Infrared spectroscopy

Basic theory

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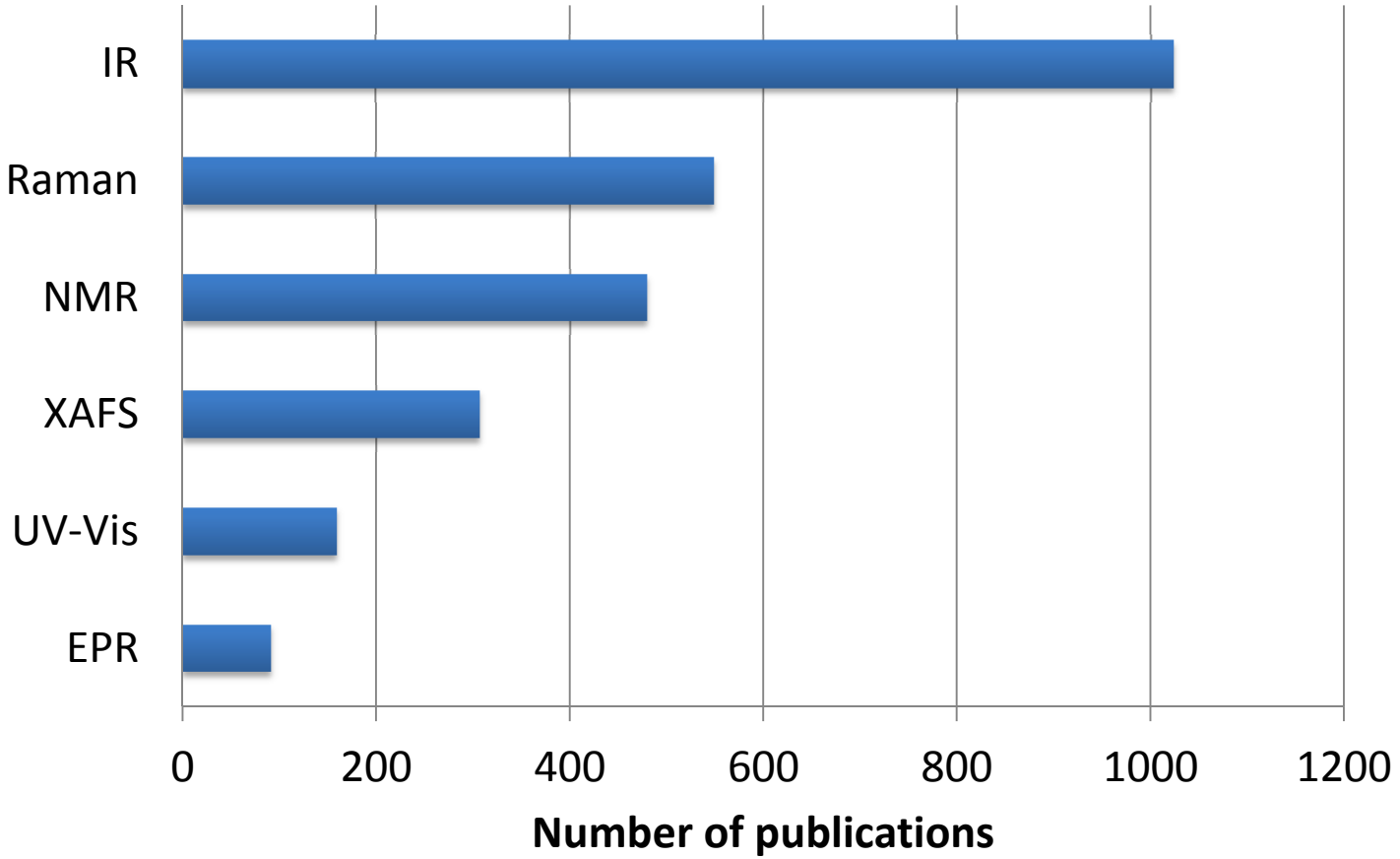
Importance of IR spectroscopy in catalysis



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

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

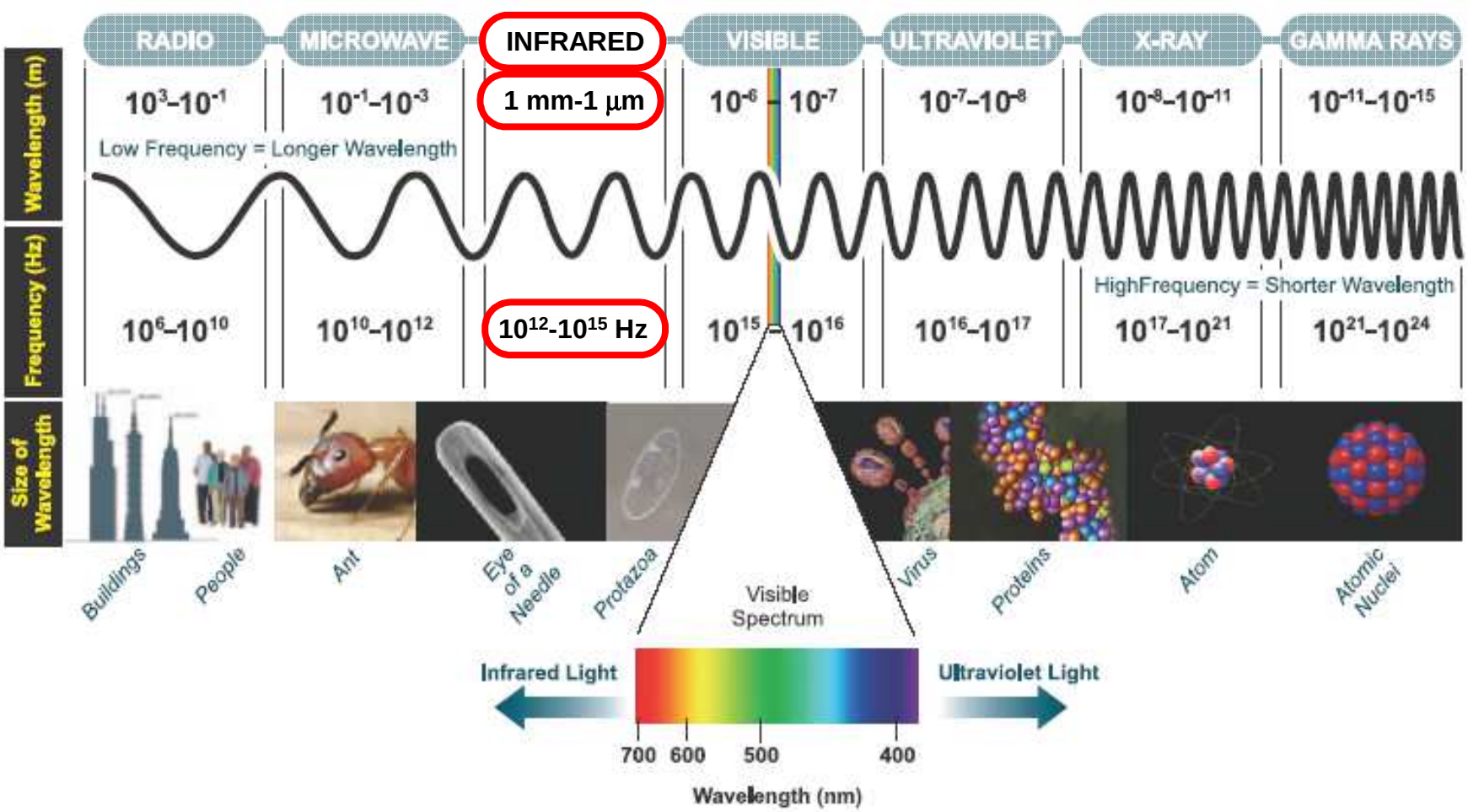
pros

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

cons

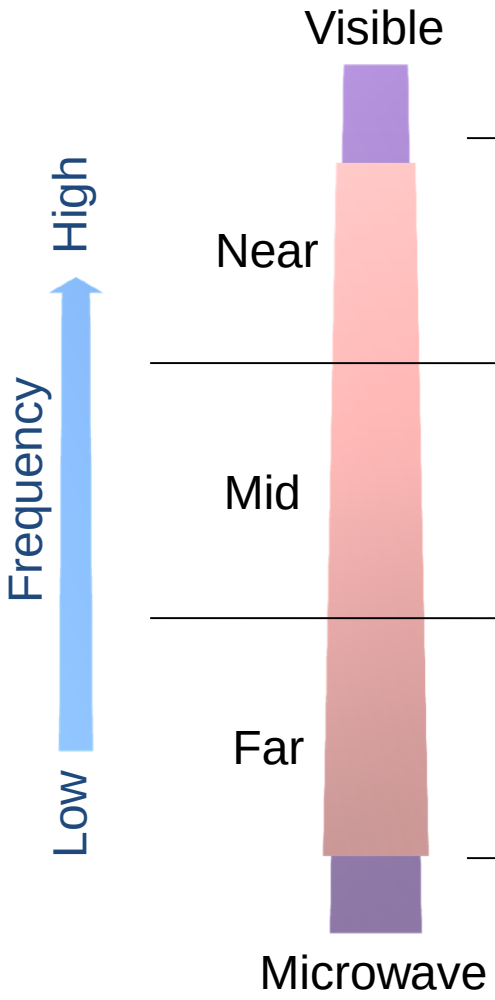
- no atomic resolution

The electromagnetic spectrum



source: Andor.com

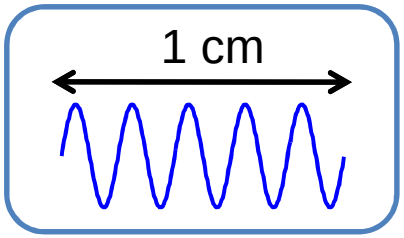
The IR region



	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 frequency unit

- Typically, the wavenumber (cm^{-1}) is used
- The number of waves in 1 cm

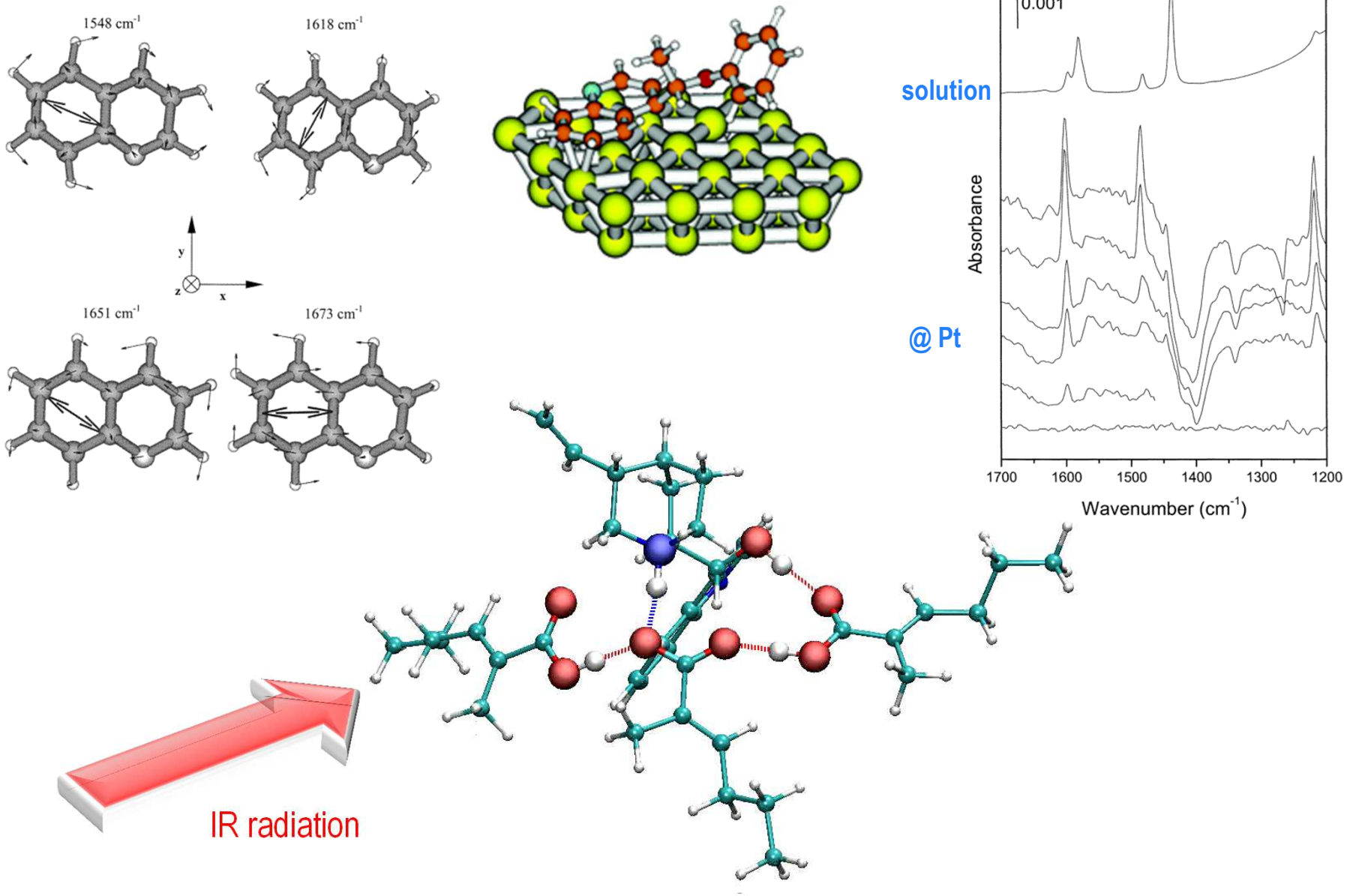


$$\tilde{\nu} = \frac{1}{\lambda} \quad [cm^{-1}]$$

Q Calculate the wavelength of the following light frequency

a) 400 cm^{-1}
b) 4000 cm^{-1}

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?

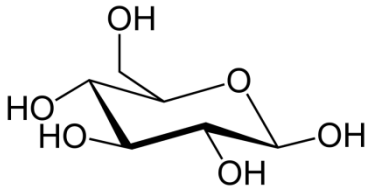
molecule	number of vibrations
linear	**3N-5**
non-linear	**3N-6**

vibrational normal modes

O=O

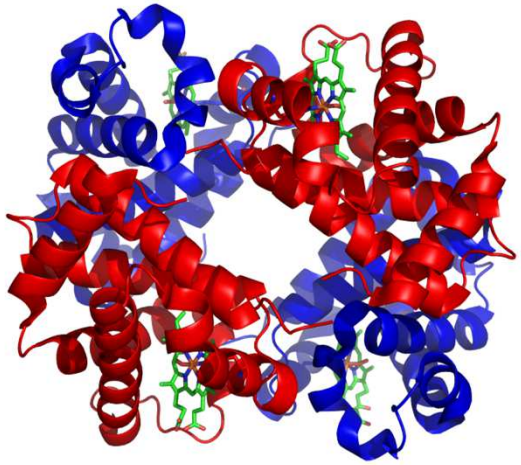
Oxygen molecule (N=2)

1 fundamental mode



Glucose (N=24)

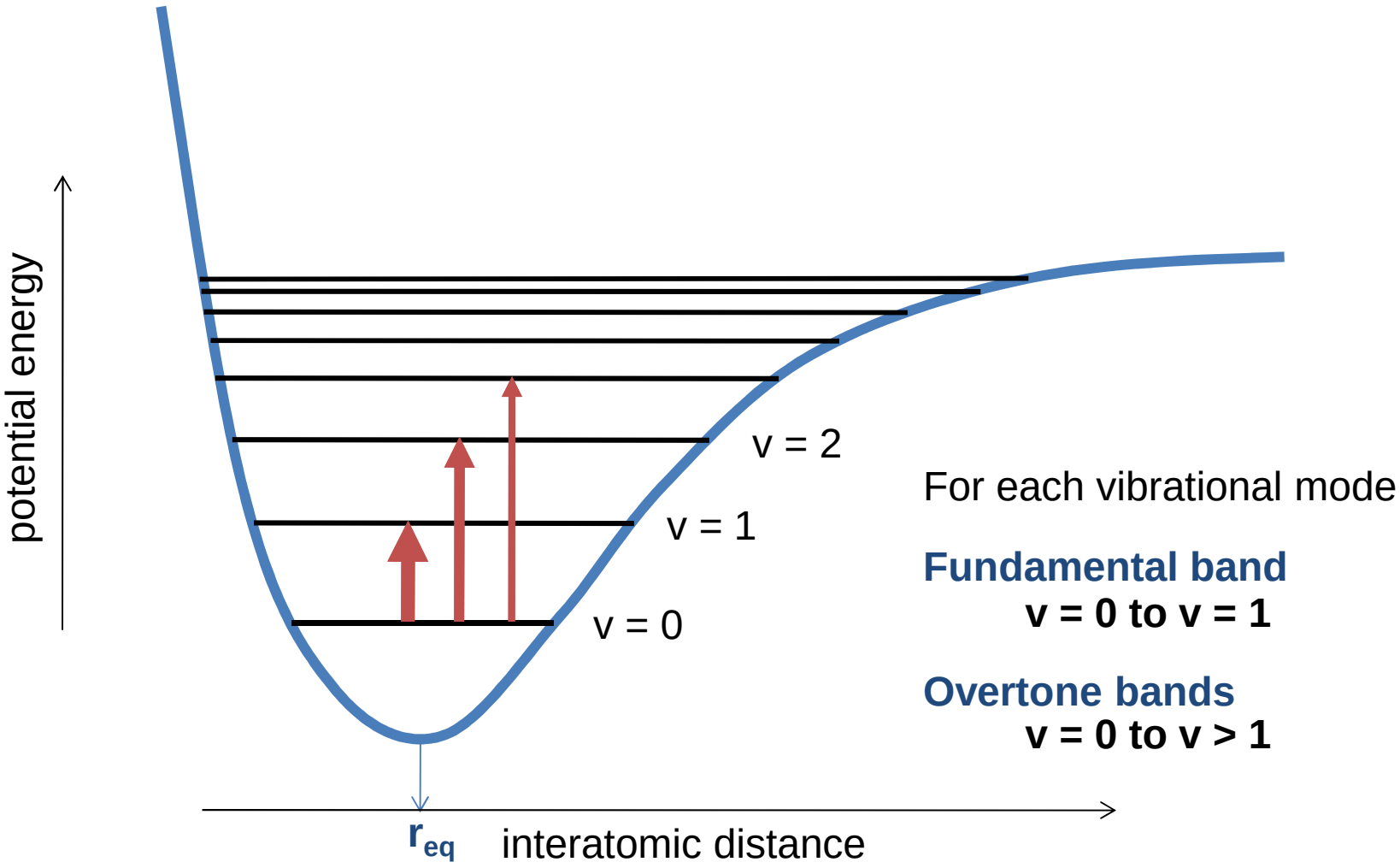
66 fundamental modes



Proteins (hemoglobin)

N typically 10'000...

Vibrational transition



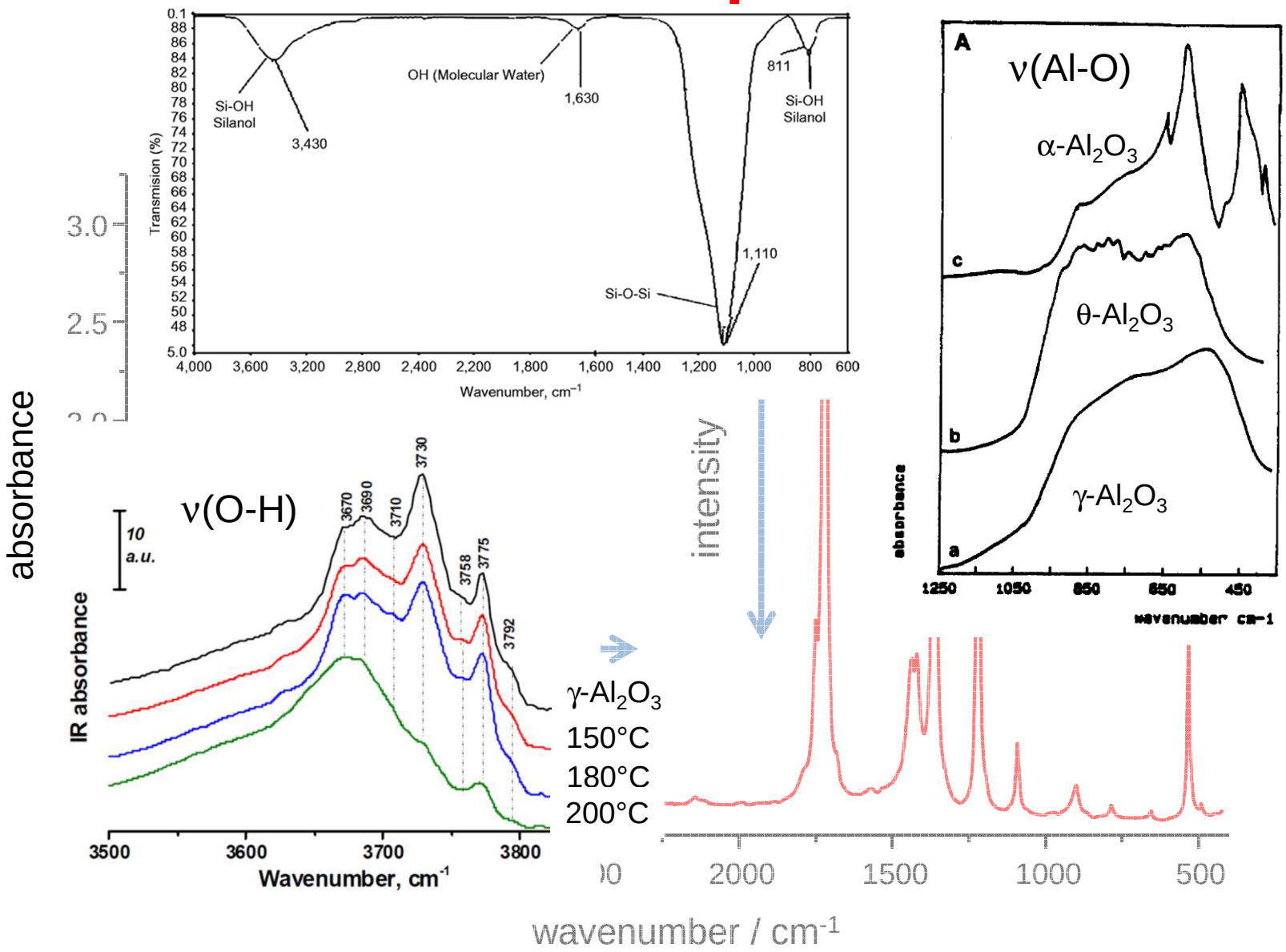
For each vibrational mode

Fundamental band
v = 0 to v = 1

Overtone bands
v = 0 to v > 1

v= vibrational number

The mid-IR spectrum



Morterra, Catal. Today 27 (1996) 497

Which vibrations do appear in a spectrum?

Selection rule

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

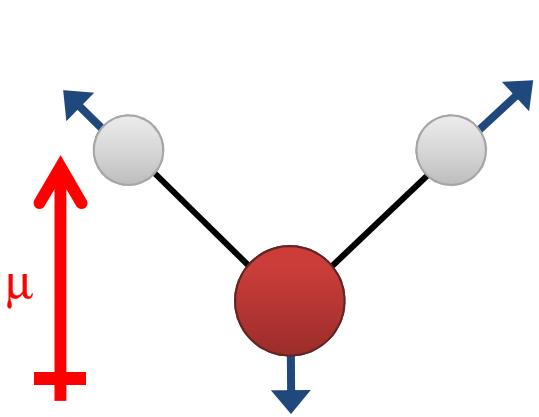
Molecular dipole moment μ must change due to vibration or rotation along its coordinate (so called, normal mode or normal coordinate, ***Q***)

Q Are these molecules infrared active or inactive?

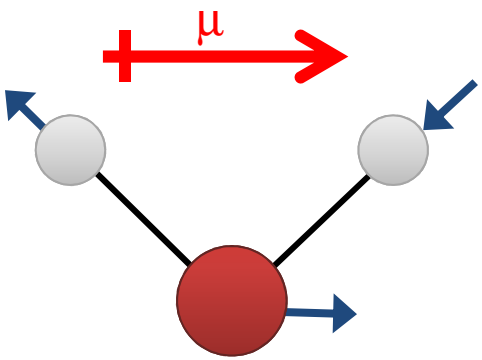
O=O H-Cl Ar

The H_2O molecule

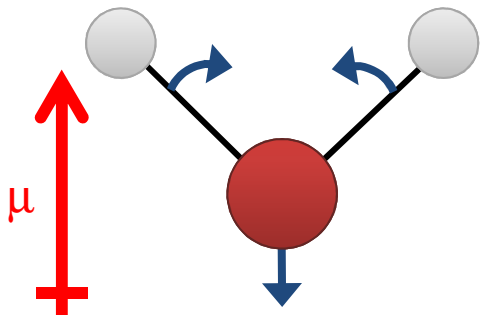
N=3, non-linear, 3 fundamental modes



3657 cm^{-1}
symmetric stretching



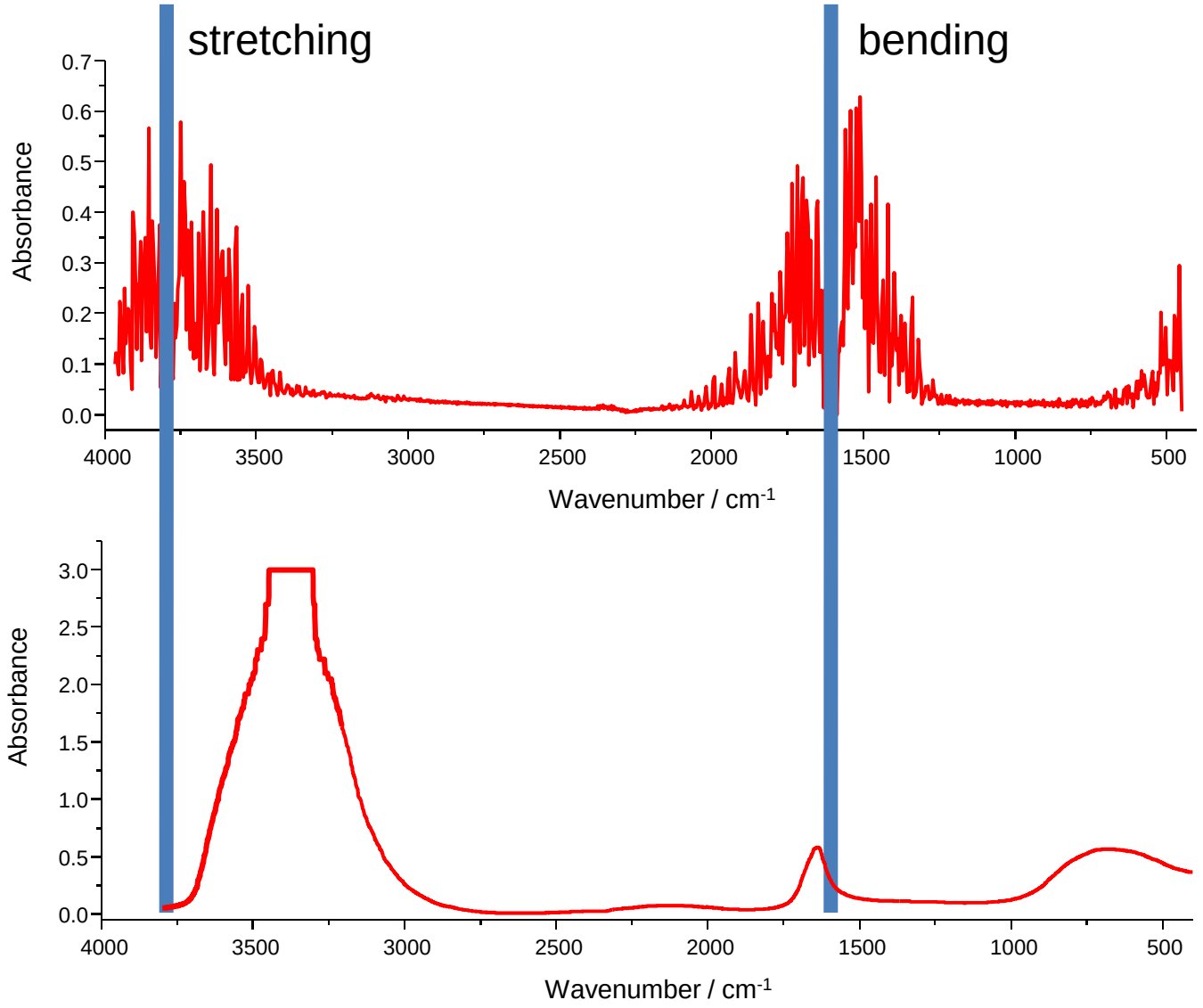
3756 cm^{-1}
asymmetric stretching



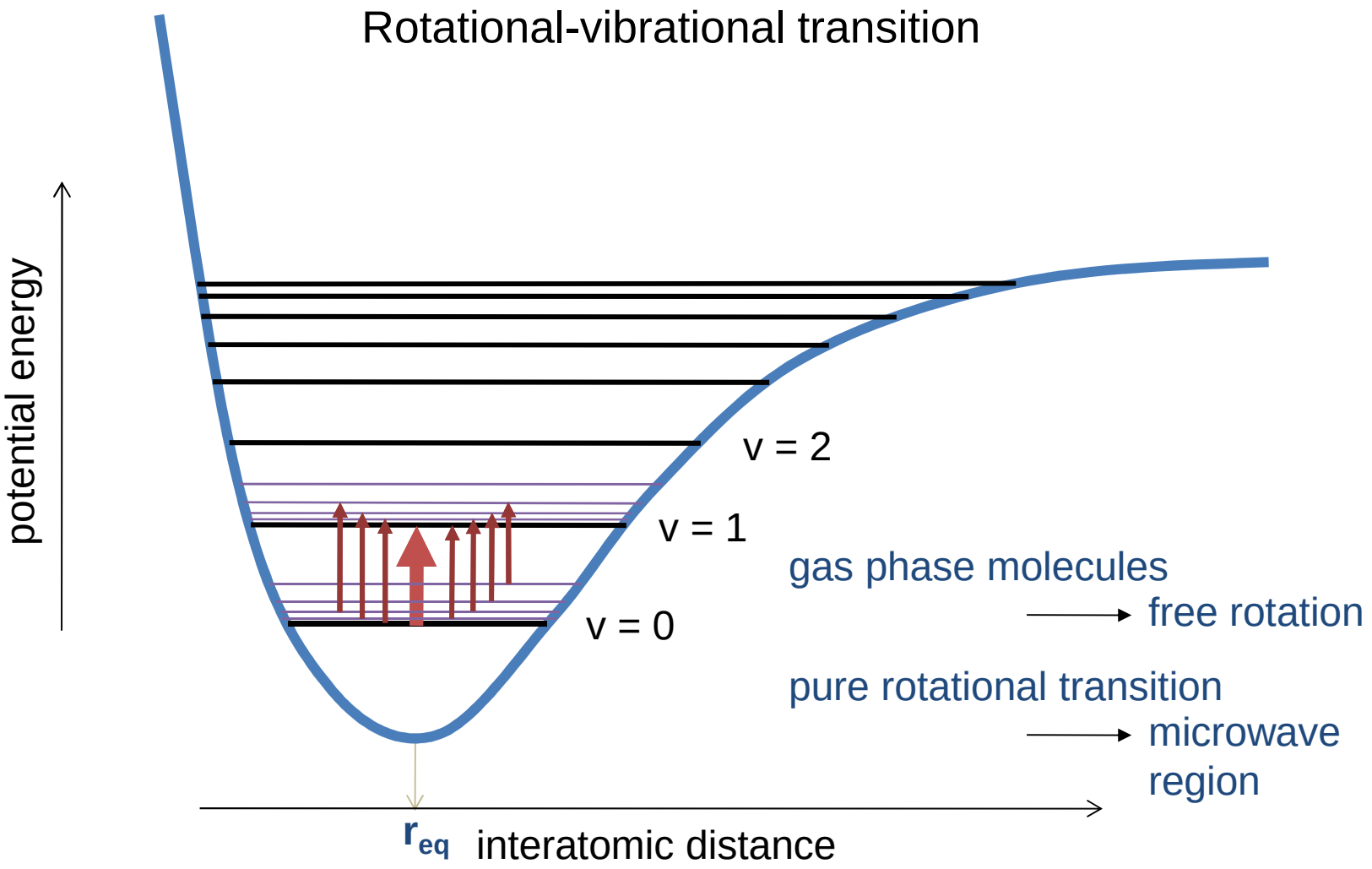
1595 cm^{-1}
scissoring (bending)

All modes IR active

Gas and liquid phase H_2O



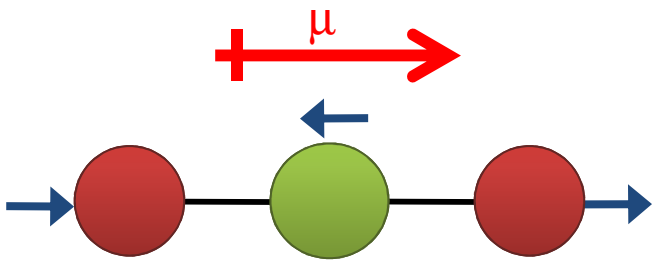
Vibrational transition (II)



v= vibrational number

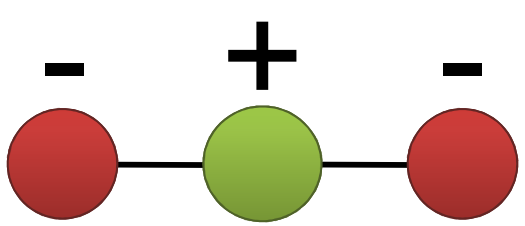
The CO_2 molecule

N=3, linear, 4 fundamental modes



2349 cm^{-1}

asymmetric stretching



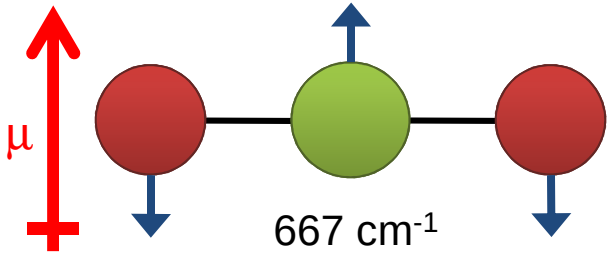
667 cm^{-1}

scissoring (or bending)

1288 cm^{-1}

symmetric stretching

IR inactive

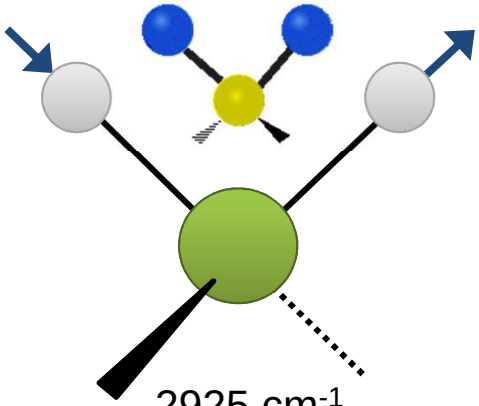


667 cm^{-1}

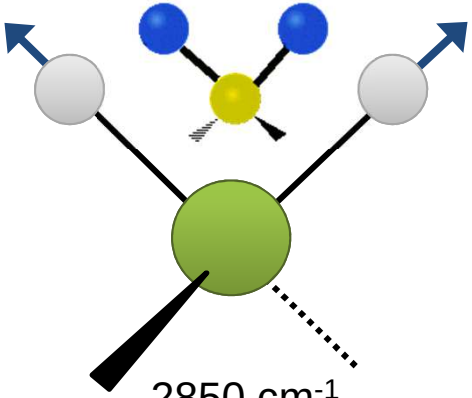
scissoring (or bending)

degenerate when isolated

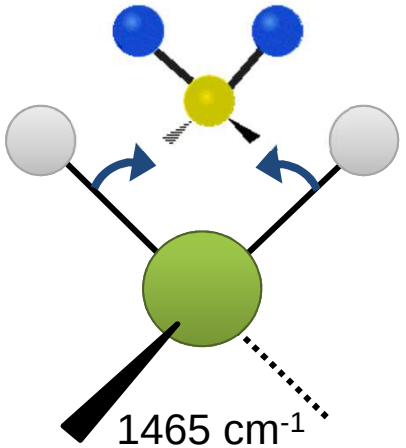
The -CH_2 group



2925 cm^{-1}
asymmetric stretching

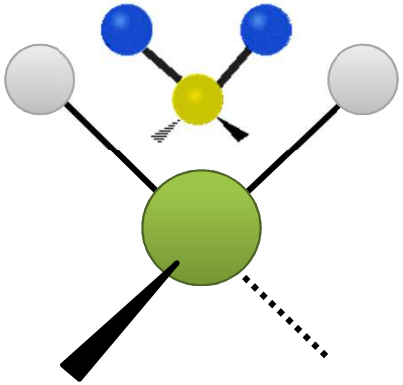


2850 cm^{-1}
symmetric stretching

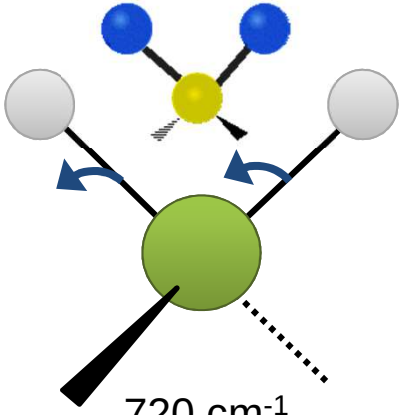


1465 cm^{-1}
scissoring /
bending in-plane

\+ -

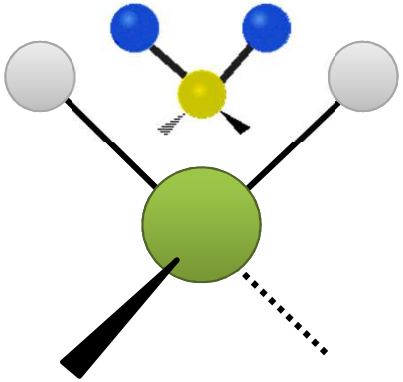


1350-1150 cm^{-1}
twisting /
bending out-of-plane



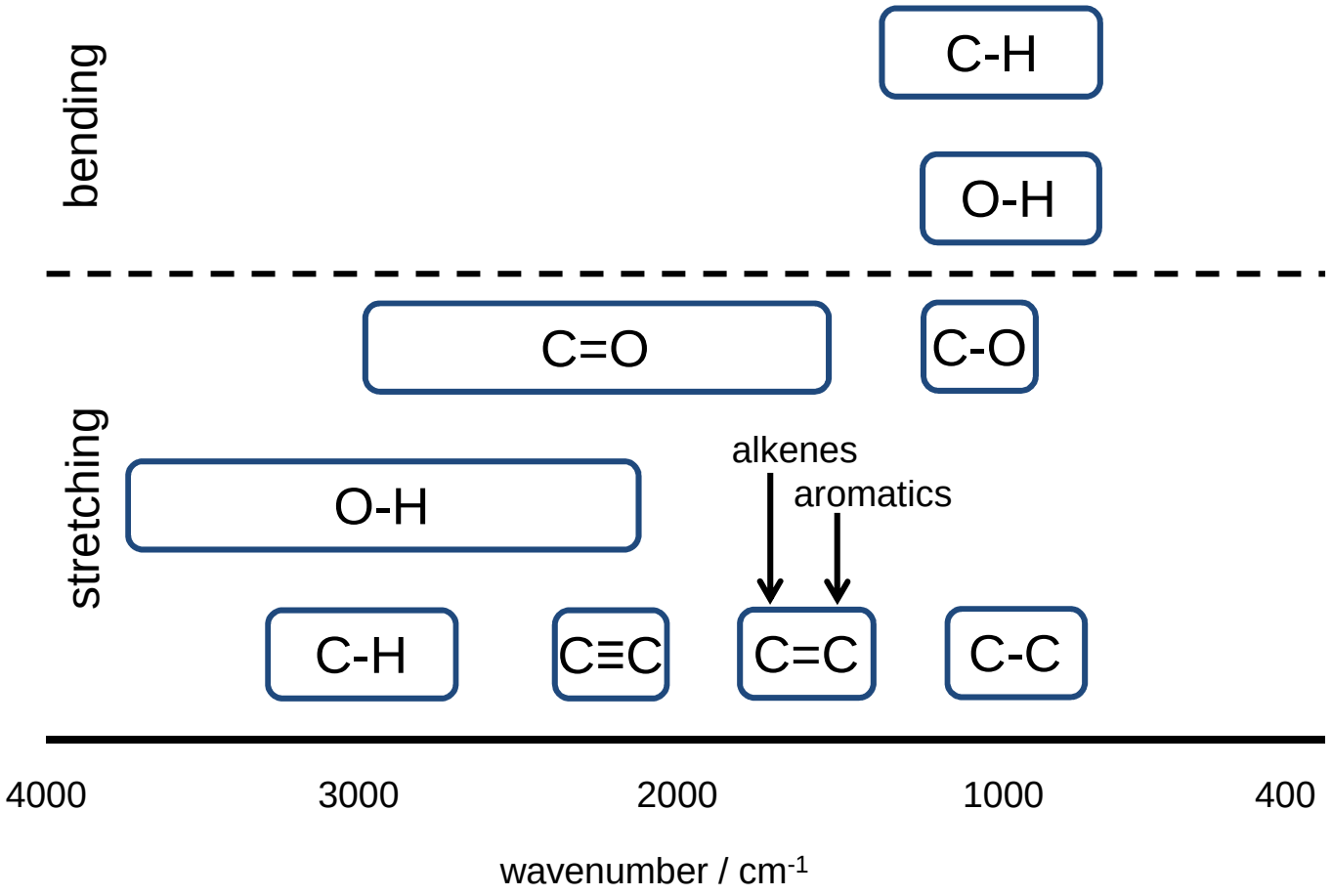
720 cm^{-1}
rocking /
bending in-plane

\+ +



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

Basic functional groups



Assignments

- **Functional groups (not complete!)**

aliphatic hydrocarbons

Wavenumber (cm^{-1})	Assignment
	Alkanes
2960	Methyl symmetric C–H stretching
2930	Methylene asymmetric C–H stretching
2870	Methyl asymmetric C–H stretching
2850	Methylene symmetric C–H stretching
1470	Methyl asymmetrical C–H bending
1465	Methylene scissoring
1380	Methyl symmetrical C–H bending
1305	Methylene wagging
1300	Methylene twisting
720	Methylene rocking
	Alkenes
3100–3000	=C–H stretching
1680–1600	C=C stretching
1400	=C–H in-plane bending
1000–600	=C–H out-of-plane bending
	Alkynes
3300–3250	=C–H stretching
2260–2100	C=C stretching
700–600	=C–H bending

aromatic compounds

Wavenumber (cm^{-1})	Assignment
3100–3000	C–H stretching
2000–1700	Overtone and combination bands
1600–1430	C=C stretching
1275–1000	In-plane C–H bending
900–690	Out-of-plane C–H bending

amines

Wavenumber (cm^{-1})	Assignment
3335	N–H stretching (doublet for primary amines; singlet for secondary amines)
2780	N–CH_2 stretching
1615	NH_2 scissoring, N–H bending
1360–1250	Aromatic C–N stretching
1220–1020	Aliphatic C–N stretching
850–750	NH_2 wagging and twisting
715	N–H wagging

amides

Wavenumber (cm^{-1})	Assignment
3360–3340	Primary amide NH_2 asymmetric stretching
3300–3250	Secondary amide N–H stretching
3190–3170	Primary amide NH_2 symmetric stretching
3100–3060	Secondary amide amide II overtone
1680–1660	Primary amide C=O stretching
1680–1640	Secondary amide C=O stretching
1650–1620	Primary amide NH_2 bending
1560–1530	Secondary amide N–H bending, C–N stretching
750–650	Secondary amide N–H wagging

oxygen-containing compounds

Wavenumber (cm^{-1})	Assignment
	Alcohol and phenols
3600	Alcohol O–H stretching
3550–3500	Phenol O–H stretching
1300–1000	C–O stretching
	Ethers
1100	C–O–C stretching
	Aldehydes and ketones
2900–2700	Aldehyde C–H stretching
1740–1720	Aliphatic aldehyde C=O stretching
1730–1700	Aliphatic ketone C=O stretching
1720–1680	Aromatic aldehyde C=O stretching
1700–1680	Aromatic ketone C=O stretching
	Esters
1750–1730	Aliphatic C=O stretching
1730–1705	Aromatic C=O stretching
1310–1250	Aromatic C–O stretching
1300–1100	Aliphatic C–O stretching
	Carboxylic acids
3300–2500	O–H stretching
1700	C=O stretching
1430	C–O–H in-plane bending
1240	C–O stretching
930	C–O–H out-of-plane bending
	Anhydrides
1840–1800	C=O stretching
1780–1740	C=O stretching
1300–1100	C–O stretching

nitrogen-containing compounds

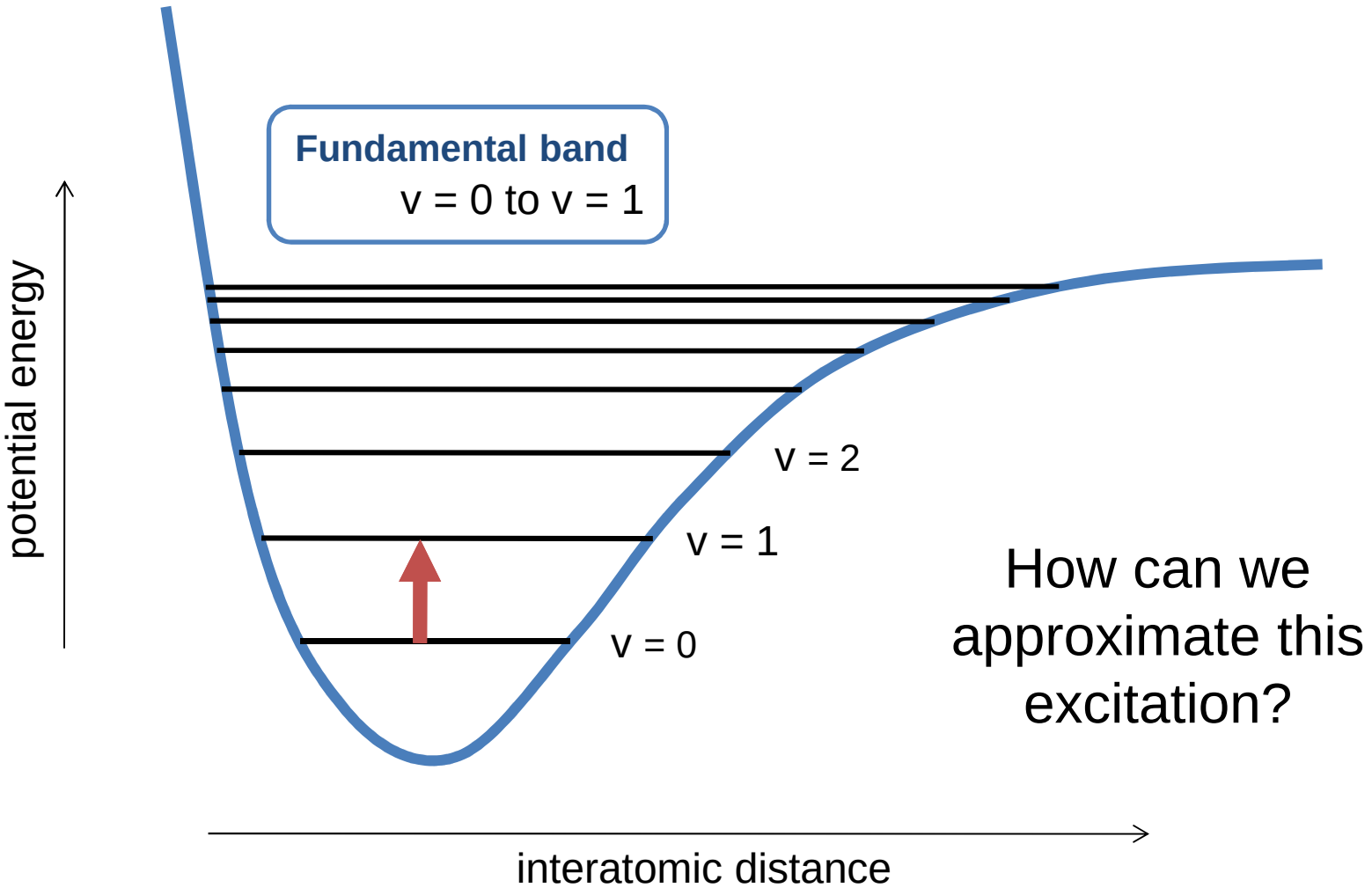
Wavenumber (cm^{-1})	Assignment
2260–2240	Aliphatic nitrile C≡N stretching
2240–2220	Aromatic nitrile C≡N stretching
2180–2110	Aliphatic isonitrile –N≡C stretching
2160–2120	Azide N≡N stretching
2130–2100	Aromatic isonitrile –N≡C stretching
1690–1620	Oxime C=N–OH stretching
1680–1650	Nitrite N=O stretching
1660–1620	Nitrate NO_2 asymmetric stretching
1615–1565	Pyridine C=N stretching, C=C stretching
1560–1530	Aliphatic nitro compound NO_2 asymmetric stretching
1540–1500	Aromatic nitro compound NO_2 asymmetric stretching
1450–1400	Azo compound N=N stretching
1390–1370	Aliphatic nitro compound NO_2 symmetric stretching
1370–1330	Aromatic nitro compound NO_2 symmetric stretching
1300–1270	Nitrate NO_2 symmetric stretching
965–930	Oxime N–O stretching
870–840	Nitrate N–O stretching
710–690	Nitrate NO_2 bending

NIR (in nm!)

Wavelength (nm)	Assignment
2200–2450	Combination C–H stretching
2000–2200	Combination N–H stretching, combination O–H stretching
1650–1800	First overtone C–H stretching
1400–1500	First overtone N–H stretching, first overtone O–H stretching
1300–1420	Combination C–H stretching
1100–1225	Second overtone C–H stretching
950–1100	Second overtone N–H stretching, second overtone O–H stretching
850–950	Third overtone C–H stretching
775–850	Third overtone N–H stretching

Frequency

- **Real potential**



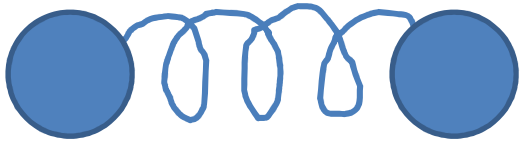
How can we approximate this excitation?

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.

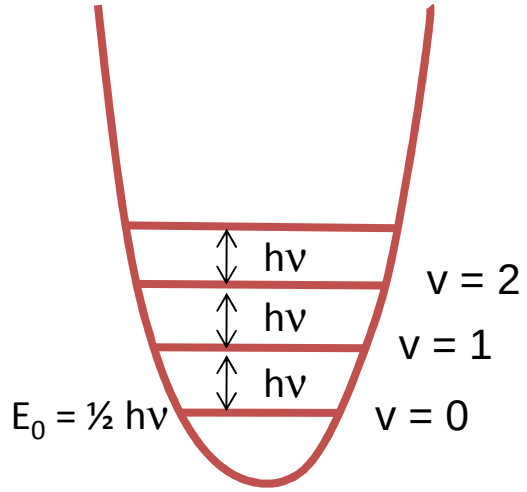


$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k: force constant

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

μ: reduced mass



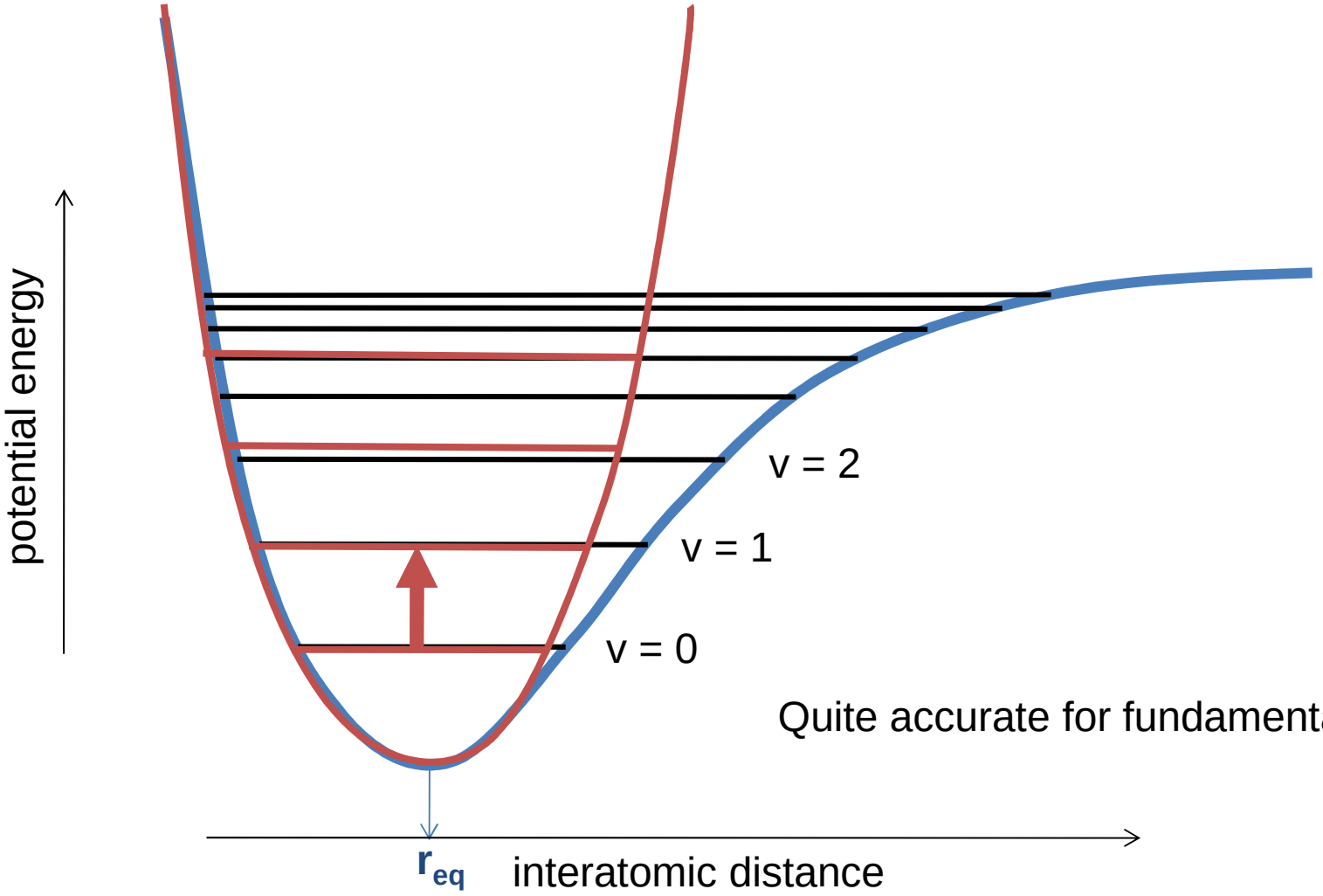
For molecules more than two atoms

→ Normal mode analysis

v= vibrational number

Frequency

- **Approximation: harmonic oscillator**



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 μ

Isotopic labeling

Q The stretching frequency of HCl is 2890 cm^{-1}. What is the frequency of DCl assuming the force constants (k_{HCl} and k_{DCl}) are the same?