All modes IR active

Gas and liquid phase H_2O



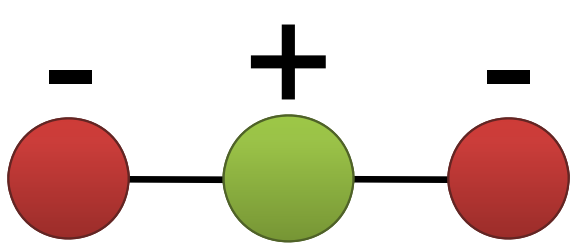
The CO_2 molecule

N=3, linear, 4 fundamental modes



2349 cm^{-1}

asymmetric stretching



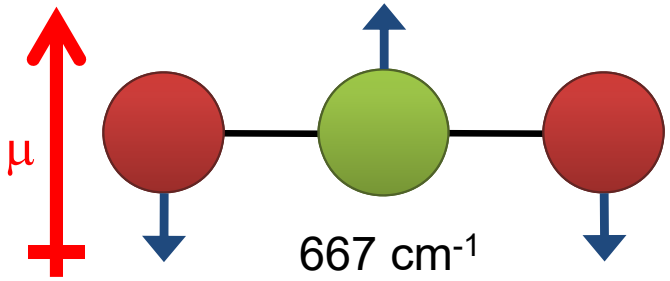
667 cm^{-1}

scissoring (or bending)

1288 cm^{-1}

symmetric stretching

not IR active

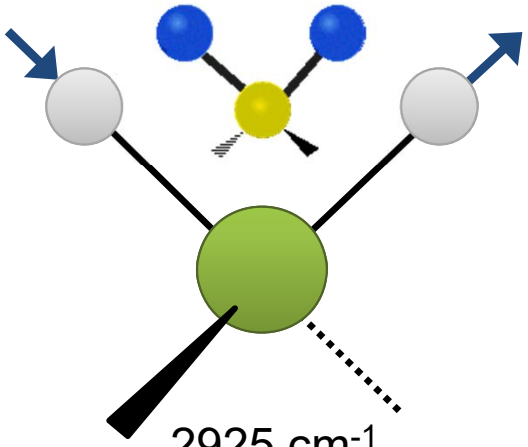


667 cm^{-1}

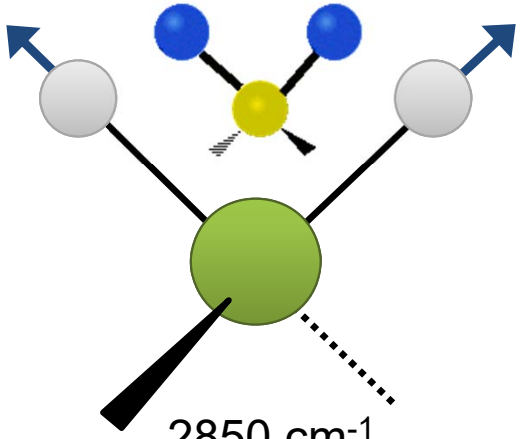
scissoring (or bending)

degenerate when isolated

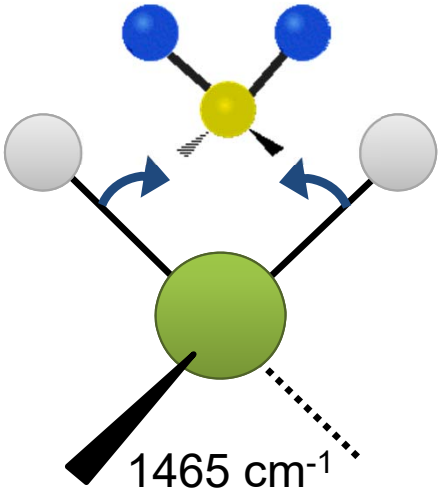
The -CH_2 group



2925 cm^{-1}
asymmetric stretching

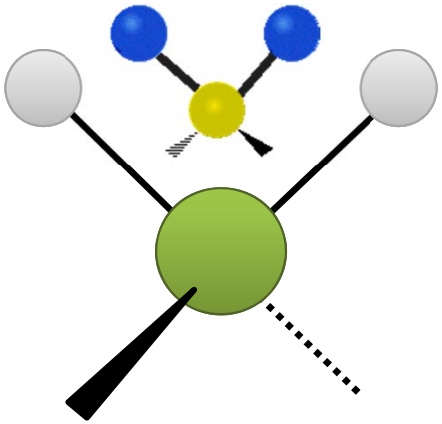


2850 cm^{-1}
symmetric stretching

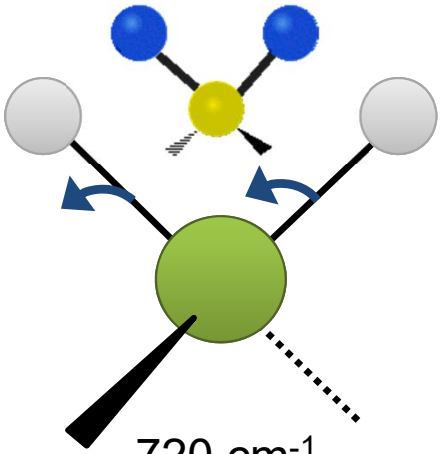


1465 cm^{-1}
scissoring /
bending in-plane

\+ -

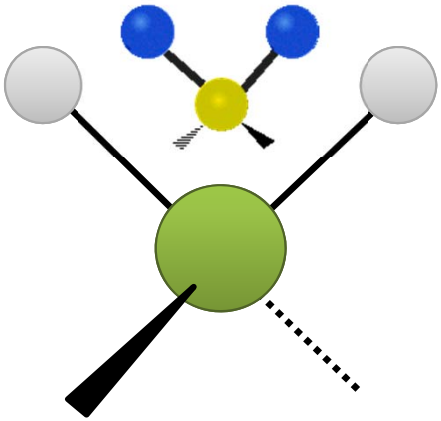


1350-1150 cm^{-1}
twisting /
bending out-of-plane



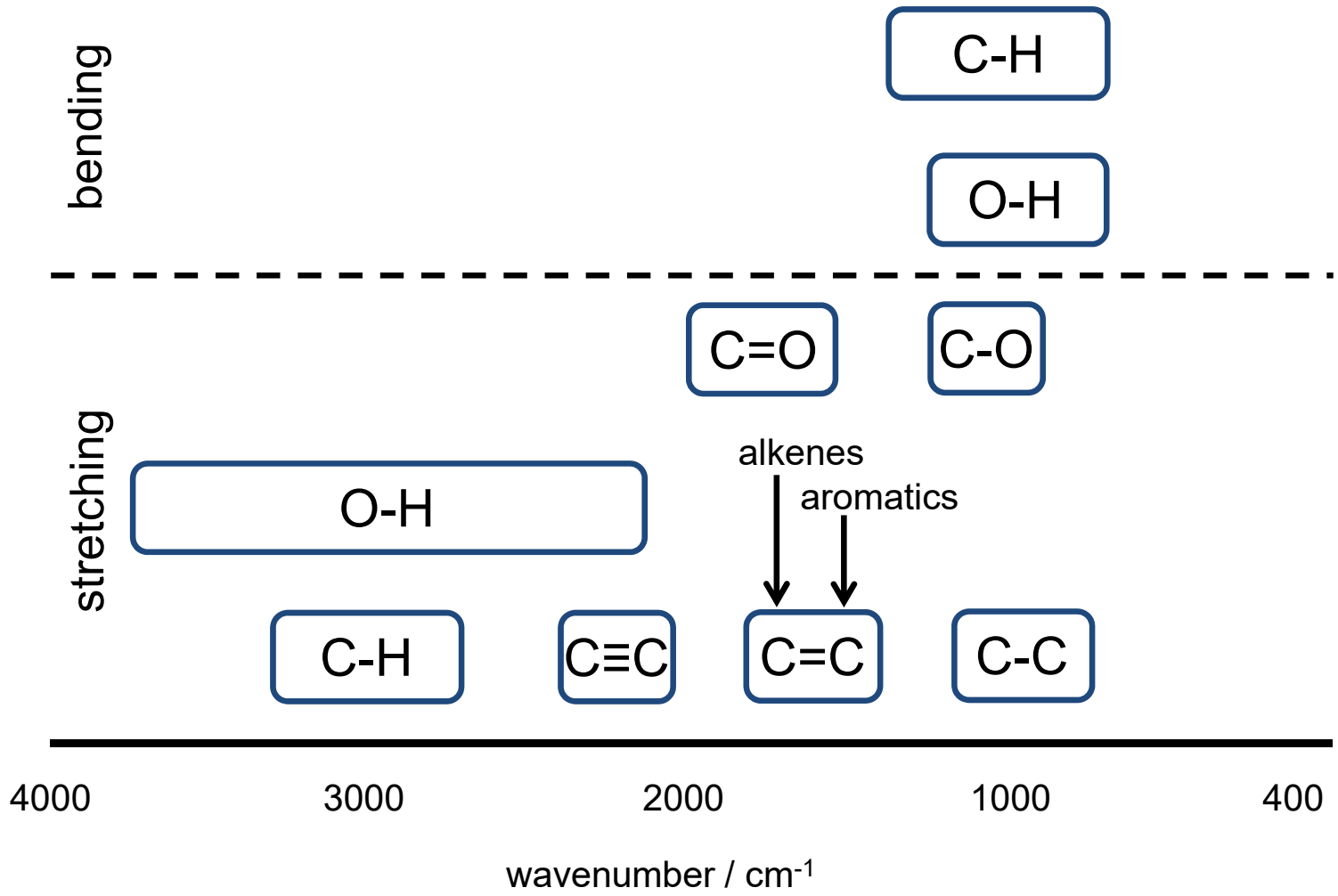
720 cm^{-1}
rocking /
bending in-plane

\+ +



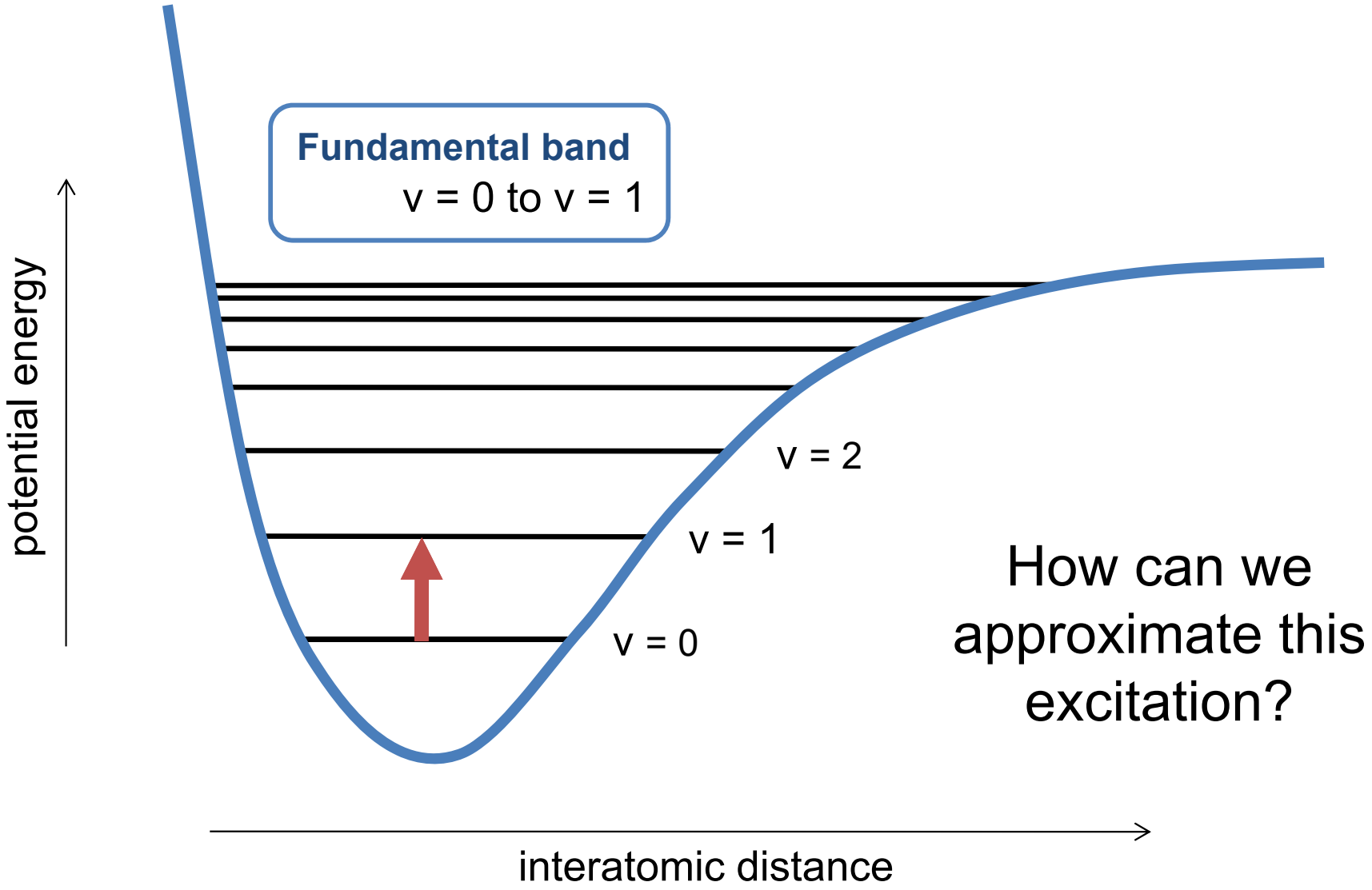
1350-1150 cm^{-1}
wagging /
bending out-of-plane

Basic functional groups



Frequency

- **Real potential**

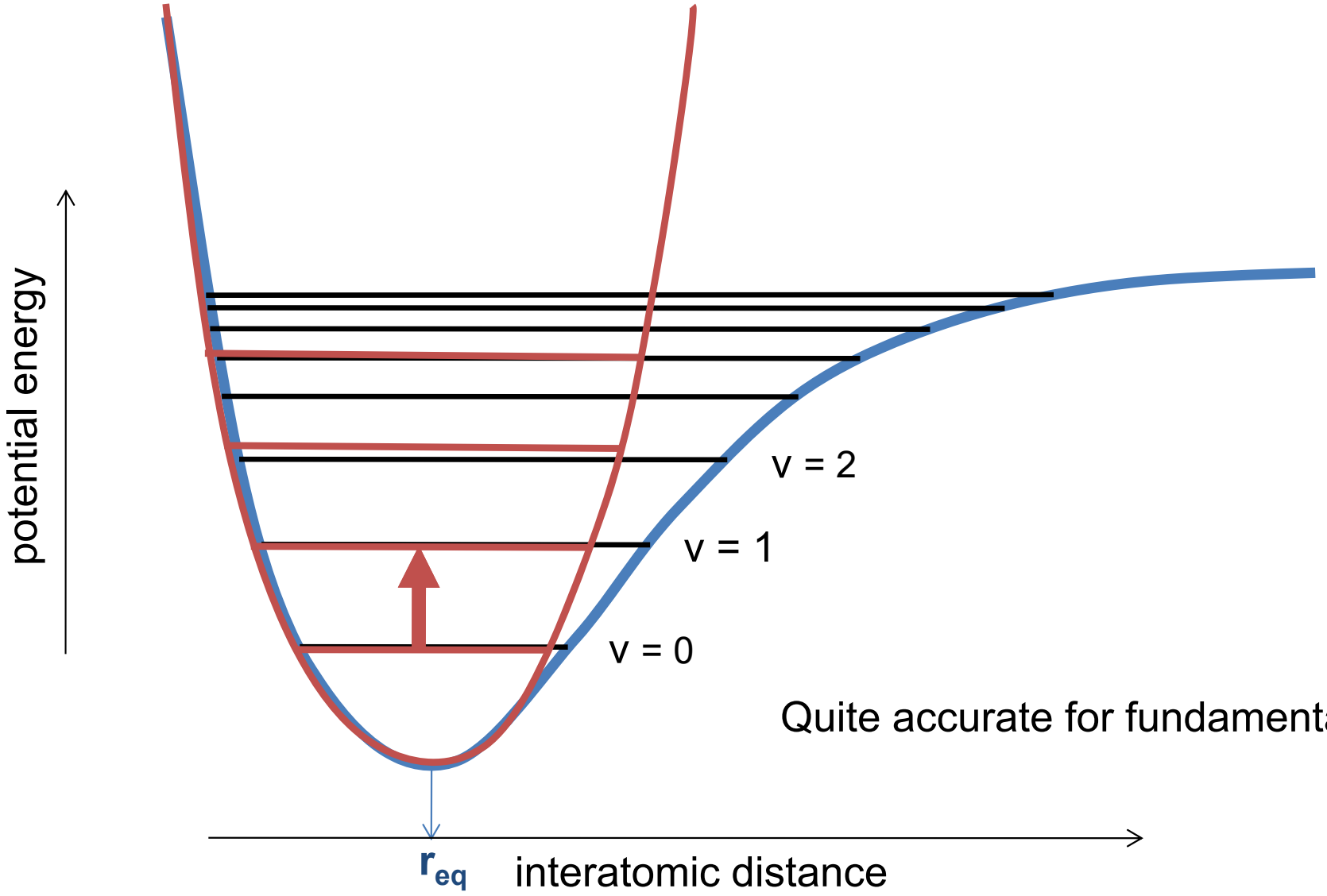


How can we approximate this excitation?

v= vibrational number

Frequency

- **Approximation: harmonic oscillator**

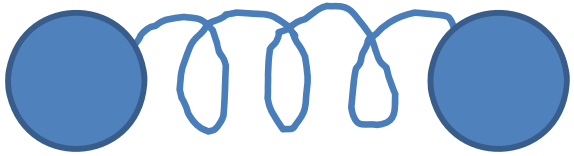


v= vibrational number

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.

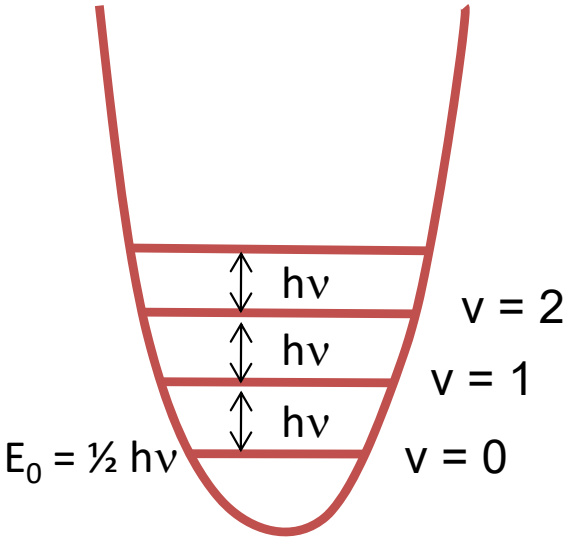


$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

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

larger k

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

larger μ