General introduction to molecular spectroscopy

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Pr Martin Schwell

- Diploma in chemistry, Free University of Berlin (1994)
- PhD in Physical Chemistry, Free University of Berlin (1998)
  - Microphysics of stratospheric aerosols studied in the laboratory with electrodynamic traps
- PostDoc @Paris Observatory (LERMA laboratory), 1998-2001
  - Vacuum UV spectroscopy of interstellar molecules
  - Photophysics of fullerenes in the UV/vis domain
- MCF @ Paris Diderot in 2001, Pr @UPEC in 2013
  - Associated to the LISA laboratory
    - Vacuum-UV spectroscopy of interstellar and planetary molecules
    - Tunable Diode Laser spectroscopy of GHG
    - Mass spectrometry of aerosols

Summary

1. **Introduction:** Why do we need spectroscopy in the atmospheric sciences ?

2. **History:** from the 19th century spectroscopes to the ascension of quantum mechanics

   - Newton, Herschel, Fraunhofer lines, Kirchhoff laws, Balmer series, photoelectric effect, quantization of energy, Bohr's model, wave mechanics

3. **Basics of Spectroscopy**

   - The electromagnetic spectrum,
   - Black body radiation
   - Absorption and emission of radiation,
   - Molecular motion and energy levels, transitions (Rotational, vibrational, electronic…)
   - The Beer-Lambert Law

4. **Experimental spectroscopy** (this afternoon…)

   - Typical experimental setup: light sources , dispersing elements (prism, diffraction gratings), monchromators, spectrographs, …
   - Introduction to laser radiation

Introduction

- What is (molecular) spectroscopy ?
  - Study the interaction of electromagnetic radiation with molecules, <u>as a function of the wavelength</u> of the radiation
- What can we do with spectroscopy ?
  - Determine the internal structure of molecules and how they interact
  - Probe matter, molecules, atmospheres & objects of the universe
- $\rightarrow$ Very important field in physical chemistry
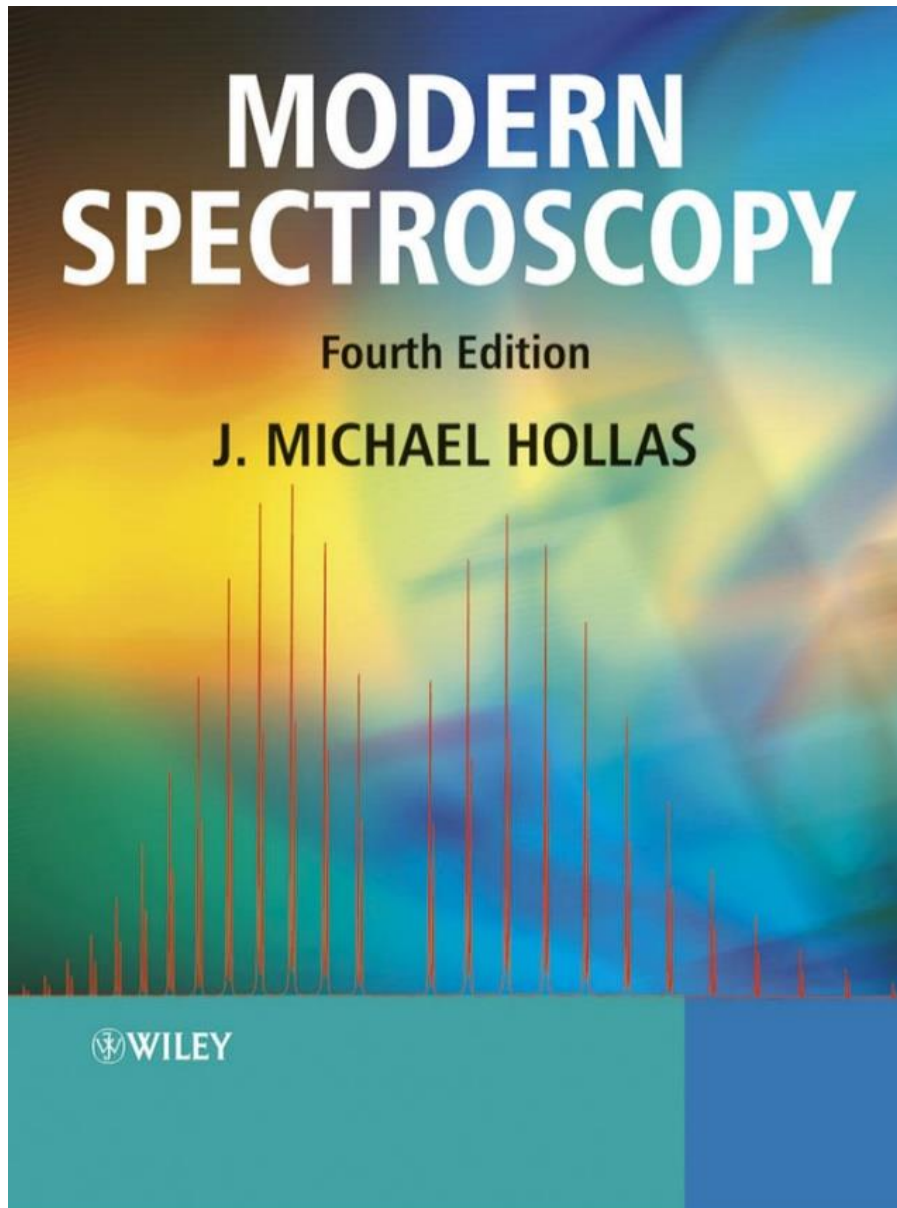
Book recommendation

- 4th edition from 2004
- 450 pages
- 42 euros
- Good basis for beginners with good knowledge of physics or chemistry (Ba3/M1 level)

Further reading, advanced spectroscopy

- "Spectra of atoms and molecules", P.F. Bernath, *Oxford University Press* (2005).

- "Rotational structure in molecular infrared spectra", C. di Lauro, *Elsevier* (2013).

- "Atoms, molecules and photons", W. Demtröder, *Springer* (2006).

- "Handbook of high resolution spectroscopy", M. Quack and F. Merkt, Editors, *Wiley* (2011).

- "Fundamentals of molecular symmetry", P.R. Bunker and P. Jensen, *Institute of Physics Publishing* (2005).
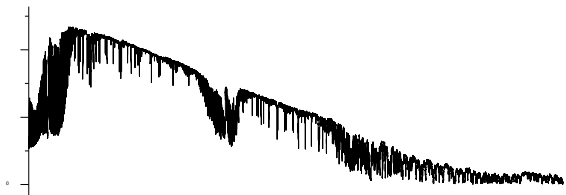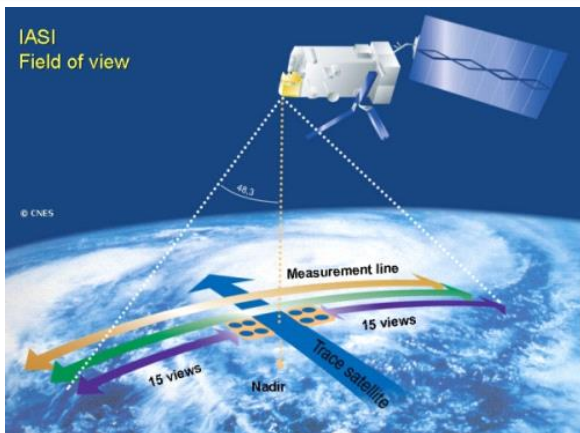
Why do we need molecular spectroscopy in the atmospheric sciences ?

1. **Remote sensing** of relevant trace gases (by **satellites** or from **ground**) by spectroscopic methods
   - GHG (CO_2, CH_4, H_2O, N_2O, CFCs, HCFCs, HFCs…)
   - Pollutants (O_3, NO_x, NH_3, BTX, Persistent organic pollutants (POP)…..)
2. **In-situ measurements** in the field
3. **Process studies** of atmospheric chemistry in simulation chambers
   - Spectroscopic methods are used to follow molecules in <u>real time</u> (optical spectroscopy, mainly IR & UV; mass spectrometry)
4. Measurement of high precision, **quantitative spectroscopic parameters** of pure compounds in the laboratory (<> theoretical spectroscopy)
   - ***Needed for everything depicted above….***
5. Input (and output) data for **atmospheric modelling**
   - Photolysis rates are calculated from quantitative absorption spectra in the ultraviolet
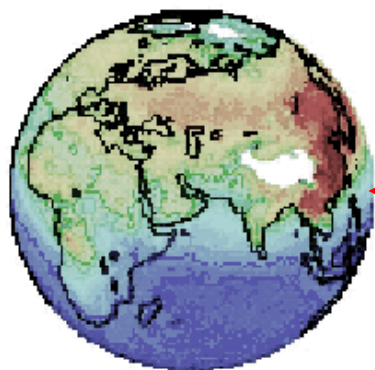   - Synthetic IR spectra of planetary atmospheres

Experimental Lab spectrum

Spectroscopic data base
(line position, intensity, shape)
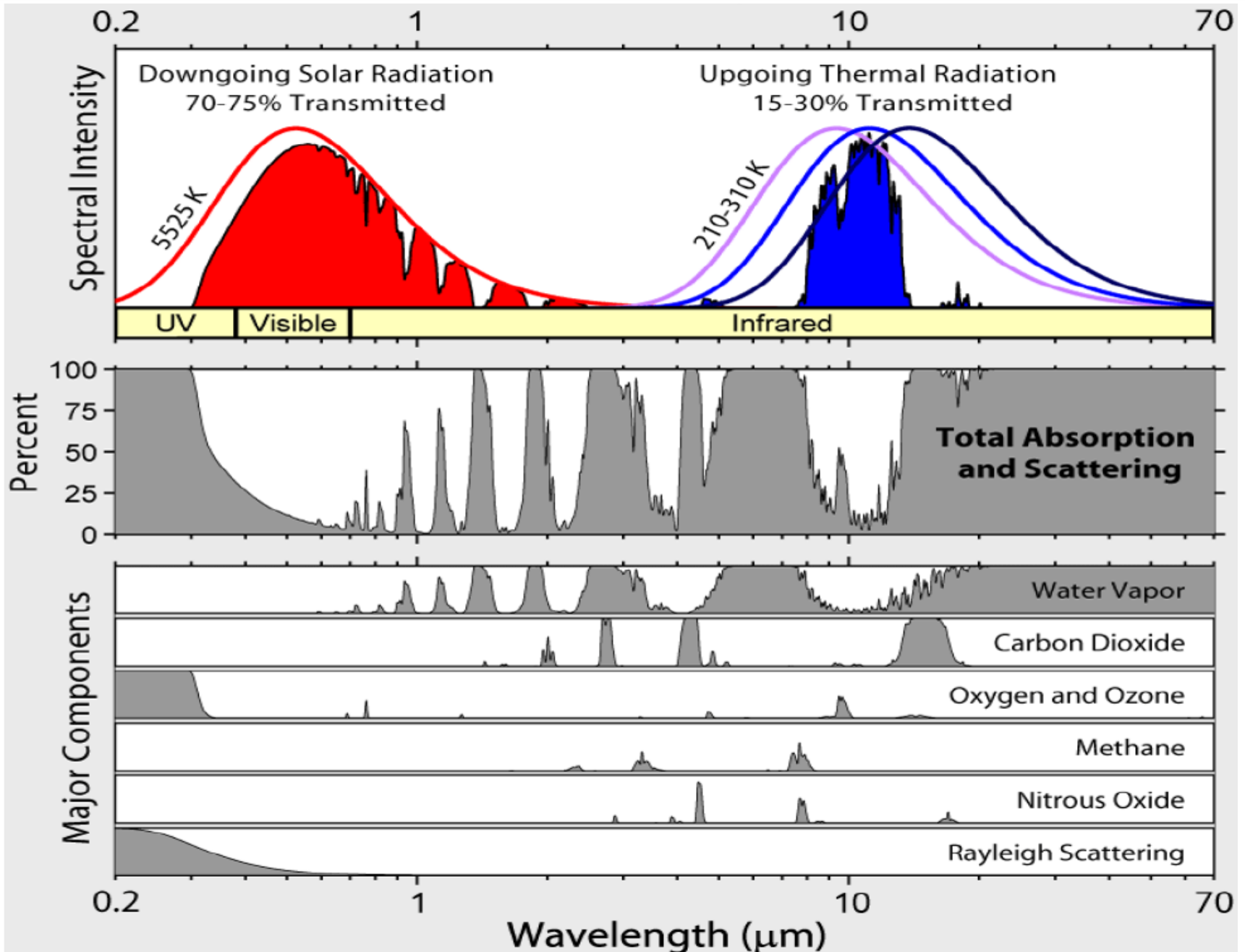
Theoretical model of a spectrum

Real world atmospheric spectrum

Inversion Method

$$\mathrm{H}\Psi = \mathrm{E}\Psi$$

Chemistry Transport model
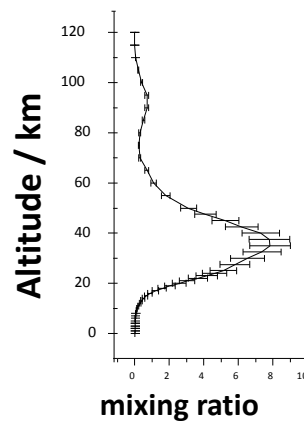
Typical result of a remote sensing experiment:
A (vertical) profile of a molecule

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Example : High resolution <u>microwave</u> spectroscopy

|		
1) Experimental spectrum	**2) Quantum chemical calculations (ab-initio)**	3) High precision spectral analysis with **effective theroretical models** to describe **rotation and torsion** in molecules (Codes : XIAM; BELGI, ERHAM…)
Rotational temperature ≈10K res. power: 10^6	→ First estimation of **rotational constants**	
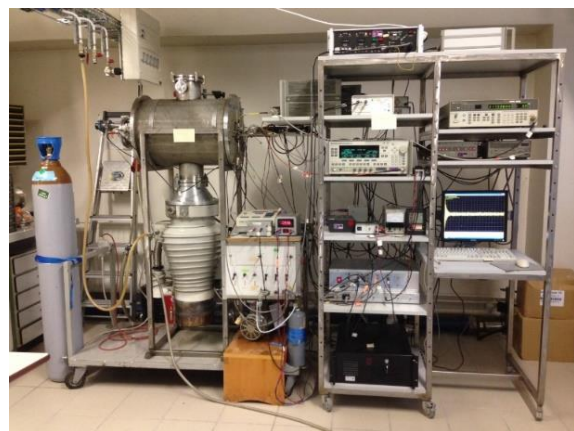
- "Small Cavity" ; 26-40 GHz experiment
- jet-cooled molecules

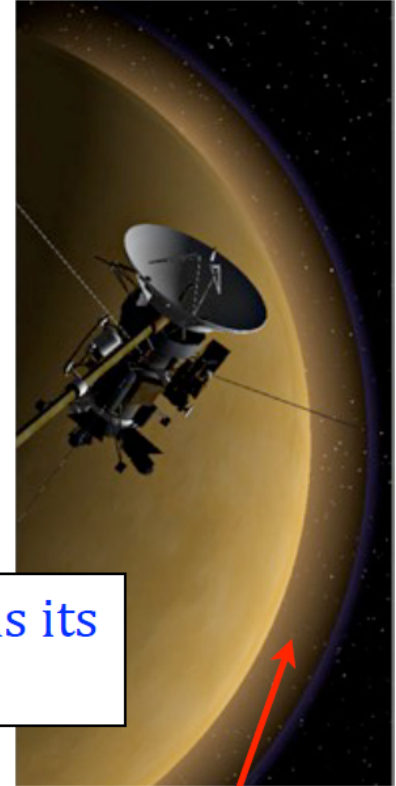*Kleiner, Nguyen et al. (LISA)*

4) **Comparison of molecular parameters:**

Ab initio calculations of rotational constants
⇔ **values obtained by fitting experimental HR spectra with effective theoretical models**

(i) Very precise determination of **molecular structures**
(ii) Validation of **ab initio quantum chemical calculations**
(iii) Line lists for remote sensing → **data base**

Limb sounding on Titan

Cassini / CIRS
Flyby T32
Latitude 50°N
Resolution = 0.5 cm^{-1}

Courtesy: A. Coustenis (LESIA)
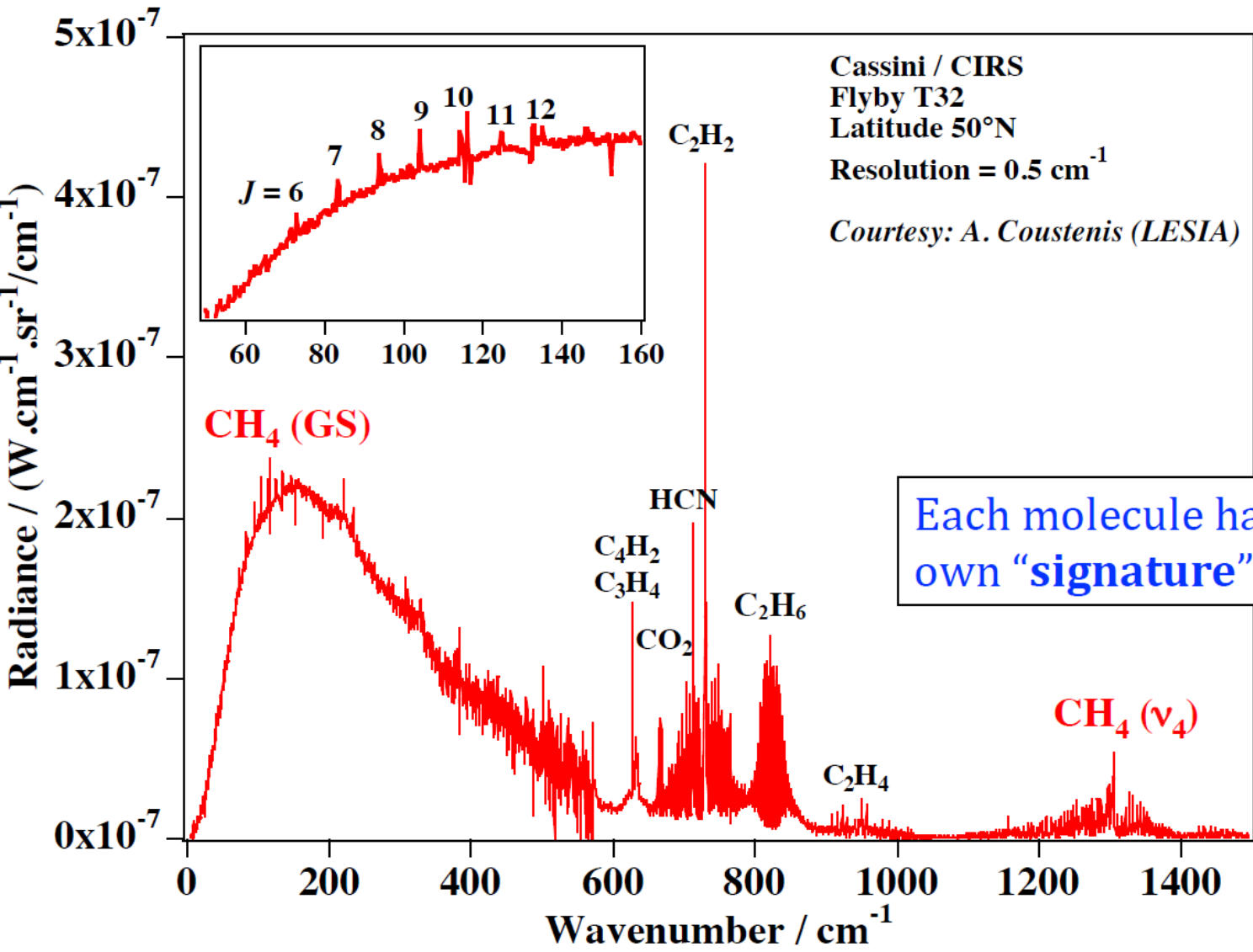
Each molecule has its own "**signature**"

Emission from the atmosphere

Table 3. Example of HITRAN line-transition format.

Mol/Iso	$\nu_{\eta\eta'}$	$S_{\eta\eta'}$	$\mathfrak{R}_{\eta\eta'}$	γ_{air}	γ_{self}	E''	n	δ	iv'	iv''	q'	q''	ierr	iref
21	800.451076	3.197E–26	6.579E–05	0.0676	0.0818	2481.5624	0.78	0.000000	14	6		P 37	465	2 2 1
291	800.454690	9.724E–22	1.896E–02	0.0845	0.1750	369.6303	0.94	0.000000	9	1	341619	331519	000	4 4 1
291	800.454690	3.242E–22	2.107E–03	0.0845	0.1750	369.6303	0.94	0.000000	9	1	341519	331419	000	4 4 1
121	800.455380	1.037E–22	1.657E–03	0.1100	0.0000	530.3300	0.75	0.000000	32	14	46 640	45 540	000	4 4 1
121	800.455380	1.037E–22	1.657E–03	0.1100	0.0000	530.3300	0.75	0.000000	32	14	46 740	45 640	000	4 4 1
101	800.456743	1.680E–23	1.659E–04	0.0670	0.0000	851.0494	0.50	0.000000	2	1	45 244 0–	44 143 0–	301	6 6 1
101	800.457045	1.710E–23	1.689E–04	0.0670	0.0000	851.0469	0.50	0.000000	2	1	45 244 1–	44 143 1–	301	6 6 1
101	800.457310	1.740E–23	1.718E–04	0.0670	0.0000	851.0442	0.50	0.000000	2	1	45 244 2–	44 143 2–	301	6 6 1
121	800.457760	4.726E–23	4.614E–03	0.1100	0.0000	920.0000	0.75	0.000000	32	14	593033	493833	000	4 4 1
121	800.457760	4.726E–23	4.614E–03	0.1100										
24	800.465942	9.792E–27	6.063E–04	0.0754										
121	800.466160	1.061E–22	2.720E–03	0.1100										
121	800.466160	1.061E–22	2.720E–03	0.1100										
35	800.472900	3.878E–26	6.919E–04	0.0686										
101	800.473083	1.270E–23	1.254E–04	0.0670										
101	800.474860	1.210E–23	1.195E–04	0.0670										
31	800.475500	1.680E–24	3.617E–05	0.0653										
291	800.476220	9.597E–23	6.010E–03	0.0845										
291	800.476220	3.199E–22	6.010E–03	0.0845										
101	800.476937	1.160E–23	1.145E–04	0.0670										
101	800.484334	1.740E–23	2.153E–05	0.0670										

Note: FORTRAN Format (I2,I1,F12.6,1P2E10.3,0P2F5.4,F10.4,F4.2,F8

Mol	I2	molecule number
Iso	I1	isotope number (1 = most abundant, 2 = second
$\nu_{\eta\eta'}$	F12.6	frequency in cm^{-1}
$S_{\eta\eta'}$	E10.3	intensity in cm^{-1}/(molecule·cm^{-2}) @ 296 K
$\mathfrak{R}_{\eta\eta'}$	E10.3	weighted transition moment-squared in Debye^2
γ_{air}	F5.4	air-broadened halfwidth (HWHM) in cm^{-1}/atm @
γ_{self}	F5.4	self-broadened halfwidth (HWHM) in cm^{-1}/atm @
E''	F10.4	lower state energy in cm^{-1}
n	F4.2	coefficient of temperature dependence of air-broad
δ	F8.6	airbroadened pressure shift of line transition in cm
iv',iv''	2I3	upper state global quanta index, lower state globa
q',q''	2A9	upper state local quanta, lower state local quanta
ierr	3I1	accuracy indices for frequency, intensity, and air-b
iref	3I2	indices for table of references corresponding to fre

The HITR

The HITRAN data base (mainly IR):
- **Few million lines for 49 species** (2016; *not counting isotopologues*)
- **"Eternal field of work"** :
  - Questions arise continuously about **correctness, completeness, accuracy, better parameters to be included…** *remote sensing is an important driving force*
  - Biennial conference (alternating in USA and France), dedicated working groups,
  - User-friendly web version: www.hitran.org

For example:

Laser Induced Fluorescence (LIF)

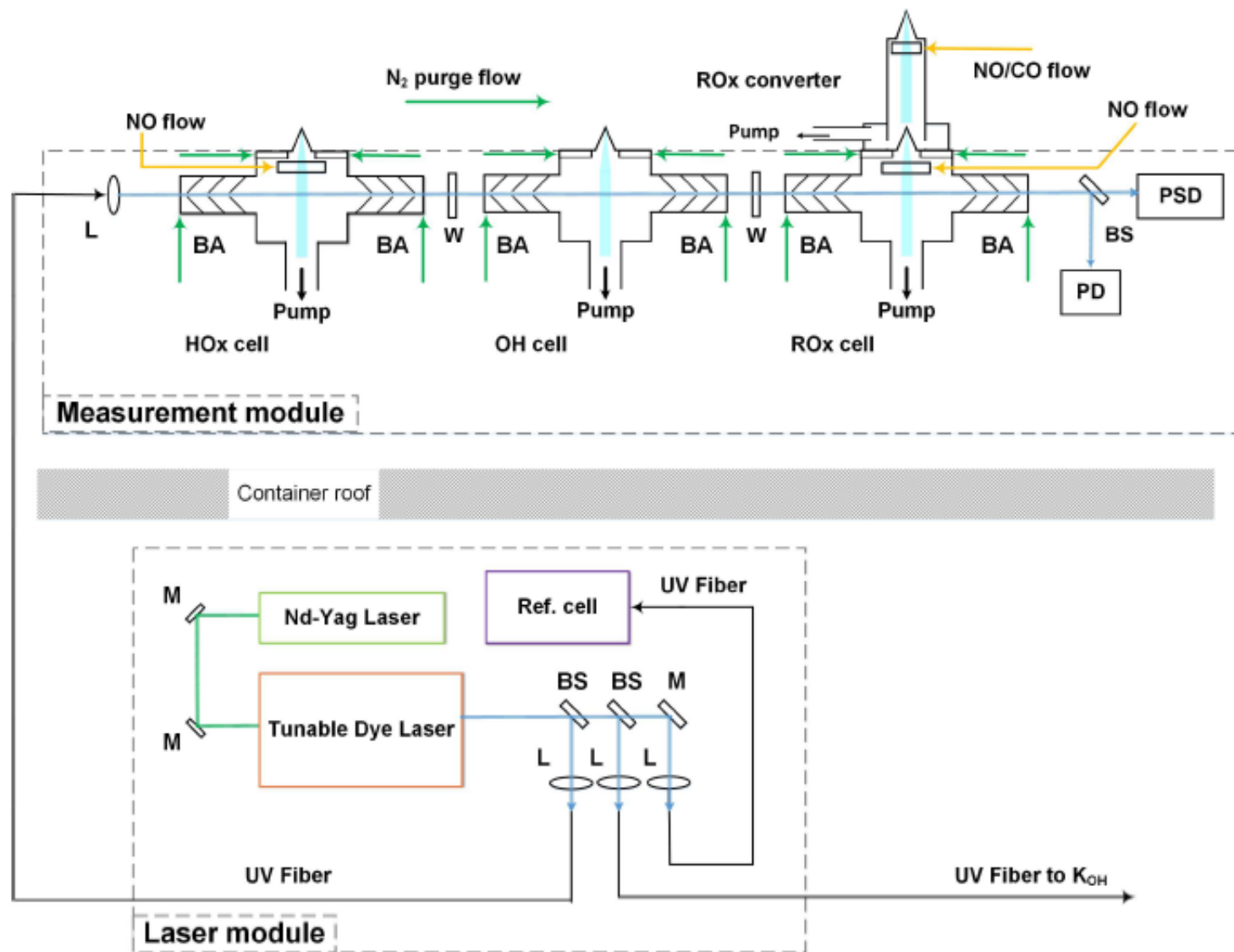Interatomic distance in a molecule A-B

Measurement principle :

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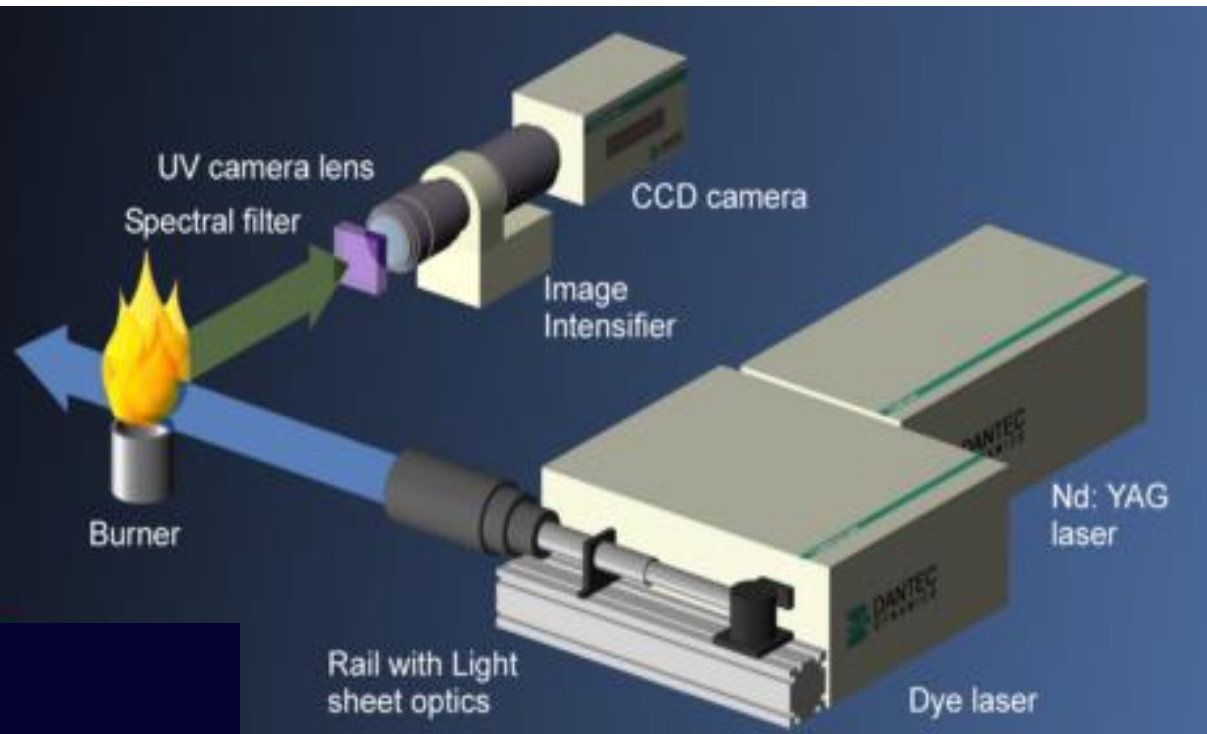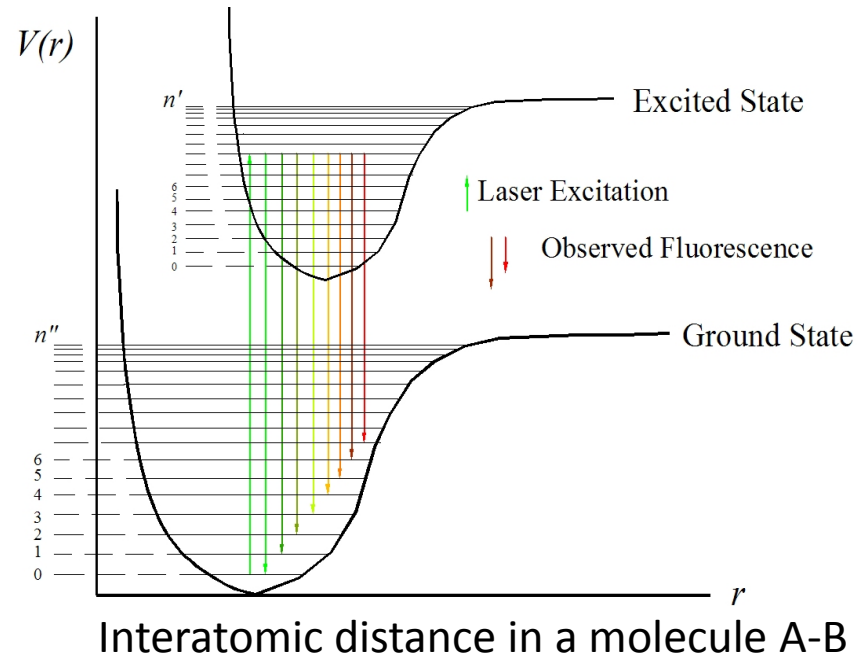
Radical chemistry at a rural sites: Observation and model calculations of **OH, HO$_2$ and RO$_2$ radicals**

LIF – technique:

Detection limits:
below ppt

Accuracy: **11-18%**

Time resolution:
32 s

Tan, Fuchs et al.,
Atmos. Chem. Phys.,
17, 663–690, 2017

Dunkerque

Créteil

CESAM : General view
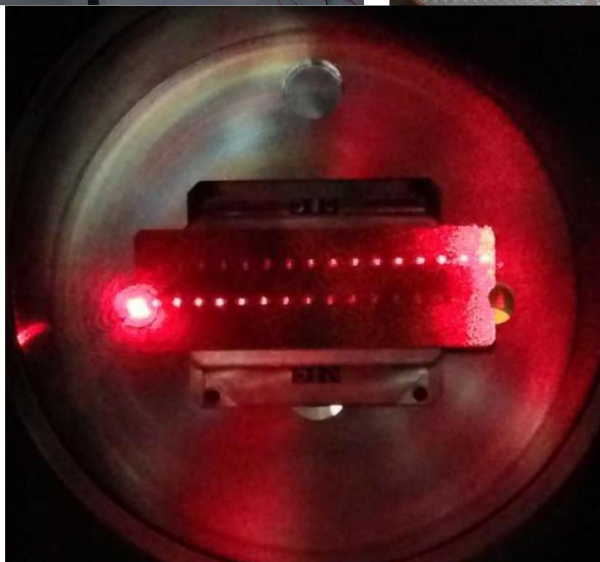
Laser Alignment of the Multi-reflection White cell inside CESAM

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Example:

High-resolution Fourier-Transform IR spectrometer @LISA (650 - 30000 cm^{-1}),
spectral resolution: 0.0019 cm^{-1}

Various absorption cells: **room temperature 298 K** : 0.8 - 8 m, 3.2 - 40 m,
12.4 cm …

A low temperature long-pass absorption cell for <u>mid-infrared to terahertz</u> spectroscopy
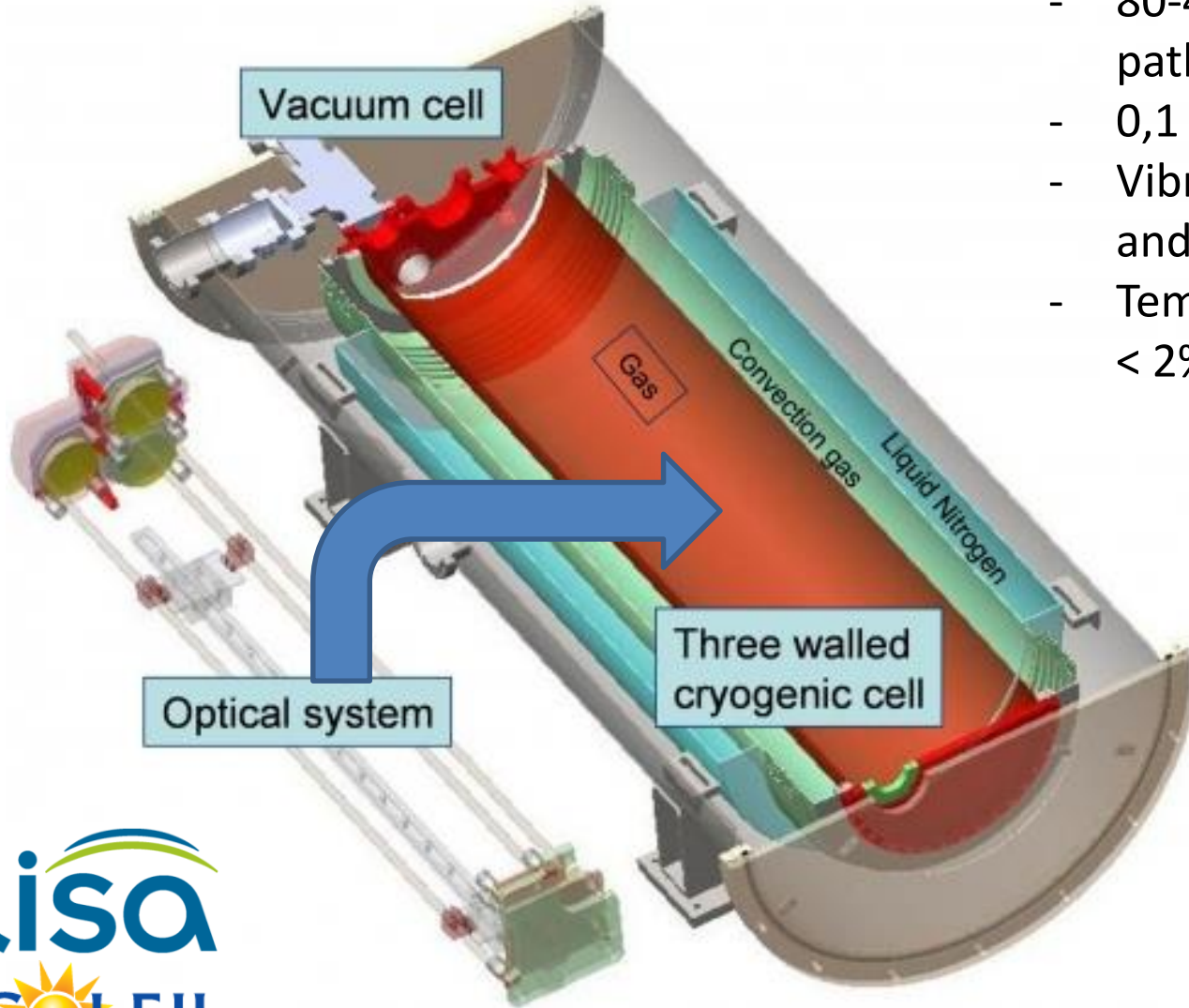
- 80-400 K, 141 m total optical path (1 m base length)
- 0,1 - 1000 mbar
- Vibration free (cooling fluid and convection gas are static)
- Temperature homogeneity : < 2%

F. Kwabia Tchana et al., Rev. Sci. Instr. 84, 093101 (2013)

Laboratory UV spectrum CO_2 @ different temperatures

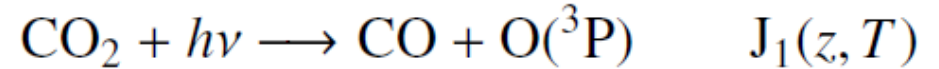## Calculation of photolysis rates J from UV spectra
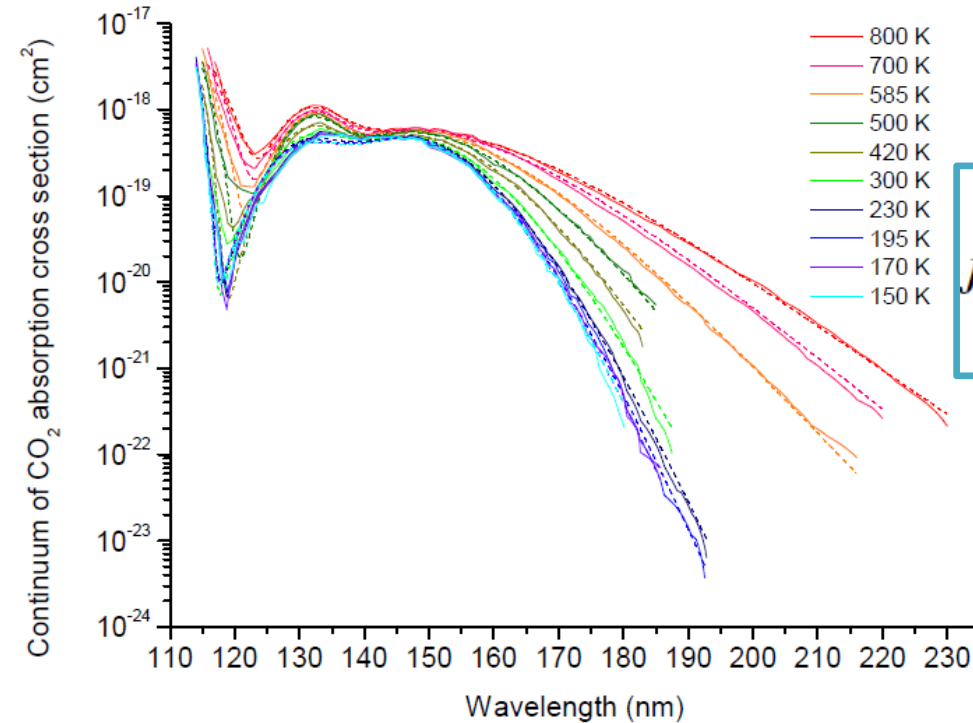
Fig. 6. Continuum of CO_2 absorption cross section (cm^2) measured between 150 K and 800 K (full lines). The continuum can be fitted by a sum of three Gaussian functions (dashed lines).

$$CO_2 + h\nu \longrightarrow CO + O(^3P) \qquad J_1(z, T)$$

$$CO_2 + h\nu \longrightarrow CO + O(^1D) \qquad J_2(z, T)$$
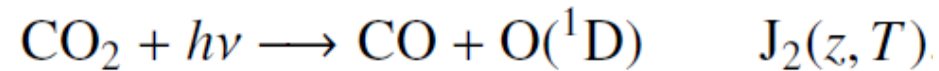
$$J_k(z, T) = \int_{\lambda_1}^{\lambda_2} \sigma_{CO_2}(\lambda, T) F(\lambda, z, T) q_k(\lambda) d\lambda,$$

- σ: absorption cross section
- F: radiation field (for ex. star)
- z : altitude in a planetary atmosphere
- q: quantum yield of photodissociation
- T : temperature
- λ : wavelength

Venot et al., Astronom. & Astrophys, 609, A 34 (2018)
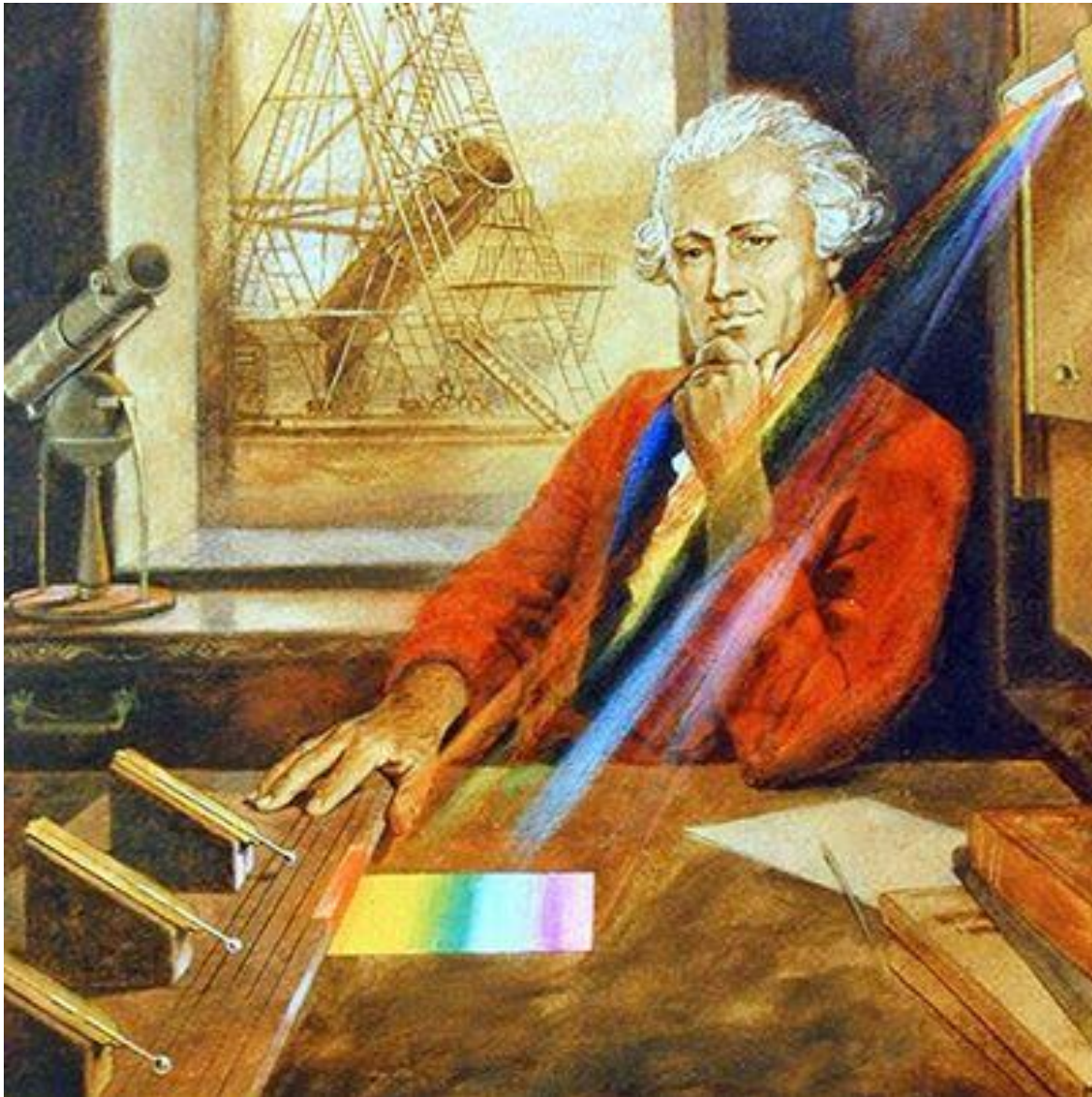
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These were just a few examples ….

….. now let's go back in time and to the basics ….

Spectroscopy: historic events

- **1665:** Newton does experiments with prisms, dispersing white light, invents the term "spectrum" (from latin: "appearance", "image", "apparition")
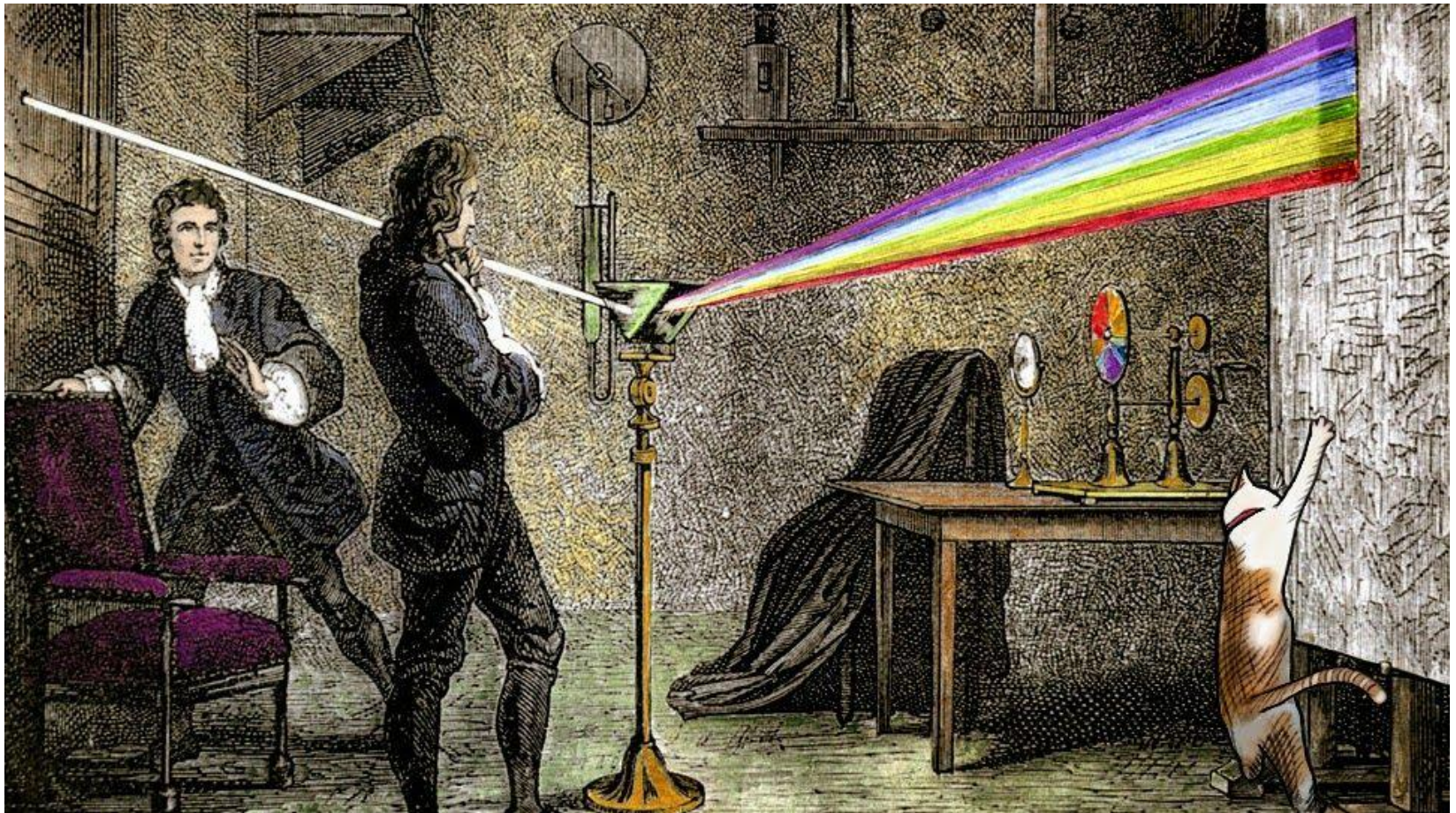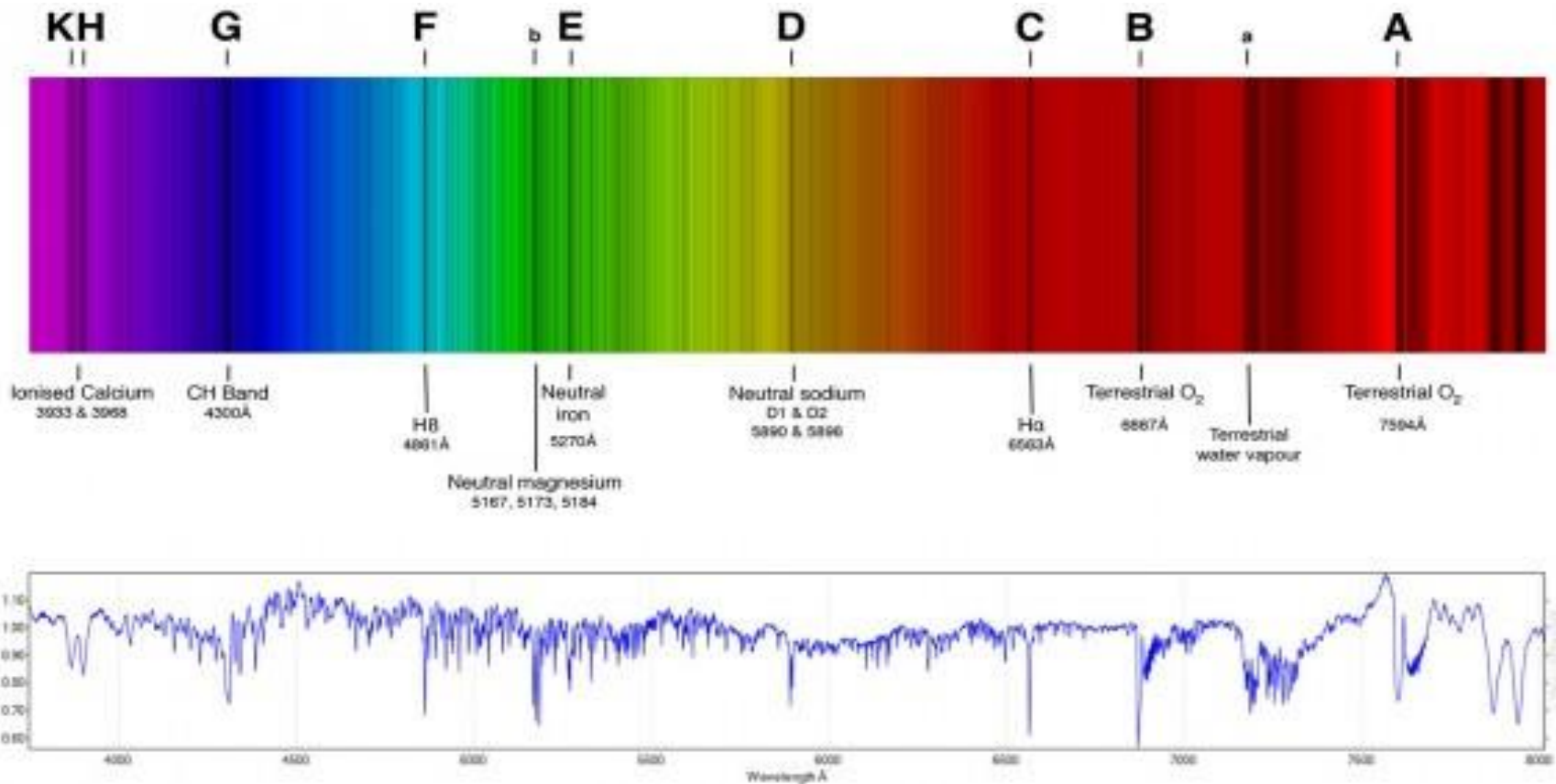
Spectroscopy: historic events

- **1800:** Friedrich Wilhem Herschel discovers **infrared light** with a thermometer


Herschel Space telescope

Spectroscopy: historic events

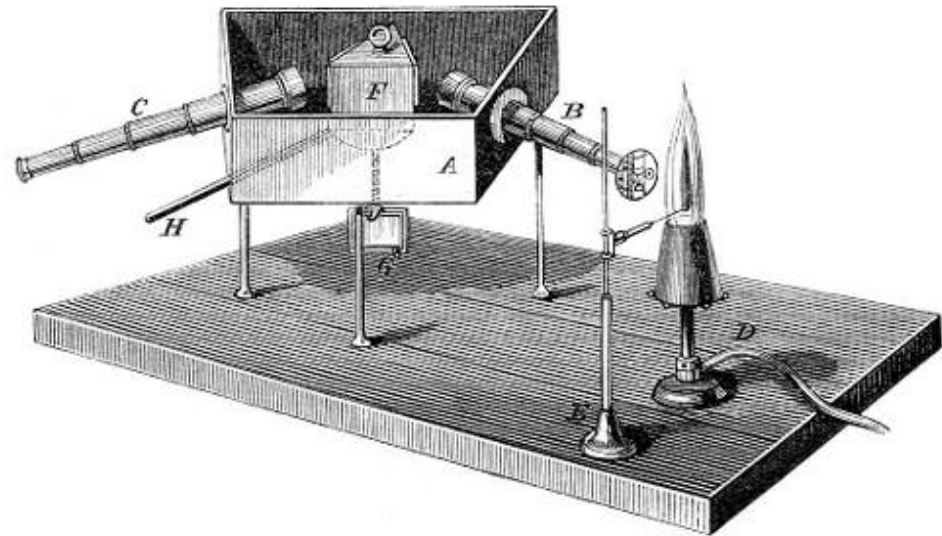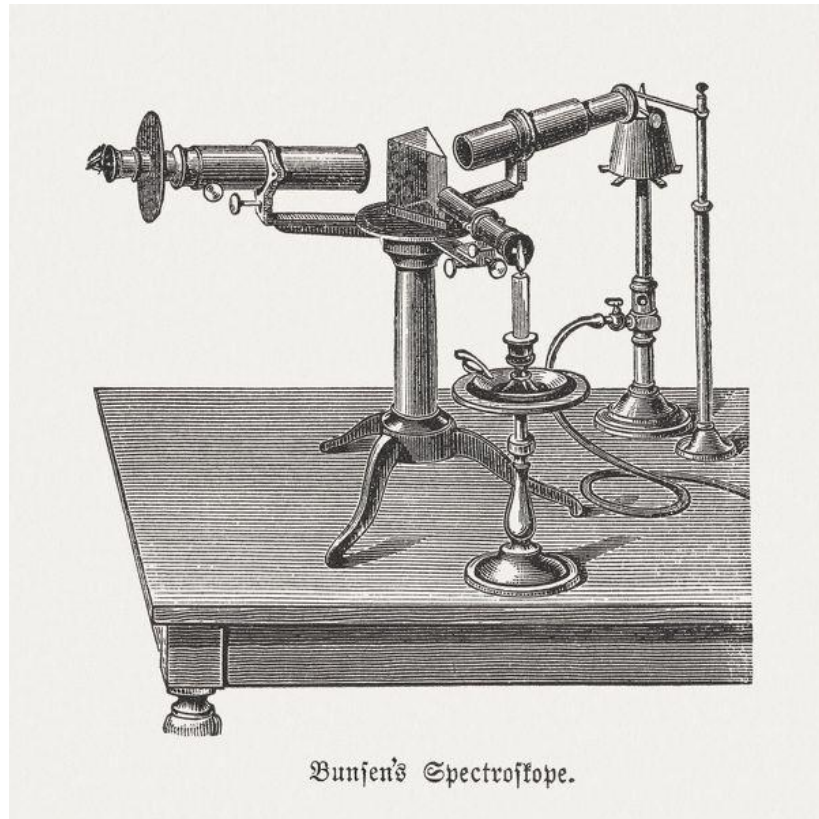- **1814:** Fraunhofer discovers "dark lines" in the spectrum of the sun

Spectroscopy: historic events

German chemists **Robert Bunsen** (1811-1899) and **Gustav Kirchhoff** (1824-1887) study the flame or spark spectra produced by the light emitted by samples of **highly purified salts**. They postulate that it takes an individual element, heated to produce a **series of bright "light" lines characteristic of the element**.
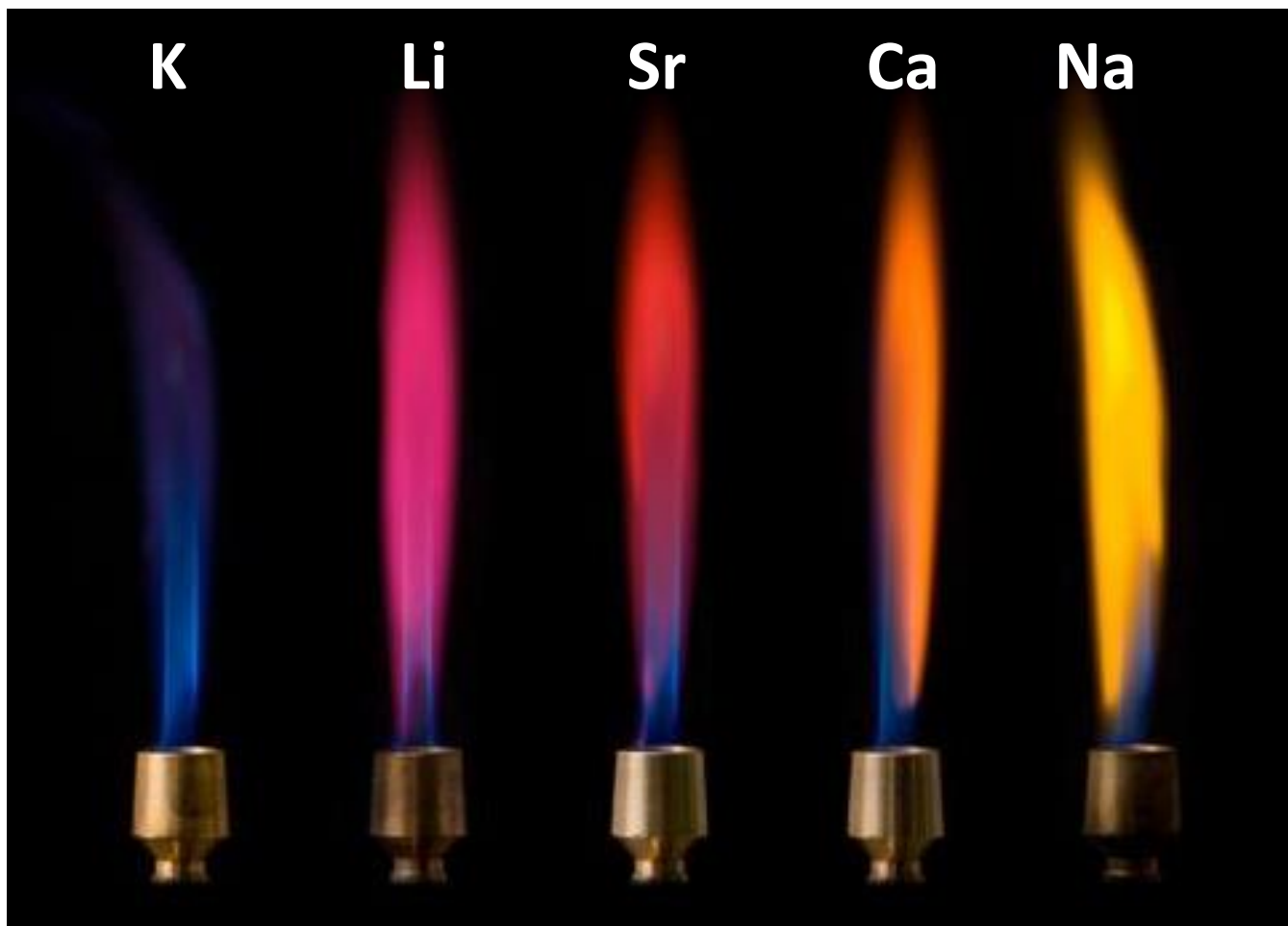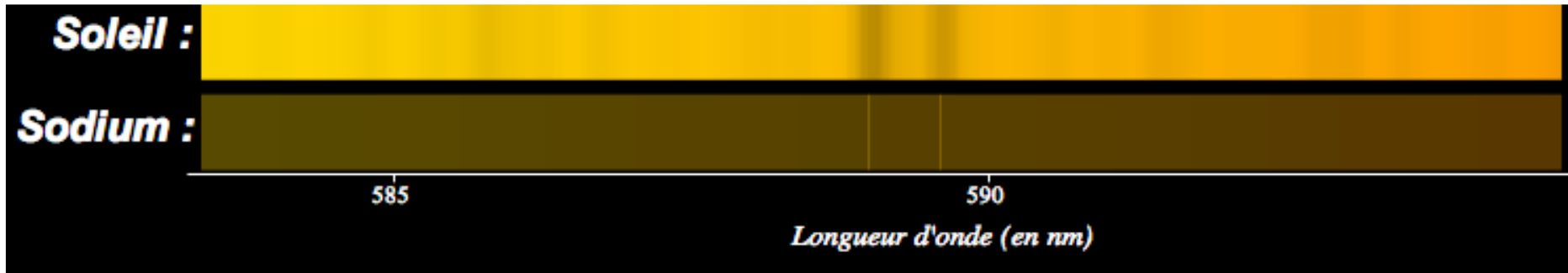
19th century spectroscopic instruments


Bunsen's Spectroskope.

Kirchhoff also observes the solar spectrum with his spectroscopes. He concludes this experiment by explaining that **Fraunhofer's dark lines in the spectrum of the sun exist because of the presence, around the sun, of the same substance which in the flame spectrum** produces the **luminous lines at the same position**.

Conclusion : There is sodium around the sun !
→ **First spectroscopic remote sensing experiment, detection of Na** (1860)
This marks the beginning of chemical analysis by spectroscopy.
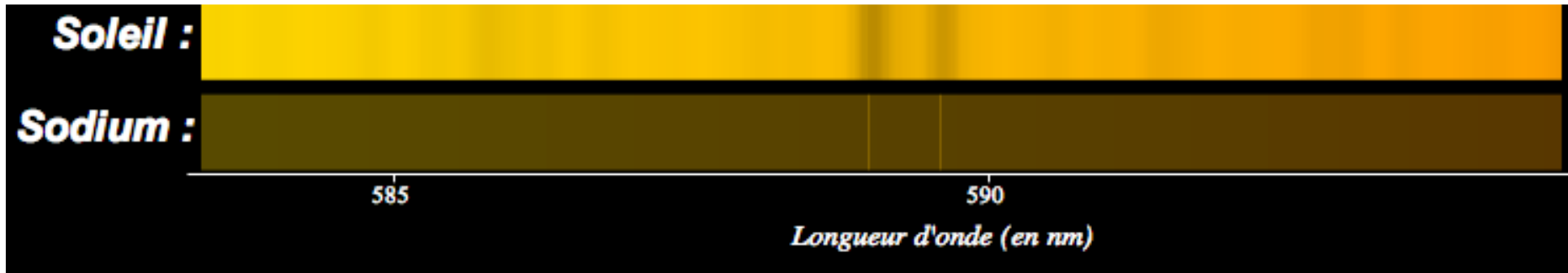
→ Famous **Three Kirchhoff Laws of spectroscopy**

1. "A **solid, liquid, or dense gas** excited to **emit light** will radiate at all wavelengths and thus produce a **continuous spectrum**"
    (→ *Black Body radiation…*)

2. "A **low-density gas** excited to **emit light** will do so at **specific wavelengths** and this produces an **emission spectrum**" → "Light lines": in the flame's spectrum

3. If light composing a continuous spectrum **passes through a cool, low-density gas**, the result will be an **absorption spectrum**.

Spectroscopy: historic events

- *1665: Newton does experiments with prism dispersing white light, invents the term "spectrum"*

- *1800: Herschel discovers infrared light with a thermometer*

- *1814: Fraunhofer discovers "dark lines" in the spectrum of the sun*

- *1860: Bunsen and Kirchhoff develop the prism spectroscope as an analytical instrument in chemistry; they identify Fraunhofer lines in flame spectra and conclude on chemical elements present in the sun*

- **1814-1874: Anders Angstrom, inspired by Kirchhoff's work** *(or vice versa ?)* studies line spectra from the sun. Further develops spectroscopic instruments with <u>diffraction gratings</u>. **Discovers the presence of hydrogen in the sun from line spectra**.
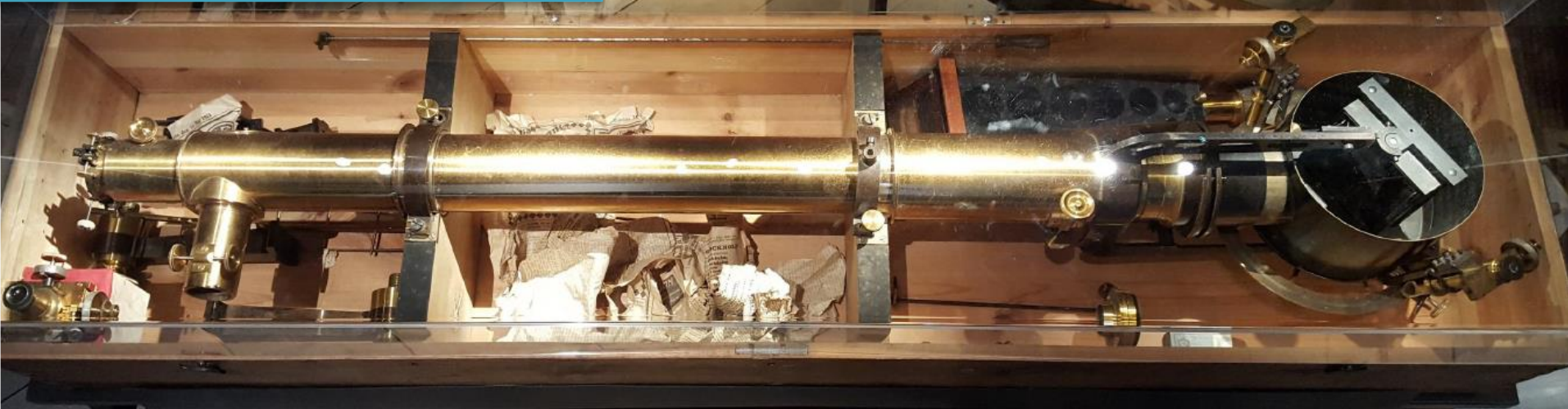
Anders Angstrom, one of the fathers of spectroscopy, has worked at the University of Uppsala
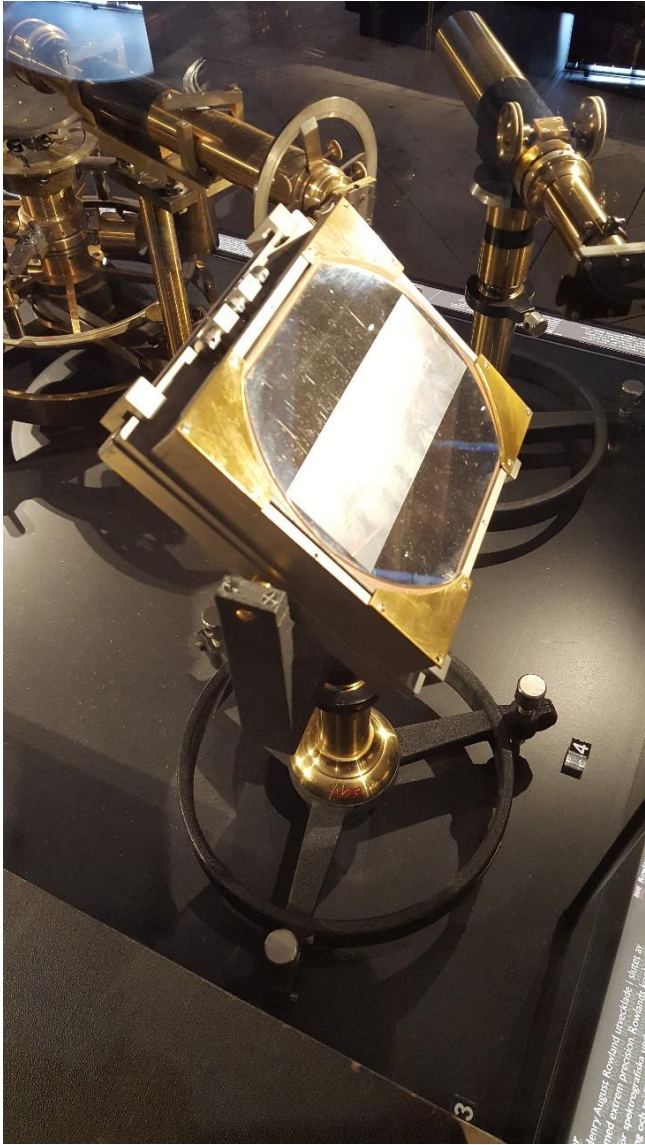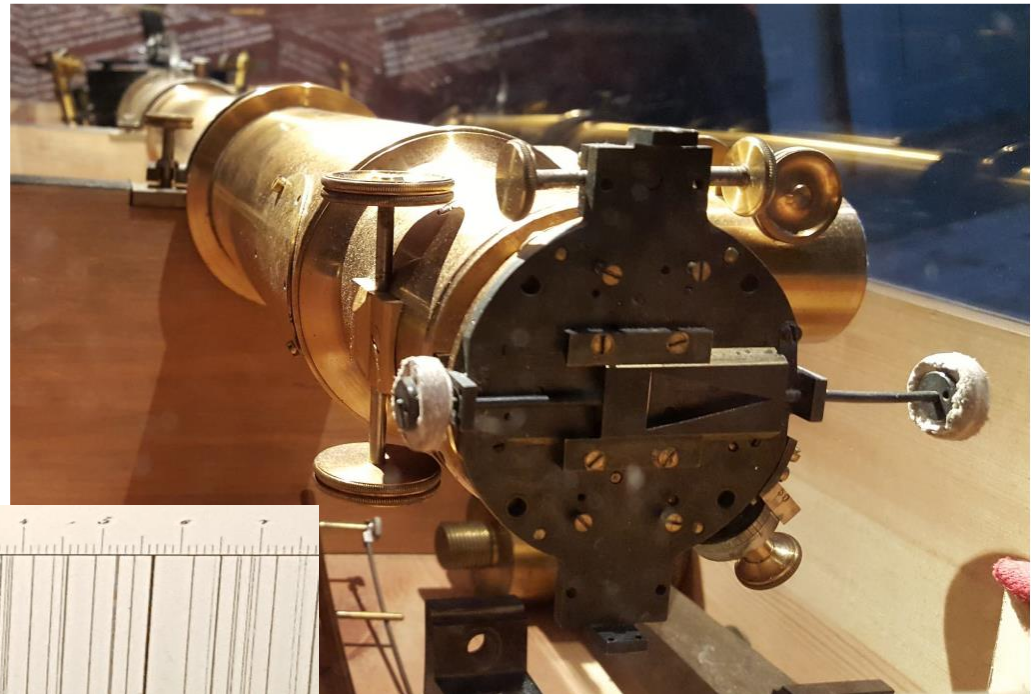

Concave diffraction grating

Sun spectrometer, University Uppsala, end of 19th century, *« to be mounted on a telescope »*

Spectroscopy and remote sensing were linked from the beginning !!

Balmer lines (1885)

The **"visible" hydrogen emission spectrum** lines in the Balmer series. H-alpha is the red line at the right. Four lines (counting from the right) are formally in the "visible range." Lines **five and six can be seen with the naked eye but considered to be "ultraviolet"** as they have wavelengths less than 400 nm.

δ   γ   β   Wavelength →   α

Balmer fitted position of H spectral lines into a mathematical formula:

$$\lambda = \frac{n'^2 G}{n'^2 - 4}$$

G: constant
n'= 3,4,5
λ: wavelength

Rydberg formula (1888):
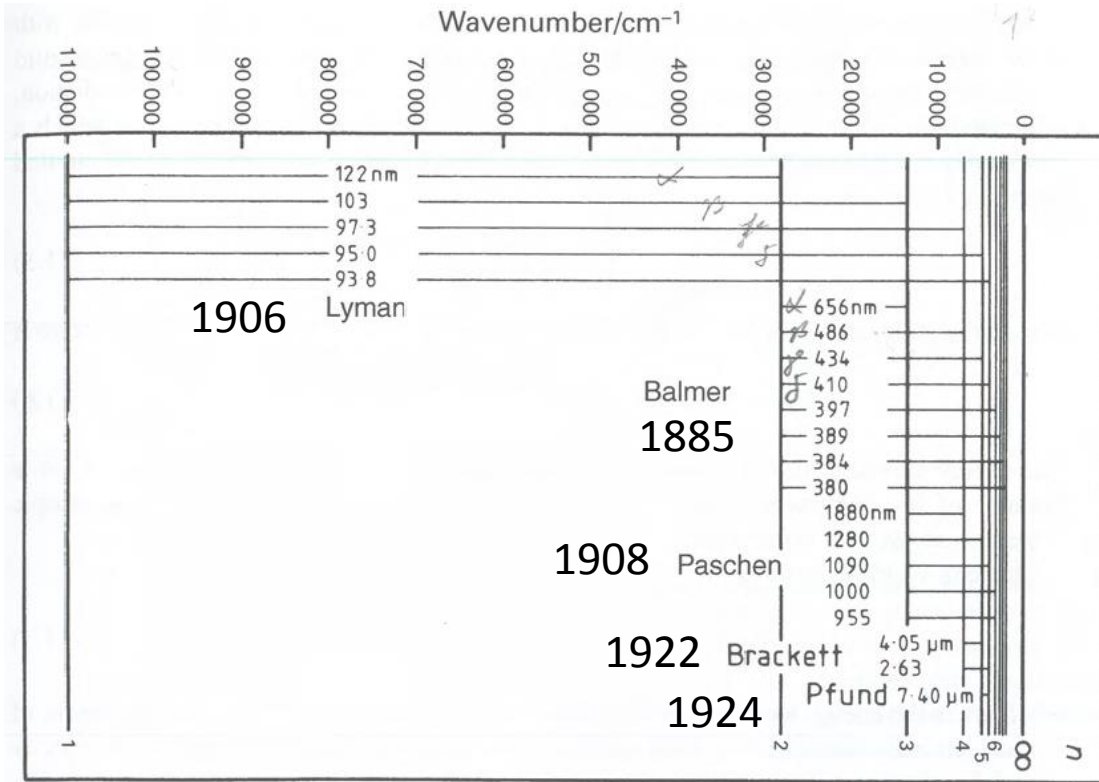
Using $\nu = c/\lambda$
c: speed of light in vacuum

$$\nu = R_H \left(\frac{1}{2^2} - \frac{1}{n'^2} \right)$$

R_H : Rydberg constant for H

This equation and the fact that the **spectrum is discrete rather than continuous** is in **contradiction with classical mechanics. Theory fails to explain line positions → ascension of quantum mechanics ….**

Rydberg's formula (1888)

$$v = R_{\mathrm{H}} \left(\frac{1}{2^2} - \frac{1}{n'^2} \right)$$

Figure 1.1 Energy levels (vertical lines) and observed transitions (horizontal lines) of the hydrogen atom, including the Lyman, Balmer, Paschen, Brackett and Pfund series
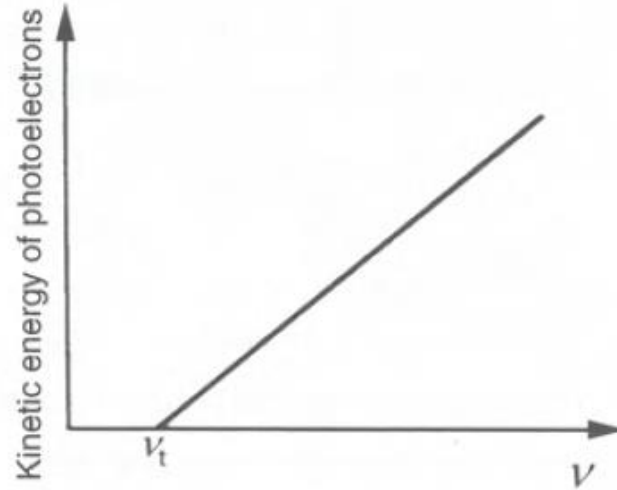
Figure 1.2   Variation of kinetic energy of photoelectrons with the frequency, v, of incident radiation

The existence of a **"threshold frequency"** from which **photoelectrons** were ejected from a metal plate **could not be explained by existing physics**.

Quantization of energy: Planck 1900

- **Line spectra, the photoelectric effect and other anomalous behaviors** such as….

  – the Heat capacity of solids at 0K

  – frequency distribution of black body radiation

  … lead **Max Planck** to the proposal of **microscopic oscillators of which a black body is made of.**

  The **oscillation frequency** ν is related to the energy E of the emitted radiation by

  $$E = n\, h\, \nu$$ with n being an integer

  and h being a constant

- Energy is quantized in discrete states (or quanta), each of energy $h\nu$.

- The accepted value of h is today:

  h = (6,626 06876 ± 0,000 000 52) × 10^{-34} J.s

- Since h is extremely small, quantization of energy is not noticed in macroscopic systems, but of course applies in all systems

- In 1906, **Einstein used Planck's quantum theory to explain the photoelectric effect**. In particular he showed that :

  $$h\nu = \tfrac{1}{2}\, m_e v^2 + I$$ (Nobel Prize 1921)

- I : ionization energy of the metal surface, $\tfrac{1}{2}\, m_e v^2$ is the kinetic energy of the ejected photoelectron with velocity v and the electron mass m_e.

Bohr's model of the H atom (1913)

- In 1913, Niels Bohr **amalgamated classical and quantum mechanics**, **explaining the Lyman, Balmer, and Paschen series** (and later the Brackett and Pfund series) of the H emission spectrum.

- Assumes that the **electron can move only in circular orbits** around the nucleus and that the angular momentum is given by $p_\theta = nh/2\pi$ (Bohr's model)

- **Energy is emitted and absorbed when the electron "hops" from one orbit to another**.

- The energy of the electron is given by :

$$E_n = \frac{\mu e^4}{8h^2 \varepsilon_0^2}\left(\frac{1}{n^2}\right)$$

- μ is called the reduced mass
  $\mu = m_e m_p/(m_e+m_p)$
- e: elementary charge
- ε_0 : permittivity in the vacuum
- n is the number of the orbit
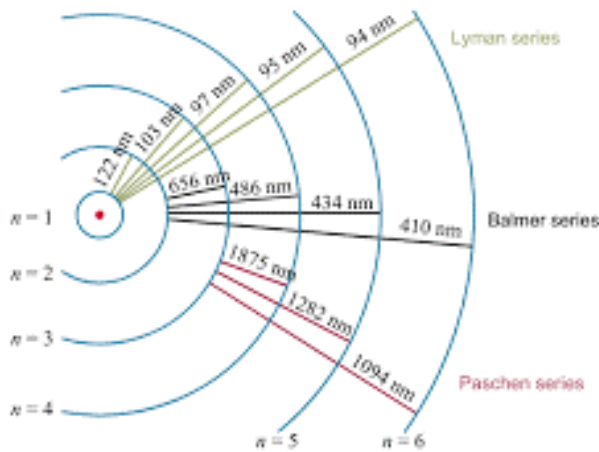
$$\Delta E = \frac{\mu e^4}{8h^2 \varepsilon_0^2}\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)$$

- n'' is the number of the lower orbit
- n' is the number of the higher orbit

Since **$\Delta E = h\nu$**

$$\nu = \frac{\mu e^4}{8h^3 \varepsilon_0^2}\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)$$

$$R_H = \frac{\mu e^4}{8h^3 \varepsilon_0^2} \quad [s^{-1}]$$

Since $\nu = c \times \tilde{\nu}$

$$\tilde{R}_H = \frac{\mu e^4}{8h^3 \varepsilon_0^2 c} = 1{,}096776 \times 10^7 \text{ m}^{-1}$$

Lyman series

Balmer series

Paschen series

$n=1$, $n=2$, $n=3$, $n=4$, $n=5$, $n=6$

94 nm, 95 nm, 97 nm, 103 nm, 122 nm, 656 nm, 486 nm, 434 nm, 410 nm, 1875 nm, 1282 nm, 1094 nm

- **Planck's quantum theory was successful** to explain **a)** the photoelectric effect, **b)** the H atom spectrum, **c)** the frequency distribution of black body radiation and **d)** the heat capacity of solids at 0K

- However, **anomalies persisted**, for example concerning the photoelectric effect: **ultraviolet light "falling on metals"** to eject electrons **behaves like a particle**, whereas **interferences and diffraction** could only be explained with the **wave nature** of light.

- The **contradiction was solved** by **de Broglie (1924)** who **related the momentum p of a particle to the picture of the wavelength** λ.

$$p = h / \lambda$$

- The **dual wave-particle nature should also apply to any other particle or radiation**. This lead to the important prediction that a **beam of electrons** travelling with uniform velocity, and therefore momentum, **should show wave-like properties** (**confirmed later**, lead to the development of electron diffraction techniques which are important tools in solid physics).

- **The dual particle-wave picture also applies to Bohr model with "electrons "circulating in orbits around the H atom ":** Combining the angular moment of the Bohr model $p_\theta = nh/2\pi$ with de Broglie $p = h/\lambda$ relation yields

$$\boxed{n \, \lambda = 2\pi r} \quad \text{« Bohr condition »}$$

- In the wave picture, **the circumference $2\pi r$ of the electron's orbit must thus be an integer multiple of the wavelength** (of the electron !)

- This leads to the picture of the **standing wave** for an electron in a orbit.
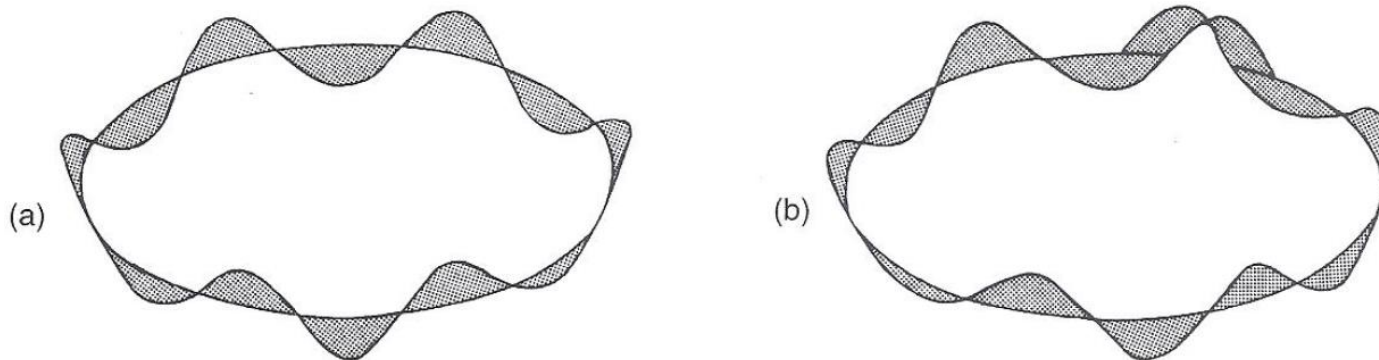
Figure 1.3 (a) A standing wave for an electron in an orbit with $n = 6$. (b) A travelling wave, resulting when n is not an integer

- This leads to the development of wave mechanics and the famous Schrödinger equation to describe the electronic structure of atoms and molecules . **Electrons are described using "wavefunctions" Ψ**

Important basics: the electromagnetic spectrum, Black body radiation, Absorption and emission of radiation, molecular motion and energy levels, the Beer-Lambert Law….

Wave : phenomenon propagating in space and time, transports energy.
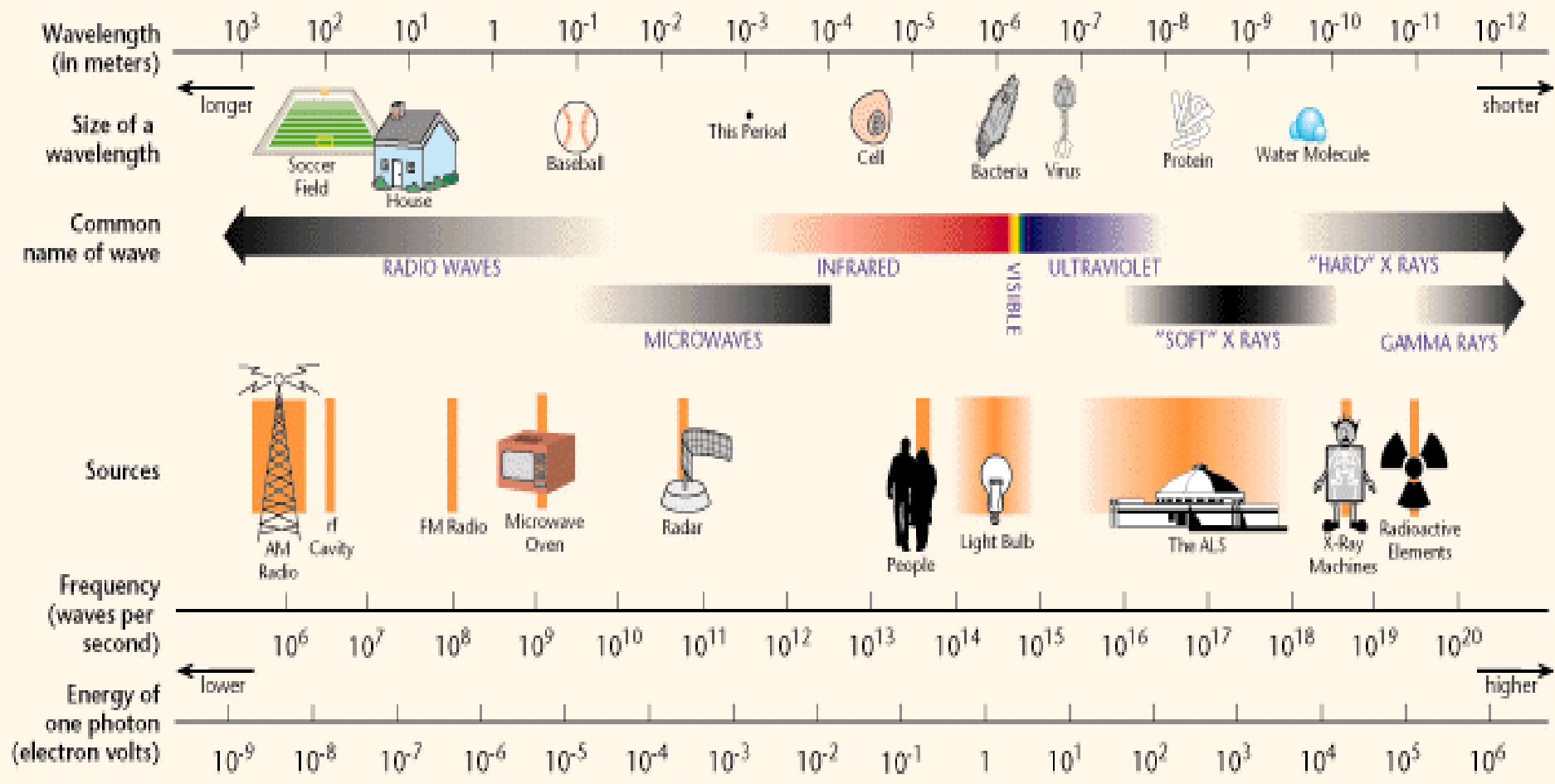*Electromagnetic radiation:*

Oscillating Electric field: $E_y = A \sin(2\pi\nu t - kx)$

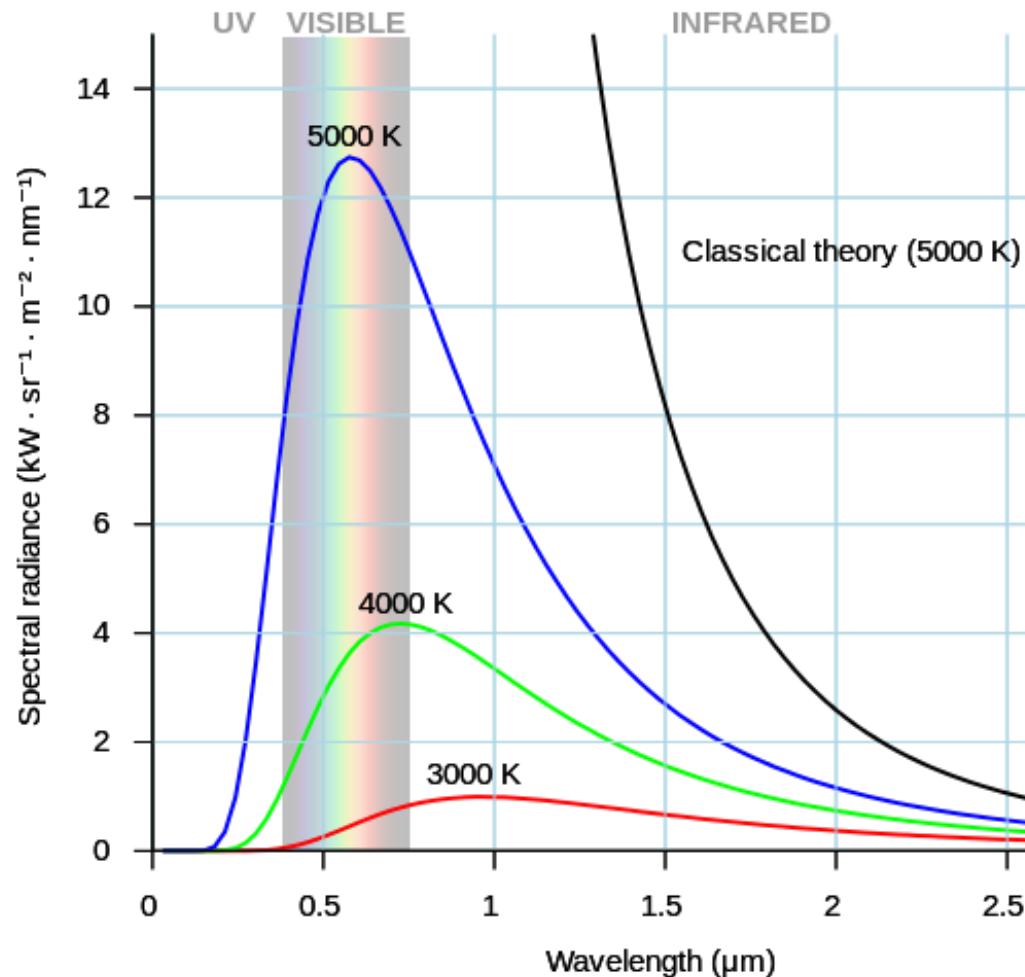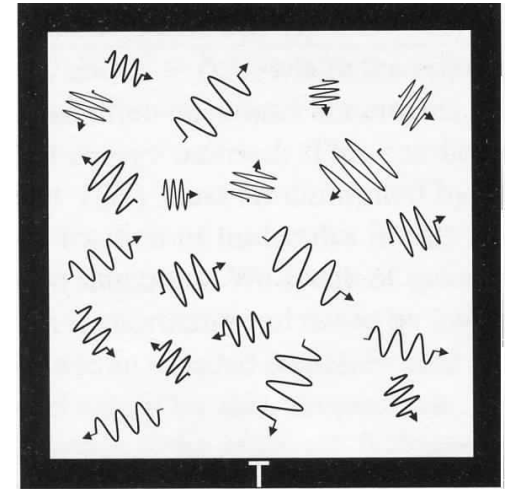Oscillating Magnetic field (perpendicular): $H_z = A \sin(2\pi\nu t - kx)$

Direction of propagation
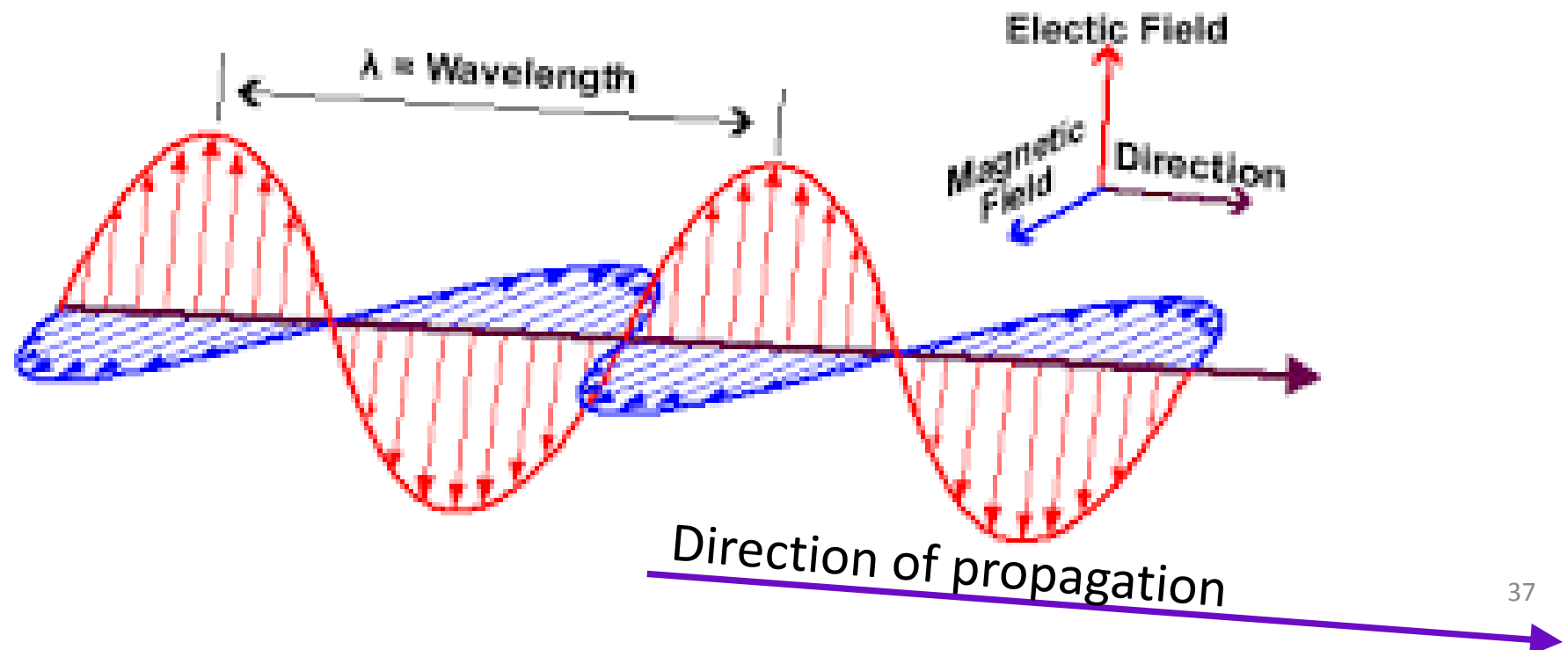
THE ELECTROMAGNETIC SPECTRUM

Black body radiation, **Planck's Law**

Black Body: An opaque container at temperature T encloses **a gas of photons emitted by its walls**. At equilibrium, the distribution of photon energies is determined solely by this temperature.

Spectral Radiance of the black body

$$\rho_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5}\left(\frac{1}{e^{hc/\lambda k_B T} - 1}\right)$$

[W m⁻² sr⁻¹ μm⁻¹]

$$\rho_\nu(\nu, T) = \frac{2h\nu^3}{c^2}\left(\frac{1}{e^{h\nu/k_B T} - 1}\right)$$

$$\rho_{\tilde{\nu}}(\tilde{\nu}, T) = 2hc^2\tilde{\nu}^3\left(\frac{1}{e^{hc\tilde{\nu}/k_B T} - 1}\right)$$

Upper Energy level 2

Energy

photon

Absorption

Excited state (unstable)

ΔE

Lower energy level 1
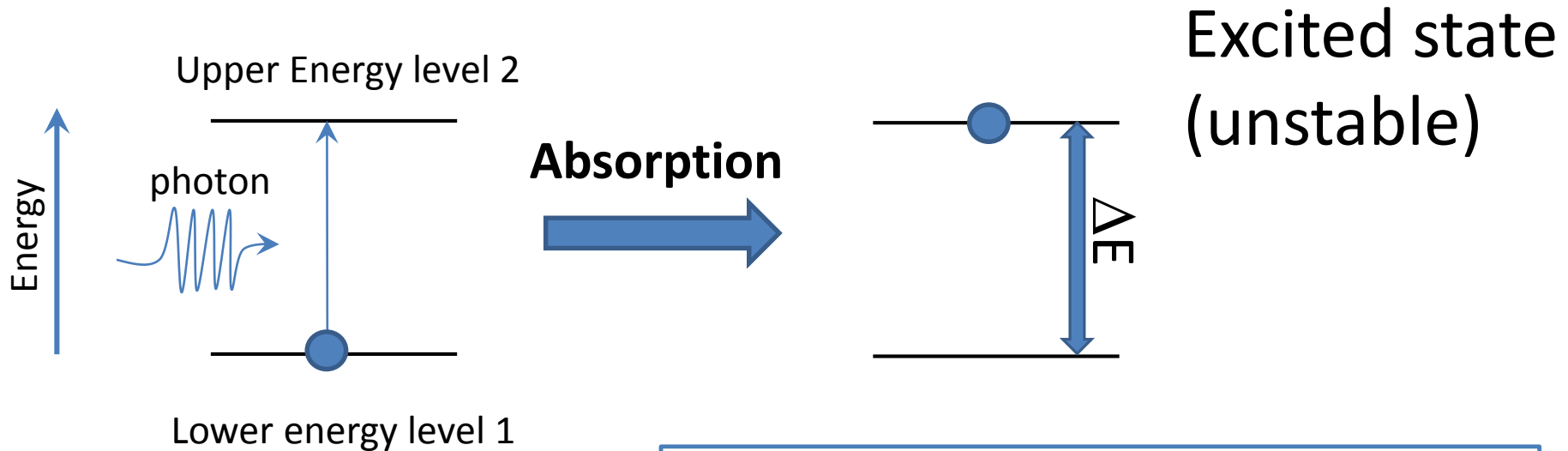
Fundamental state (stable)

Resonance : $\Delta E = h\nu_{photon}$

- N_1, N_2: number of molecules in respective level
- $\rho(\tilde{\nu})$: spectral radiance
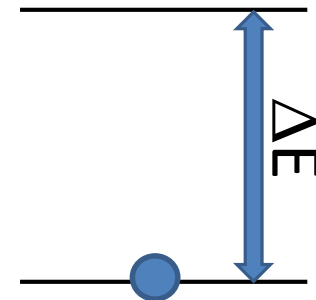- B_{12} : Einstein coefficient of absorption

Probability of absorption :

$$\frac{dN_2}{dt} = N_1 \times B_{12} \times \rho(\tilde{\nu})$$

The Einstein coefficient is linked to the absorption cross section σ [cm²] of a molecule

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Level 2

photon

Level 1

Emission

ΔE
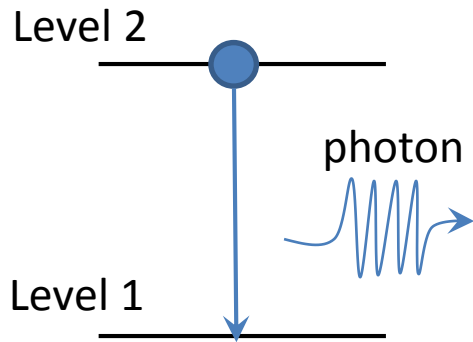
$\Delta E = h\nu_{photon}$

Excited state (unstable)

Fundamental (or intermediate) state

Probability of spontaneous emission :

$$\boxed{\frac{dN_2}{dt} = -N_2 \times A_{21}}$$

Einstein coefficient for **spontaneous emission** :

$$\boxed{A_{21} = \frac{8\pi\nu^3}{c^3} \times B_{12}}$$

$$A_{21} \propto \nu^3$$

Molecular motion and energy levels

- A molecule has **3N degrees of freedom to store energy**, with **N being the number of atoms** constituting de molecule
    - 3 degree of freedom for **translation** : movement of the molecule in direction x,y,z
    - 3 degrees of freedom for **rotation** around the three space axes x,y,z (2 for linear molecules)
    - **3N-6** (or **3N-5 for linear molecules**) degrees of freedom for **vibrational motion**
- The more atoms a molecule has, the more energy it can store in itself.

bending

symmetric stretching

asymmetric stretching

vibrational motion

rotational motion

translational motion
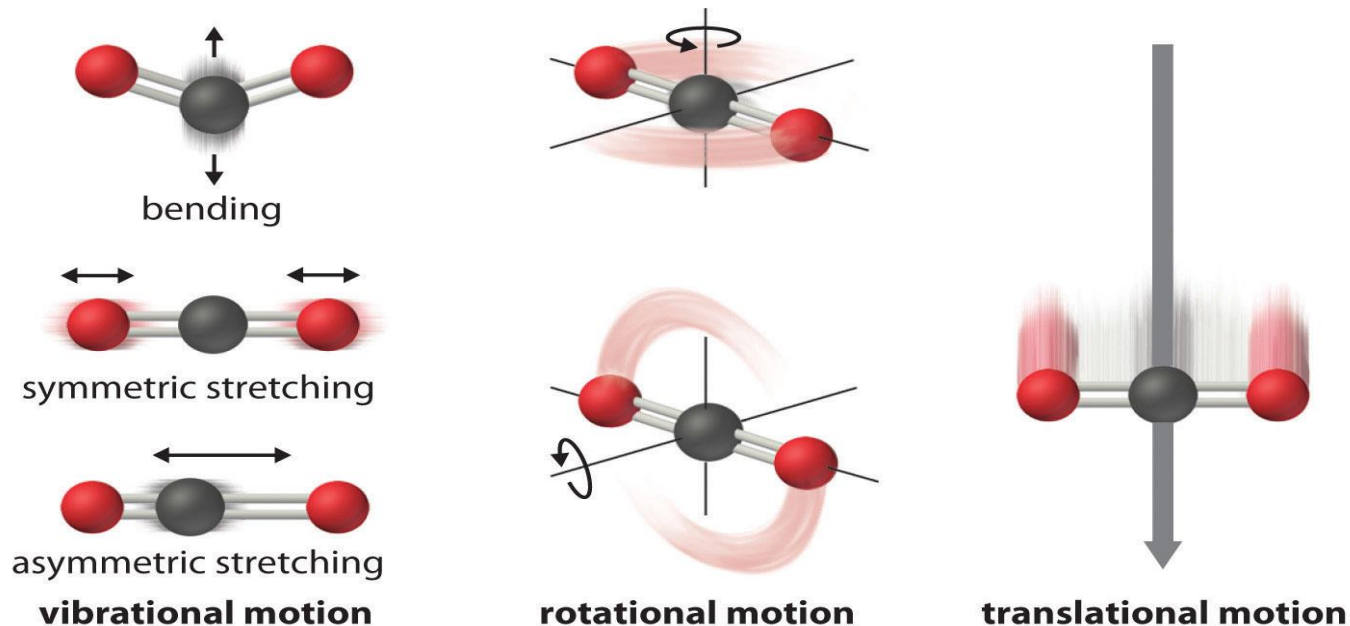
Molecule = ensemble of interacting electrons and atomic nuclei
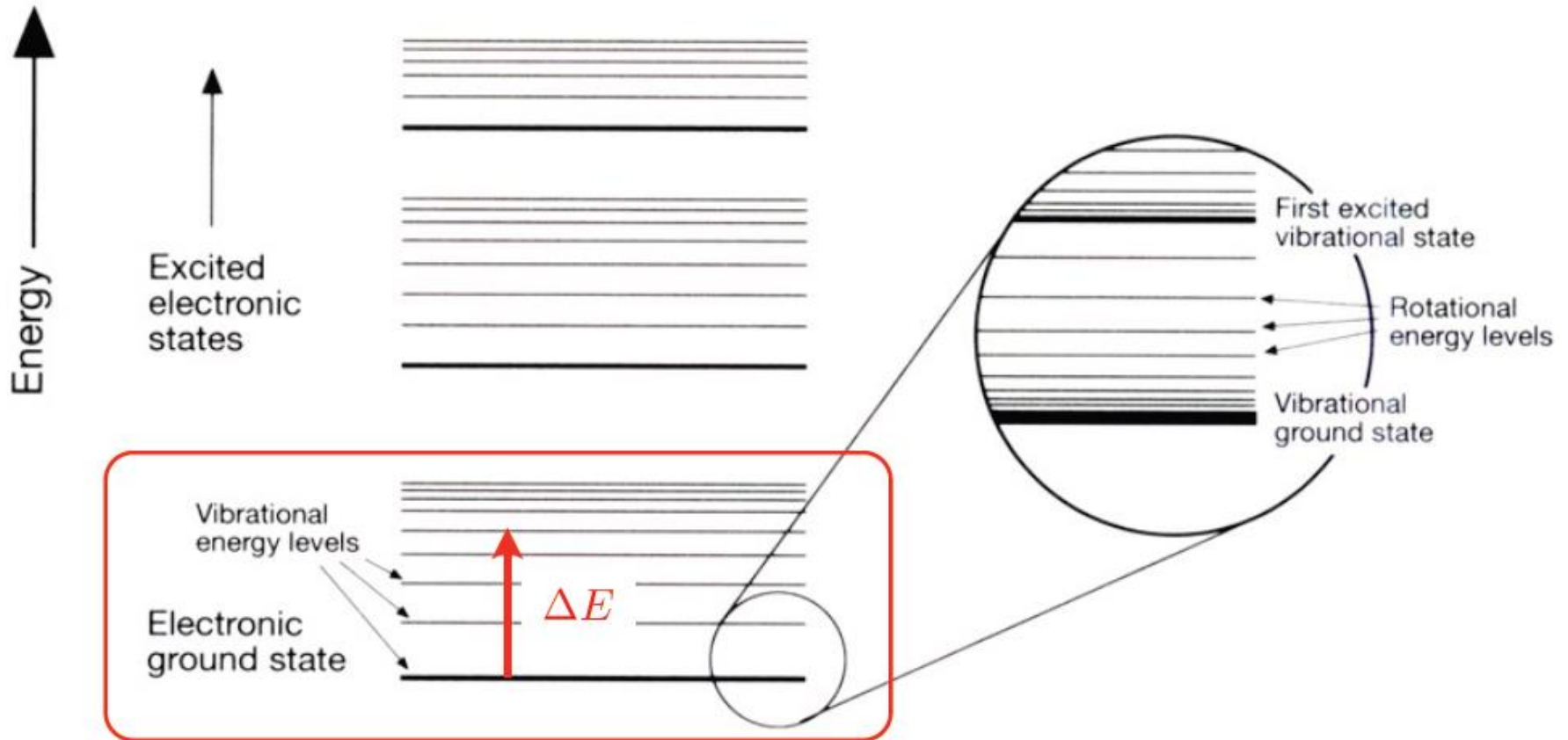
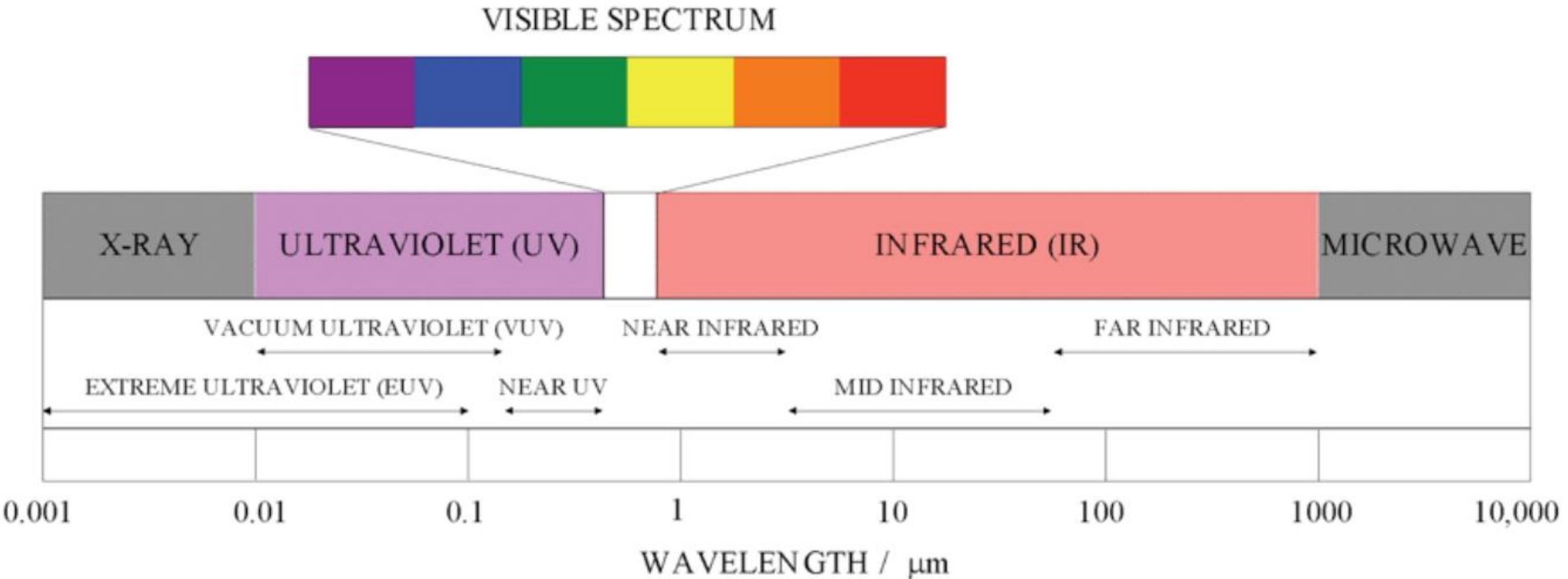Quantized energies $\rightarrow$ E_{total} = E_{elec} + E_{vib} + E_{rot}

Energy of electrons

Motion of nuclei

Spectroscopy: **_Allowed_ transitions between energy levels:**

$$\rightarrow \Delta E_{total} = \Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot}$$

VISIBLE SPECTRUM

X-RAY	ULTRAVIOLET (UV)	INFRARED (IR)	MICROWAVE

VACUUM ULTRAVIOLET (VUV) NEAR INFRARED FAR INFRARED

EXTREME ULTRAVIOLET (EUV)   NEAR UV   MID INFRARED

| 0.001 | 0.01 | 0.1 | 1 | 10 | 100 | 1000 | 10,000 |

WAVELENGTH / μm

electronic transitions

vibrational transitions

rotational transitions

Rotational Spectroscopy (micro-wave, far-infrared)

- **The molecules rotate among themselves**, around the 3 axes of space defined by their symmetry. By consequence there are three moments of inertia I_a, I_b, I_c

- By convention, the three moments of inertia are such that $I_c \geq I_b \geq I_a$. **a is thus the axis for which the moment of inertia has its minimum value**.

- In the model of the **rigid rotor** the bond lengths of the molecule stay constant like rigid rods (without mass) between the atomic nuclei.

- However, there can be **centrifugal distortion of the bond upon rotation** (when excited with many quanta), in which case the molecule becomes a **semi-rigid rotor** (bonds gets elongated).

Linear molecules $(I_a = 0; \ I_b = I_c)$

Hydrogen cyanide   Carbon dioxide
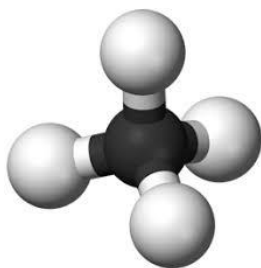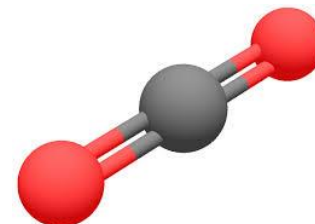
Spherical top molecule $(I_a = I_b = I_c)$
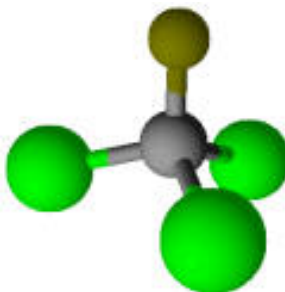
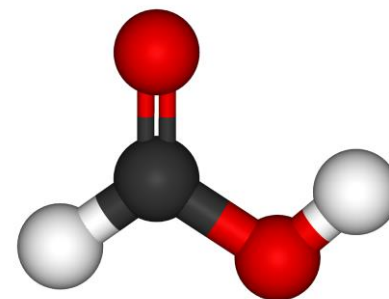Methane (CH_4)   sulfur hexafluoride (SF_6)

Oblate (pancake) symmetric top molecule $(I_a = I_b < I_c)$

Trichlorofluoromethane (CCl_3F), *also called freon-11, CFC-11*

Prolate symmetric top molecule $(I_a < I_b = I_c)$

Chloromethane (CH_3Cl)

Asymmetric top $(I_a < I_b < I_c)$

Acetic acid

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Solving the Schrödinger equation gives quantized energy levels of rotation for **a linear rigid rotor**

$$F(J) = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic}J(J+1) = BJ(J+1)$$

$F(J)$:   energy level, expressed in cm^{-1}
E_J :   energy level, expressed in Joule
B :   rotational constant, expressed in cm^{-1}
J :   rotational quantum number, dimensionless
c :   speed of light (vacuum)
h :   Planck's constant

Energy levels in a rigid rotor : $F(J) = \dfrac{E_J}{hc} = \dfrac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1)$
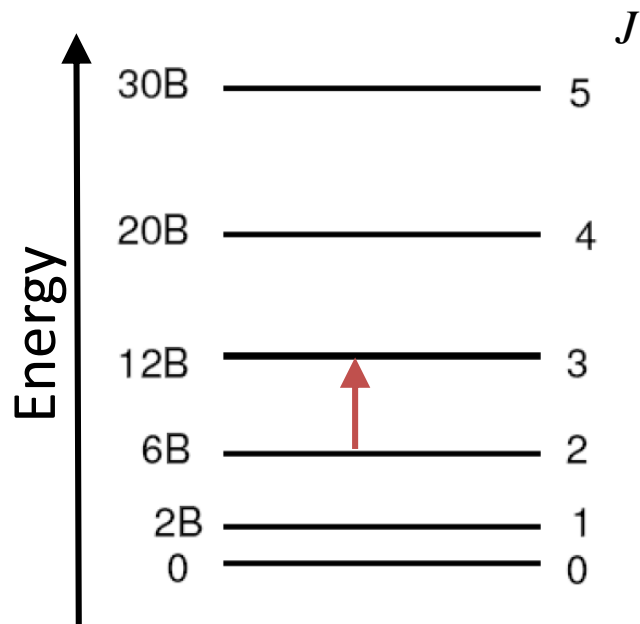
- B is called the rotational constant
- For example, the B value for the molecule C≡O is B= 1,9212 cm^{-1}
- Selection rules (deduced from the quantum mechanical treatment):
  - The molecule must have a **permanent dipole moment μ**
  - **ΔJ = ± 1**

Calculation of the **transition frequency σ** between two adjacent levels:

$\sigma = \mathbf{F(\textit{J}+1) - F(\textit{J})} = B(J+1)(J+2) - BJ(J+1) =$
$BJ^2 + BJ + 2B(J+1) - BJ^2 - BJ = \mathbf{2B(\textit{J}+1)}$

$\Rightarrow \quad \sigma = \mathbf{2B(\textit{J}+1)}$
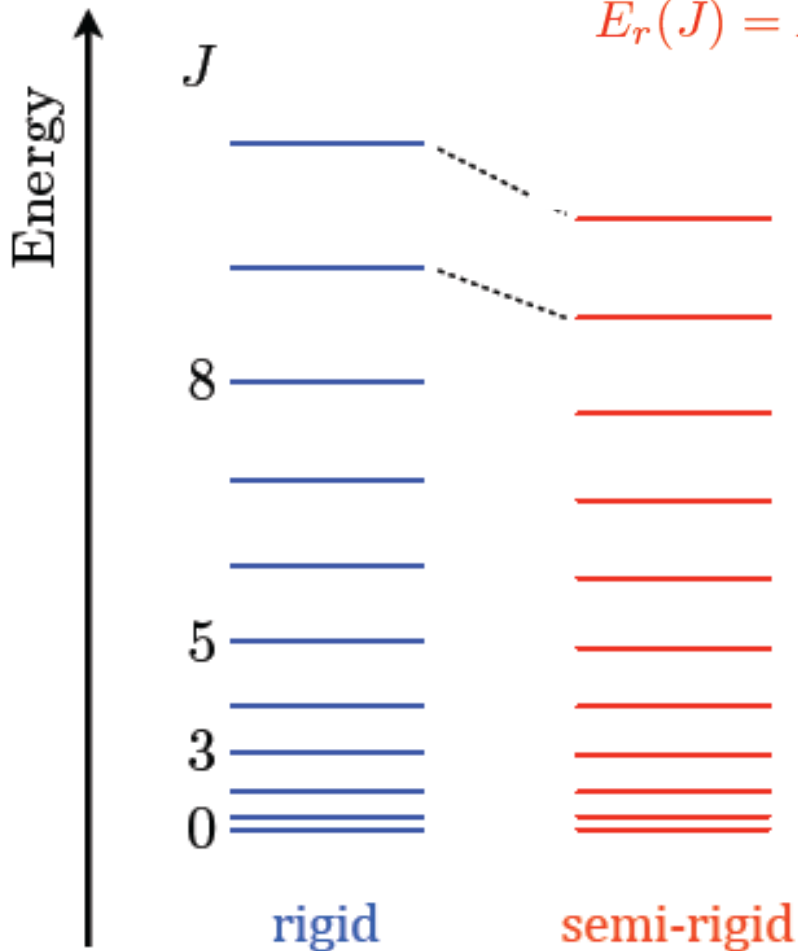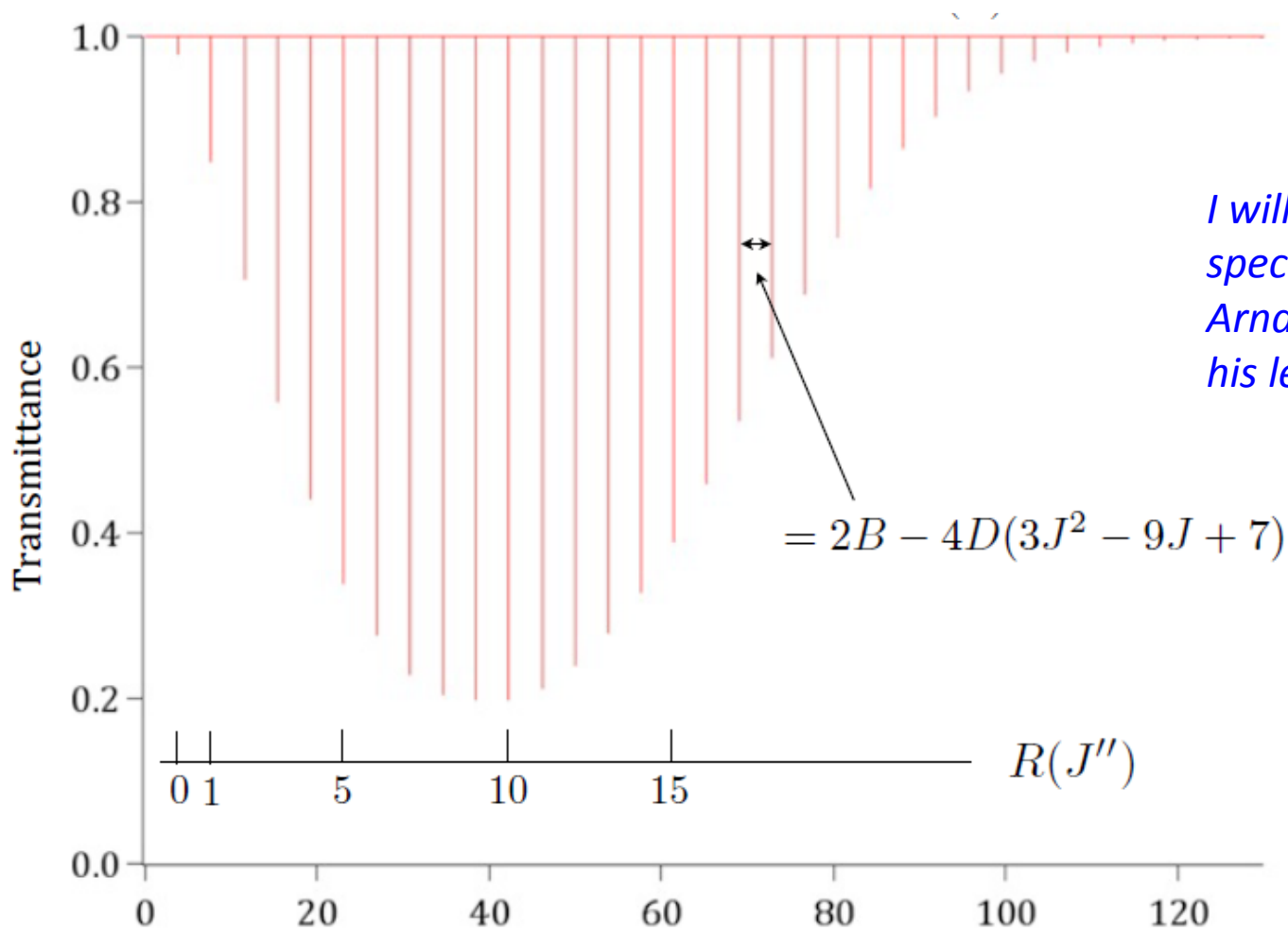
- Semi-rigid rotor

$$E_r(J) = BJ(J+1) - DJ^2(J+1)^2 + \ldots$$

$$\text{CO}_2 : D = 1.334 \times 10^{-7} \text{ cm}^{-1}$$

D = constant of centrifugal distortion

rigid   semi-rigid

I will stop on rotational. spectroscopy here since Arnaud will go further in his lecture.

$$= 2B - 4D(3J^2 - 9J + 7)$$

$R(J'')$

Transmittance

Wavenumber [cm^{-1}]

# Vibrational Spectroscopy & normal modes of vibration

- Vibration spectroscopy measures **changes in the vibrational energy of molecules** when it absorbs or emits a resonant frequency

- A vibration movement corresponds to a **variation of the interatomic distance, the binding angle or the torsion angle**

- For a **diatomic molecule A-B, the only possible internal movement is the variation of the distance r_{AB}. (3N-5** rule).

- For polyatomic molecules, any molecular movement of vibration is described as the **superposition of movements** of the typical vibrations characteristic of the system, the so-called **normal modes of vibration (NMV)**.

- By definition, a **NMV corresponds to a synchronized movement of atoms. All atoms vibrate at the same frequency**, and go simultaneously through their equilibrium position. **During a vibration, the center of gravity of the molecule remains unchanged**. **NMVs are independent of each other.**

Example : **water** H_2O:
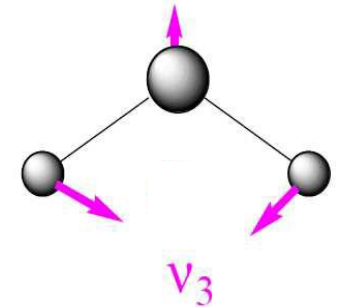3N-6 = 3 normal modes
of vibration ν_1, ν_2, ν_3

ν_1 ν_2 ν_3
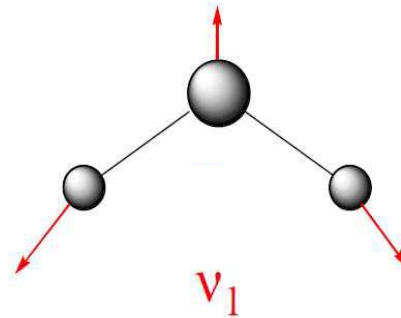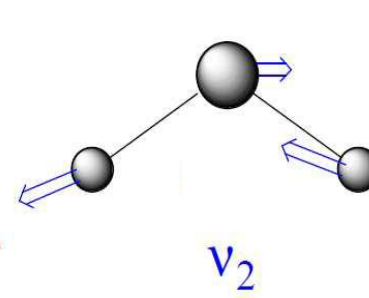
Symmetric stretch   Asymmetric stretch   Bend
ν_1 = 3657 cm^{-1} ν_2 = 3756 cm^{-1} ν_3 = 1595 cm^{-1}
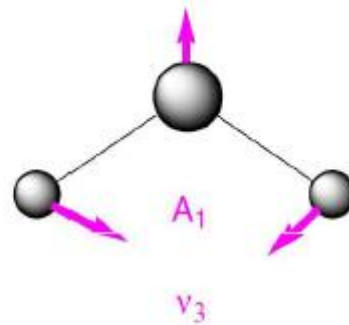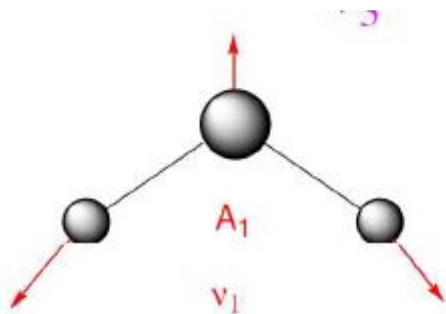
A$_1$ is called the « symmetry species Γ » of the vibrations ν_1, ν_3
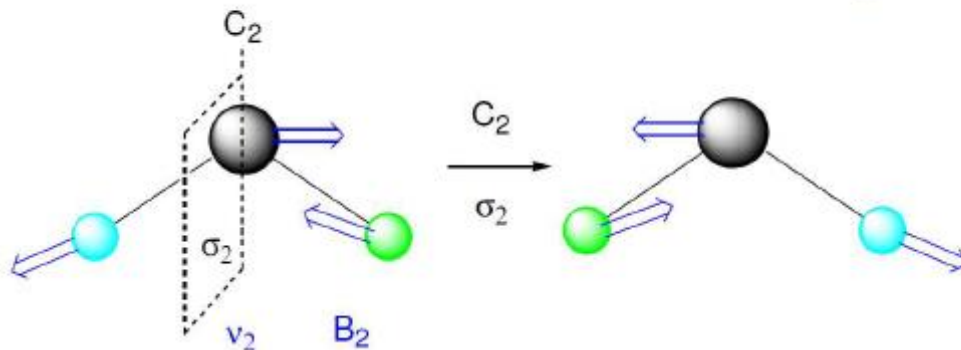
B$_2$ is called the « symmetry species Γ » of the vibrations ν_2

Vibrational Spectroscopy & symmetry

- Especially small molecules of atmospheric interest are **often highly symmetric**

- Group theory permits a qualitative treatment of molecular movements: **All molecules are classified, according to their symmetry, into point groups.**

- **Molecular motions can also be classified by their symmetry**. The ensemble of possible symmetry operations of a given molecule are listed in the **character table of the point group**.

- **Quantum mechanics : In order to be IR active, a molecule must change its dipole moment during the movement. The symmetry of the motion can tell if this is the case**

- Water belongs to the **C_{2v} point group** with the character table shown below:

Name of the group

Symmetry elements

Symmetry species Γ

Particular motion

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	R_z
B_1	1	−1	1	−1	x, R_y
B_2	1	−1	−1	1	y, R_x

1 : molecule is symmetric with respect to the element
-1 : molecule antisymmetric with respect to the element

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Formaldehyde, H_2CO

- 3N-6 = 6 **normal modes**

- **Point group C2v** (same than water)

- Vibrations are all IR active :

- CO et CH stretching

- Bending in plane

- Bending out of plane.

A_1 ν_{CO} 1744

A_1 ν_{CH} 2780

B_2 ν_{CH} 2874

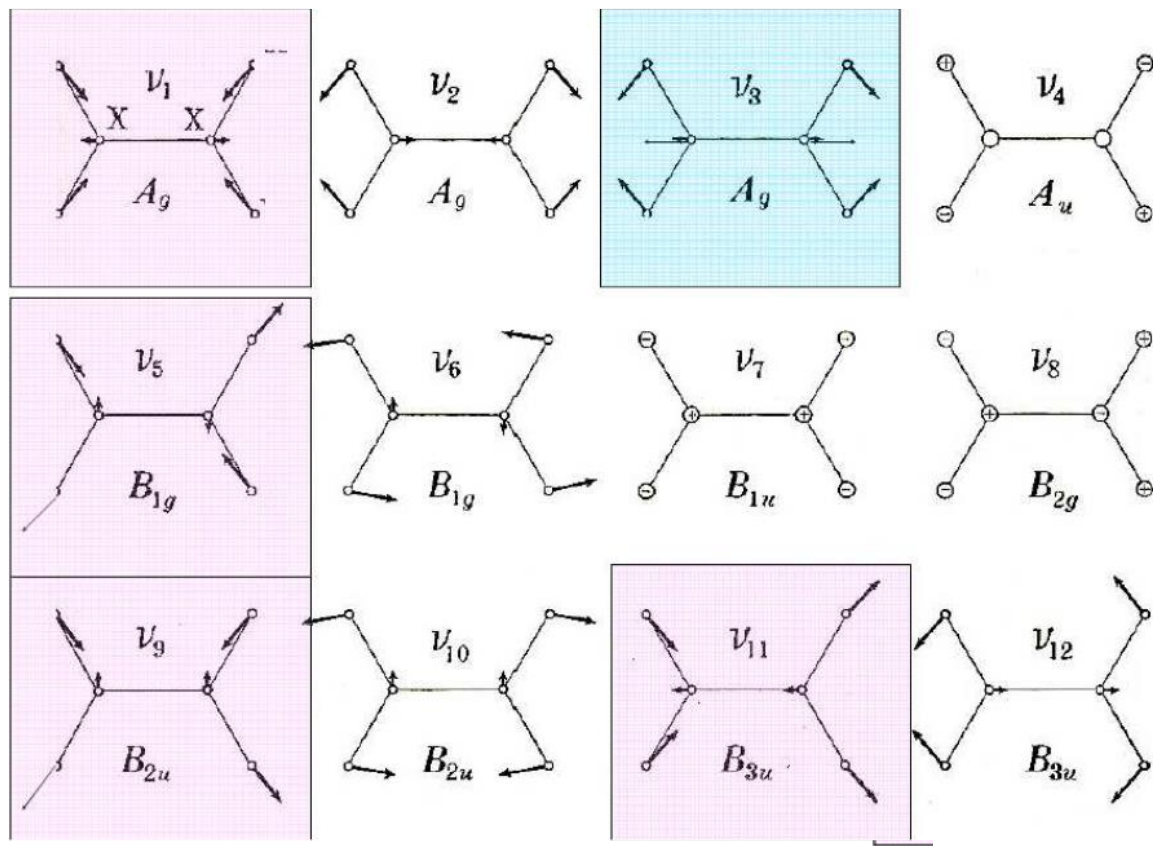A_1 $\delta(p)$ 1503

B_2 $\delta(p)$ 1280

B_1 $\delta(hp)$ 1167
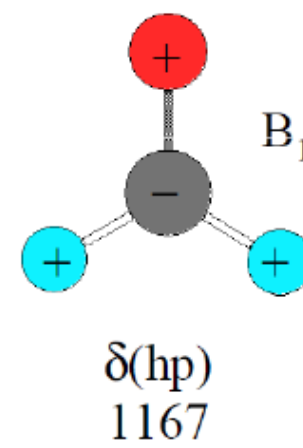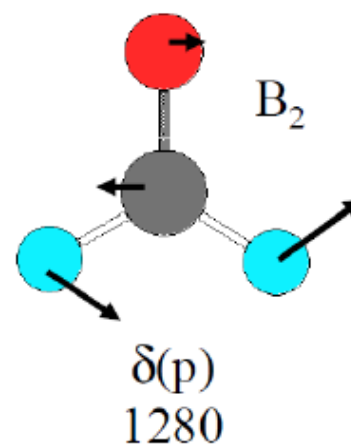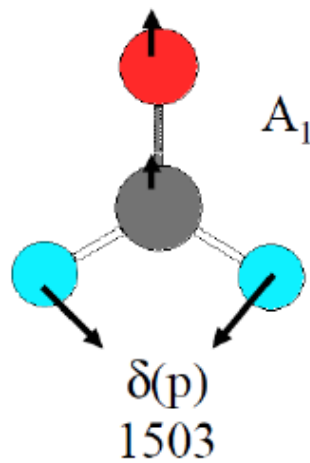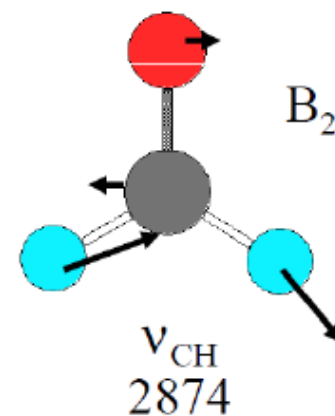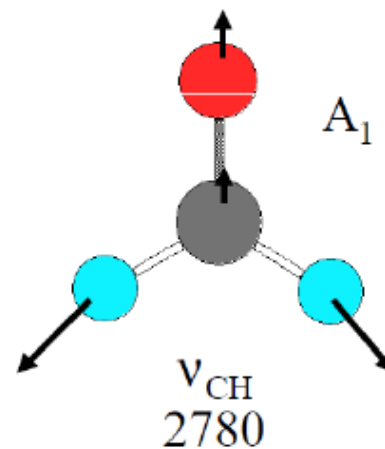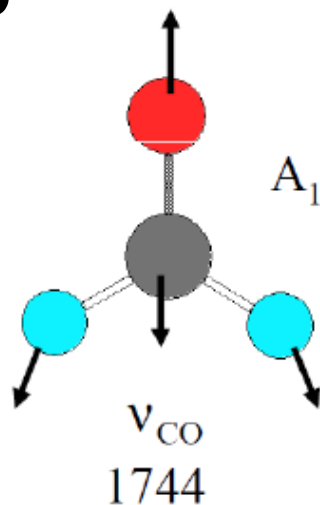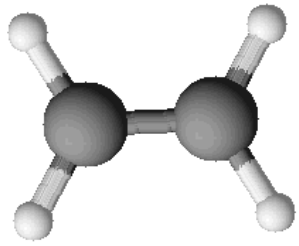
Ethylene (C$_2$H$_4$)

- 12 normal modes
- **Only 5 are actives in the IR**
- **No permanent molecular dipolement μ** in its the equilibrium geometry
- Any *symmetric* deformation of the molecule will leave μ unchanged

D2h	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A$_g$	1	1	1	1	1	1	1	1	
B$_{1g}$	1	1	−1	−1	1	1	−1	−1	R_z
B$_{2g}$	1	−1	1	−1	1	−1	1	−1	R_y
B$_{3g}$	1	−1	−1	1	1	−1	−1	1	R_x
A$_u$	1	1	1	1	−1	−1	−1	−1	
B$_{1u}$	1	1	−1	−1	−1	−1	1	1	z
B$_{2u}$	1	−1	1	−1	−1	1	−1	1	y
B$_{3u}$	1	−1	−1	1	−1	1	1	−1	x

55

Reference data (10 μm region of C_2H_4)
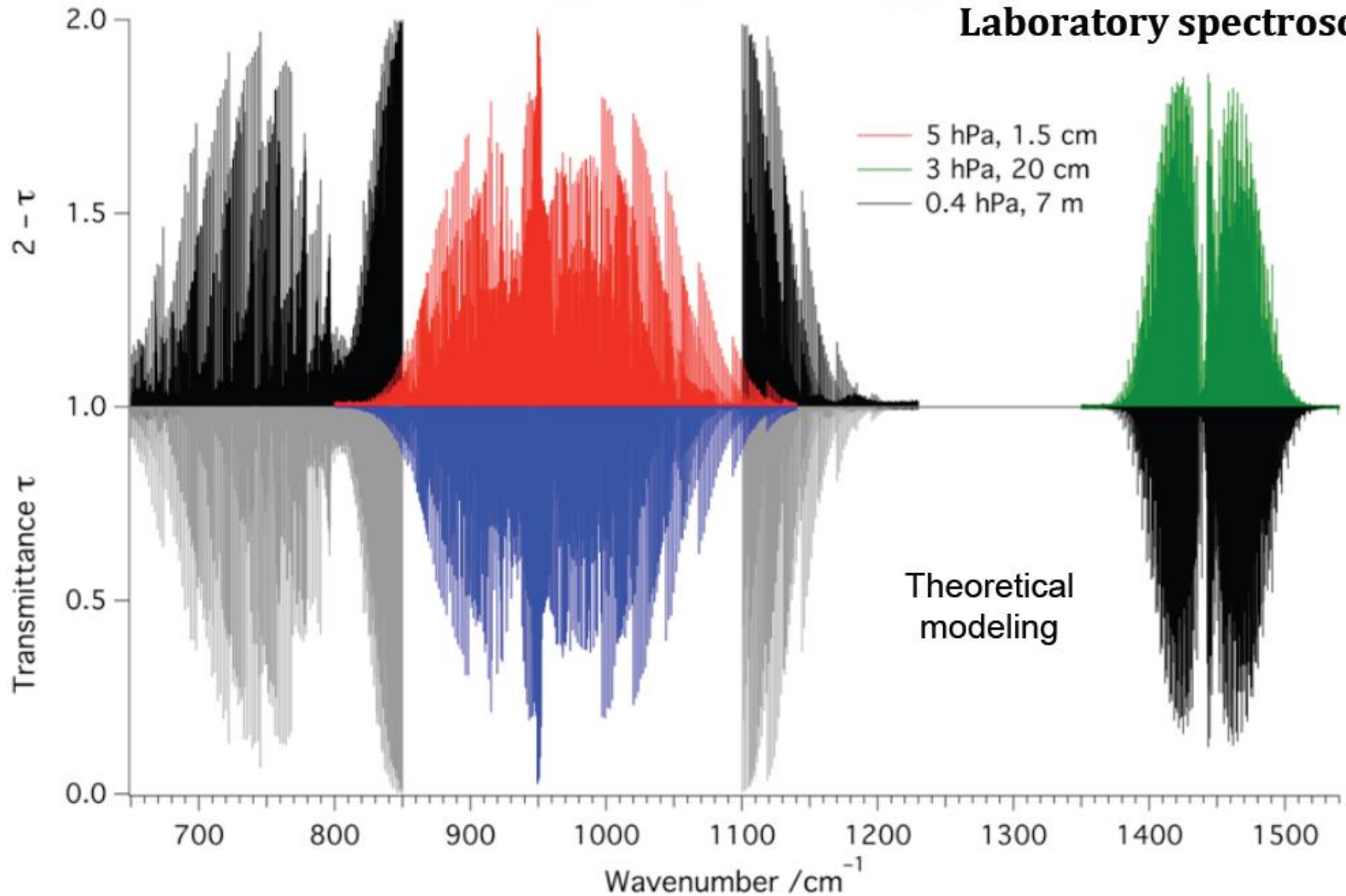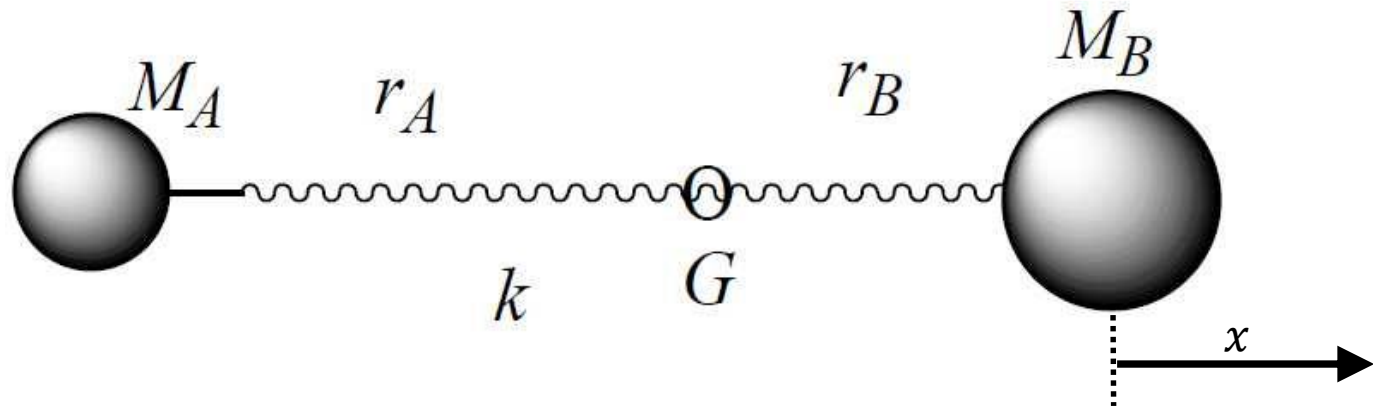

Courtesy: Jean Vander Auwera, Free University of Brussels

The harmonic oscillator

In the **classical treatment** a diatomic molecule A-B is modeled by two masses M_A and M_B at a respective distance r_A and r_B from their center of gravity G and connected by a **spring with the force constant k**.

In the classical approximation, **the force F exercised by the spring is proportional to the elongation x = Δr$_A$ + Δr$_B$ of the masses of the nuclei** (with respect to their equilibrium positions (x = 0):

$$F = -kx \quad \Longrightarrow \quad \frac{dV}{dx} = F = -kx \quad \Longrightarrow \quad V = \frac{1}{2}kx^2 \qquad \text{V : potential energy}$$

The kinetic energy T of motion in a diatomic molecule is: $\quad T = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 \; ; \quad \mu = \frac{M_A \times M_B}{M_A + M_B}$

Potential & kinetic energy of motion in a diatomic molecule:

$$V = \frac{1}{2}kx^2 \qquad T = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2$$
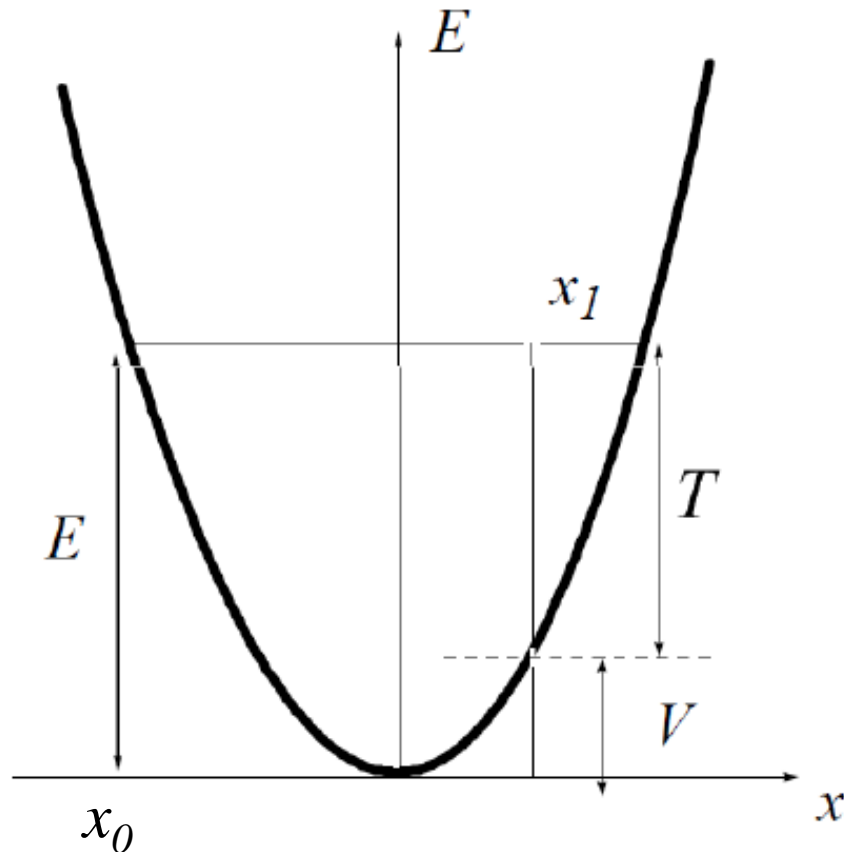
Motion equation and frequency ν_0 of the vibration :

$$x = x_0\cos(2\pi\nu_0 t + \varphi) \quad \text{avec} \quad \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

At $x = 0 \Rightarrow V = 0$ and T = max

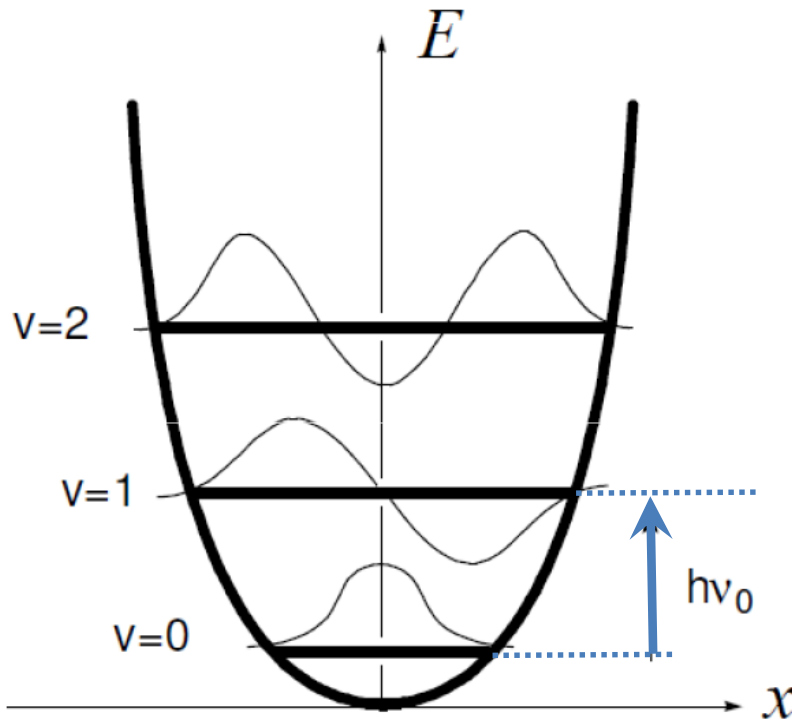At maximum position of the stretching (x_0):
$T = 0$ and V = max

Quantum-mechanical treatment gives quantized energy levels:

$$E_v = h\nu_0 \left(v + \frac{1}{2}\right) \quad \text{with} \quad \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

v is the vibrational quantum number

- **Wave functions of the first 3 vibrational levels** of a diatomic molecule in the harmonic approximation.

- The **vibrational levels are equidistant** and separated by the energy $h\nu_0$.

- The energy in the lowest (fundamental) state of v = 0 is not zero but $\frac{1}{2} h\nu_0$: this is called the **zero point energy**

- Note that, due to quantum mechanics, there is a non-zero probability to find an atomic nucleus at $x > x_0$: **quantum tunneling**

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Molecular vibration : diatomic molecule

$$V = \frac{1}{2}kx^2$$

Dissociation
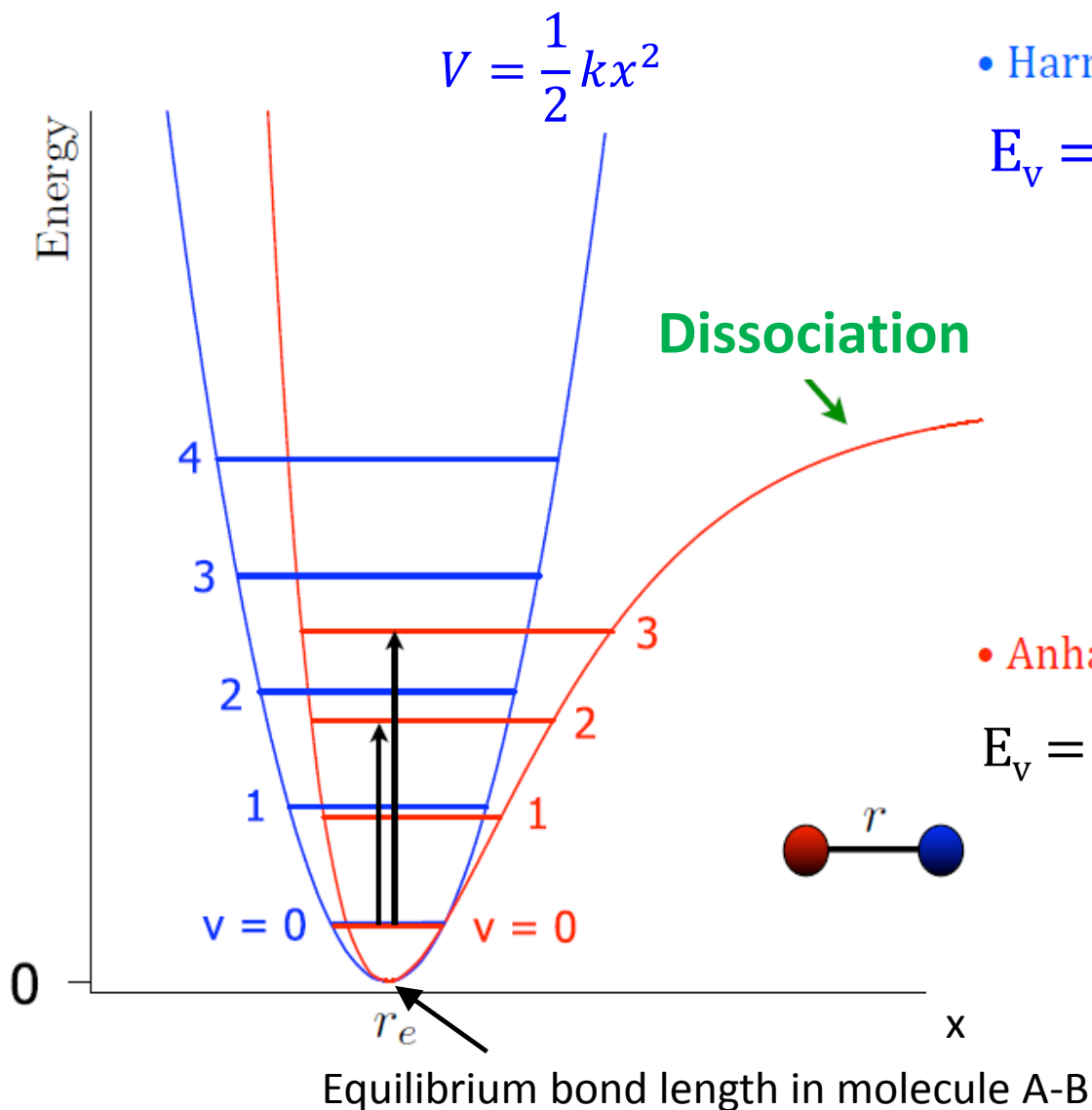
- Harmonic oscillator :

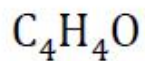$$E_v = h\nu_0 \left(v + \frac{1}{2}\right)$$

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad ; \quad \mu = \frac{M_A \times M_B}{M_A + M_B}$$

- Anharmonic oscillator :

$$E_v = h\nu_0 \left(v + \frac{1}{2}\right) - h\nu_0 \, x_e \left(v + \frac{1}{2}\right) + \ldots..$$

x_e Anharmonicity constant

Energy

4

3

2

1

$v = 0$

3

2

1

$v = 0$

r_e

r

0

x

Equilibrium bond length in molecule A-B

Fundamental bands of furane

C_4H_4O

21 modes of vibration

Courtesy: Jean Vander Auwera, Free University of Brussels
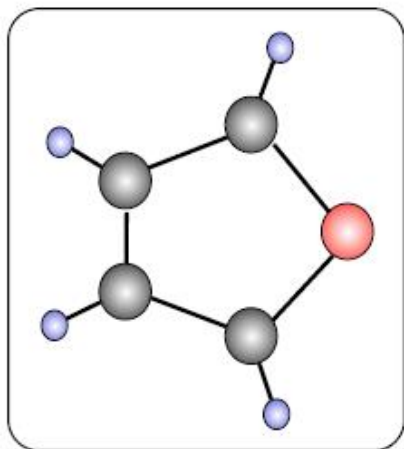
Ro-vibrational spectroscopy
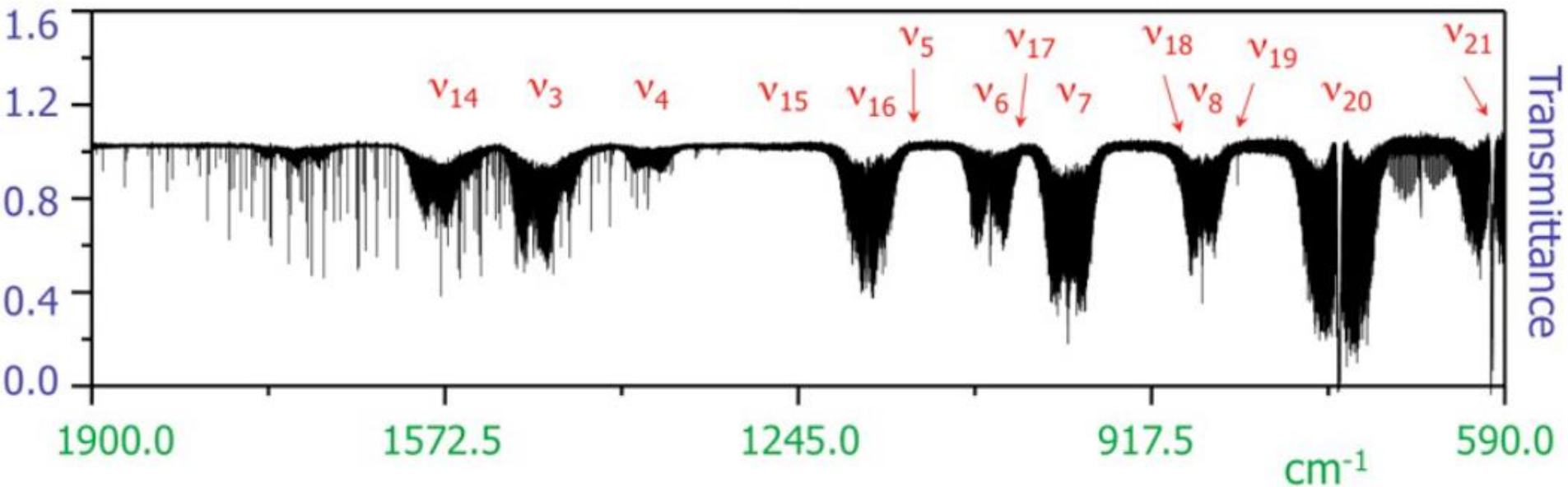
- The **excitation of vibrational mode goes simultaneously with the excitation of rotational levels** !

- This gives rises to **characteristic envelopes P,Q,R** of any excited vibrational level in the infrared.

- **P branch** : $\Delta v = +1$; $\Delta J = -1$

- **Q branch:** $\Delta v = +1$; $\Delta J = 0$

- **R branch:** $\Delta v = +1$; $\Delta J = +1$

- The Q branch might consist of only one line or of lines very close (if B of the excited vibration level is different). P,R branches are thus much larger than the Q

- $\Delta J = 0$ is forbidden for diatomics and for parallel movement of linear molecules
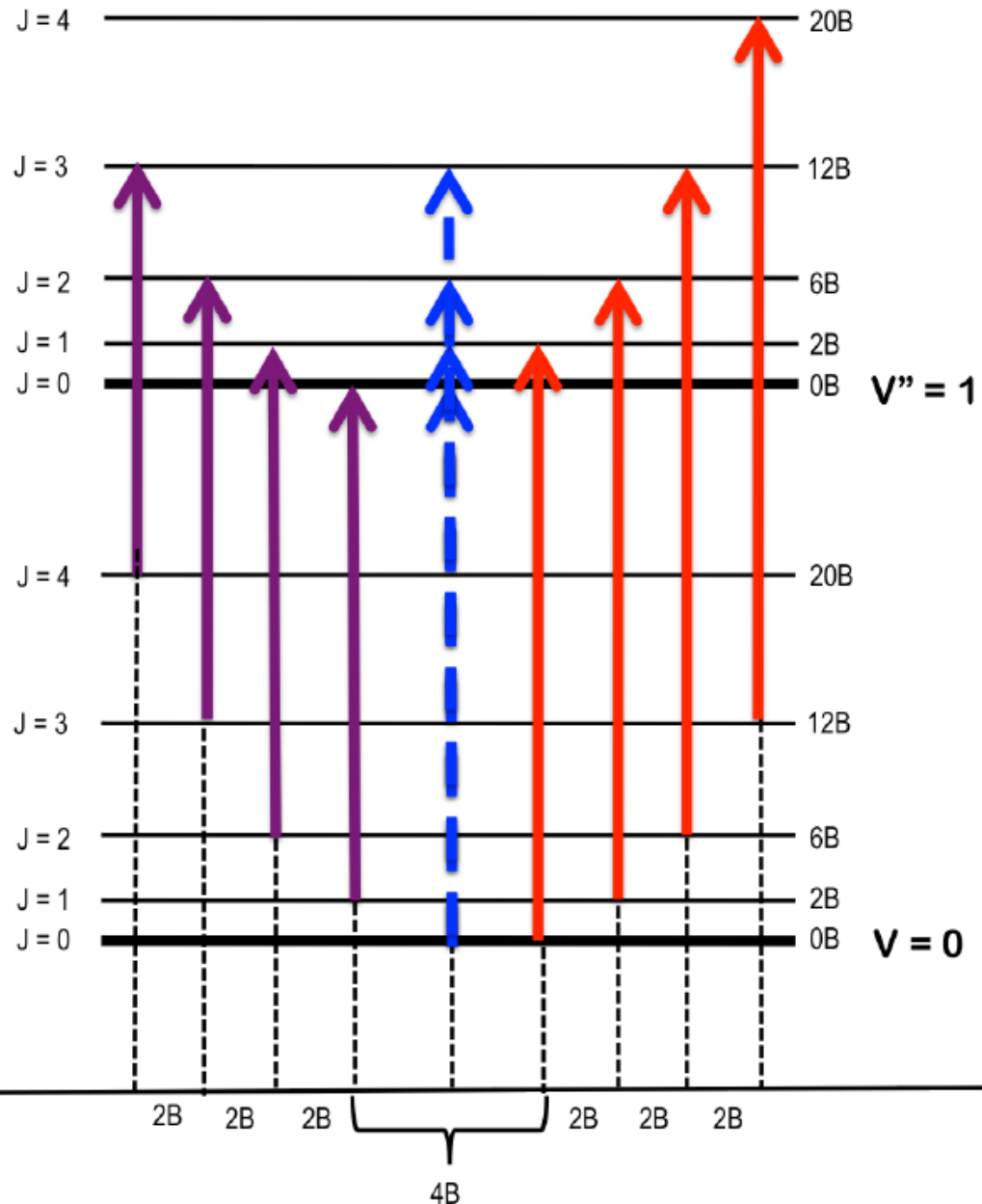
- Spectrum (simulated) of the asymmetric stretching (parallel) band of carbon dioxide, $^{12}C^{16}O_2$ (Q branch absent)
- The weak superimposed spectrum is due to **absorption of the first vibrationally excited level** ($v = 1 \rightarrow v = 2$) since $v = 1$ is also populated at room temperature (this is called a **hot band**)
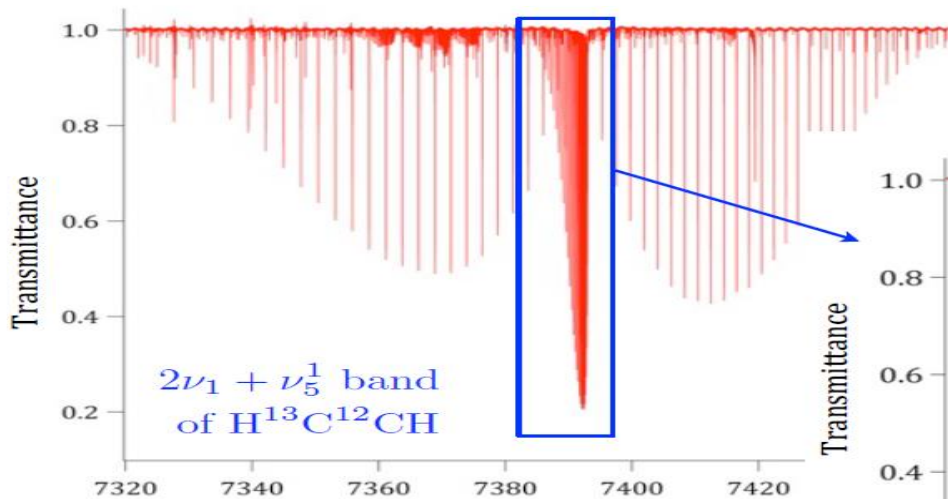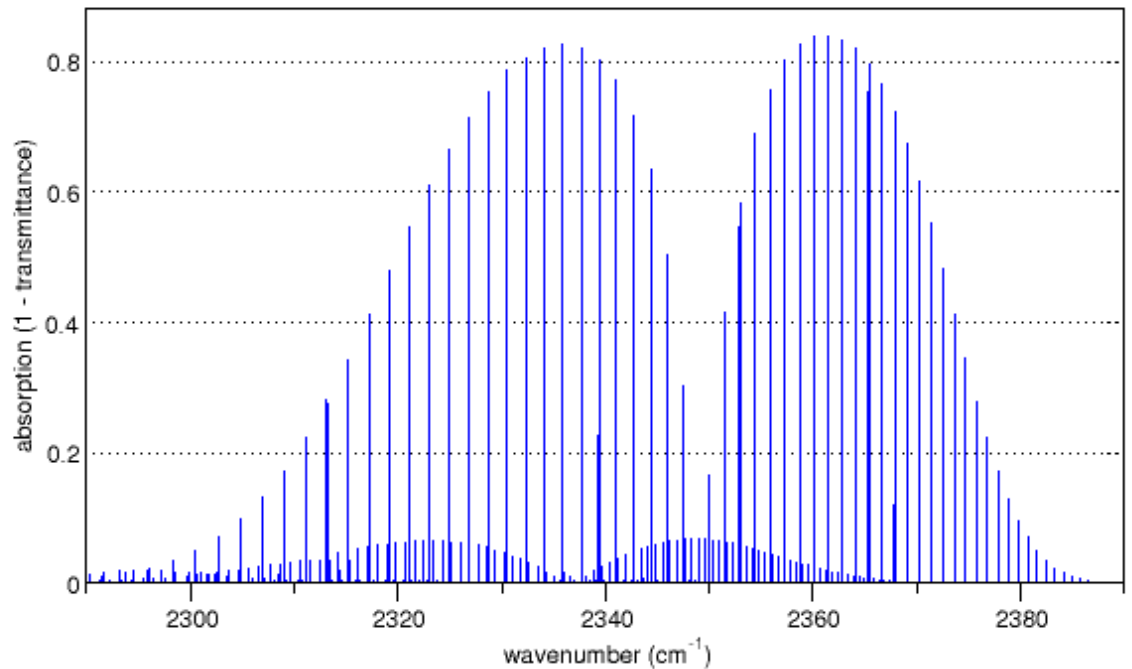
Combination band of Acetylene (C_2H_2)

$2\nu_1 + \nu_5^1$ band of $H^{13}C^{12}CH$

Q branch ($\Delta J = 0$)
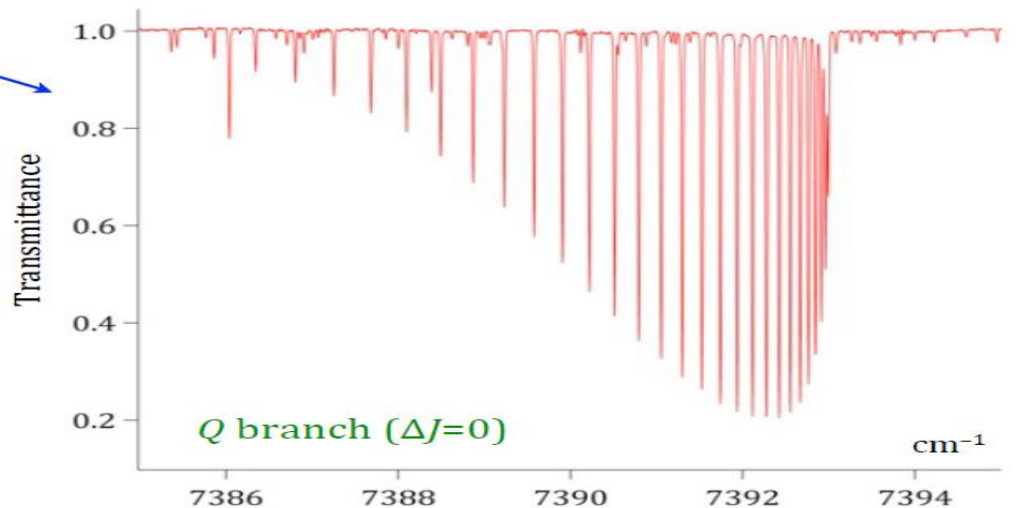
Link to chemistry …

- In general, a normal mode of vibration involves a **displacement of all the atoms** of the molecule.

- Nevertheless, under certain conditions, the **movement is more or less localized in a part of the molecule**: we say that the vibration bands are characteristic of groups or **chemical functions**.

- Many normal modes involve couplings between the vibrational movements of atoms: we speak then of **skeleton vibrations**, very specific to a given molecule : the region between ~1300 cm^{-1} and several hundreds of cm^{-1} is considered to be a **fingerprint region**

Stretching

Groupe	ω / cm^{-1}
$\equiv C-H$	3 300
$=C\stackrel{H}{\diagdown}$	3 020
sauf $O=C\stackrel{H}{\diagdown}$	2 800
$>C-H$	2 960
$-C\equiv C-$	2 050
$>C=C<$	1 650
$>C-C<$	900
$>Si-Si<$	430
$>C=O$	1 700
$-C\equiv N$	2 100
$>C-F$	1 100
$>C-Cl$	650
$>C-Br$	560
$>C-I$	500

Stretching

Groupe	ω / cm^{-1}
$-O-H$	3 600[a]
$>N-H$	3 350
$>P=O$	1 295
$>S=O$	1 310

Bending

	ω / cm^{-1}
$\equiv C-H$	700
$=C\stackrel{H}{\diagdown}_{H}$	1 100
$-C\stackrel{H}{\underset{H}{\diagdown}}_{H}$	1 000
$\stackrel{H}{\underset{H}{\diagup}}$	1 450
$C\equiv C-C$	300

The Beer-Lambert Law → "classical spectroscopy"

Optical path, l

| Source of radiation | $\rightarrow$ $I_0(\lambda)$ | Sample to be probed | $\rightarrow$ $I_x(\lambda)$ | Detector |
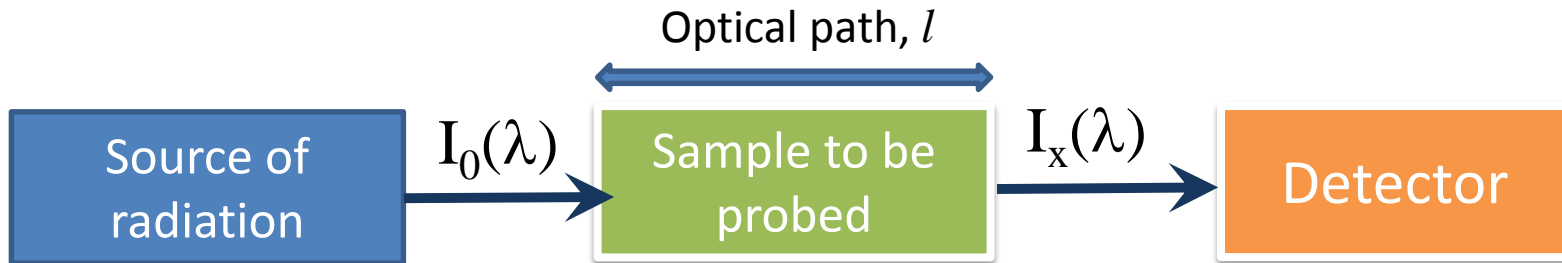
$$dI = -\alpha(\lambda) \times I \times dl \qquad \Longrightarrow \qquad I = I_0 \times e^{-\alpha(\lambda)\, l}$$

$$\ln \frac{I_0}{I_x} = \alpha\, l$$

$$\ln \frac{I_0}{I_x} = \tau$$

$$\frac{I_x}{I_0} = T = e^{-\tau}$$

l : optical path length

α : **absorption coefficient** (λ) **(molecule specific)** **[cm^{-1}]**

I_0 : incoming intensity (λ)

I_x : transmitted intensity (λ)

τ : **optical depth;** or **optical density "OD"; or absorbance**

T : **Transmittance** (number 0..1; usually expressed in %) (λ)

1-T: Absorption (number 0..1; usually expressed in %) (λ)

$$\ln \frac{I_0}{I_x} = \alpha \times l = \sigma \times N \times l$$

Absorption coefficient [cm^{-1}]

Optical path length [cm]

Absorption cross section [cm^2]

Molecule number density [cm^{-3}]
- Can be calculated from the **ideal gas law**:

$$N = p / (k_B T)$$

...if the measured pressure is only due to the absorbing gas

Einstein coefficient for absorption B$_{12}$ *(molecule specific)*

- The intensity of an absorption band
  - Is very specific for the molecule under consideration
  - Can be expressed in : Einstein coefficients, **cross sections**, oscillator strength (« *f*-value »), transition dipole moments (theory)…
  - Is **absolutely needed for a remote sensing measurement** in order **to restitute reliable mixing ratios of key molecules** (i.e. partial pressures) in a real planetary atmosphere
  - The intensity is often difficult to measure in a typical laboratory experiment since the absolute number density must be known precisely (in a gas cell….). However, gases can be reactive or thermolabile, or exist only in equilibrium with other species…
  - The intensity generally depends on temperature…
  - Measuring precisely the intensities of absorption bands is called "**quantitative spectroscopy**"
  - Whereas quantum chemistry does generally a good job for the prediction of lines positions (energy levels inside molecules…), the theoretical calculation of in lines intensities is far more difficult