Vibrational spectroscopies: infrared and Raman

From theory to pharmaceutical and biomedical applications

1

- History of infrared and basics of molecular vibrations

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Lipides: systèmes analytiques et biologiques
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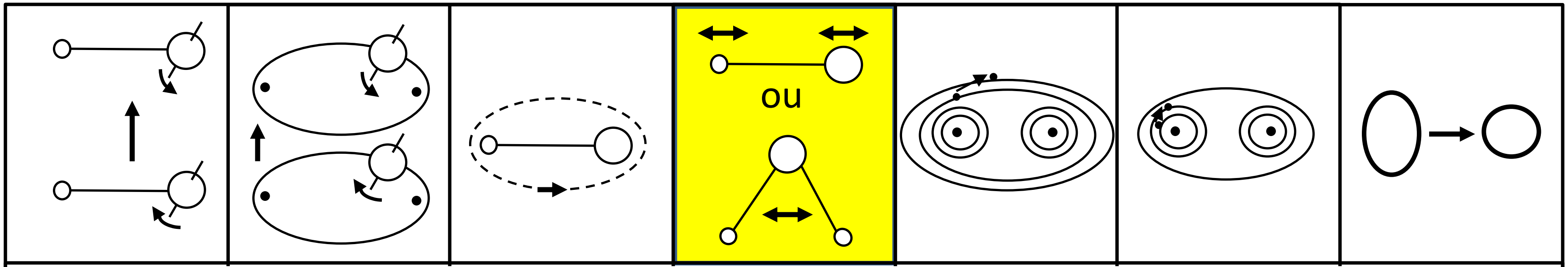
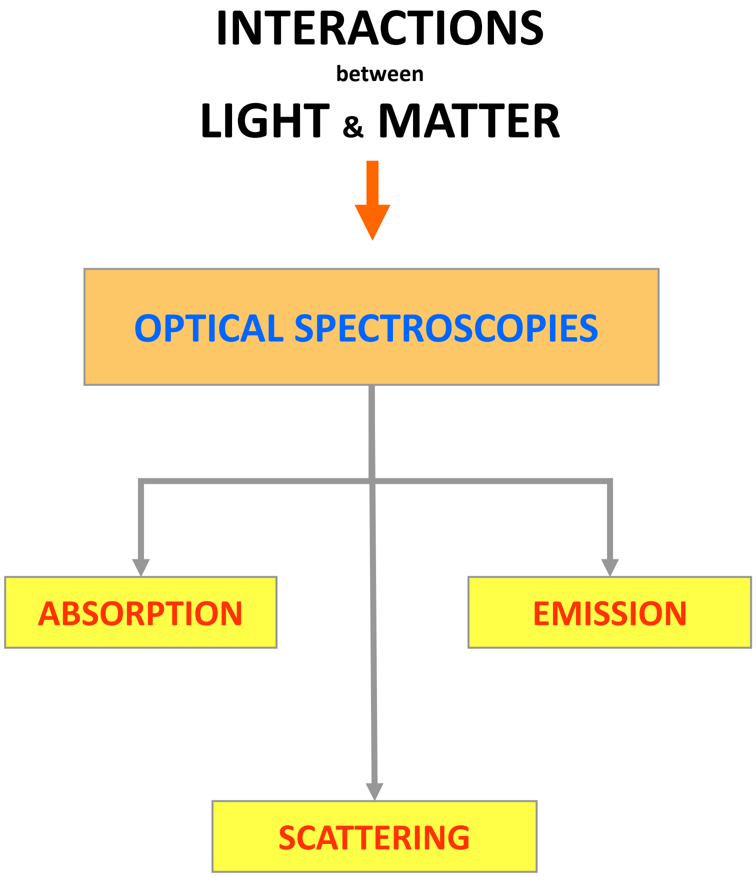
INTERACTIONS between LIGHT & MATTER



	Spin changes		Orientation changes	Configuration changes	Changes in the electronic distribution		Changes in the nuclear configuration
Wavenumber (cm^{-1})	10^{-4}	10^{-2}	1	100	10^{4}	10^{6}	10^{8}
Waveltength	10 m	100 cm	1 cm	100 µm	1000 nm	10 nm	100 pm
Frequency (Hz)	3.10^{6}	3.10^{8}	3.10^{10}	3.10^{12}	3.10^{14}	3.10^{16}	3.10^{18}
Energy ($J.mol^{-1}$)	10^{-3}	10^{-1}	10	10^{3}	10^{5}	10^{7}	10^{9}
	NMR	EPR	Micro-wave	IR	Visible & UV	X rays	γ rays

C.N. Banwell, Fundamentals od Molecular spectroscopy, 3rd edition, New York; McGraw-Hill 1983,P7

Vibrational spectroscopies



INTERACTIONS

between

LIGHT & MATTER

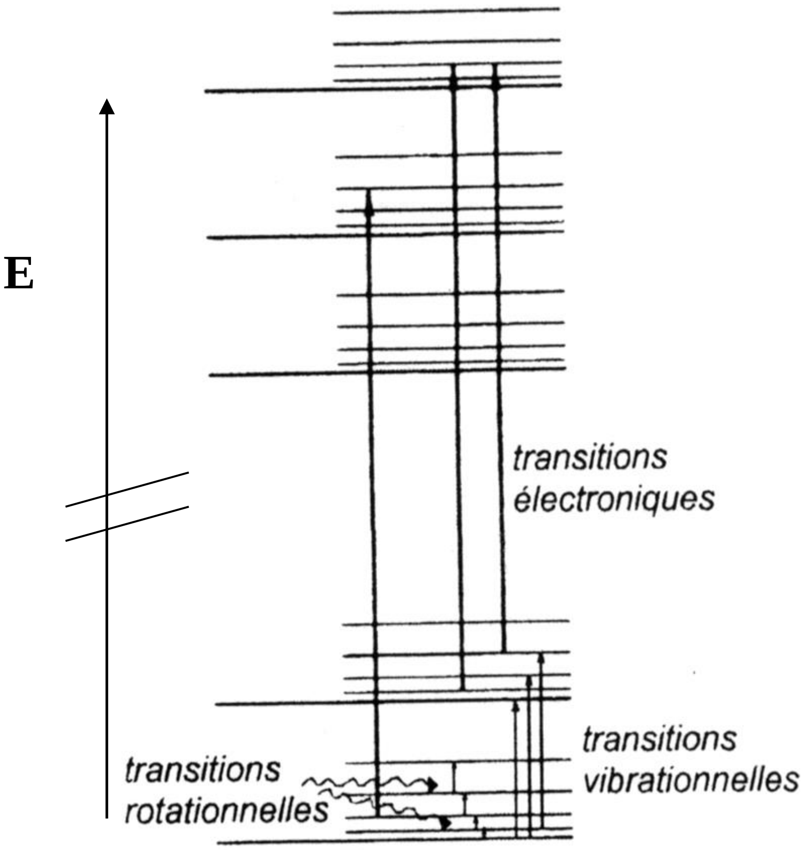
OPTICAL SPECTROSCOPIES

ABSORPTION

EMISSION

SCATTERING

Jablonski Diagram

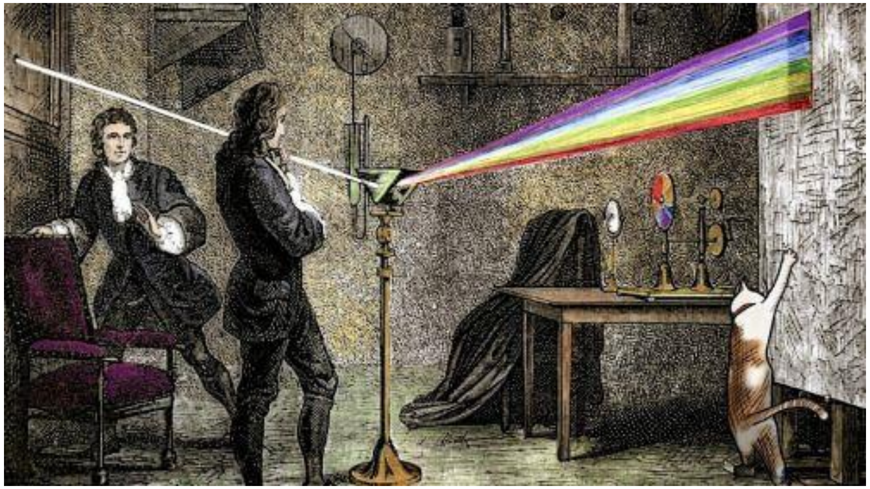


$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$

$E_{vib} \approx 1$ kCal $E_{ele} \approx 100$ kcal

What is infrared spectroscopy?

The story of infrared spectroscopy begins with Sir Isaac Newton.
He set up an experiment in which a beam of sunlight passed through window shutters into a dark room



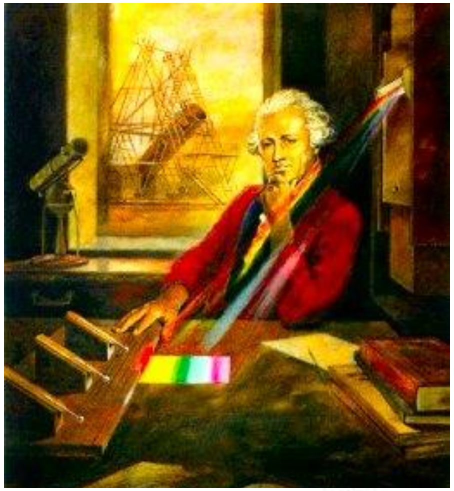
By placing a prism in the beam of light, he showed that ***<u>white light is composed of different colors</u>***. Violet light is bent the most of the prism while red light is bent the least. Although this was known before Newton, he was the first to describe it accurately

http://rstl.royalsocietypublishing.org/content/6/69-80/3075.full.pdf

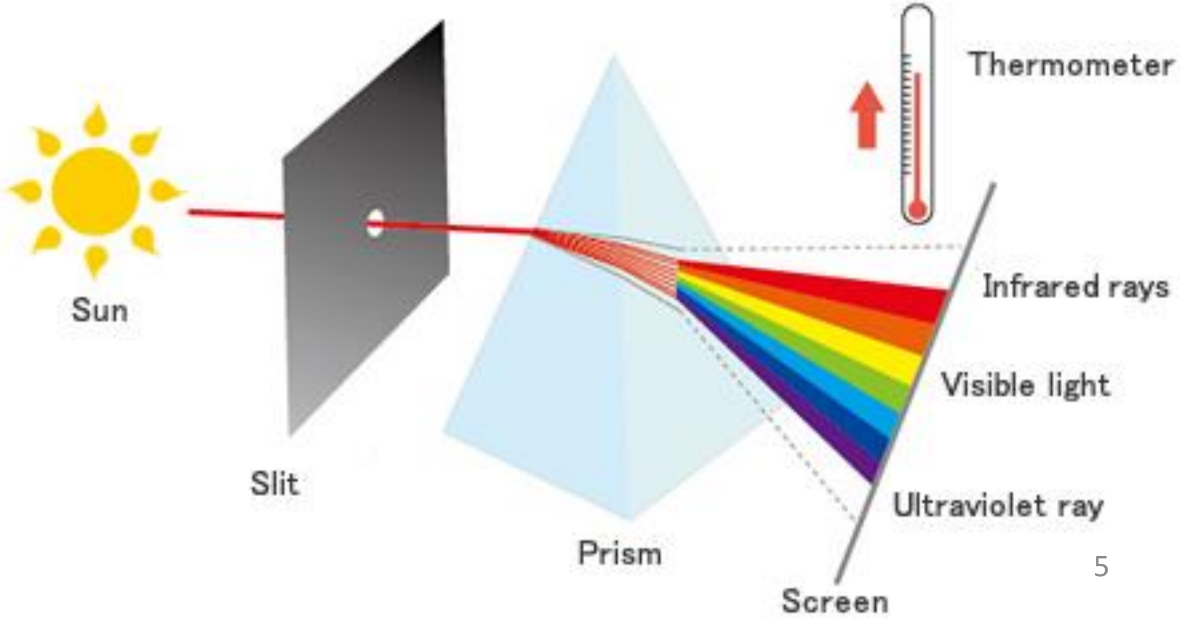
IR tutor

What is infrared spectroscopy?

Much later, Frederic William Herschel explored the existence of other components of white light, outside the visible region.
The region after the red part of the visible spectrum: the **infrared (IR) region**



Since this region is invisible to the human eye, Herschel needed a way to detect it. A blackened thermometer bulb was the answer.
When placed in the beam of infrared light, the thermometer warms above room temperature.

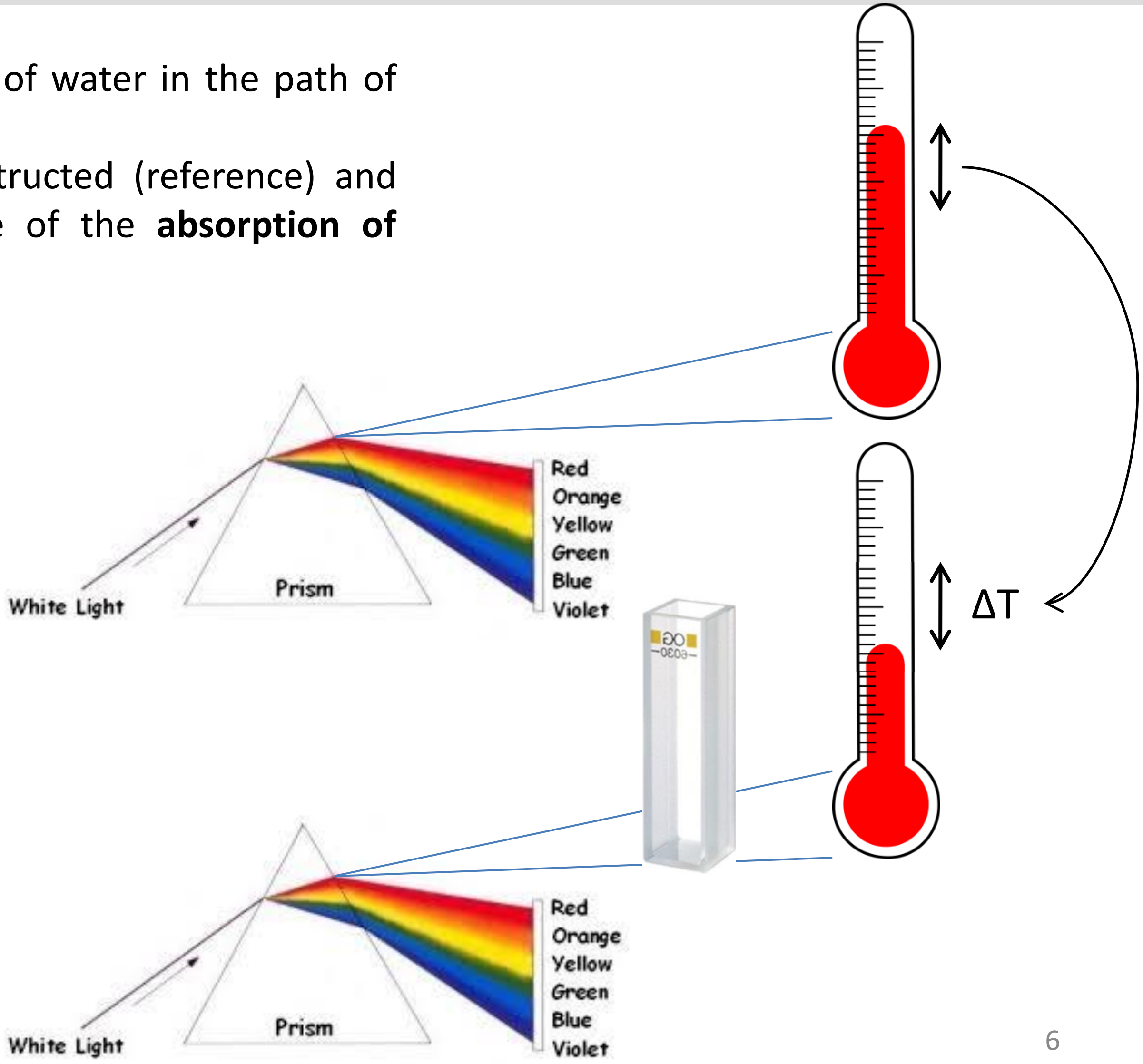


IR tutor

What is infrared spectroscopy?

In March 1800, Herschel put a well of water in the path of the beam.
The difference between the unobstructed (reference) and sample temperatures is a measure of the **absorption of infrared light.**

By changing the part of the spectrum that shines through the sample, Herschel showed that **the absorption varies with wavelength** (or ‘color”) of infrared light.



IR tutor

What is light?

Infrared spectroscopy is thus the measurement of the absorption of infrared light by a sample.

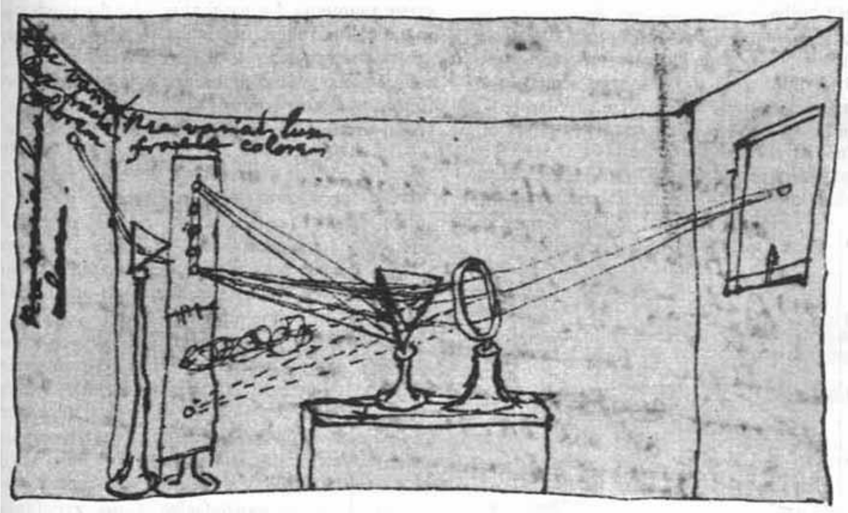
But what is light?

Observations of Isaac Newton showed that white light is composed of different visible colors.

Much later Herschel proved the presence of “invisible” colors such as infrared

IR tutor

Nature of light: waves or particles?



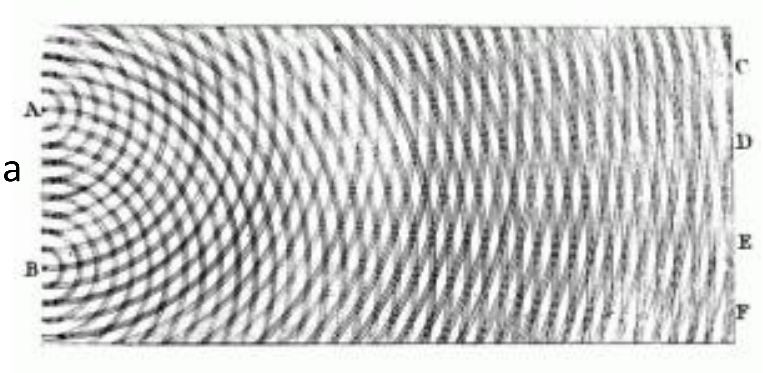
Particles: **Newton** argued vehemently that light was comprised of streams of particles that he dubbed "corpuscles."

http://rstl.royalsocietypublishing.org/content/6/69-80/3075.full.pdf

Waves: Descartes, Huygens, Fresnel and **YOUNG**

Young shone the light onto a barrier in which he'd cut two narrow, parallel slits, about a fraction of an inch apart. On the other side was a white screen.

Thomas Young's sketch of his observed interference pattern
He reasoned that if light were made of particles, as Newton claimed, the screen would show two bright parallel lines where the light particles had passed through one slit or the other. But if light were a wave, it would pass through both slits, separating into secondary waves that would then recombine on the other side -- i.e, they interfere with each other.

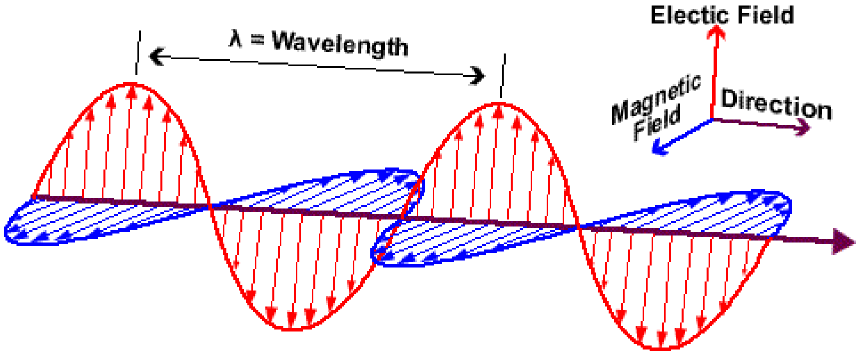


http://photonterrace.net/en/photon/history/ https://blogs.scientificamerican.com/cocktail-party-physics/the-photon-has-two-faces/

Nature of light: electromagnetic waves of photons

Electromagnetic wave: **Maxwell** predicted that light was an electromagnetic wave

Several observations could not be explained by any wave model of electromagnetic radiation,



Photons:

Planck: the energy of any system that absorbs or emits electromagnetic radiation of frequency ν is an integer multiple of an energy quantum $E = h\nu$.

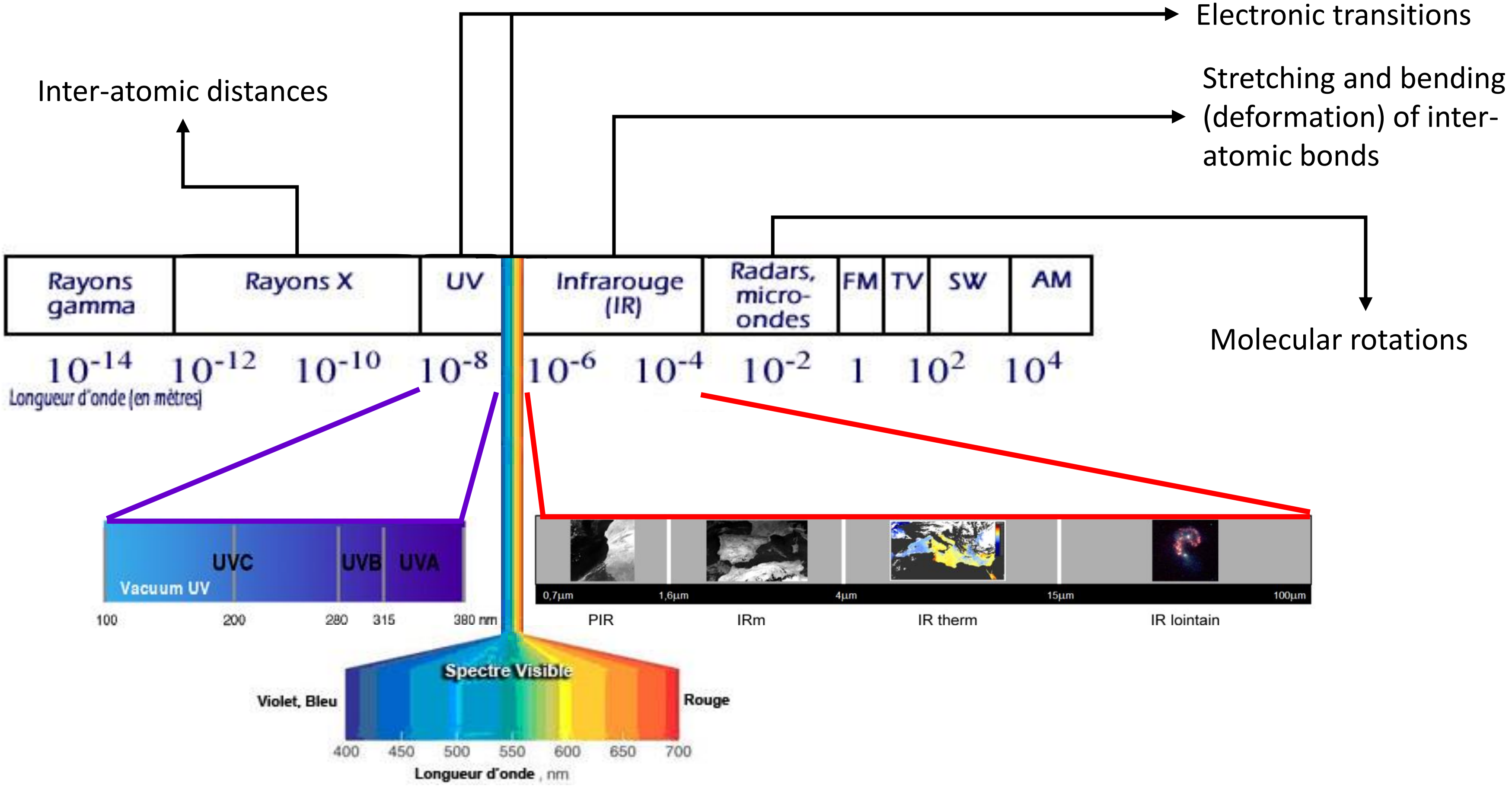
Albert Einstein: some form of energy quantization must be assumed to account for the thermal equilibrium observed between matter and electromagnetic radiation;

Einstein: energy quantization was a property of electromagnetic radiation itself, but many anomalous experiments could be explained if the energy of a Maxwellian light wave were localized into point-like quanta that move independently of one another. Einstein showed that, if Planck's law of black-body radiation is accepted, the energy quanta must also carry momentum $p = h/\lambda$, making them full-fledged particles.

Arthur Compton observed this photon momentum experimentally

Electromagnetic spectrum

Visible and infrared light constitute just a small part of the electromagnetic spectrum, which is the continuous range of light energy



Electronic transitions

Inter-atomic distances

Stretching and bending (deformation) of inter-atomic bonds

Molecular rotations

http://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/raman_ir.html

Electromagnetic spectrum

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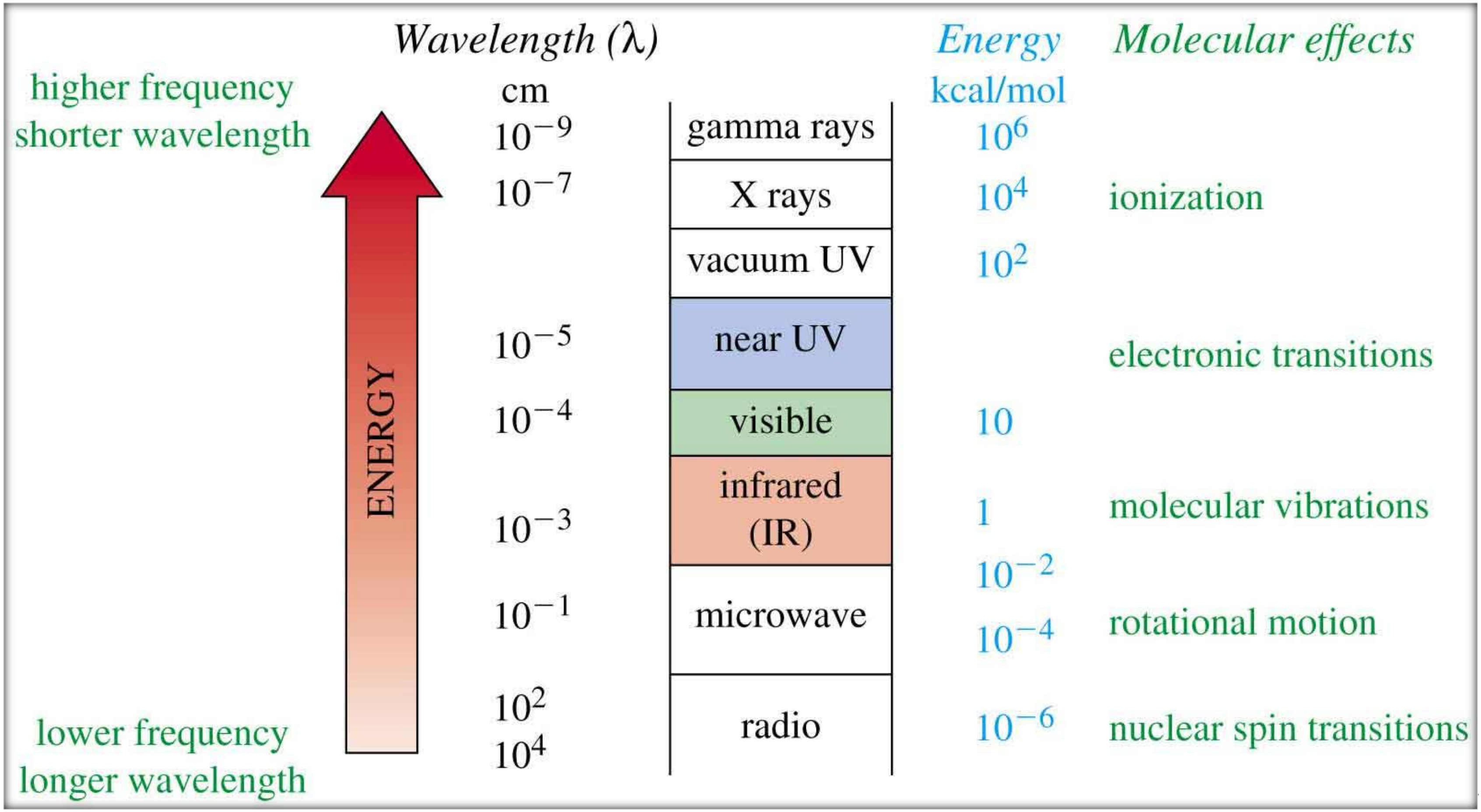
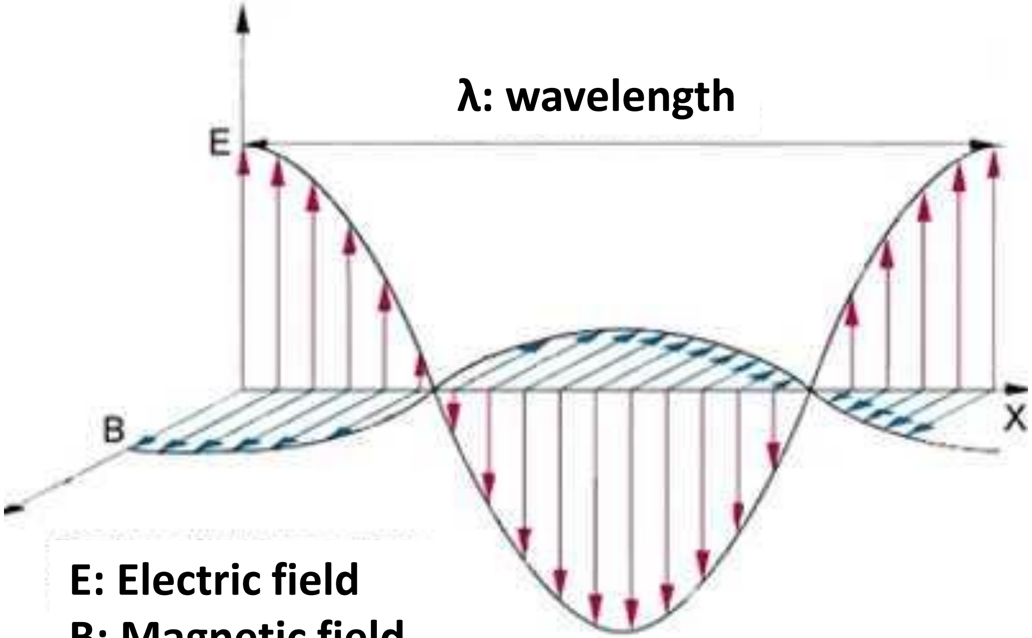


Electromagnetic spectrum

The electromagnetic spectrum can be described as a combination of oscillating electric, and magnetic fields,



λ: wavelength

E: Electric field
B: Magnetic field

This scheme presents a polarized light, as the electric field lies in one plane

Wave properties:

- Wavelength **λ** (nm): the distance between two maxima or minima
- Frequency **ν** (hertz): number of cycles that pass a point in one second

$\nu = C/\lambda$

(C is the speed of light: 2.99792458 .108 m/s)

- Wavenumber **ω** (cm^{-1}): number of cycles in 1 cm.

$\omega = \nu/C$

(the symbols $\bar{\nu}$ or σ are also used for wavenumber)

$\omega = 1/\lambda$

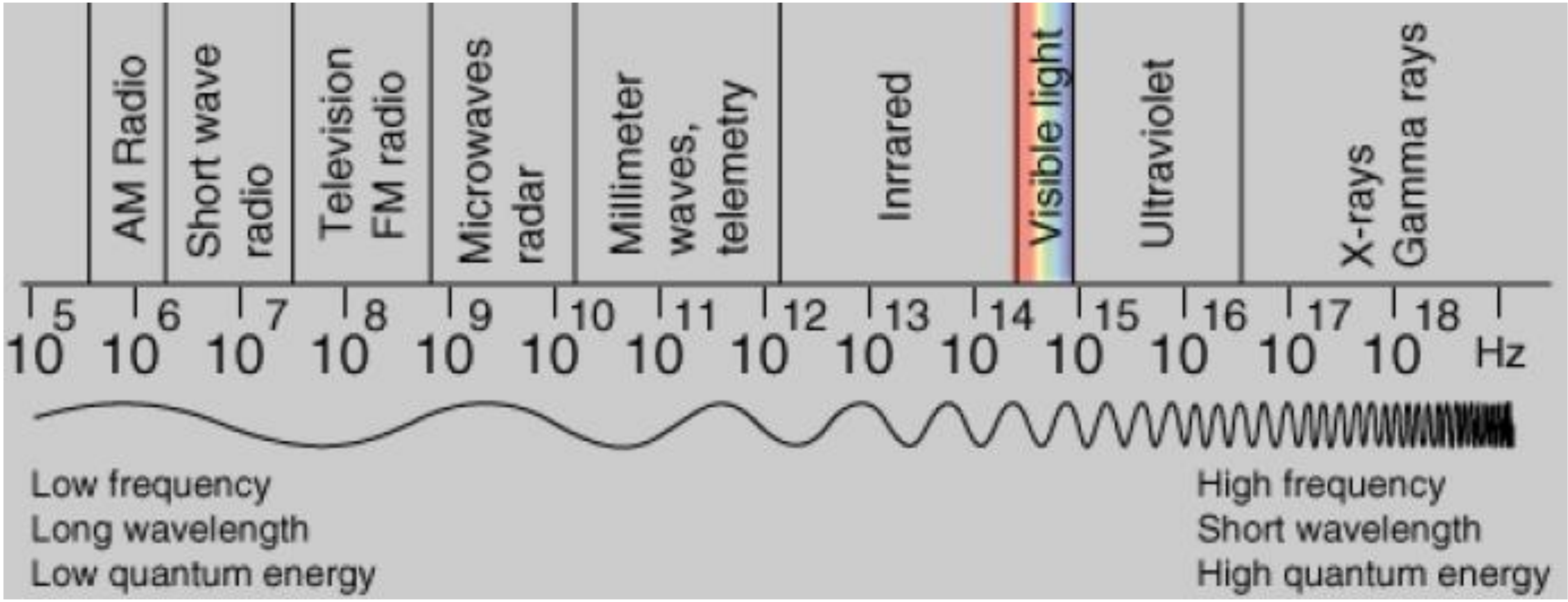
Particles properties:

- The Energy **E** (Joules):

$E = h.\nu = h.\omega.C$

h: Planck's constant

Electromagnetic spectrum



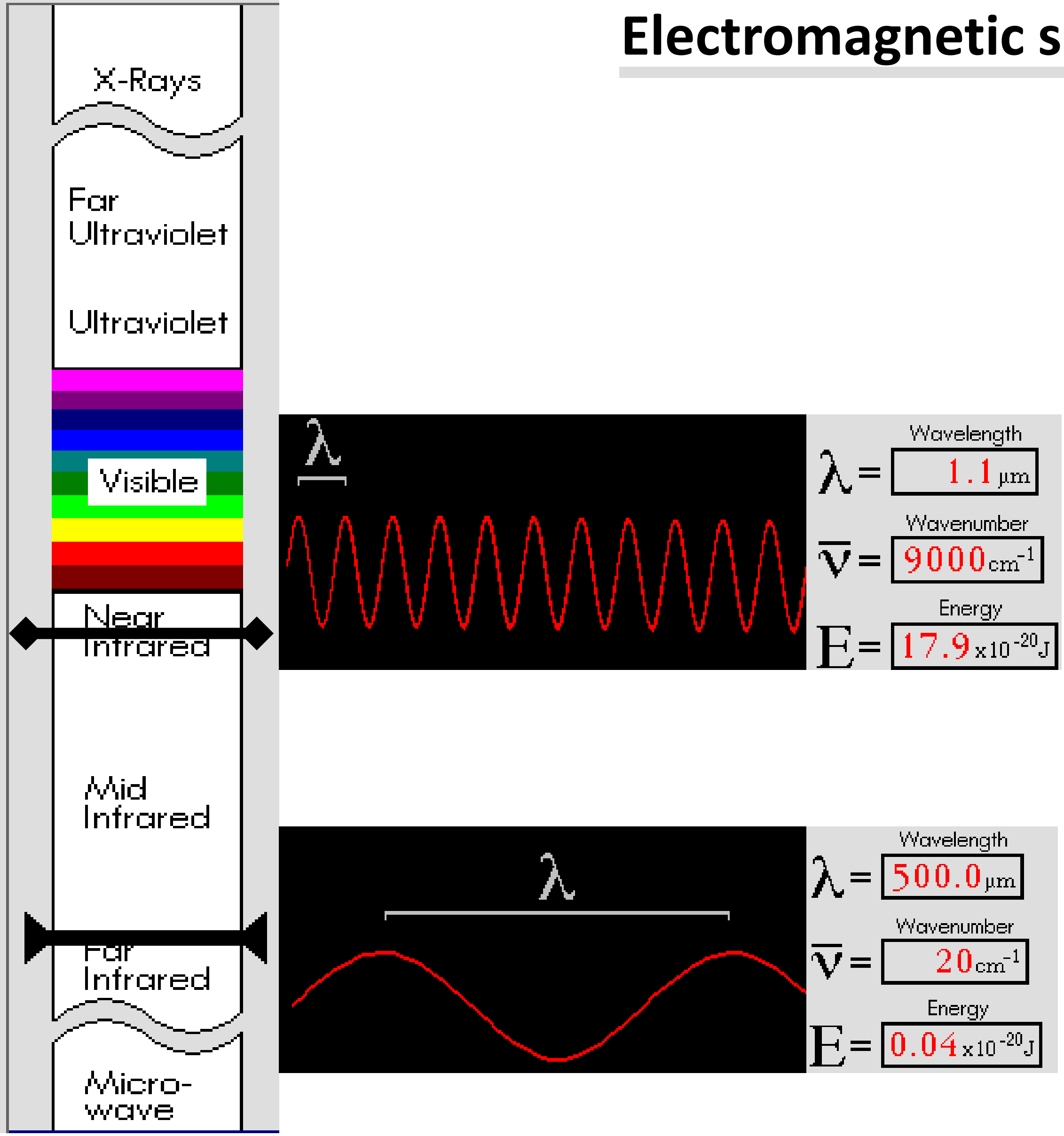
$\nu = C/\lambda$

$\omega = \nu/C$

$\omega = 1/\lambda$

$E = h.\nu = h.\omega.C$

Electromagnetic spectrum



$$\nu = C/\lambda$$

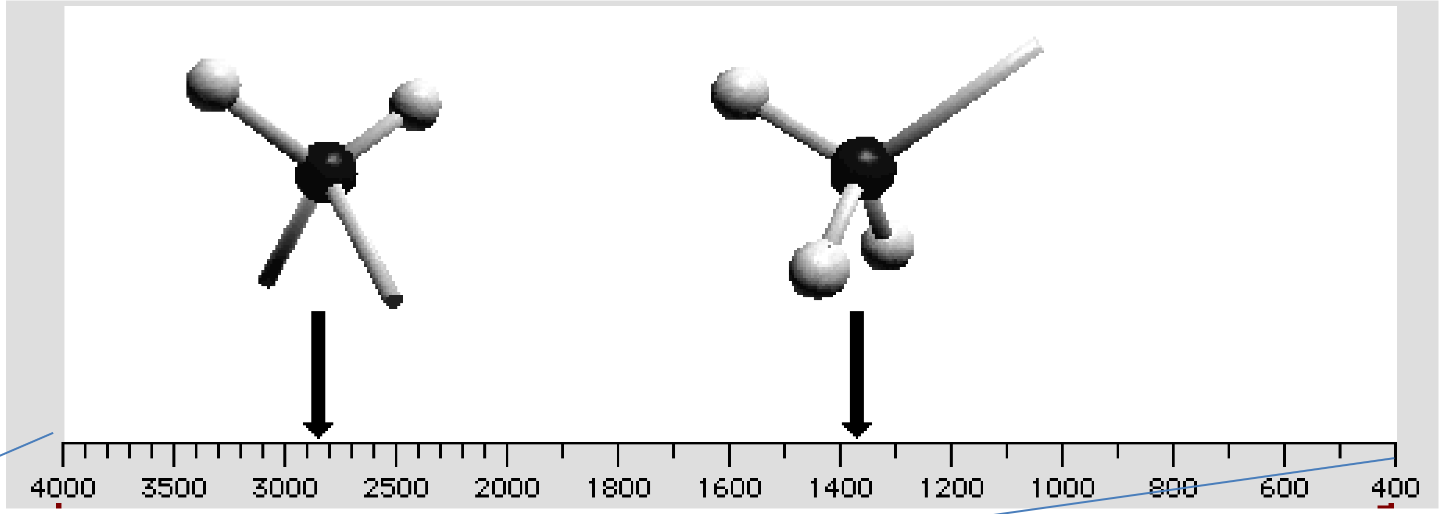
$$\omega = \nu/C$$

$$\omega = 1/\lambda$$

$$E = h.\,\nu = h.\,\omega\,.C$$

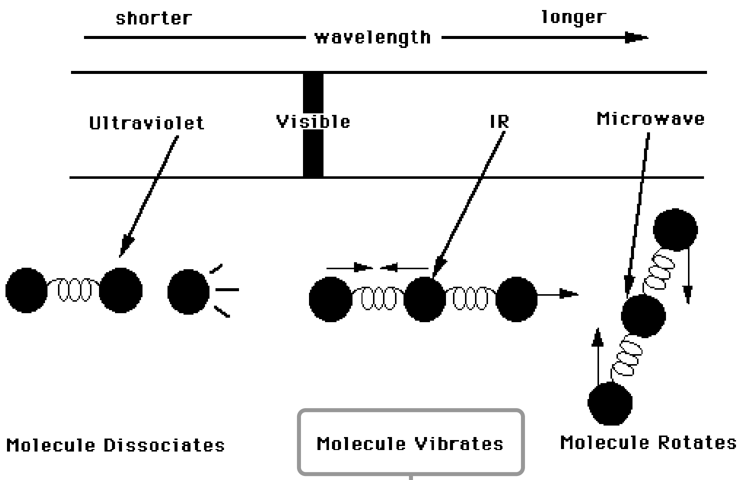
Vibrational spectroscopies: infrared and Raman

Infrared	λ (µm)	ω (cm^{-1})
Near	0,78-2,5	128000-4000
Mid	2,5-50	4000-200
Far	50-1000	200-10
Most common for mid	2,5-25	4000-400



Radiation in the mid infrared region (4000-400 cm^{-1}) correspond to the vibrational frequencies of molecules.
The theory of molecular vibration explains the appearance of infrared spectra.

Theory of molecular vibrations



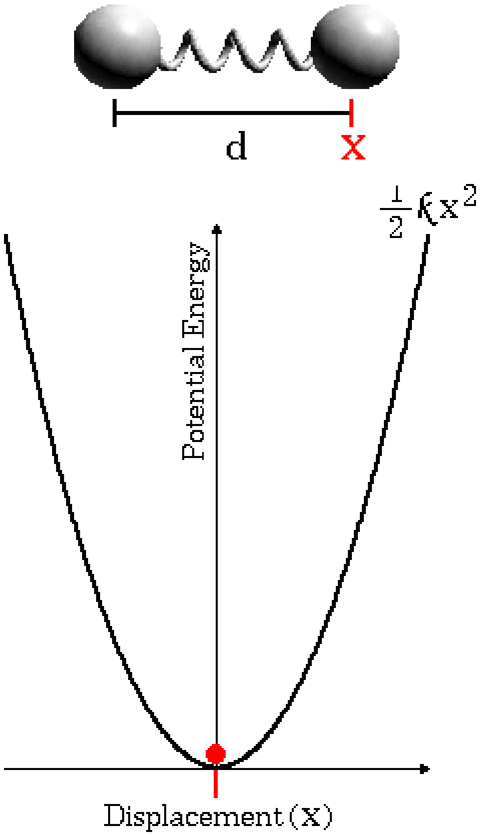
- A molecule vibrates at all temperature values higher than 0°K (-273.15°C)

- The energies of vibrations are comprised between 0.5 et 0.006 eV → 2.5 à 200 µm → 4000-50 cm^{-1}

Theory of molecular vibrations

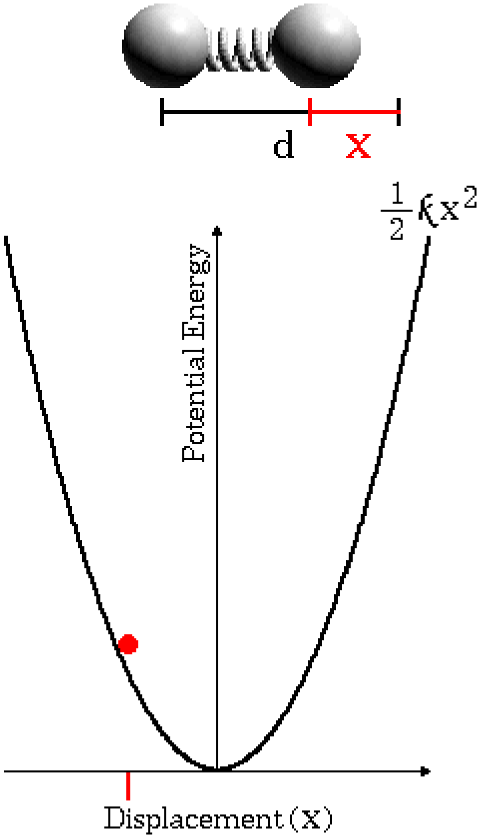
Model of a Simple Molecule

A diatomic molecule can be modelled by a spring with force constant **K** attached to two balls of mass **m**. This is called the **classical harmonic oscillator** model

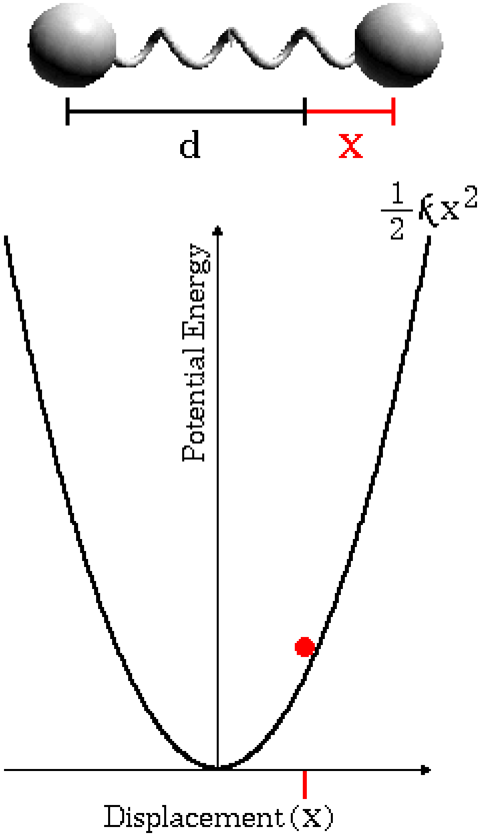


At the equilibrium length d, the spring has zero (relative) potential energy. As the spring is stretched or compressed, the potential energy increases along a parabola. This curve is called the **harmonic potential.**

Theory of molecular vibrations



Compressed spring: the potential energy increases along a parabola.



Stretched spring: the potential energy increases along a parabola.

Theory of molecular vibrations

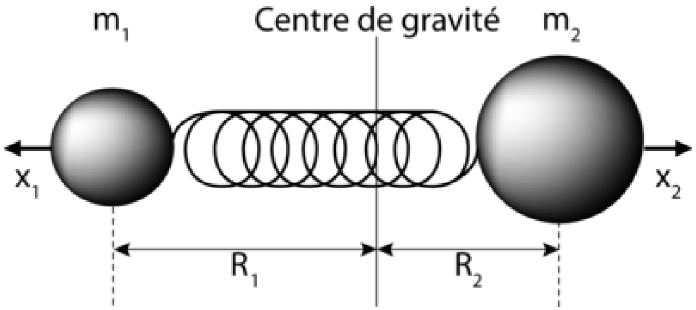
The vibration frequency is related to the force constant **k** and masses of atoms **A** and **B** : **m_A** and **m_B** respectively by **Hooke's law**:

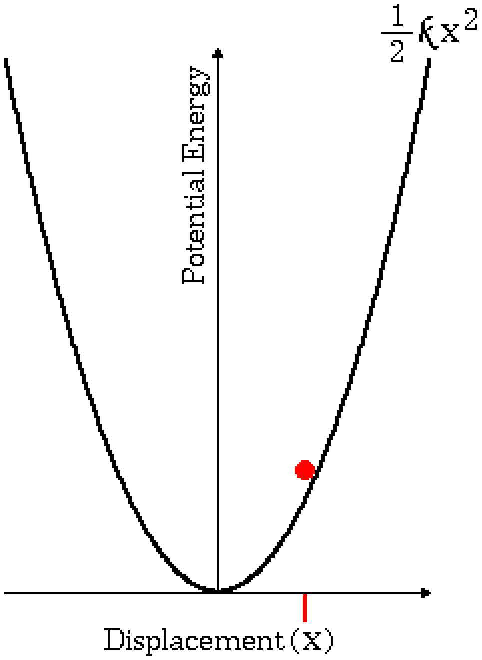
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

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

$\bar{\nu}$ = wavenumber, ν = frequency, μ = reduced mass

$$\mu = \frac{m_A . m_B}{m_A + m_B}$$





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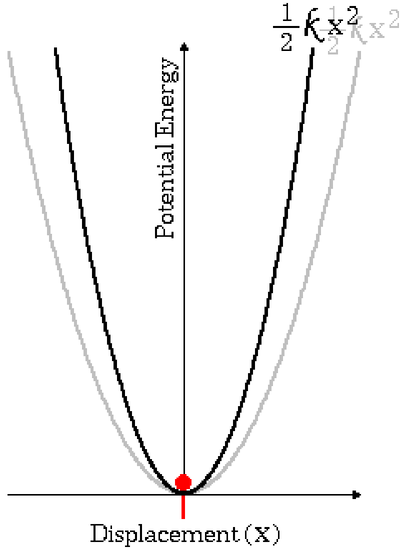
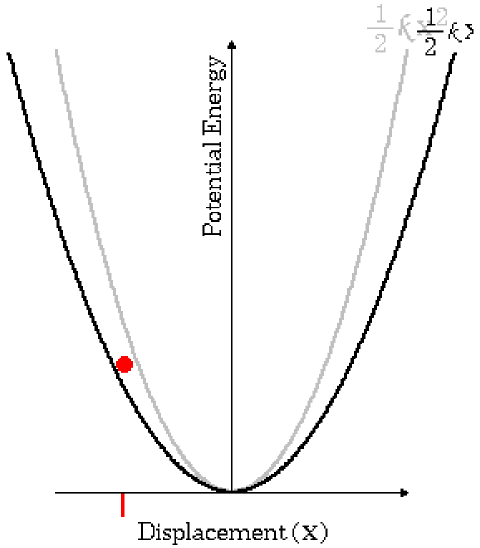


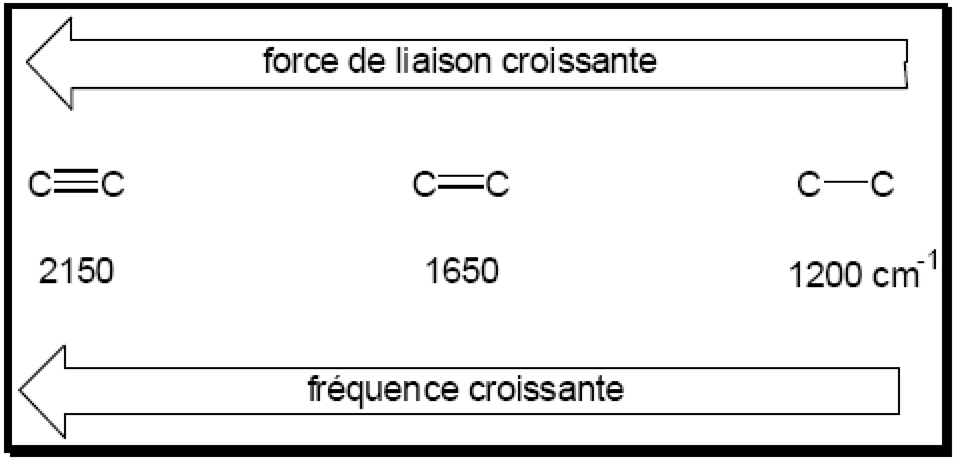
Therefore, a larger force constant (stronger spring) results in a higher frequency…

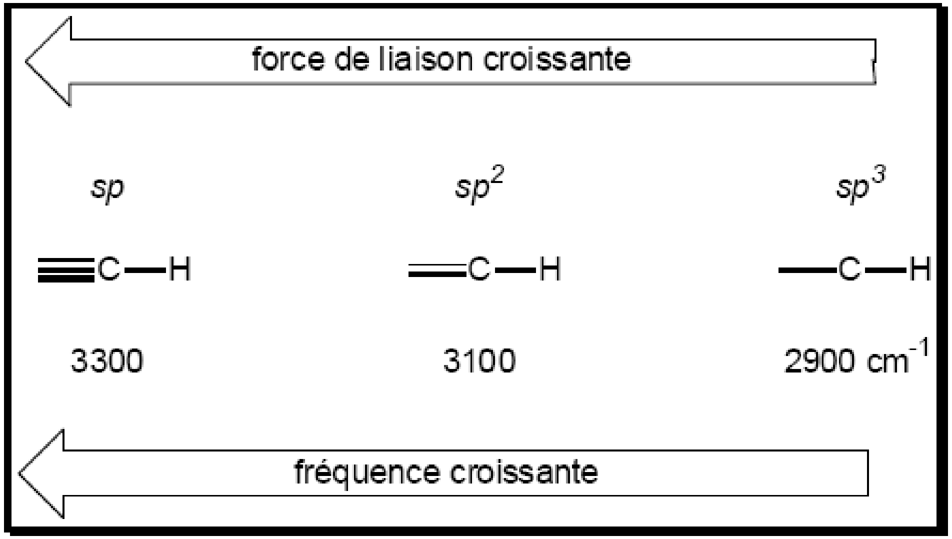


And a smaller force constant results in a lower frequency

Theory of molecular vibrations

The vibration frequency is related to the force constant





Theory of molecular vibrations

Classical model

IR absorption bands calculated with Hooke’s law

Type of bonds	**Force constant (dyne/cm)**	**Spectral region (cm^{-1})**	
		Calculated	**Observed**
C-O	5,0 .10^5	1113	1300-800
C-C	4,5 .10^5	1128	1300-800
C-N	4,9 .10^5	1135	1250-1000
C=C	9,7 .10^5	1657	1900-1500
C=O	12,1 .10^5	1731	1850-1600
C≡C	15,6 .10^5	2101	2150-2100
C-D	5,0 .10^5	2225	2250-2080
C-H	5,0 .10^5	3032	3000-2850
O-H	7,0 .10^5	3553	3800-2700

Theory of molecular vibrations

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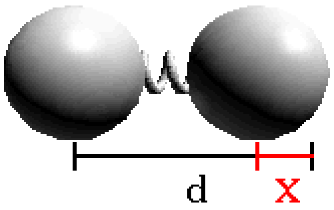
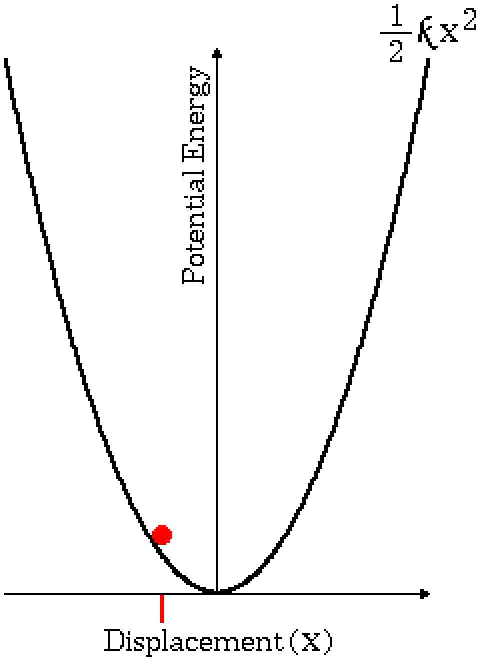
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

A larger mass results in a lower frequency, but the potential curve does not change.





Theory of molecular vibrations

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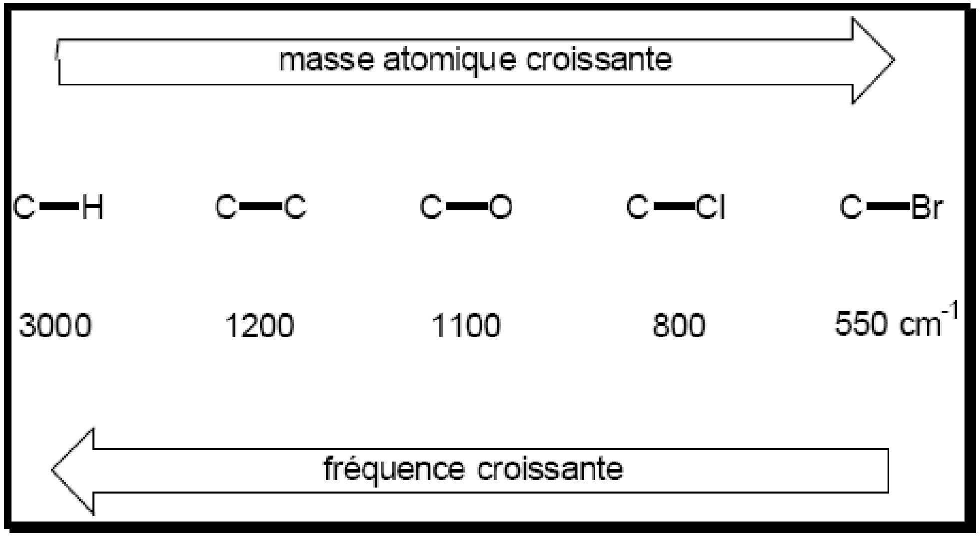
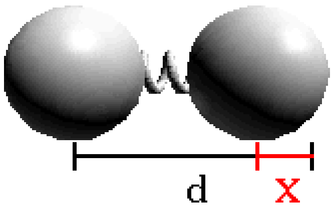
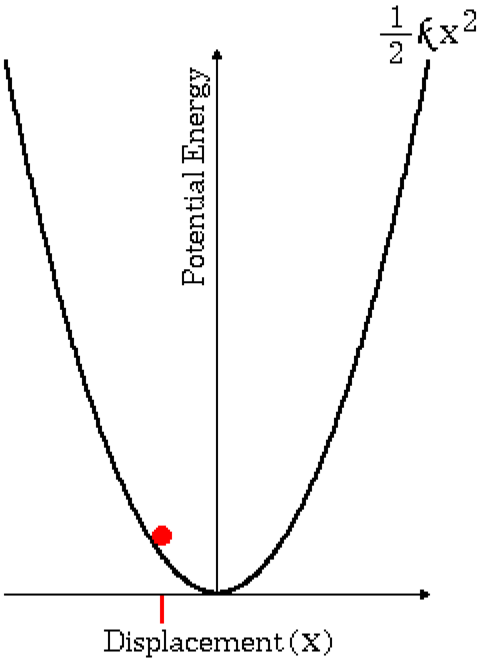


C—H	C—C	C—O	C—Cl	C—Br
3000	1200	1100	800	550 cm^{-1}

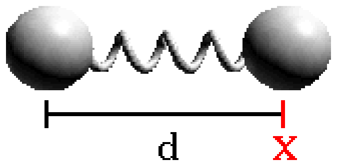


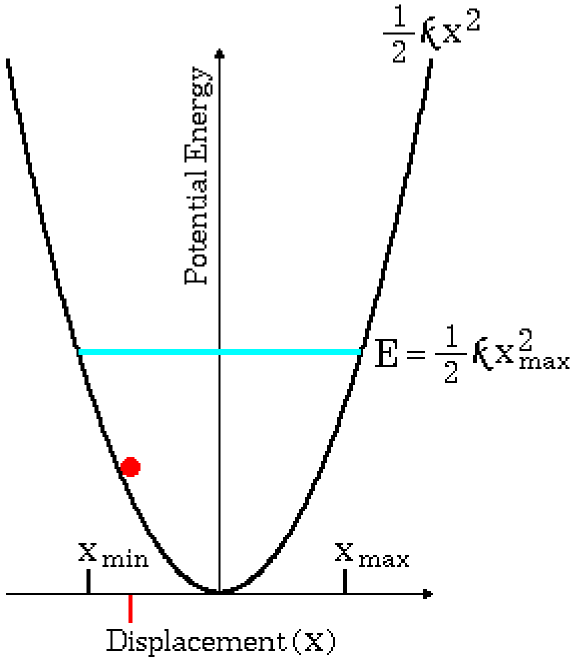


Theory of molecular vibrations

The molecule vibrates with a total energy equal to the potential energy at the stretched or compressed position

$$E = \frac{1}{2} k X^2{}_{\max}$$





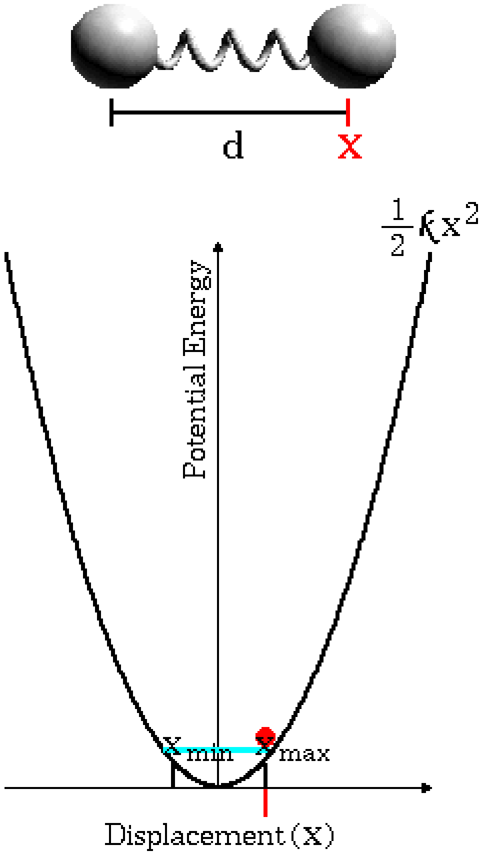
Theory of molecular vibrations

When the spring is stretched an arbitrary amount X_{max} and then released, it vibrates with a total energy equal to :

$$E = \frac{1}{2} k X^2{}_{max}$$

The model therefore predicts that the molecule can vibrate at **any** total energy. While this is true for a real ball and spring, it is **incorrect for a molecule**

A more accurate model, **quantum mechanics,** must be used to predict the observed behavior of molecules.



Theory of molecular vibrations

Quantum mechanics predicts the same relationships between vibration frequency, force constant, and mass that are predicted by classical physics. However, quatum mechanics predicts that **the molecule may vibrate only at energy levels which with the formula:**

$$E = h\bar{\nu}c\left(n + \frac{1}{2}\right)$$

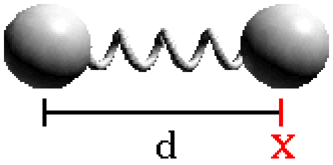
n = 0, 1, 2 …

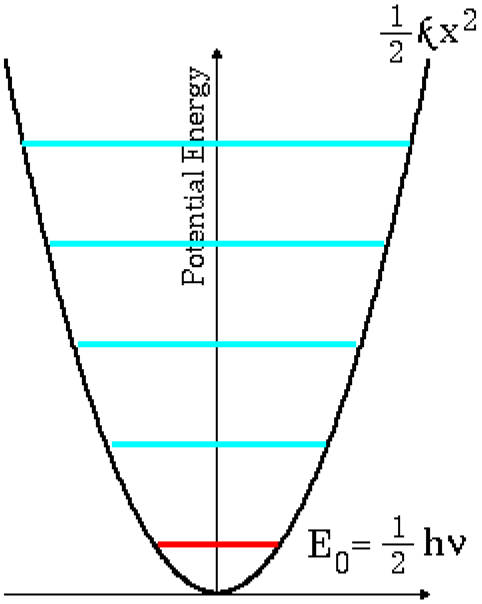
The energy is said to be **quantized**

In this model, a molecule may only absorb (or emit) light of an energy equal to the spacing between two levels. Furthermore, for a harmonic oscillator these transitions can only occur from one level to next higher (or lower) level, i.e. **Δn = ±1**.

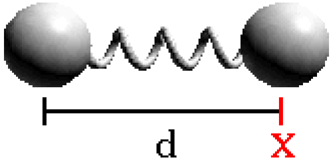
This is called selection rule

$$E = E_{n+1} - E_n = h.\nu$$





Theory of molecular vibrations

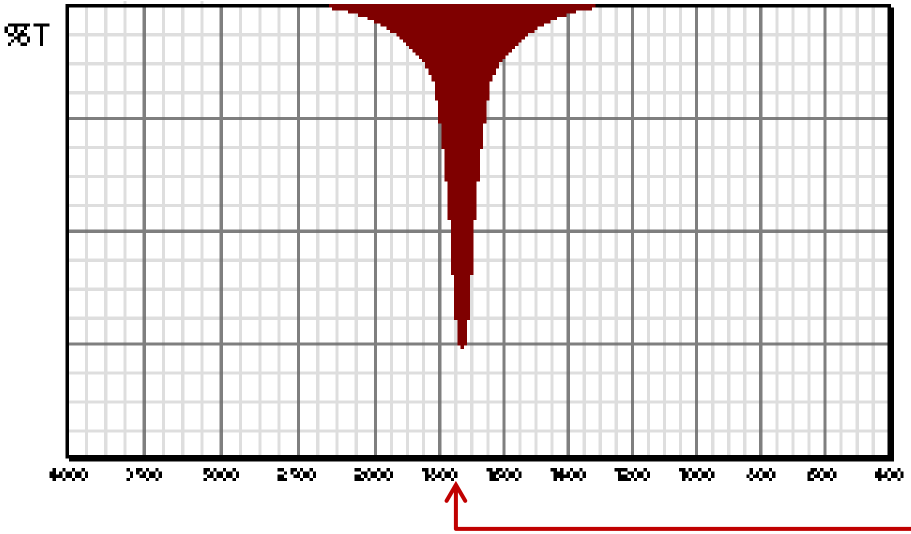


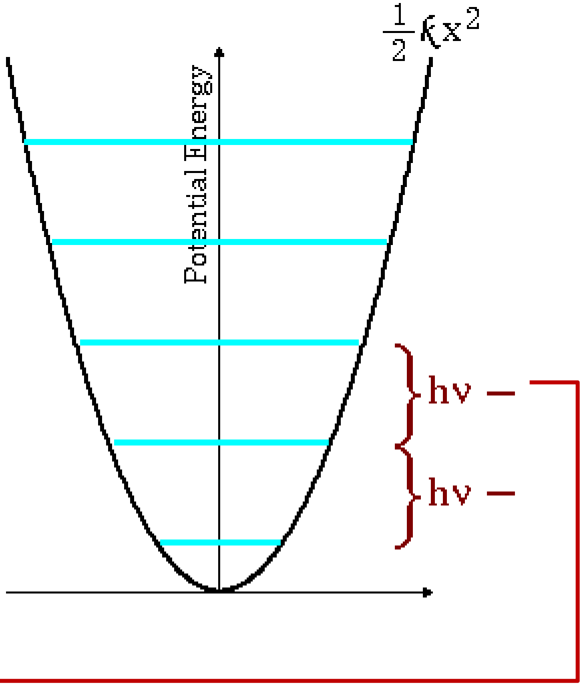
Quantum mechanics

Because of the selection rule, a molecule can only absorb light with energy equal to h.ν .

Therefore, the infrared spectrum of this molecule should have a single peak at the frequency corresponding to that energy.

$$E = E_{n+1} - E_n = h.\nu$$

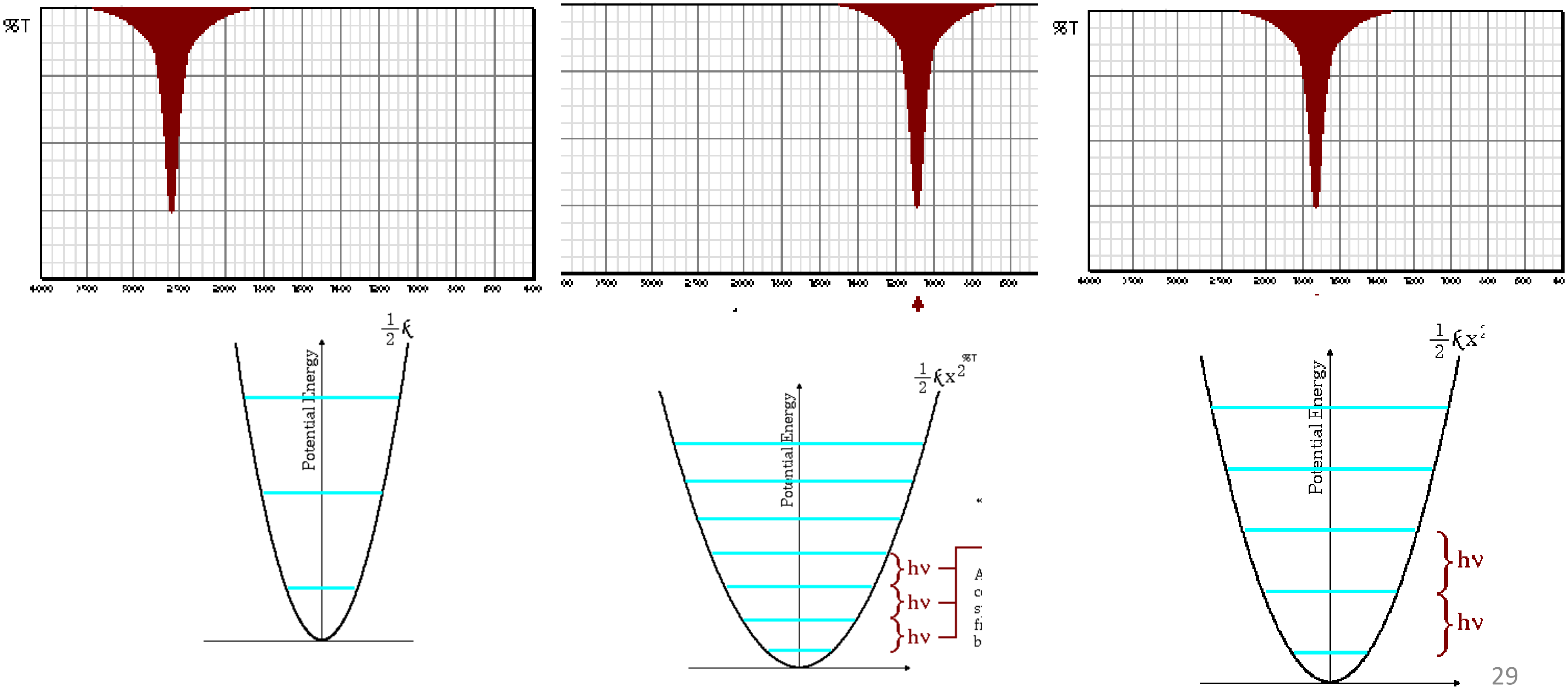




Theory of molecular vibrations

Quantum mechanics

A higher freqyency (due to a larger force constant or a smaller mass) results in a larger spacing between the levels… and a lower frequency results in a smaller spacing between the levels.

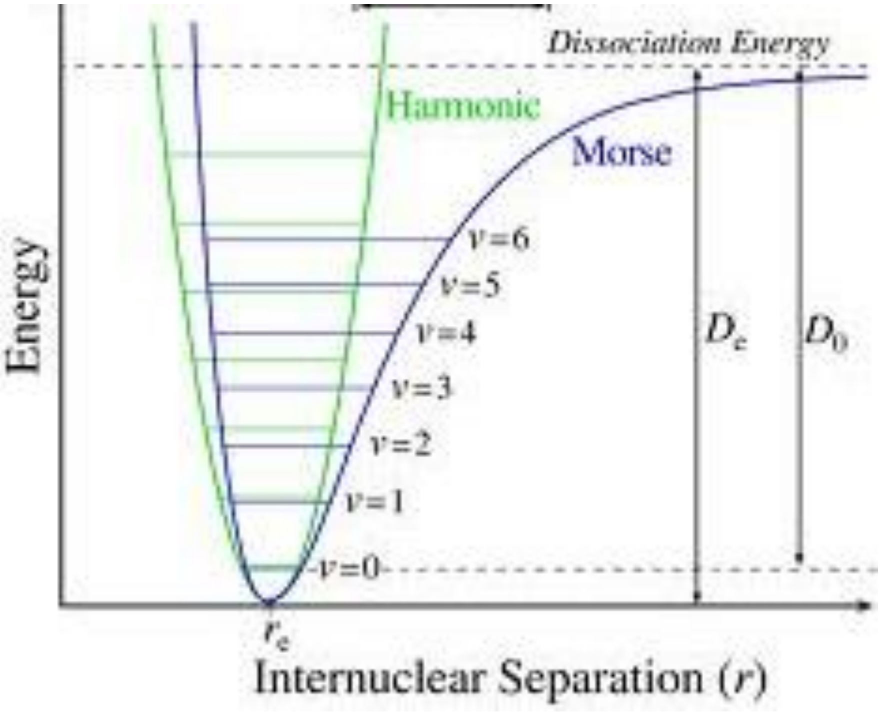


Theory of molecular vibrations

Quantum mechanics

An actual spectrum is more complicated.
1- A real molecule is not a harmonic oscillator. When atoms are pushed very close together, they repel more strongly than a spring.
When pulled apart far enough, the bond breaks.
This behavior can be modelled with an **anaharmonic potential.**
In this model, the energy levels are equally spaced only in the region shaped like harmonic potential.

2- The selection rule, which allowed transitions between one level and the next higher (or lower) is not rigorously true. A transition with Δn = +2, called an **overtone**, corresponds to ΔE approximately 2.h.v
The overtone band appears at a little less than twice the frequency of the fundamental band, and is less intense. Often the overtone band is so small it cannot be found.



$$E = h\bar{\nu}c\left(n+\frac{1}{2}\right)-\left(n+\frac{1}{2}\right)^2 h\bar{\nu}cX_e$$

X_e= anharmonicity constant

Theory of molecular vibrations

A final limitation:
In order to absorb light, the mocleular dipole must change when a transistion occurs.

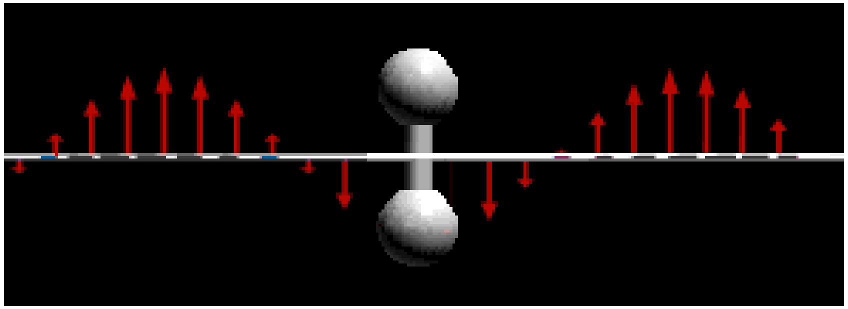
$$\frac{d\mu}{dr} \neq 0$$

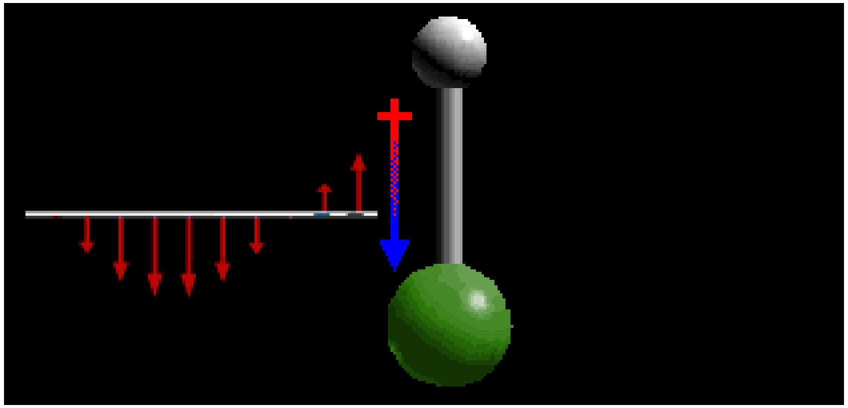
For example:

H_2 always has a net zero dipole, and does not absorb infrared light.

HCl does have a dipole change as it stretches. When this dipole aligns with the electric field of a beam light, the light is absorbed (so long the frequency is correct).

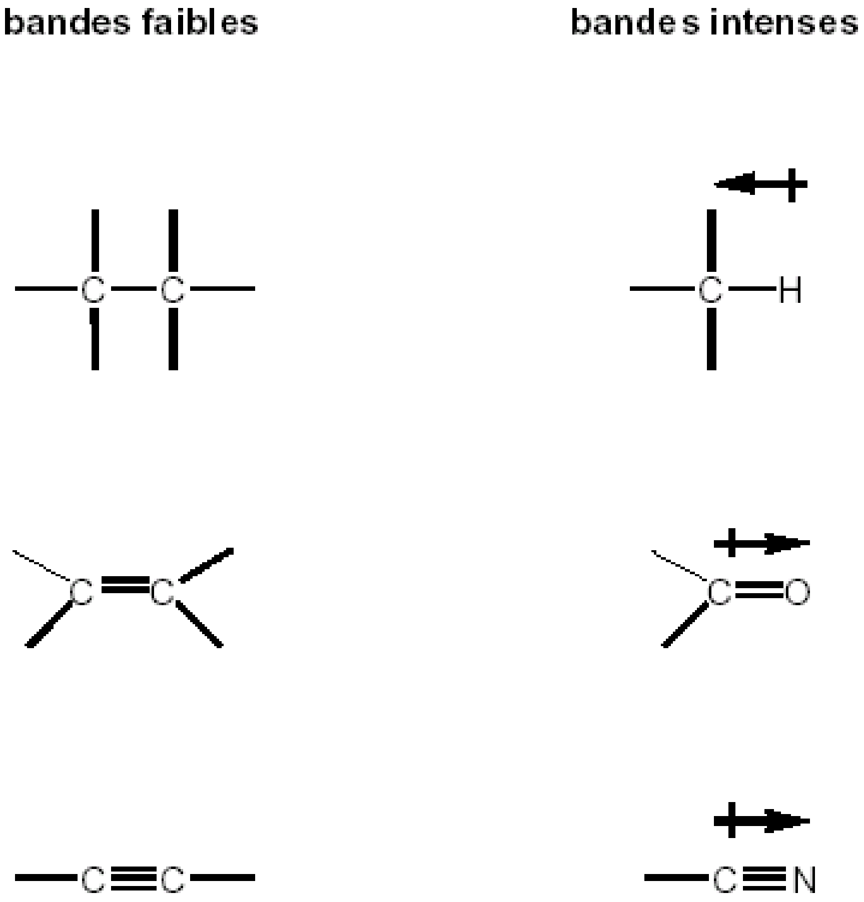
The intensity of the absorption is related to the magnitude of the dipole change.





Theory of molecular vibrations

The intensity of the absorption is related to the magnitude of the dipole change.



Theory of molecular vibrations

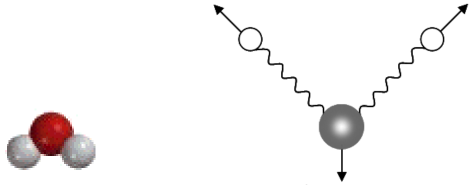
Molecules bigger than two atoms have more complicated infrared spectra:

Vibration types :

2 types of molecular vibrations :

- Stretching ν :

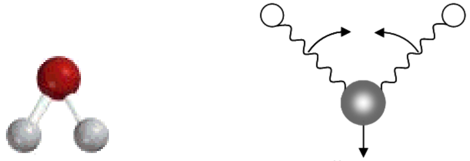
Movement along the covalent bond axis



Elongation
symétrique OH
3652 cm^{-1}

- Deformation (bending) δ :

Angular movement (change in the angle between covalent bonds)



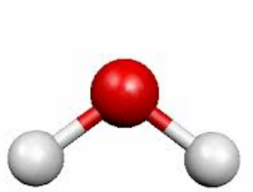
Cisaillement OH
1596 cm^{-1}

Theory of molecular vibrations

Molecular movements :

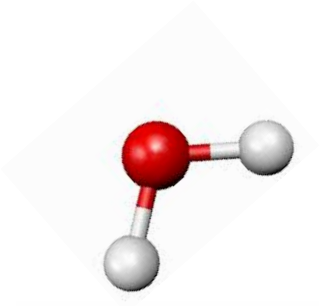
A molecule with N atoms has 3N degrees of freedom:

- **Translation:** 3 degrees of freedom (x,y et z coordinates)



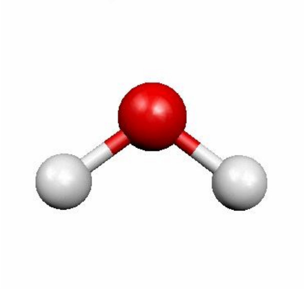
- **Rotation:** 3 degrees of freedom for non linear molecules

  2 degrees of freedom for linear molecules



- **Vibration:** 3N-6 degrees of freedom for non linear molecules

  3N-5 degrees of freedom for linear molecules



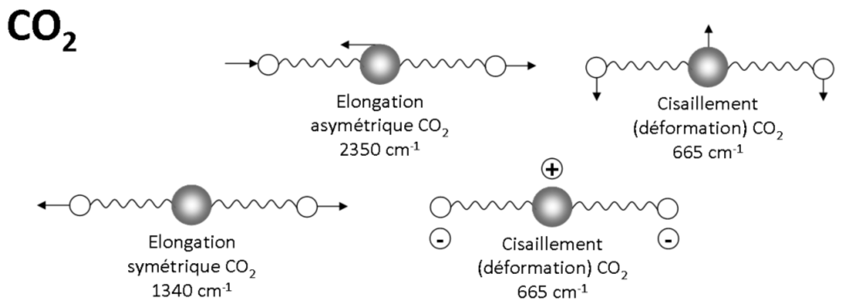
Theory of molecular vibrations

Modes of vibrations:

3N – 6 fundamental modes of vibrations
(3N – 5 pour les molécules linéaies)

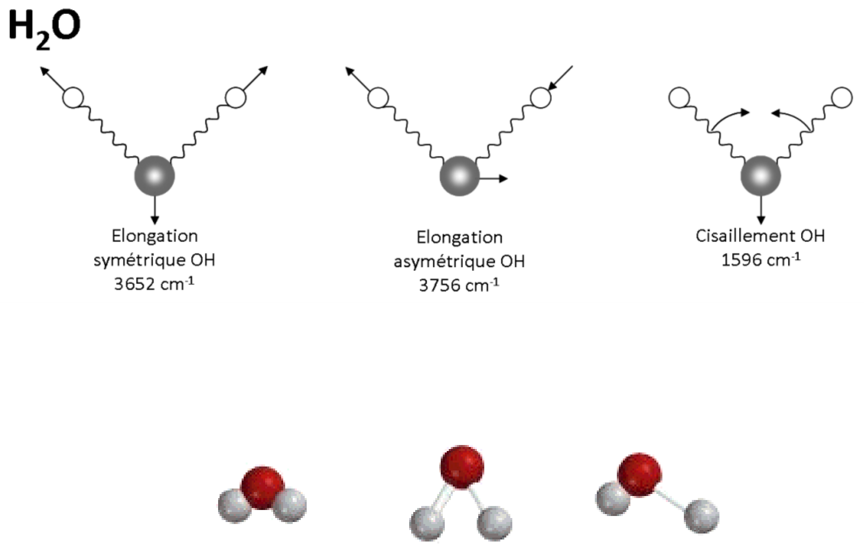
CO_2

3N- 5 = 3x3 – 5 = 4 degrees of freedom



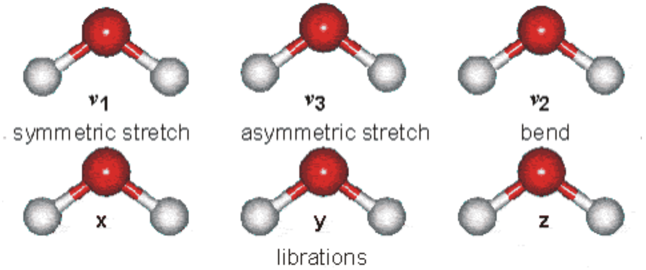
Water

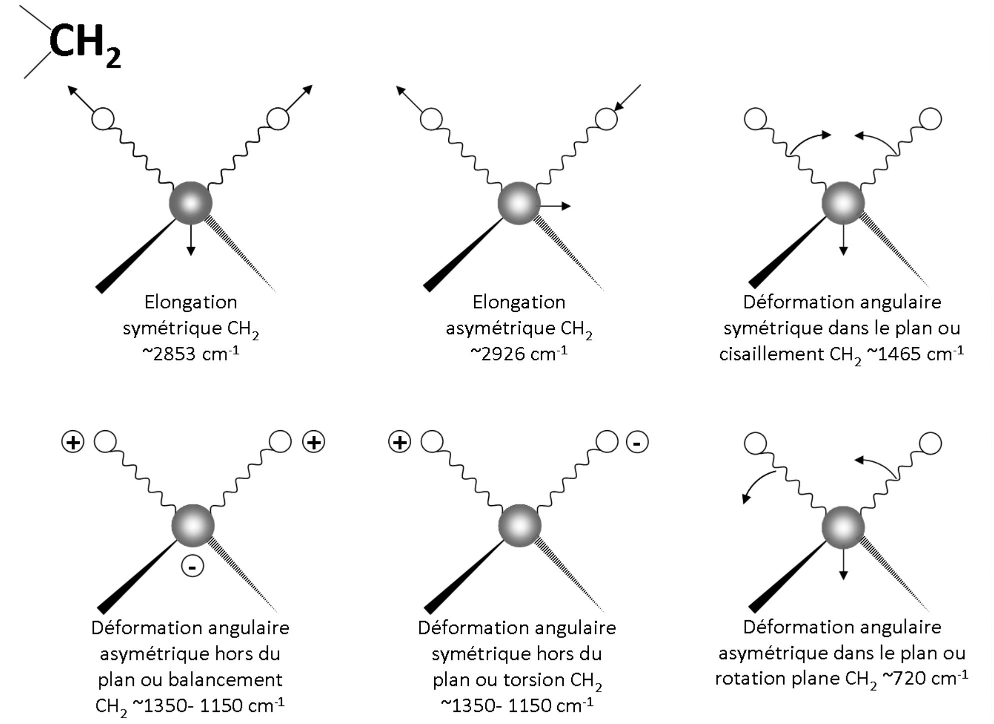
3N- 6 = 3x3 – 6 = 3 degrees of freedom



Theory of molecular vibrations

Modes of vibrations:





Elongation symétrique CH$_2$ ~2853 cm^{-1}

Elongation asymétrique CH$_2$ ~2926 cm^{-1}

Déformation angulaire symétrique dans le plan ou cisaillement CH$_2$ ~1465 cm^{-1}

Déformation angulaire asymétrique hors du plan ou balancement CH$_2$ ~1350- 1150 cm^{-1}

Déformation angulaire symétrique hors du plan ou torsion CH$_2$ ~1350- 1150 cm^{-1}

Déformation angulaire asymétrique dans le plan ou rotation plane CH$_2$ ~720 cm^{-1}

Theory of molecular vibrations

Modes of vibrations:

The number of vibrations is different than the 3N-6 (3N-5) fundamental modes

Increasing number of IR bands	Decreasing number of IR bands
Overtones (O): multiples of fundamental wavenumber	wavenumbers > 4000 cm^{-1} or < 400 cm^{-1}
Combination bands (C): sum or difference between 2 other bands, ex: aromatic rings 2000-1600cm^{-1}, aldehydes between 2820-2700 cm^{-1}	Very low intensity bands « inactive » (symmetric : $\Delta\nu = 0$). No changes in the dipole
Mechanical coupling : (ν/ν (common atom); δ/δ (common bond) ou ν/δ) : ex NH_2	Coalescence of very close bands
Fermi resonance : between FV and (H or C)	

Theory of molecular vibrations

Factors influencing the vibrations wavenumbers

Hydrogen bonds

Donors: O=C-OH; OH; NH; O=C-NH
Acceptors: O; N ;Cl ; Br ; I

Weakened heteroatom – hydrogen bond:

Shift to lower wavenumbers

Conjugation

e^- delocalization of double bonds: weakened constant force

Shift to lower wavenumbers

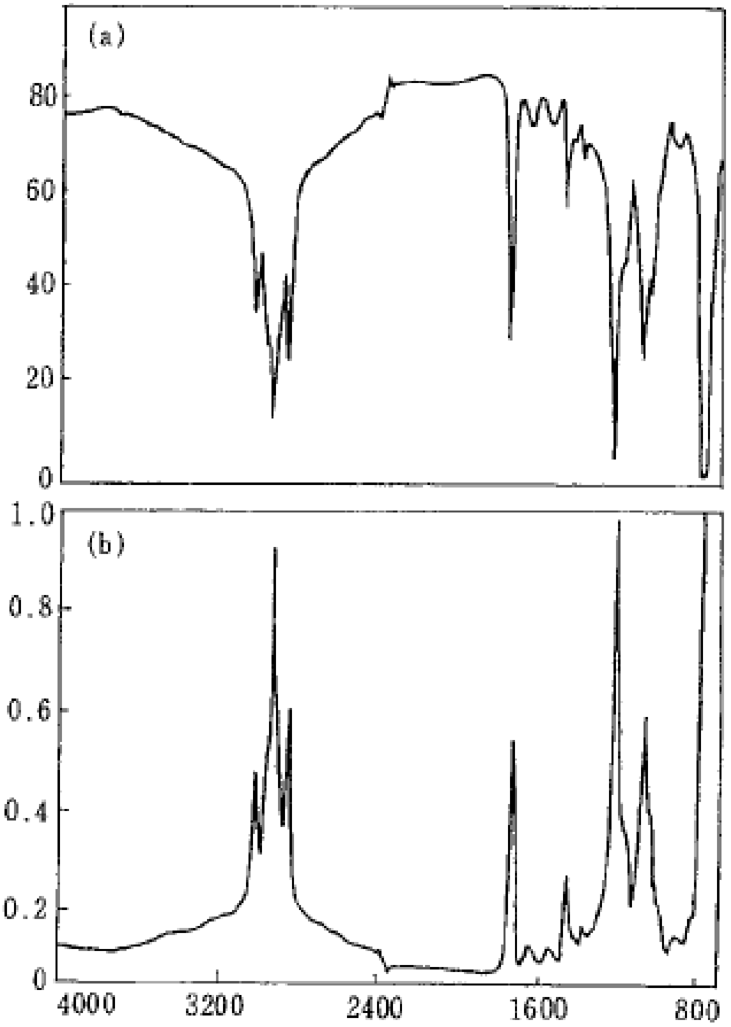
Ex: aromatic molecules against double bonds
Ex: C=O: -aliphatic ester ($1735 cm^{-1}$)
-phenol ester ($1760 cm^{-1}$)
-amide ($\sim 1680 cm^{-1}$)

Middle infrared spectroscopy

Wavenumber $\bar{\nu}\,(cm^{-1})$

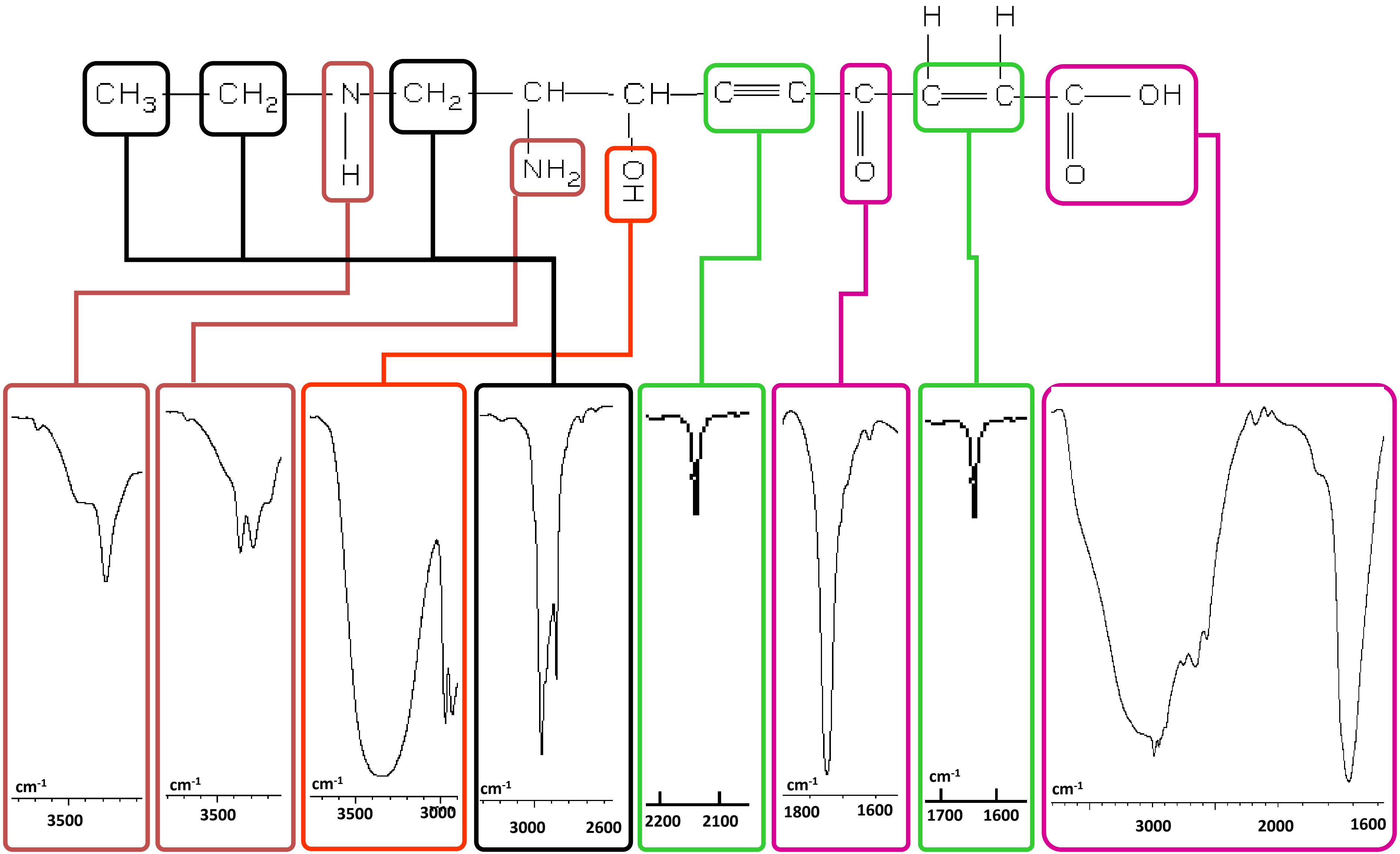
Transmission $$T = \frac{I_{withsample}}{I_{withoutsample}}$$

Absorbance $$A = \log(\frac{1}{T})$$

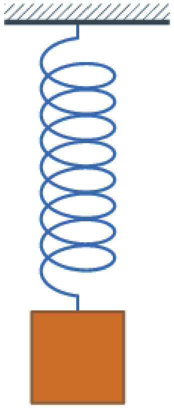


Skoog/Leary, « Principles of Instrumental Analysis » 4th edition, Saunders College Publishing, 1992

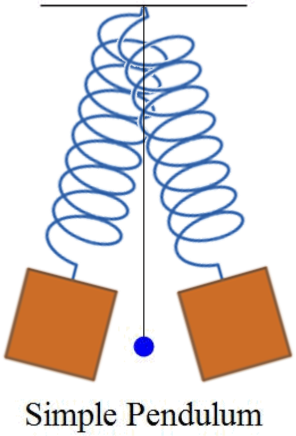
A fake infrared spectrum



ν: stretching
δ: bending



stretching



bending

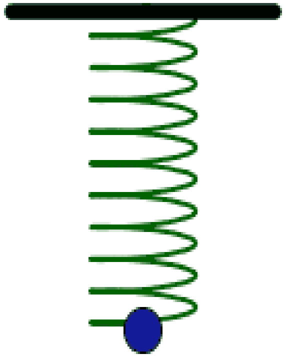
For the same molecular bond

$$\delta \boldsymbol{X}-\boldsymbol{Y} \ll\ll \boldsymbol{\nu}\boldsymbol{X}-\boldsymbol{Y}$$

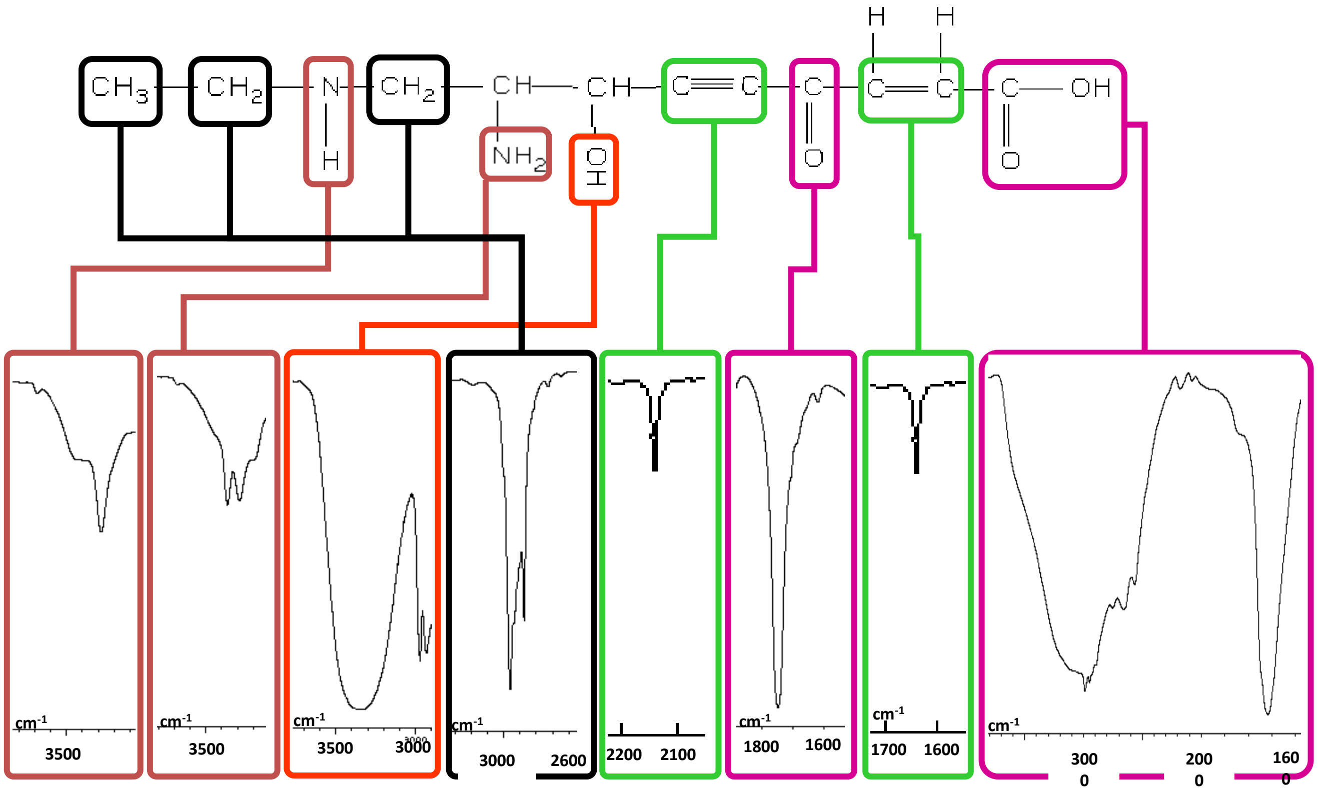
Stretching

<u>Attention:</u> this is a fake spectrum

ν: stretching



$$\nu X - H > 2500 cm^{-1}$$

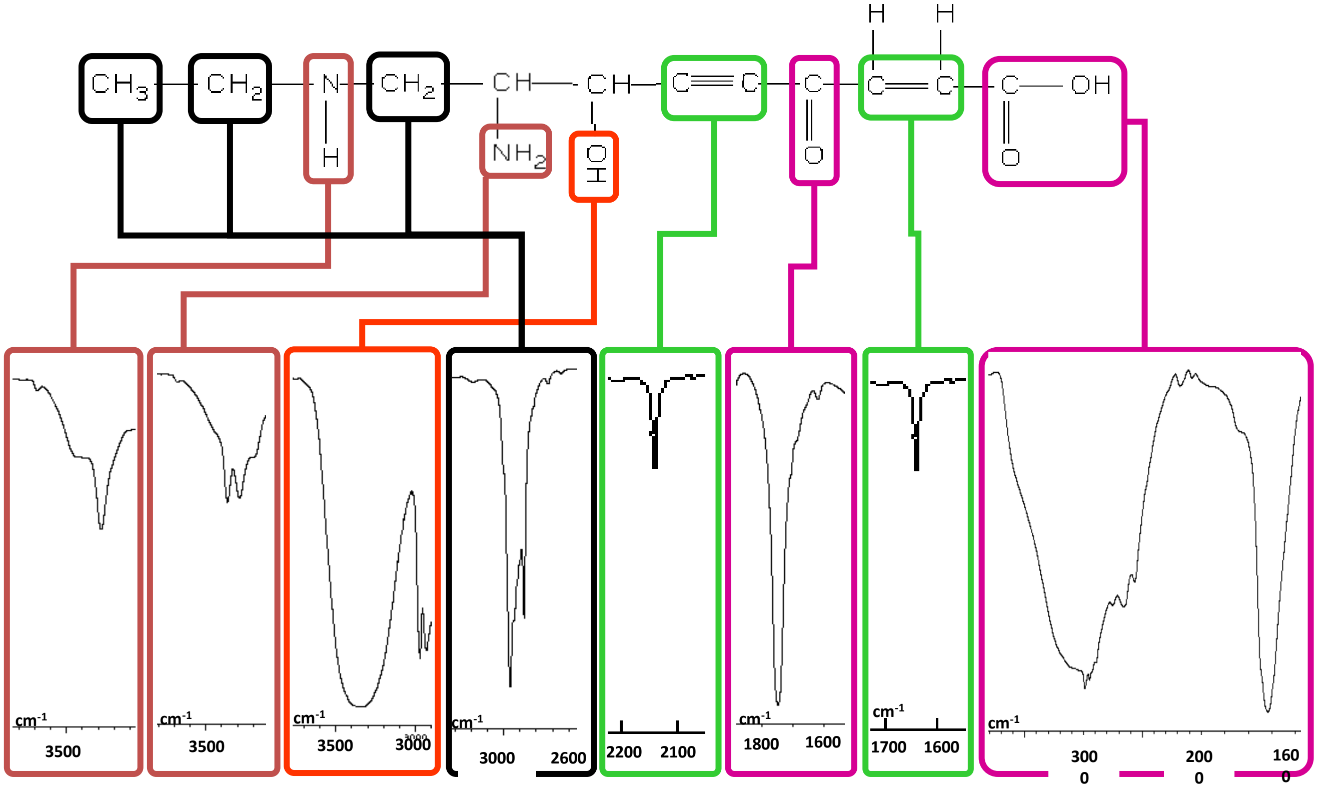


Stretching

Attention: this is a fake spectrum

ν: stretching

$$\nu X-Y<1500cm^{-1}$$



Quick spectral analysis