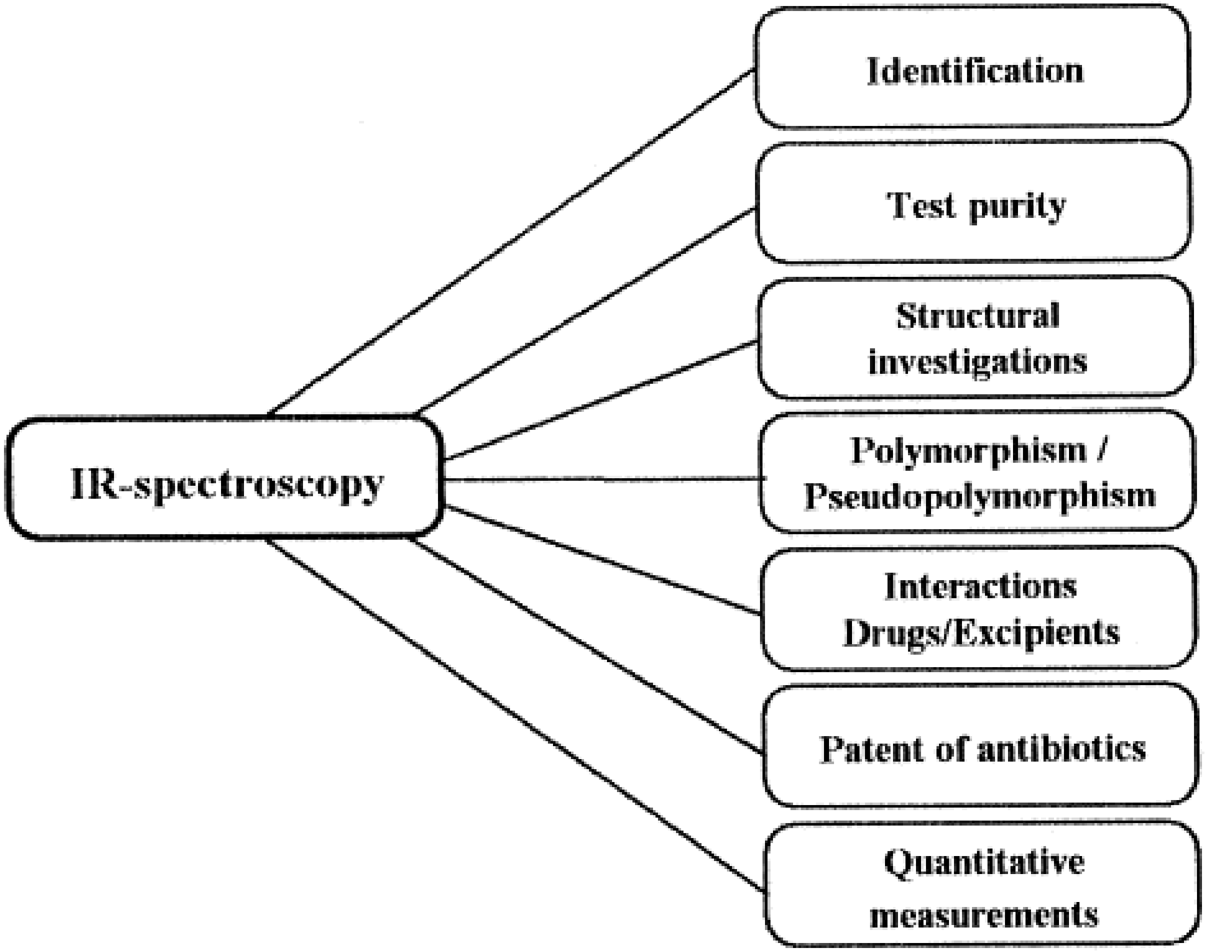
Infrared (IR) spectroscopy

ver. 20191119

Application of IR spectroscopy in pharmacy



G.N.Kalinkova: Infrared spectroscopy in pharmacy
Vibrational Spectroscopy **19**, 1999, 307-320
doi: 10.1016/S0924-2031(99)00017-X

Interaction of materials with IR light

infrared bulb

Naturally, molecules are in motion. Possible ways of motion:

- displacement
- vibration
- rotation

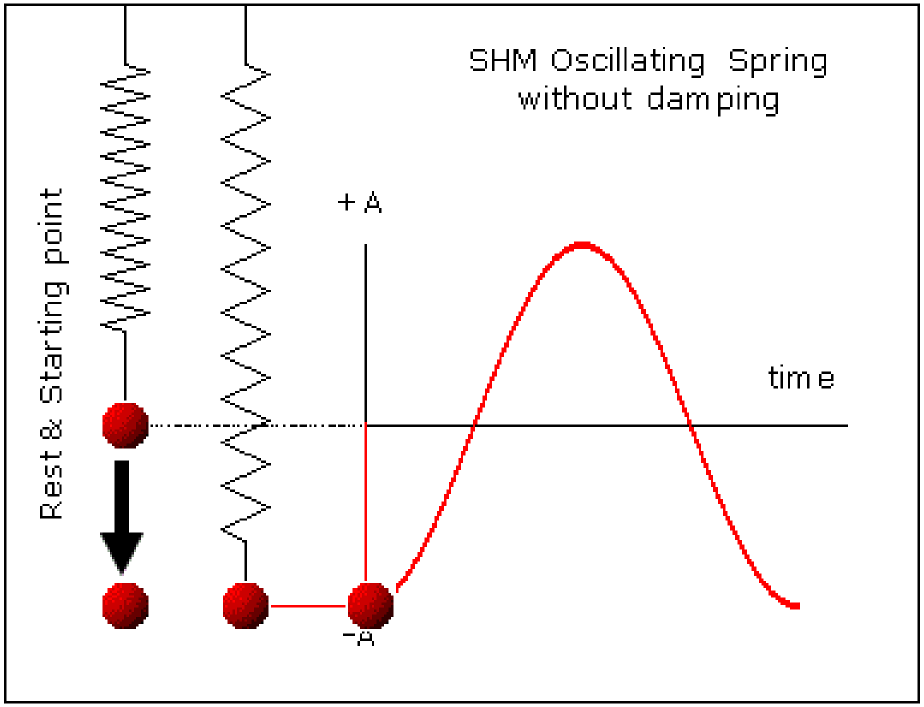
The infrared light gives its energy to vibration and rotation motion.

The vibration energies are higher than the rotational ones, therefore we have vibrational spectrum with superimposed rotational spectrums.

Note: if the energy is converted to displacement it directly increases the temperature of the system.

Physics of vibrations
The spring and ball model

Chemical bonds, which can be thought of spring connectors between atoms, serve as **constrains** to the motion of atoms leading to well defined vibrational modes.



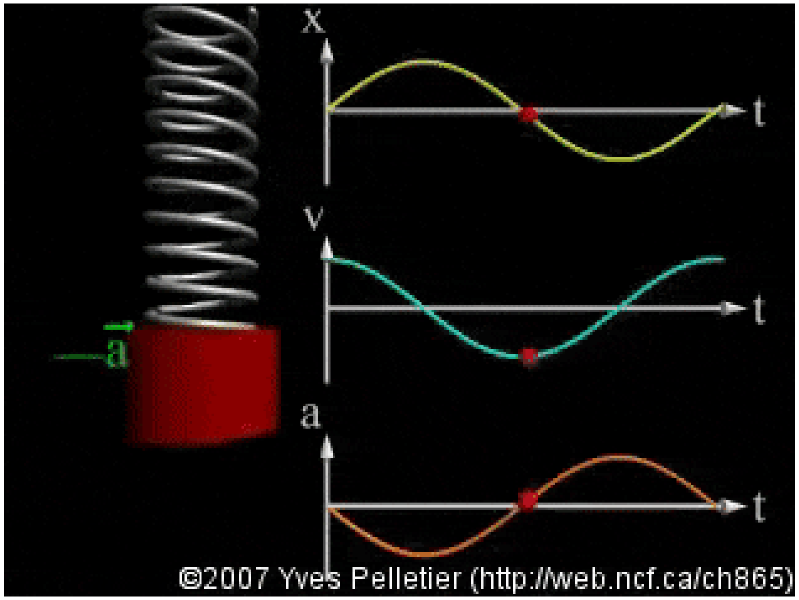
The vibrating body (here ball) has a periodic motion between two extreme positions (-A, +A).

In a **simple harmonic oscillator** the force acting is proportional to

- the force constant, *k*
- the dispalcement to the equilibrium position (x)

$$F = -k \cdot x$$

Physics of vibrations
The spring and ball model



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According to Newton's second law the force causes proportional acceleration:

$$F = m \cdot a$$

In one equation: $-k \cdot x = m \cdot a = m \cdot \frac{\mathrm{d}^2 x}{\mathrm{d}t^2}$

Solving this equation with certain boudary conditions we get:

$$x = A \cdot \cos(2\pi\nu t + b)$$

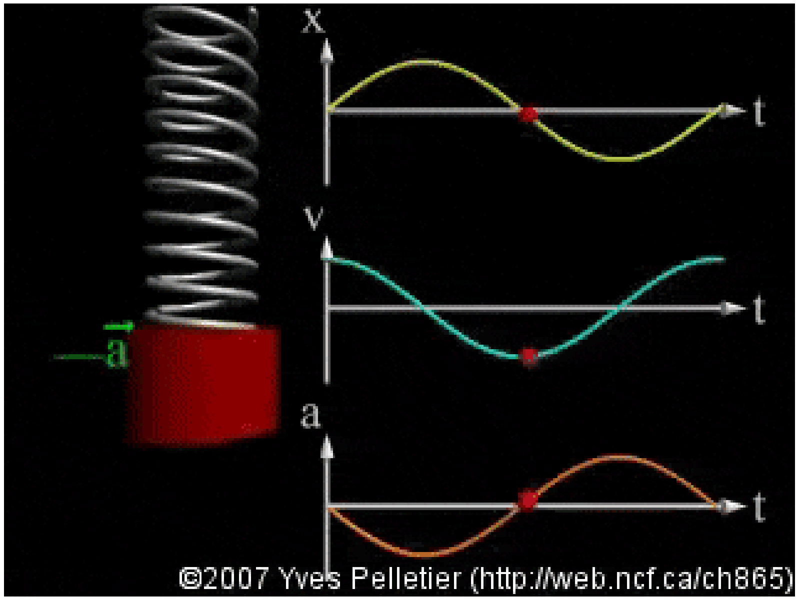
where A is the amplitude of motion, ν is the frequency of motion, t is time variable and b is the phase of vibration.

Physics of vibrations
The spring and ball model

The vibration frequency depends on the force constant and the mass of ball:

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

The frequency does not depend on the amplitude!



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Physics of vibrations
Diatomic molecules

The displacement variable is the distance of the atoms relative to the equilibrium distance:

$$x = r_{\text{actual}} - r_{\text{equilibrium}}$$

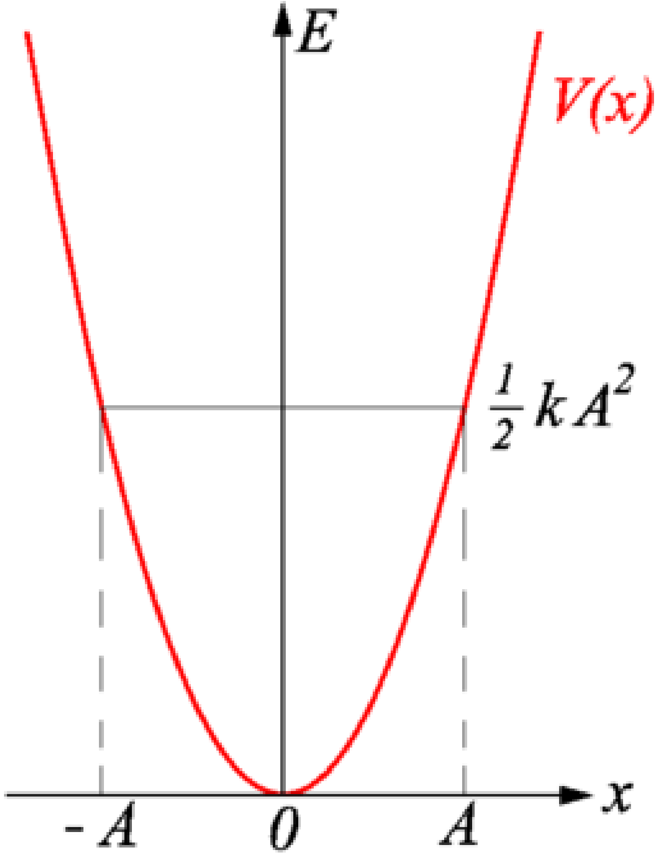
The frequency of the vibration has similar equation, but with the reduced mass, μ:

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

where $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

The potential energy is a parabolic function:

$$V = \frac{1}{2}k \cdot x^2$$



Physics of vibrations
Classical description vs. quantum mechanics

In the **quantum mechanical description** only **discrete energies** are accessible.

There is a **minimum energy**, $E_0 = \pi\hbar\nu = \frac{1}{2}\hbar\omega$. ($\omega = 2\pi\nu$, the angular frequency)

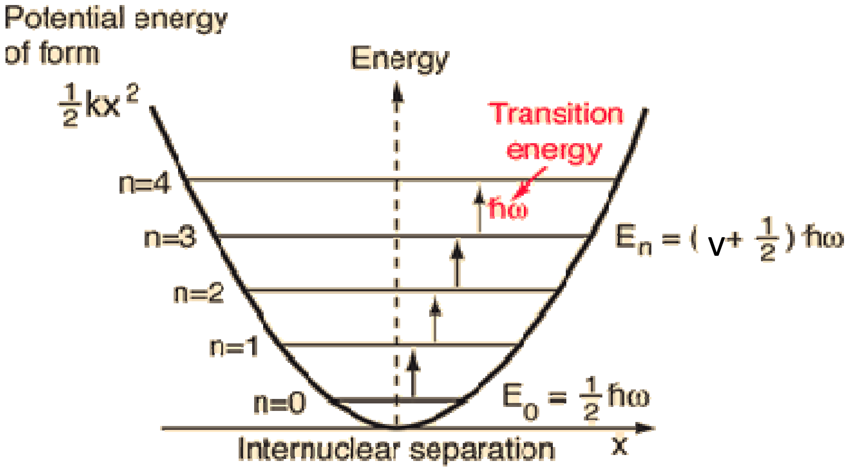
The simplest quantum mechanical model is the **harmonic oscillator**.

The distances between the rotational energy levels are $\hbar\omega$. The **energy difference** of the neigbouring levels is **independent** of the energy levels.

Vibrational selection rule: during light absorption the vibrational quantum number (v) may change only by one:

$$\boldsymbol{\Delta \mathrm{v} = \pm 1}$$

Larger changes ($\Delta\mathrm{v} = \pm 2 \text{ or } \Delta\mathrm{v} = \pm 3$) are forbidden!



Physics of vibrations
Anharmonic oscillators

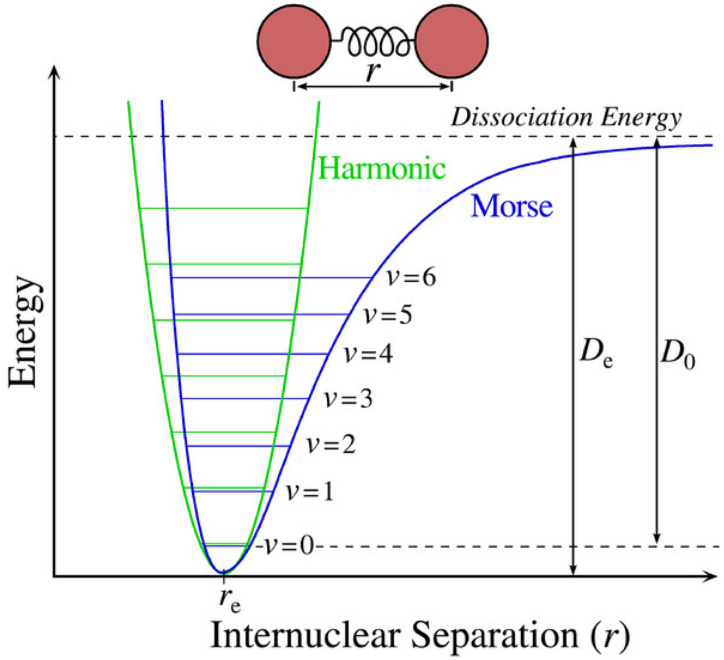
Harmonic oscillators are good approximations for low energy vibrations (e.g. at room *T* mainly the lowest energy state is populated), but poor for high energy ones. For the **anharmonic oscillators** the forces are nonsymmetrical to the equilibrium positions. A purely empirical expression fits the experimental data for diatomic molecules well was derived by P. M. Morse, called **Morse function**.

The **energy difference** of the neigbouring levels **depends on the energy levels**.

Vibrational selection rule: during light absorption the vibrational quantum number (v) may change by any number:

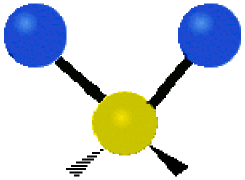
$$\Delta \mathbf{v} = \pm \mathbf{1}, \pm \mathbf{2}, \pm \mathbf{3} \ldots$$

Absrption peaks corresponding to $\Delta \text{v} \geq \pm 2$ are overtones.

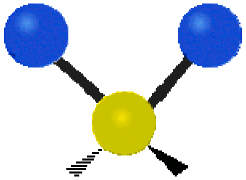


Vibrational motions

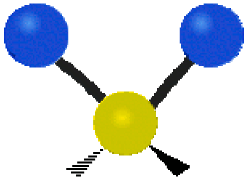
Symmetrical stretching



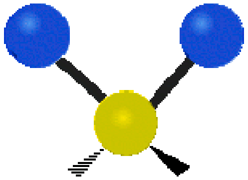
Asymmetrical stretching



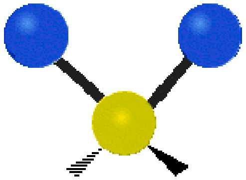
Scissoring (Bending)



Rocking



Wagging



Twisting

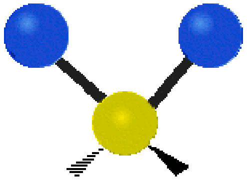
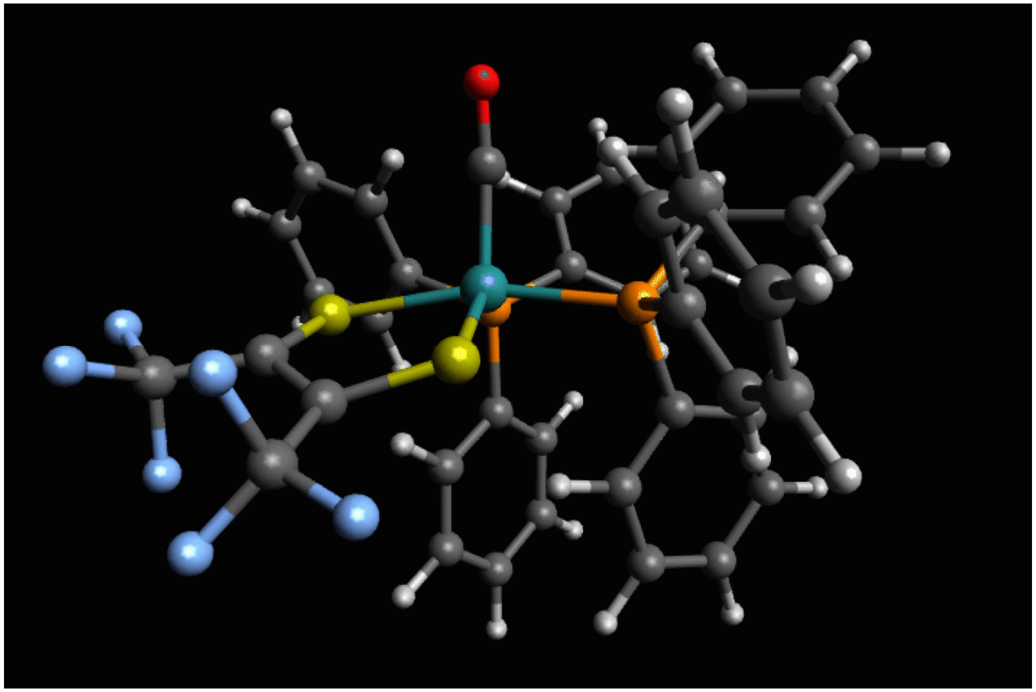


Illustration of vibrations of a methylene group ($–CH_2–$) (*wikipedia, Public Domain; Tiago Becerra Paolini*)

Physics of vibrations
Normal modes for polyatomic molecules

In molecules having more than 2 atoms the vibrations are more difficult, can not be described easily using simple variables, like atomic distances. The motions are overlapping, build on each.

The description of the vibrations can be simplified if we consider complex, polyatmic motions as **normal mode**s. These motions has one normal coordinate which progress describes the vibration (forces, acceleration).



T M Porter et al, Chem. Sci., 2018, DOI: 10.1039/c8sc03258k

Number of vibrations

An **N-atomic molecule** has **3N motional degrees of freedon** (3 for each atom according the Cartesian coordinates).

The number of vibrations can be calculated if we substract the translational (3) and rotational degrees (2 or 3) from the total one (3N)

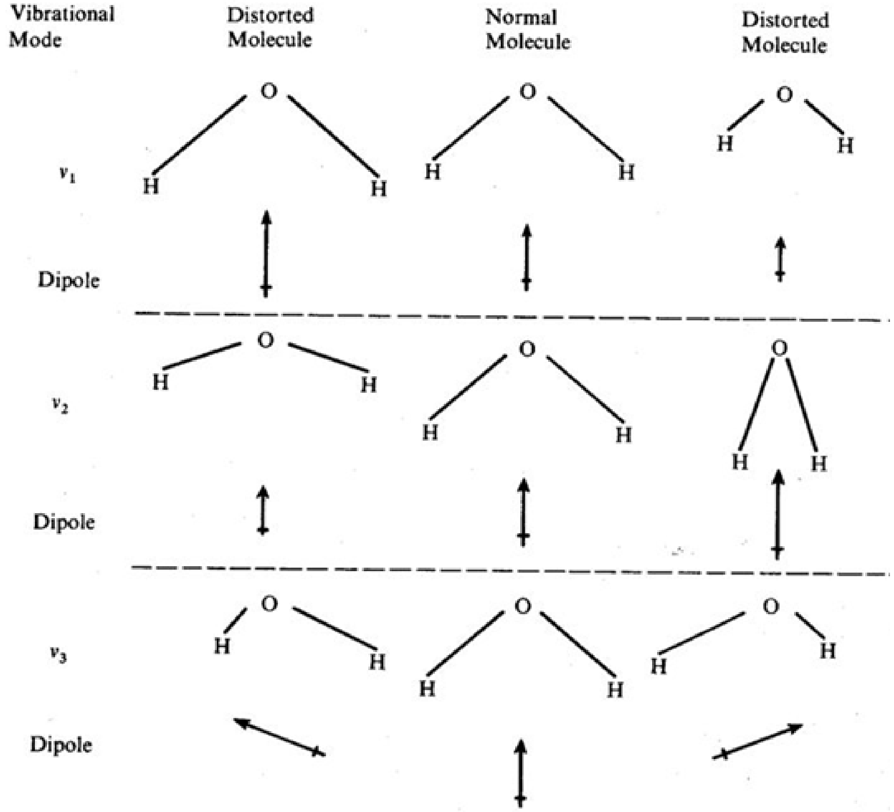
Linear molecules have only two unique rotations. The rotation about the bond axis does not count, since it changes neither positions of the atoms, nor does the angular momentum change. Therefore, the number of vibrations is **3*N*-5**.

Non-linear molecules have three unique rotations, therefore,
the number of vibrations is **3*N*-6**.

Change of the permanent dipole moment during a vibration

IR light can excite only vibrations which change the permanent dipole moment of the molecule (IR active vibrations). Other vibrations do not cause absorption, they are IR inactive.

How can change the permanent dipole moment during a vibration?



Physical condition for IR light absorption

IR light can excite only vibrations which change the permanent dipole moment of the molecule (IR active vibrations). Other vibrations do not cause absorption, they are IR inactive.

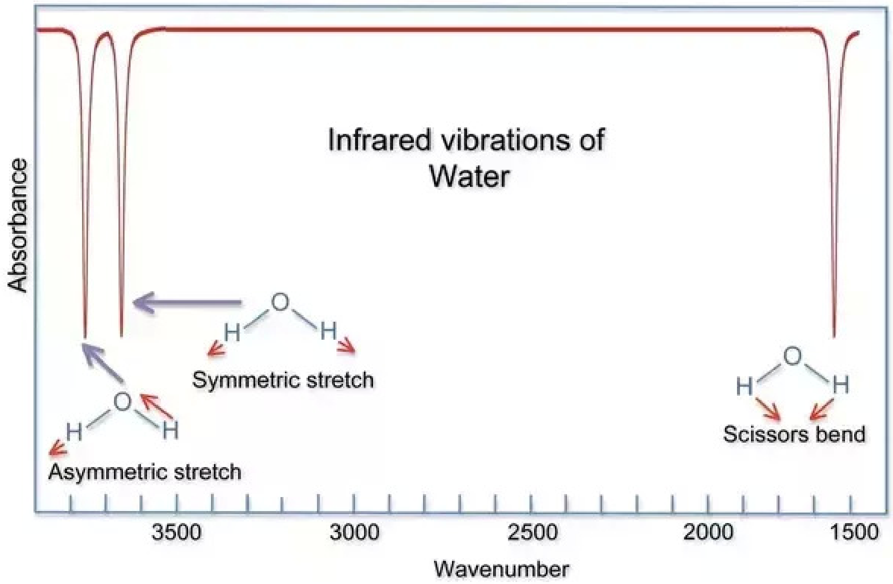
The absorption intensity is proportional to the dipole moment change due to the vibration (described by its derivative by the normal coordinates).

The same electromagnetic range is used in the **Raman spectroscopy** which relies on the Raman scattering. IR light interacts with the electrons of the molecules and during the absorption not only the vibrational, but the rotational state changes. It results a little shift of energies.
Raman effect is proportional to the change of the polarizability of the molecule due to vibrations.
IR and Raman spectroscopies **complement each other**, because many complementarily active vibrations exist.

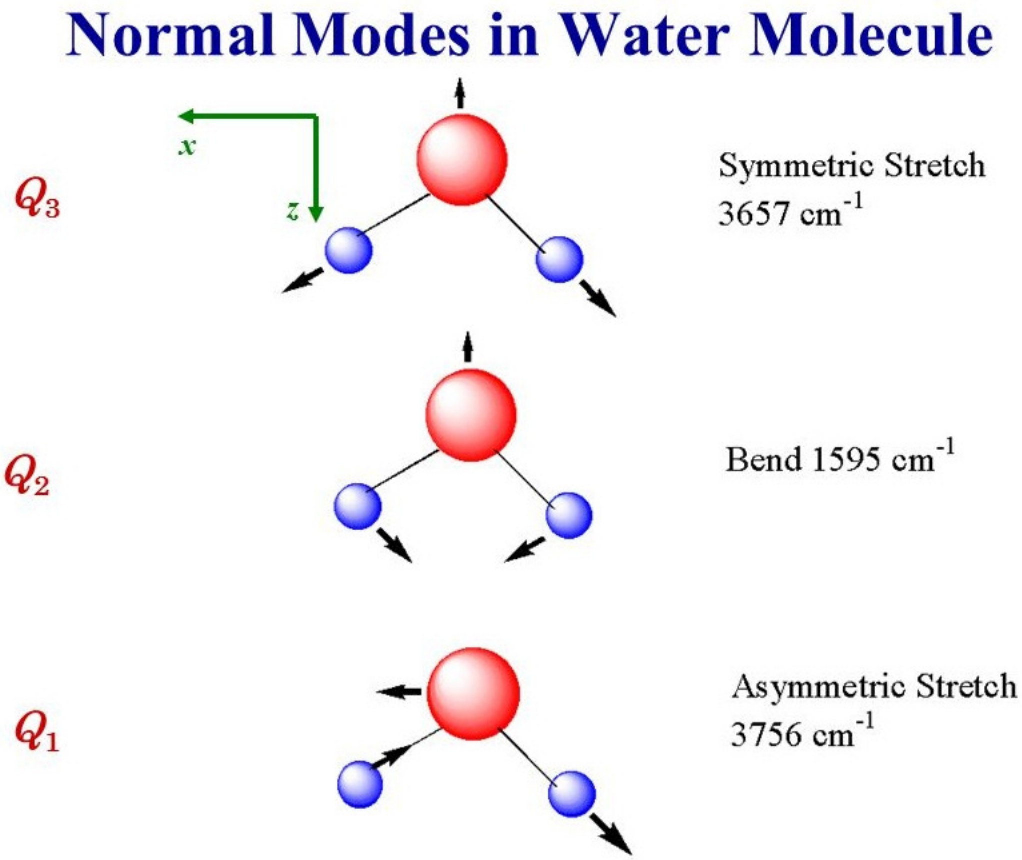
The vibration modes of water

Water has 3 atoms, therefore the number of vibration modes is 3·3-6=3.

All vibrational motions change the molecular dipole moment, so all are infrared active.



https://www.quora.com/At-what-temperature-does-water-absorb-the-most-infrared-radiation



Isotope effect on the vibrational frequencies

Let us consider a two atomic molecule, hydrogen chloride!

Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl. Is the vibration frequency of HCl the same for the two isotopes?

No! The frequencies are different, because the reduced mass of hese molecules differs:

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{k}{\mu}} \qquad \text{where } \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

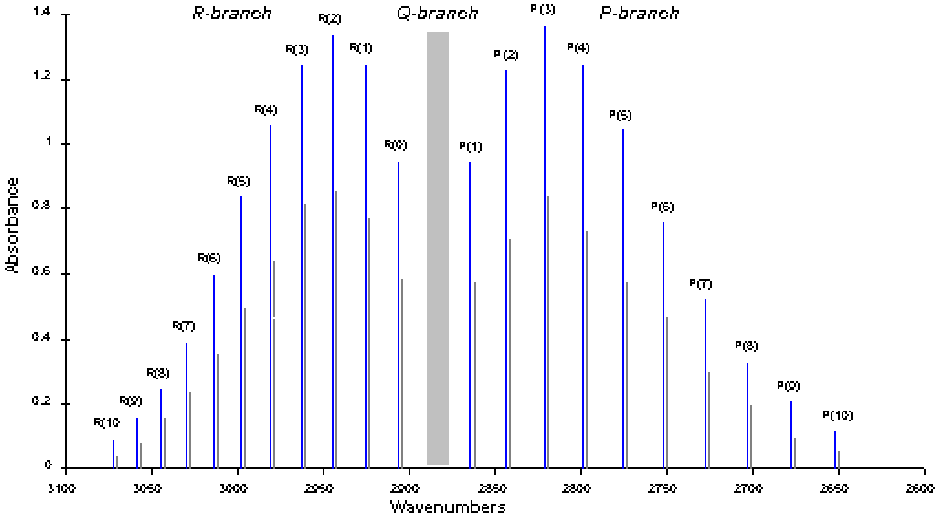
Reordering: $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$

$$\mu_{\mathrm{H^{35}Cl}} = \frac{1 \cdot 35}{1+35} = 0.9722\ ;\ \mu_{\mathrm{H^{37}Cl}} = \frac{1 \cdot 37}{1+37} = 0.9737$$

$$\nu_{\mathrm{H^{35}Cl}} / \nu_{\mathrm{H^{37}Cl}} = \sqrt{\frac{\mu_{\mathrm{H^{37}Cl}}}{\mu_{\mathrm{H^{35}Cl}}}} = \sqrt{\frac{0.9737}{0.9722}} = 1.001$$

The lighter isotope has larger vibrational frequency.

In gas phase the rotational fine structure is well visible!



Isotope effect on the vibrational frequencies

Let us consider a two atomic molecule, hydrogen chloride!

Hydrogen has two stable isotopes, ^{1}H and ^{2}H. How the IR spectrum of the two HCl with these isotopes look like?

$$\mu_{1\mathrm{HCl}} = \frac{1 \cdot 35}{1+35} = 0.9722\ ;\ \mu_{2\mathrm{HCl}} = \frac{2 \cdot 35}{2+35} = 1.8919$$

$$\nu_{1\mathrm{HCl}} / \nu_{2\mathrm{HCl}} = \sqrt{\frac{\mu_{2\mathrm{HCl}}}{\mu_{1\mathrm{HCl}}}} = \sqrt{\frac{1.8919}{0.9722}} = 1.395$$

40% difference in the frequencies!

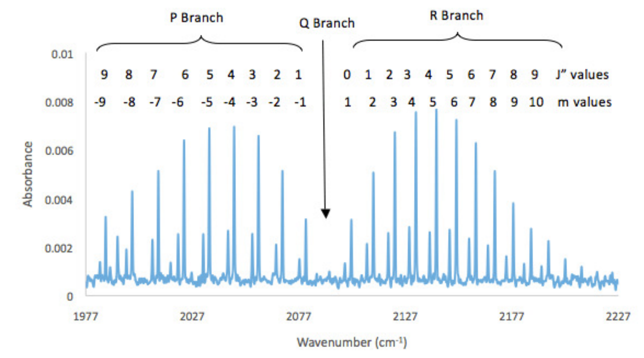
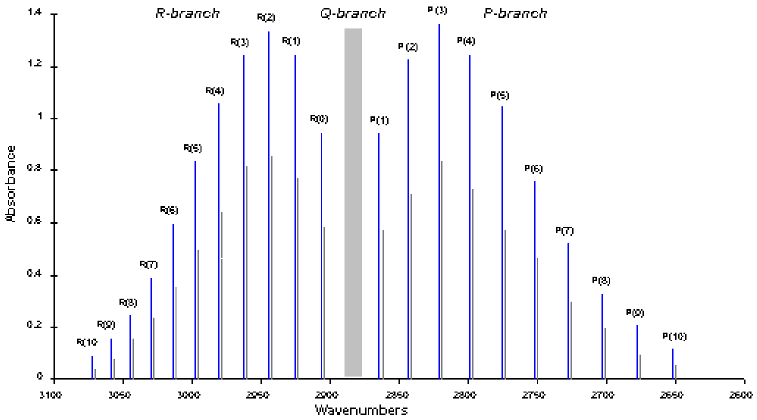


Figure 7. Spectrum of DCl with J and m values and labeled P and R branch. Vibrational rotational infrared spectrum for diatomic DCl.



On the rovibrational spectrum

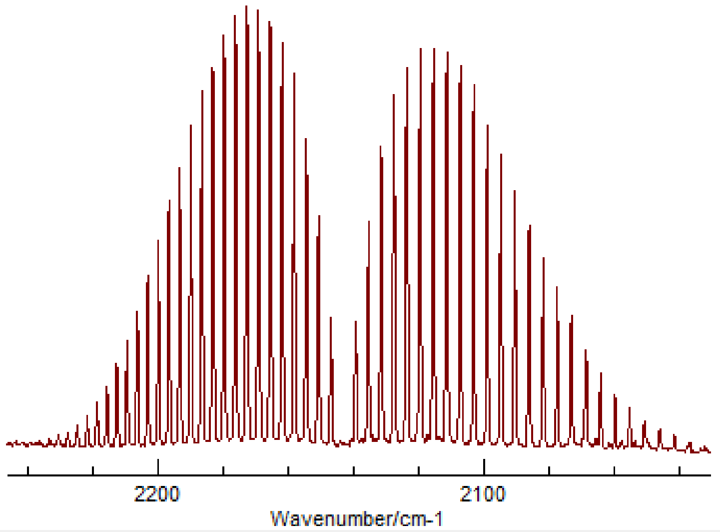
IR light absorption causes **simultaneous change of vibrational and rotational states**.

The rotational state must change by ±1!

This leads to the **missing peak at pure vibrational energies** (missing Q-branch), but a **series of peaks for vibrational ± rotational energies**. (in R-branch rotation is excited, in P-branch rotational state is decreased)

Rotational energy levels are quite well populated at room temperature, therefore many lines appear.

See the rotational spectroscopy for details!



Carbon monoxide rotational-vibrational spectrum
Ian13 wikimedia commons

IR spectrometers

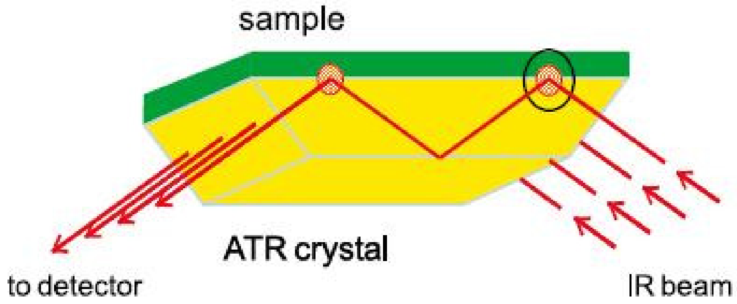
IR spectrometers are absorption spectrometers specific to the requirements of the IR light.

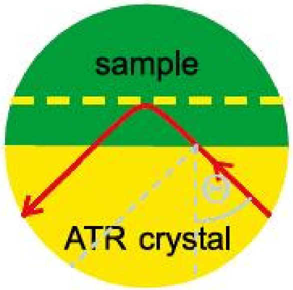
E.g. water has strong absorption peaks, so all samples and the internal of the spectrometers must be dry.

Both dispersive and Fourier transform spectrometers are available, but FTIR is more common.

Solid and liquid samples can be measured with a specific technique:

Attenuated total reflection (ATR).

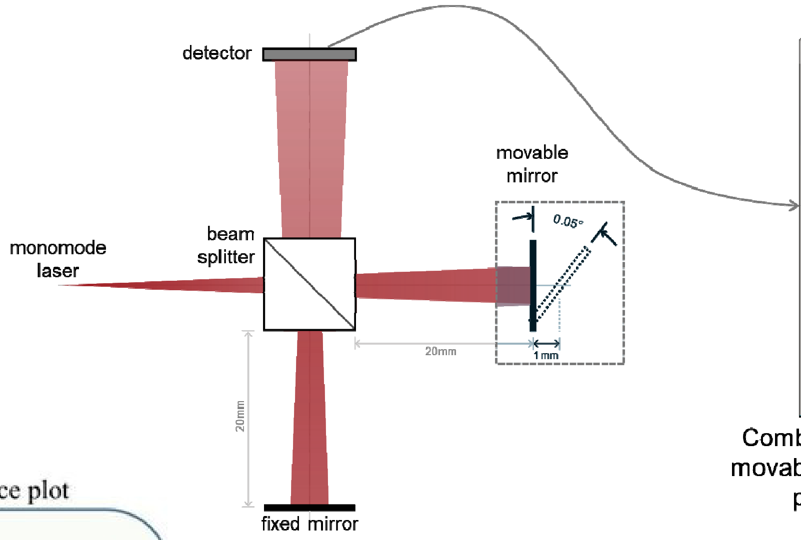


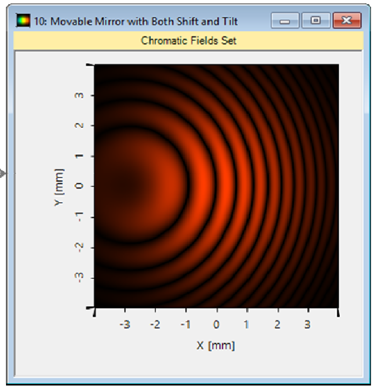


Refractive index
Crystal > Sample

Working principle of the FTIR spectrometers

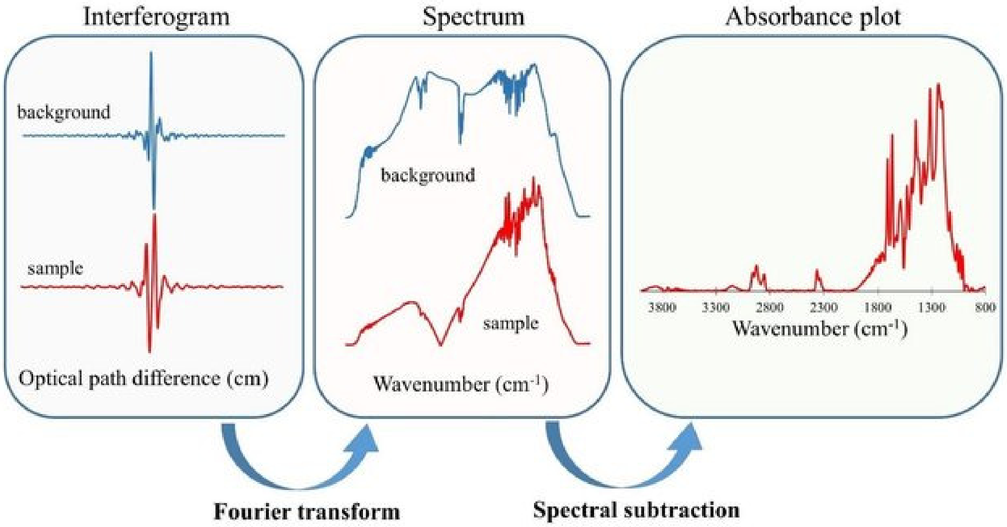
In the FTIR instruments light is not dispersed to different wavelengths, but the interferogram of the whole spectrum is measured.





Combination of both shift and tilt of the movable mirror gives rise to shifted ring pattern in the interference fringes.

Michelson interferometer



The original frequency spectrum can be reconstructed using Fourier transformation.

IR light sources

Inert solid heated to 1,500 - 2,200 K temperature.

- The Nernst glower: constructed of rare earth oxides in the form of a hollow cylinder. Platinum leads at the ends of the cylinder permit the passage of electricity. Nernst glowers are fragile. They have a large negative temperature coefficient of electrical resistance and must be preheated to be conductive.

- The globar source: a rod of silicon carbide (5 mm diameter, 50 mm long). Water cooling of the electrical contacts is needed to prevent arcing. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than 5 mm) where it's output becomes larger.

Tunable carbon dioxide laser

- A tuneable carbon dioxide laser is used as an infrared source for monitoring certain atmospheric pollutants and for determining absorbing species in aqueous solutions.

IR detectors

Thermal detectors

- can be used over a wide range of wavelengths
- operate at room temperature
- disadvantage: slow response time and lower sensitivity relative to other types of detectors

Thermocouple

A thermocouple consists of a pair of junctions of different metals; for example, two pieces of bismuth fused to either end of a piece of antimony. The potential difference voltage) between the junctions changes according to the difference in temperature between the junctions. Several thermocouples connected in series are called a thermopile.

Bolometer

A bolometer functions by changing resistance when heated. It is constructed of strips of metals such as platinum or nickel or from a semiconductor.

IR detectors

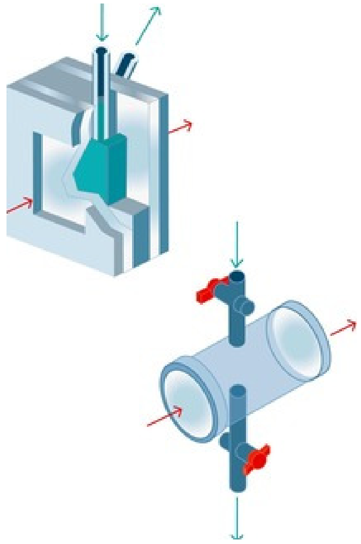
Pyroelectric detectors

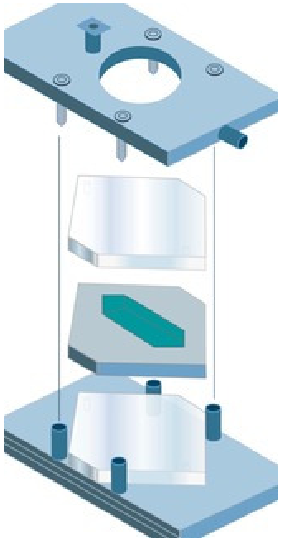
- consists of a pyroelectric material which is an insulator with special thermal and electric properties, e.g. triglycine sulphate
- the pyroelectric effect depends on the rate of change of the detector temperature rather than on the temperature itself
- much faster response time, makes these detectors well suitable for Fourier transform spectrometers where rapid response is essential.

Photoconducting detectors

- the most sensitive detectors
- rely on interactions between photons and a semiconductor. The detector consists of a thin film of a semiconductor material (e.g. lead sulphide) deposited on a nonconducting glass surface and sealed into an evacuated envelope to protect the semiconductor from the atmosphere.
- must be cooled with liquid nitrogen to minimize disturbances

IR sample handling


gas samples


liquid samples

The **sample cell** must be **transparent to IR light**.

The **sample material** must be **free from water**.

The **windows** are usually made of sodium chloride, potassium chloride or cesium bromide.

Liquids are usually analysed in **pure form** or **in solution**.

Solids reduced to small particles can be examined as a **thin paste** or **mull** (grinding a few milligrams of the sample with a few drops of a hydrocarbon oil) as a film between flat salt plates.

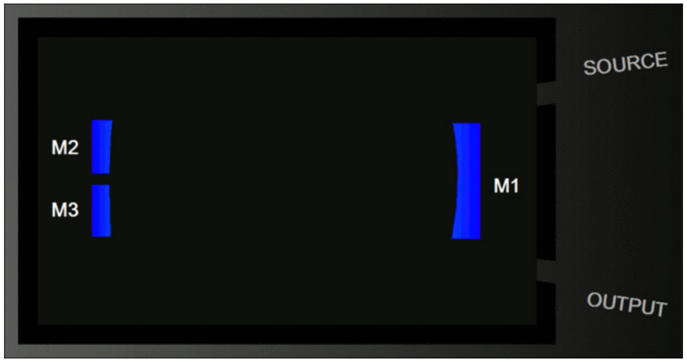
Solids can be investigated **in pastilles**: ground a milligram or less of the sample with about 100 milligram potassium bromide. The mixture is then pressed in an evacuable die to produce a transparent disk.

Optical pathlengths in IR measurements

In simple cases the light goes through the sample once.

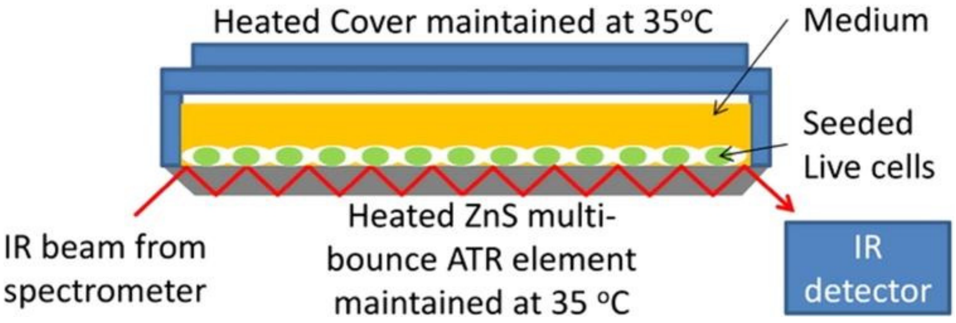
If you want to measure low-concentration components or to observe weak spectra in gases or liquids you must use multiple-pass od long path absorption cells.

E.g. the White cell (first described in 1942 by John U. White) has 8 passes.



ATR element and cell culture setup for live cells' FTIR measurement

P.L. Fale, A. Altharawi and K.L.A. Chan, In situ Fourier transform infrared analysis of live cells' response to doxorubicin, Biochimica et Biophysica Acta 1853 (2015), 2640–2648. doi:10.1016/j.bbamcr.2015.07.018.



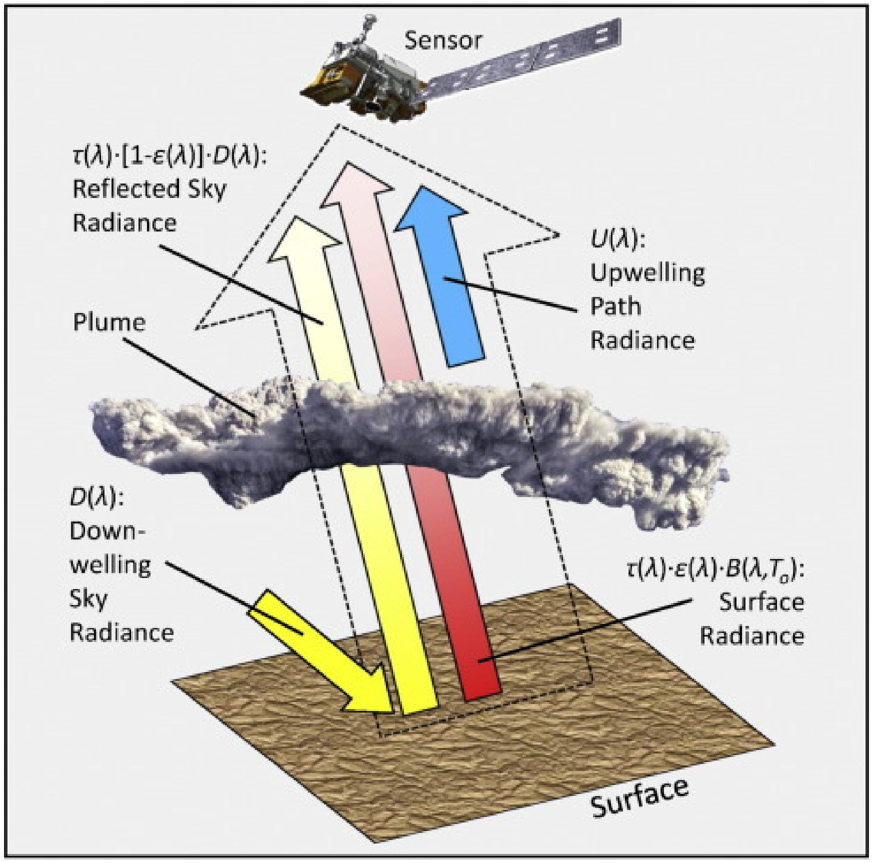
Optical pathlengths in IR measurements

In special cases we cen measure without a physical cell.

Thermal infrared sensing of volcanic plumes using IR radiation.

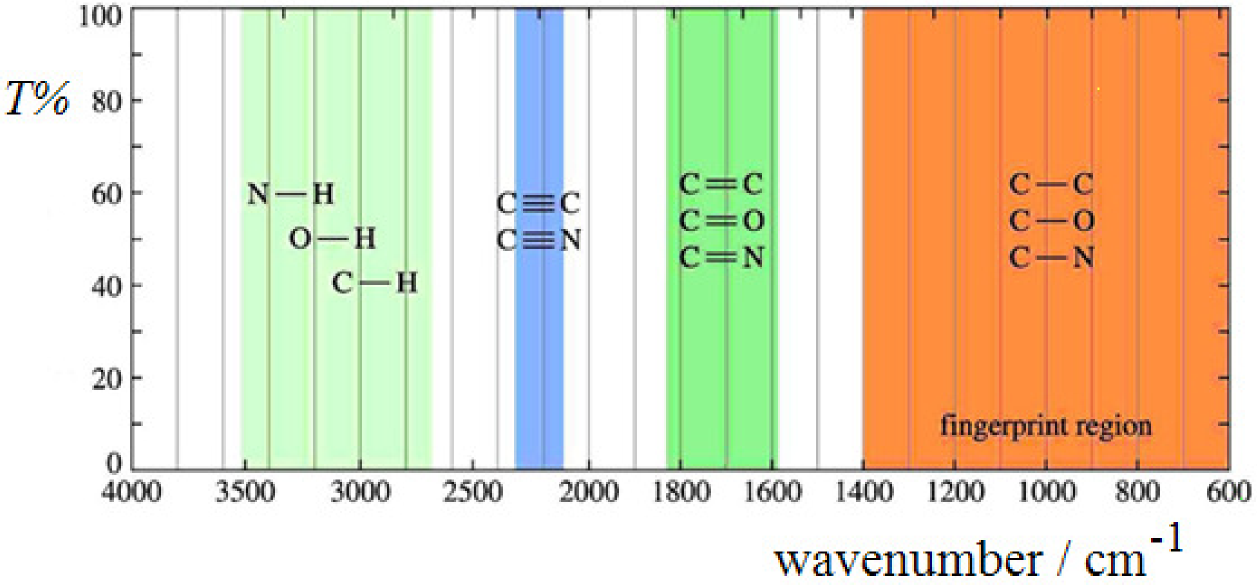
„The use of multispectral thermal infrared (TIR) image data to estimate the quantity of SO2 in volcanic plumes and clouds has become an established tool for remote sensing volcanologists.”

Journal of Volcanology and Geothermal Research
327, 2016, 55-69
Plume Tracker: Interactive mapping of volcanic sulfur dioxide emissions with high-performance radiative transfer modeling
Vincent J. Realmuto, Alexander Berk
doi: 10.1016/j.jvolgeores.2016.07.001

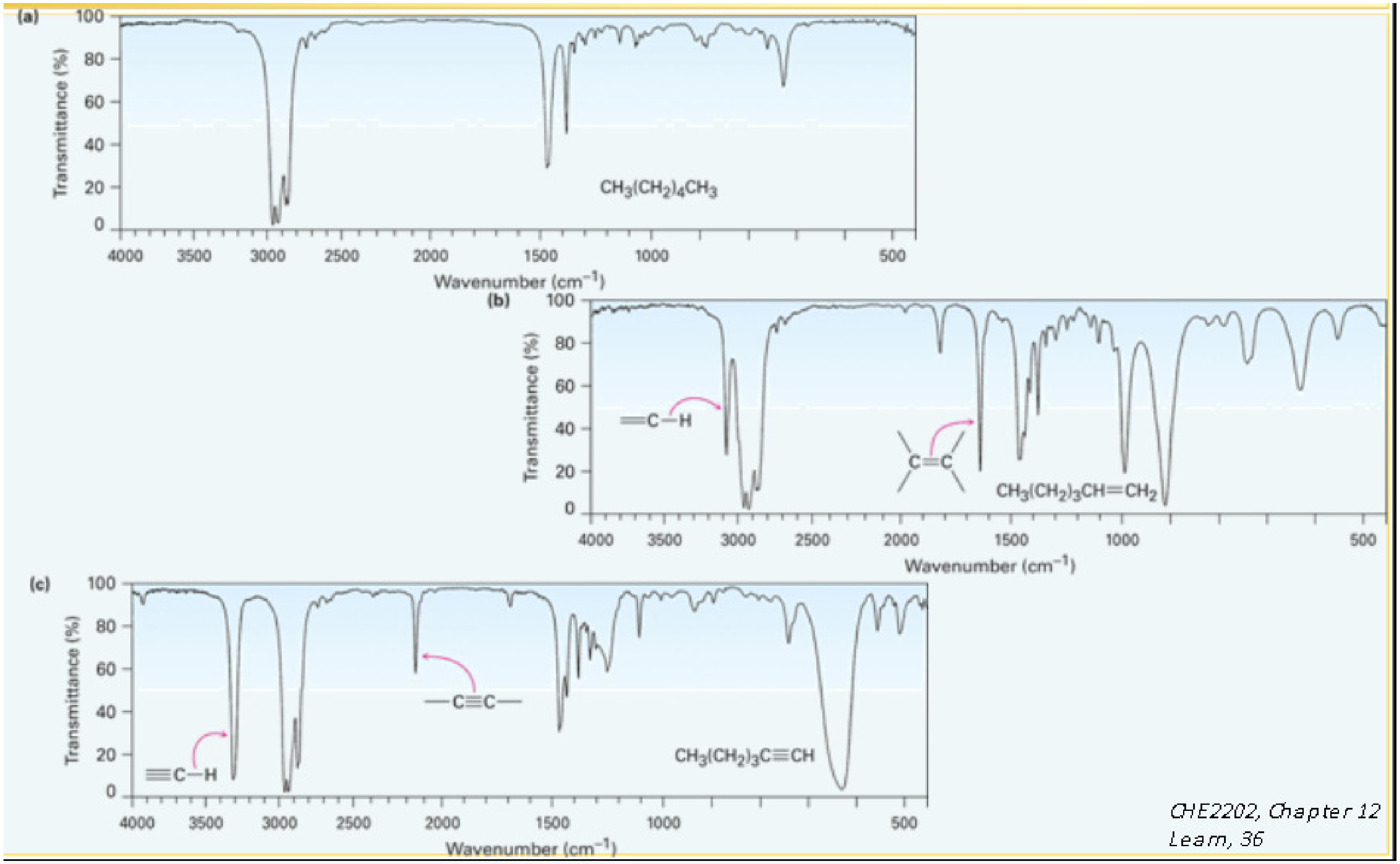


Absorption bands in IR – practical considerations

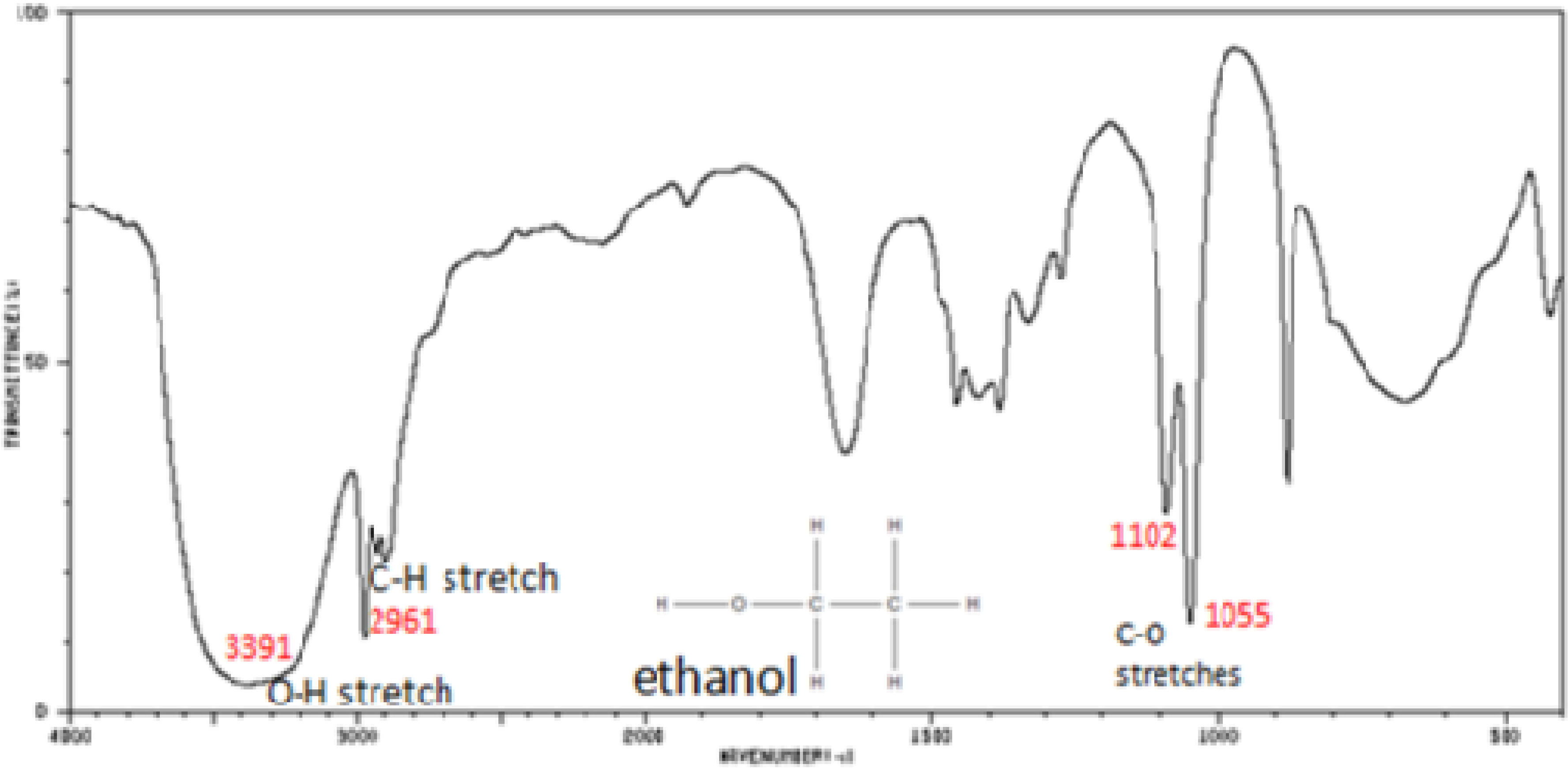
The infrared spectrum can be split to characteristic regions.
Vibrations related to single bonds with H atom come 2700-3500 cm^{-1}.
Vibrations related to triple bonds come around 2300 cm^{-1}.
Vibrations related to double bonds come around 1700 cm^{-1}.
Below 1400-1500 cm^{-1} many non-H containing bond has characteristic band, but typically overlapping. This region is called fingerprint region (very specific to a compound).



IR spectra of n-hexane, 1-hexane and 1-hexyne



IR spectrum of ethanol



IR spectra of 2-butanone and butyraldehyde