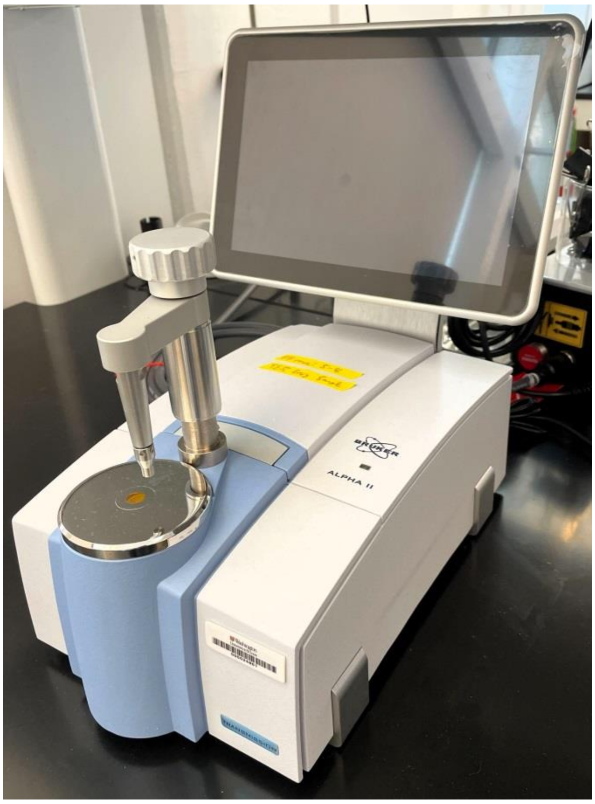
Chapter N° 3: Infrared spectroscopy (IR)

1. Introduction

The atoms that make up molecules are not fixed in place. In fact, a covalent chemical bond can be considered like a spring, capable of stretching and deforming. Thus, the positions of atoms are not fixed; they are constantly vibrating. Each pair of atoms involved in a chemical bond vibrates at its own characteristic frequency.

When such molecules are irradiated with photons (from the electromagnetic spectrum) that match the natural (fundamental) vibrational frequencies of the target molecules, some of the energy of these photons will be absorbed, resulting in an increase in the amplitude of the vibrations. In reality, the natural vibrational energy of atoms is comparable in magnitude to the energy of photons in the infrared spectrum (mid-infrared).

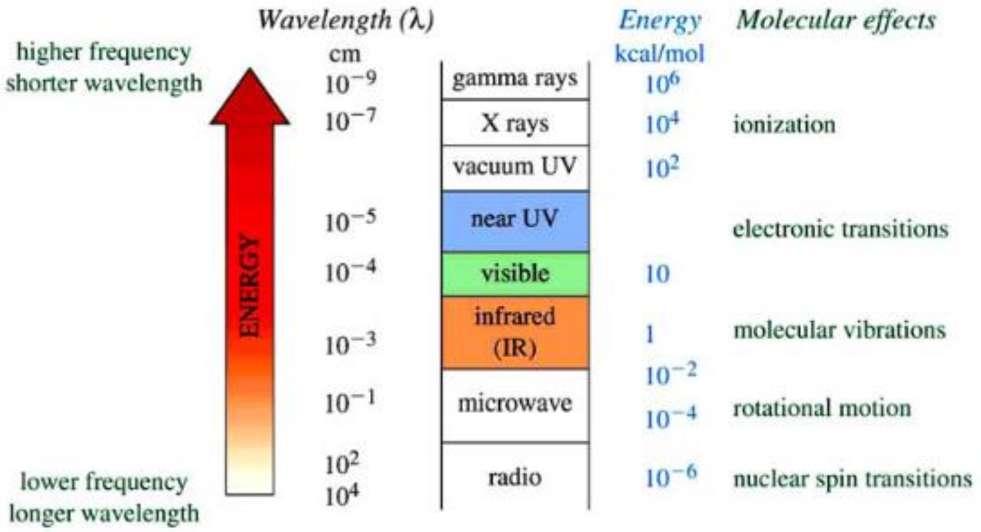
Infrared spectroscopy is a physical analytical method based on the **absorption** of low-energy **photons**, which modifies the fundamental **vibrational** energy of molecules. This technique allows the identification of organic and inorganic molecules based on their vibrational properties. Infrared radiation excites specific vibrational modes (such as stretching and bending) of chemical bonds. When the wavelength of the light beam closely matches the vibrational energy of the molecule, the molecule absorbs the radiation, leading to a reduction in the intensity of the reflected or transmitted light. This technique is ideal for confirming the presence of certain functional groups in molecules.



2. Spectral Range

Organic molecules are capable of absorbing infrared radiation in the range of **4000 cm^{-1}** to **400 cm^{-1}**, which corresponds to energy absorption between **11 kcal/mol** and **1 kcal/mol**. This amount of energy initiates transitions between vibrational states within the molecules.

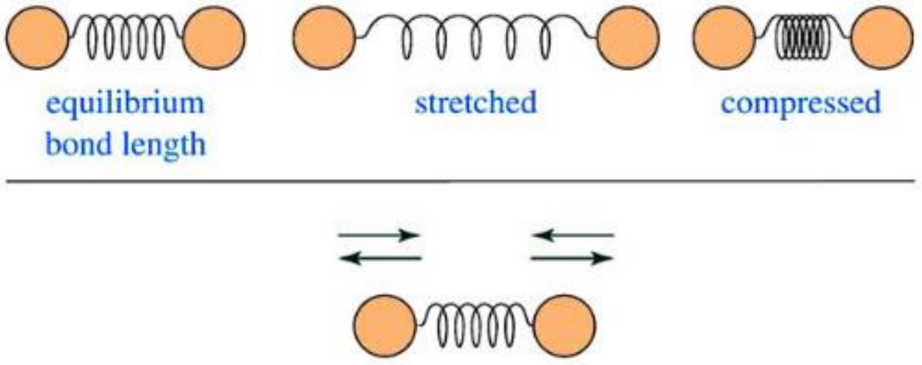
2.1. Effect of electromagnetic radiation on molecules



3. Vibration Frequency

The infrared range used in typical spectroscopic analyses lies between 400 and 4000 cm^{-1}, corresponding to energies around **30 $kJ \cdot mol^{-1}$**. Such energy is insufficient to induce electronic transitions, as observed in UV-Visible spectroscopy. Instead, this energy primarily affects molecular vibrations and rotations.

To model these vibrations and rotations, the harmonic oscillator model is employed: two masses connected by a spring.



If the two masses are displaced from their equilibrium distance re and then released, the system begins to oscillate with a period that depends on the spring constant **k** (stiffness constant, in **N·m⁻¹**) and the masses of the atoms involved.

The vibration frequency ν is given by Hooke's law:

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

Where **μ** is the reduced mass of the vibrating atoms, calculated as:

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

With **m_1**and **m_2** being the masses of the vibrating atoms.

In practice, it is convenient to use the wavenumber instead of the frequency, while retaining the relationship to the frequency:

$$\boldsymbol{\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}}$$

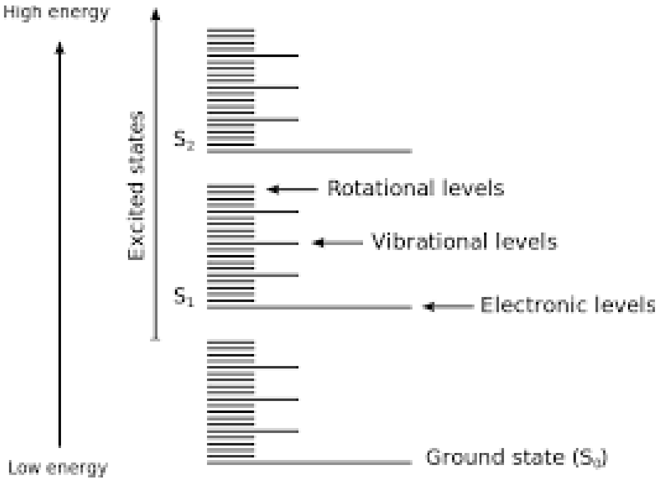
Thus:

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

4. Vibrational Energy (Vibrational Levels)

Electronic energy levels are composed of multiple vibrational levels, and each vibrational level is further divided into rotational levels. The vibrational energy is given by:

$$\mathbf{E_v = (v + \frac{1}{2})\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}}$$



Where **v** is the vibrational quantum number (v = 0, 1, 2,…).

At room temperature, most molecules are in the vibrational ground state (v = 0), meaning they vibrate at the lowest energy level allowed by quantum mechanics:

$$\mathbf{E_0} = \frac{\mathbf{1}}{\mathbf{2}}\left(\frac{\mathbf{h}}{\mathbf{2\pi}}\sqrt{\frac{\mathbf{k}}{\boldsymbol{\mu}}}\right)$$

5. VIBRATIONAL MODES

The absorption of IR radiation causes the molecule to vibrate by altering bond angles and bond lengths. Two main types of vibrations are distinguished: stretching vibrations and bending vibrations.

5.1. Stretching Vibrations

These occur when two atoms periodically move closer together or farther apart along their common axis. Two types of stretching vibrations can be observed:

Symmetric stretching: Both atoms move simultaneously toward or away from each other in a synchronized manner.

Asymmetric stretching: Atoms move in opposite directions, with one moving closer while the other moves farther apart.

Asymmetric stretching vibrations typically result in stronger absorption bands compared to symmetric stretching.

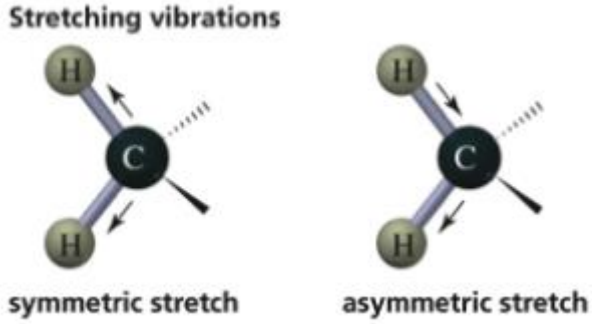
5.2. Bending Vibrations

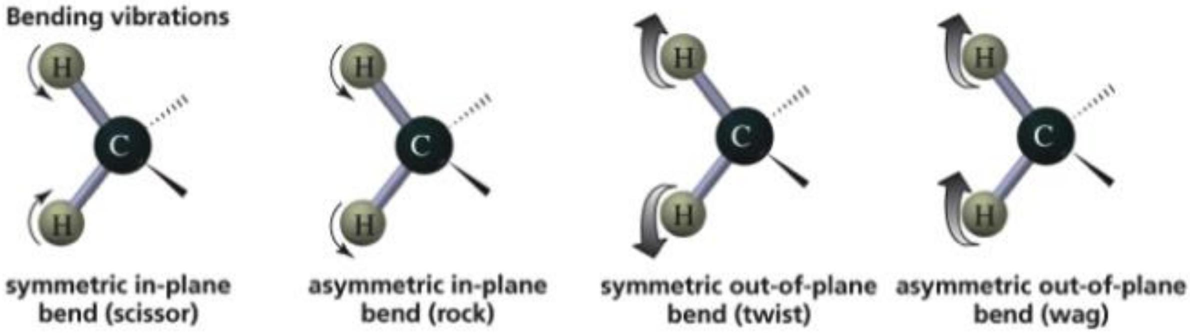
These involve changes in bond angles rather than bond lengths. Various types of bending vibrations can occur, both in-plane and out-of-plane. Bending vibrations are characterized by the following:

- Their corresponding absorption bands are less intense compared to stretching vibrations.
- They are more numerous.
- They are more sensitive to their environment (e.g., steric hindrance).

- They can occur in-plane or out-of-plane.
- They are typically observed in the region of 1600 to 600 cm^{-1}.
- They are more difficult to assign specific identifications.
- They can help determine the position of substituents (ortho, meta, or para) in aromatic compounds.

For a functional group composed of several identical bonds (involving three atoms), the following bending vibration modes can be observed.





6. Types (Modes) of Vibration

The types (or modes) of vibration depend on the degrees of freedom of the molecule. As the size of the molecule increases, the number of vibration modes also increases:

- **Diatomic molecule:** 1 stretching vibration.
- **Linear molecule:** $3n-5$ vibrational modes (e.g., CO_2).
- **Non-linear molecule:** $3n-6$ vibrational modes, where n is the number of atoms in the molecule.

Example:

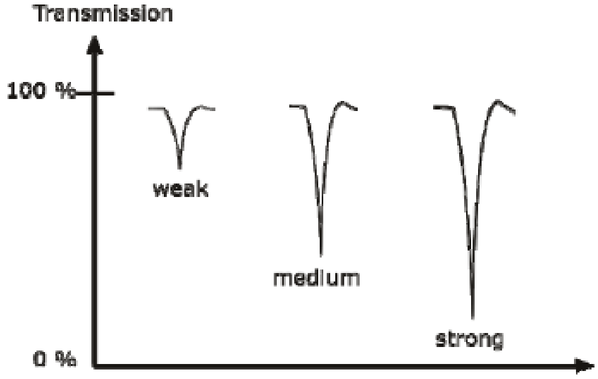
- **H_2O:**

  For water (H_2O), $3n-6 = 9 - 6 = 3$ types of vibrations:

- 1 symmetric stretching vibration.
- 1 asymmetric stretching vibration.
- 1 bending vibration.

7. Classification of IR bands

IR bands can be classified as **strong** (**s**), **medium** (**m**), or **weak** (**w**), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.

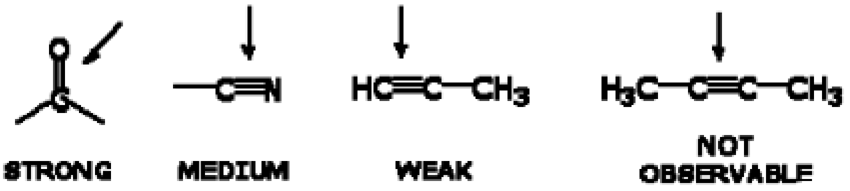


7.1. Infrared active bonds

Not all covalent bonds display bands in the IR spectrum. Only polar bonds do so. These are referred to as IR active.

The intensity of the bands depends on the magnitude of the dipole moment associated with the bond in question:

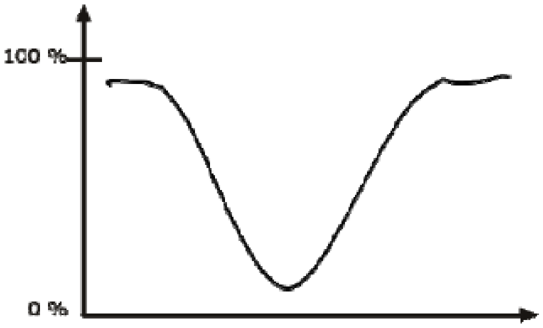
- **Strongly polar bonds** such as carbonyl groups (**C=O**) produce **strong** bands.
- **Medium polarity bonds** and asymmetric bonds produce **medium** bands.
- **Weakly polar bond** and symmetric bonds produce **weak** or non-observable bands.



7.2. Infrared bands shapes

Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are **thin** and **pointed**, like a dagger. **Broad bands** are **wide** and **smoother**.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.

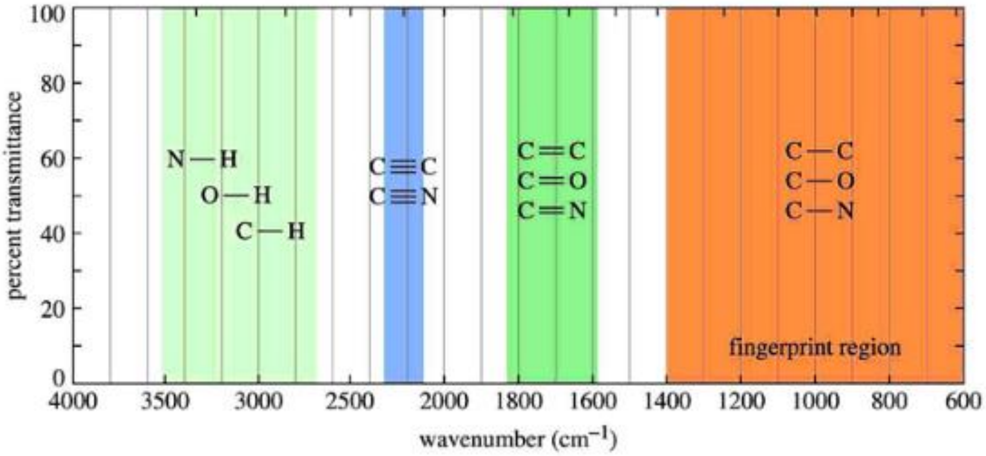


7.3. Information obtained from IR spectra

- IR is most useful in providing information about the presence or absence of specific functional groups.
- IR can provide a molecular fingerprint that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR does not provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

7.4. IR absorption range

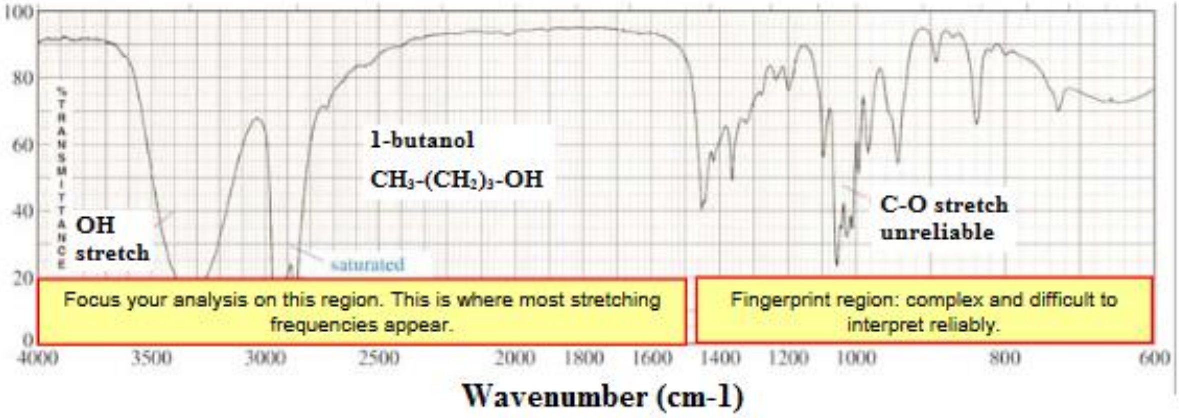
The typical IR absorption range for **covalent bonds** is **600 - 4000 cm^{-1}**. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a **sharp band** around **2200-2400 cm^{-1}** would indicate the possible presence of a **C-N** or a **C-C triple bond**.



7.5. The fingerprint region

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the fingerprint region.

This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum that is the region to the left of **1400 cm^{-1}.**



7.6. Functional groups and IR tables

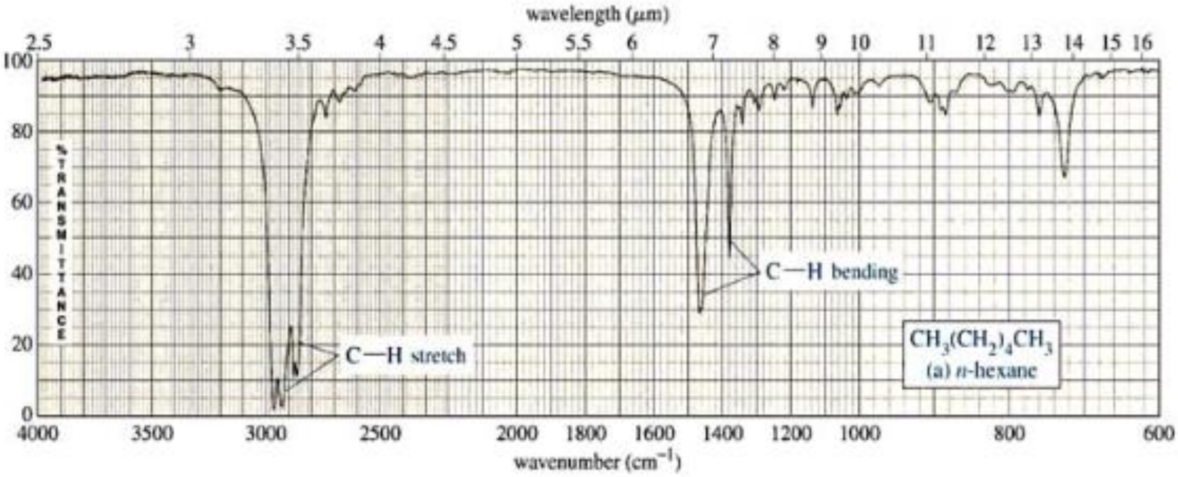
The remainder of this presentation will be focused on the IR identification of various functional groups such as alkenes, alcohols, ketones, carboxylic acids, etc. Basic knowledge of the structures and polarities of these groups is assumed.

$\bar{\nu}$ (cm^{-1})	**Structure**	**$\bar{\nu}$ (cm^{-1})**	**Structure**
1050-1400	C-O (ether, alcool et ester	**2700-2800**	H-C=O (C-H du l'aldéhyde)
1150-1360	SO_2 (dérivé sulfoniques)	**2500-3000**	O-H (acide carboxylique)
1315-1475	C-H (alcanes, vibration de déformation)	**3000-3100**	C-H (fait partie d'un cycle aromatique
1340-1500	NO_2 (dérivés nitrés)	**3300**	C-H (fait partie d'un acétylène $H-C\equiv C$
1450-1600	C=C (cycle aromatiques)	**3020-3080**	C-H (fait partie d'un acétylène $H-C=C$
1620-1680	C=C (alcènes insaturés)	**2800-3000**	C-H (alcanes)
1630-1690	C=O (amides)	**3300-3500**	N-H (amides et amines)
1690-1750	C=O (aldéhyde cétone et ester)	**3200-3600**	O-H (R-OH et Ar-OH avec liaisons hydrogènes)
1700-1725	C=O (acide carboxylique)	**2100**	O-D (composés deutérés)
1770-1820	C=O (Chlorure d'acide)	**690-710**	C-H (monosubstitution)
2100-2200	$C\equiv C$ (alcynes)	**735-770**	Ortho (di substitution)
2210-2260	$C\equiv N\ (Nitriles)$	**780-810**	Méta (di substitution))
2500	S-H (thiol)	**810-840**	Para (di substitution)

8. IR Spectrum

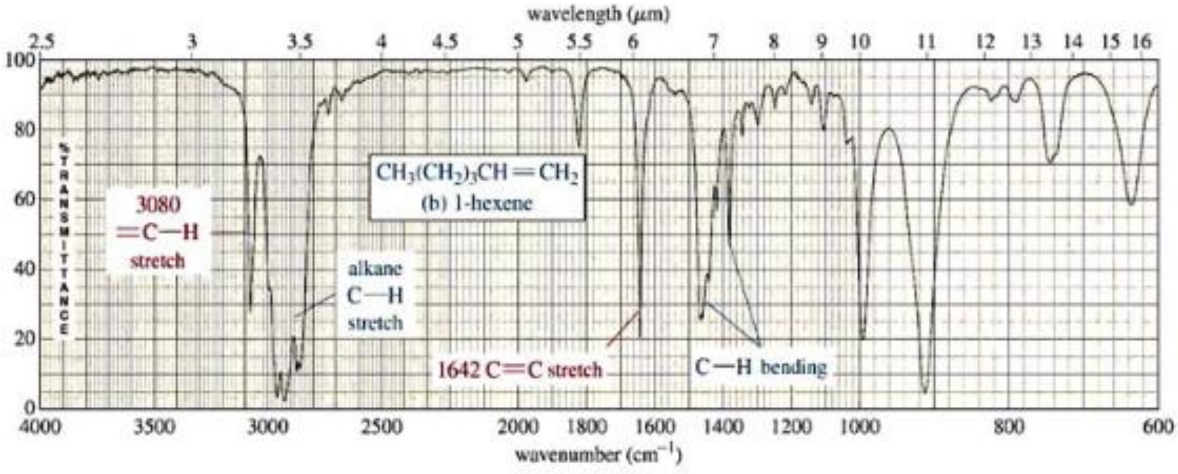
8.1. Alkanes

Alkanes have no functional groups. Their **IR** spectrum displays only **C-C** and **C-H** bond vibrations. Of these the most useful are the **C-H** bands, which appear around **2800-3000 cm^{-1}**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.

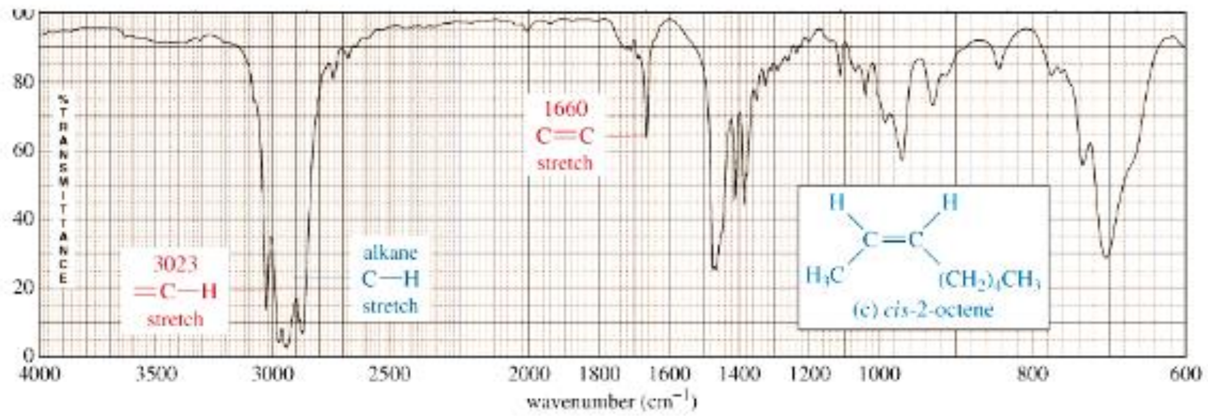


8.2. Alkenes

Besides the presence of **C-H** bonds, alkenes also show sharp, medium bands corresponding to the **C=C** bond stretching vibration at about **1600-1700 cm^{-1}**. Some alkenes might also show a band for the **=C-H** bond stretch, appearing around **3080 cm^{-1}** as shown below. However, this band could be obscured by the broader bands appearing around **3000 cm^{-1}**.



This spectrum shows that the band appearing around **3080 cm^{-1}** can be obscured by the broader bands appearing around **3000 cm^{-1}**.



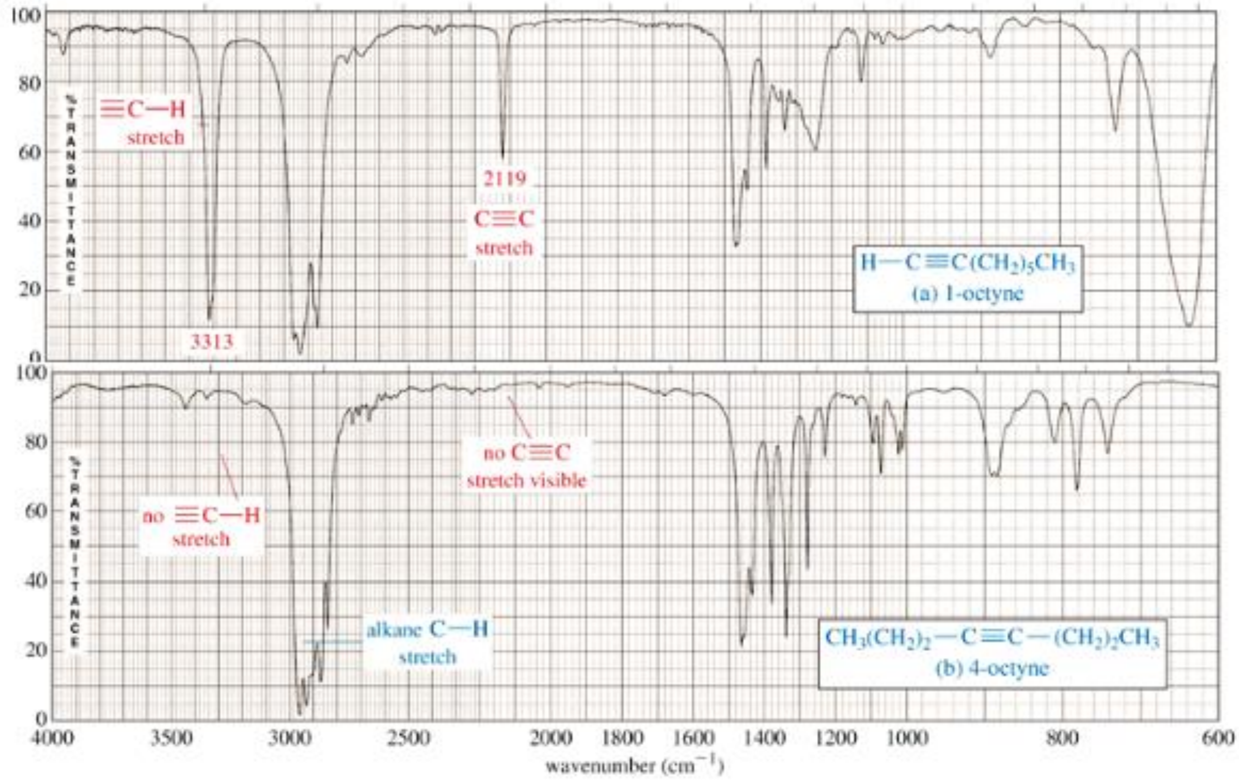
8.3. Alkynes

The most prominent band in alkynes corresponds to the **carbon-carbon triple bond**. It shows as a **sharp**, **weak** band at about **2100 cm^{-1}**. The reason it's weak is because the triple bond is not very polar. In some cases, such as in highly symmetrical alkynes, it may not show at all due to the low polarity of the triple bond associated with those alkynes.

Terminal alkynes, that is to say those where the triple bond is at the **end** of a carbon chain, have C-H bonds involving the **sp carbon** (the carbon that forms part of the triple bond). Therefore they may also show a sharp, weak band at about **3300 cm^{-1}** corresponding to the **C-H stretch**.

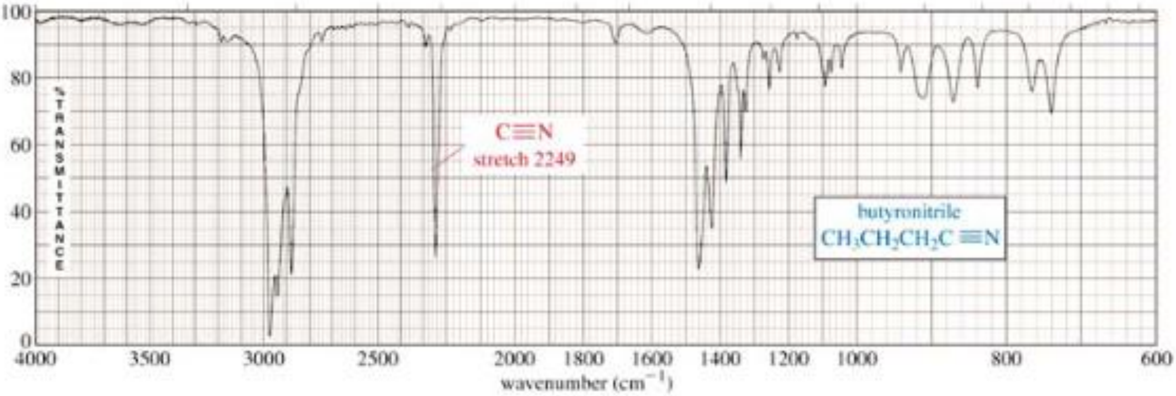
Internal alkynes, that are those where the triple bond is in the **middle** of a carbon chain, do not have C-H bonds to the sp carbon and therefore lack the aforementioned band.

In the following spectrum shows a comparison between an unsymmetrical terminal alkyne (**1-octyne**) and a symmetrical internal alkyne (**4-octyne**).



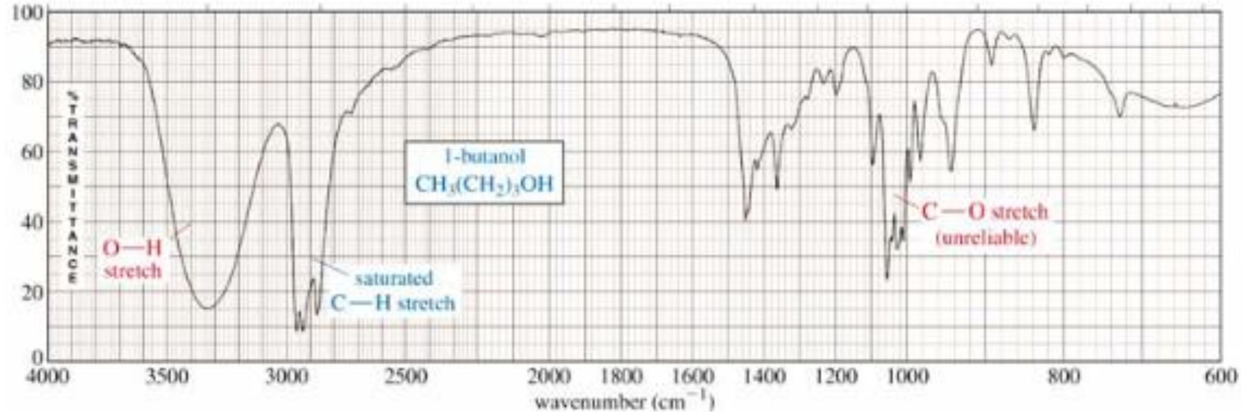
8.4. Nitrile

In a manner very **similar to alkynes**, **nitriles** show a prominent band around **2250 cm^{-1}** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne **C-C** triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



8.5. Alcohol

The most prominent band in alcohols is due to the **O-H** bond, and it appears as a **strong**, **broad band** covering the range of about **3200 - 3600 cm^{-1}**. The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.



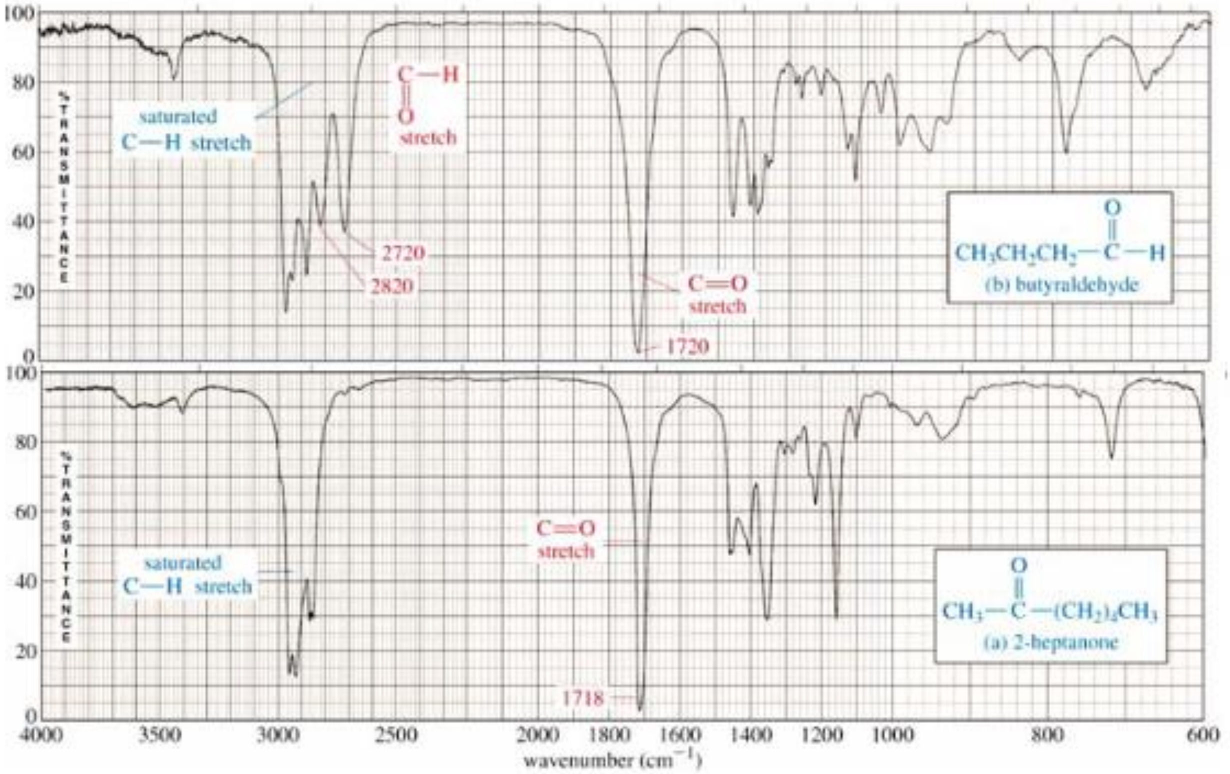
8.6. Aldehyde and ketone

Carbonyl compounds are those that contain the **C=O** functional group. In aldehydes, this group is at the **end** of a carbon chain, whereas in ketones it's in the **middle** of the **chain**. As a result, the carbon in the **C=O** bond of **aldehydes** is also bonded to another **carbon** and a **hydrogen**, whereas the same carbon in a **ketone** is bonded to **two** other **carbons**.

Aldehydes and ketones show a **strong**, prominent, stake-shaped band around **1710-1720 cm^{-1}** (right in the middle of the spectrum). This band is due to the highly **polar C=O** bond. Because of its position, shape, and size, it is hard to miss.

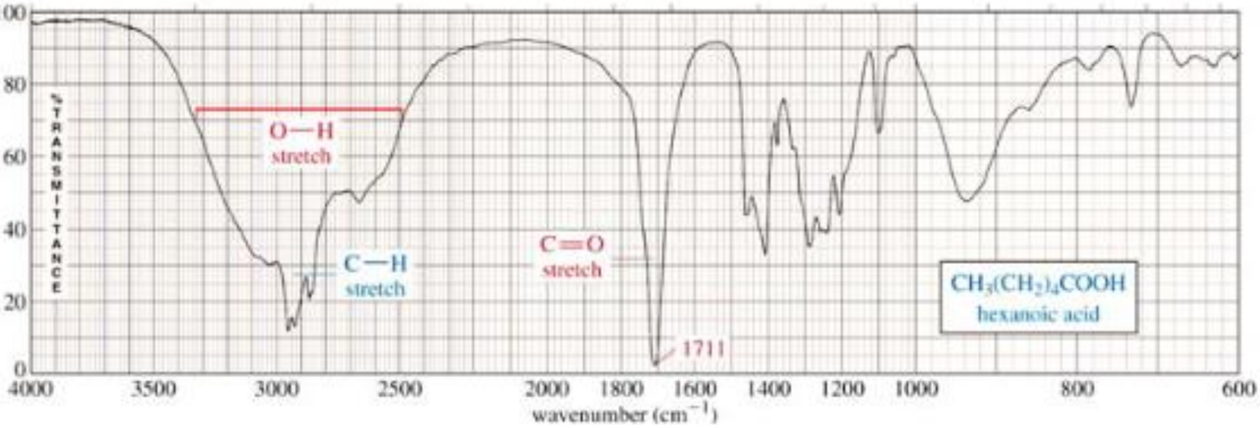
Because **aldehydes** also contain a **C-H bond** to the **sp2** carbon of the **C=O** bond, they also show a pair of **medium strength** bands positioned about **2700** and **2800 cm^{-1}**. These bands are missing in the spectrum of a ketone because the **sp2** carbon of the ketone lacks the **C-H** bond.

The following spectrum of an aldehyde and a ketone, study the similarities and the differences so that you can distinguish between the two:



8.7. Carboxylic acid

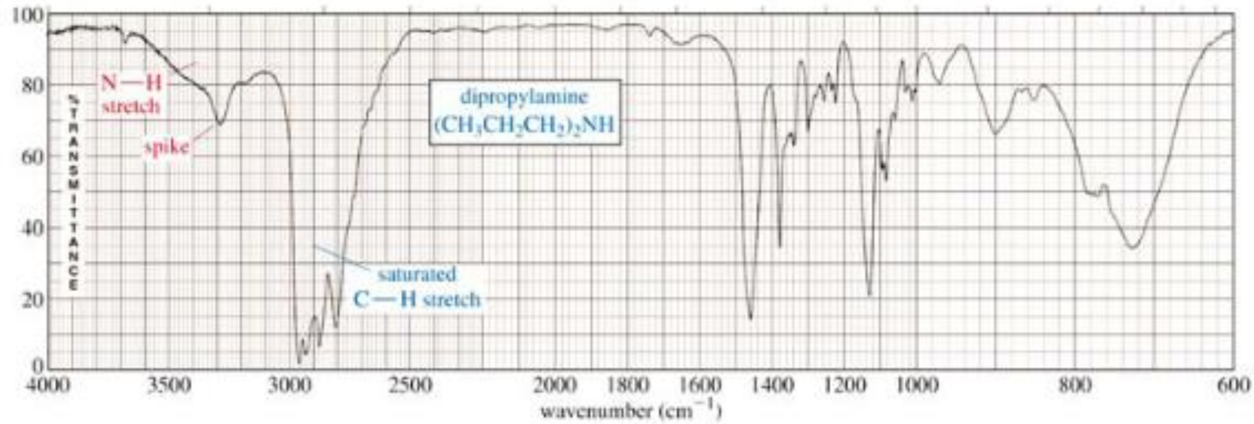
A **carboxylic acid** functional group combines the features of **alcohols** and **ketones** because it has both the **O-H** bond and the **C=O** bond. Therefore carboxylic acids show a **very strong** and **broad band** covering a wide range between **2800** and **3500 cm^{-1}** for the **O-H** stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1700-1725 cm^{-1}** corresponding to the **C=O** stretch.



8.8. Amine

The most characteristic band in **amines** is due to the **N-H** bond stretch, and it appears as a **weak** to **medium**, somewhat broad band (but not as broad as the O-H band of alcohols). This band is positioned at the **left** end of the spectrum, in the range of about **3200 - 3600 cm^{-1}**.

Primary amines have **two N-H** bonds; therefore they typically show **two spikes** that make this band resemble a molar tooth. **Secondary amines** have **only one N-H** bond, which makes them show only **one spike**, resembling a canine tooth. Finally, **tertiary amines** have no **N-H** bonds, and therefore this band is **absent** from the IR spectrum altogether. The spectrum below shows a secondary amine.



9. SPECTRAL ANALYSIS METHOD

The analysis process typically follows these steps:

- Determine the degree of unsaturation of the molecule.
- Examine the spectrum, starting with the highest wavenumbers.
- Identify the most characteristic bands using reference tables.
- Note the absence of bands in characteristic regions.
- Avoid attempting to interpret all the bands, especially in the fingerprint region (< 1400 $\mathrm{cm^{-1}}$).

9.1. Calculation of the Degree of Unsaturation:

The degree of unsaturation for a molecule is given by the formula:

$$\boldsymbol{i} = \frac{\mathbf{2n_c - n_H + n_N - n_X + 2}}{\mathbf{2}}$$

Where:

$\mathbf{n_C}$: number of carbon atoms,

$\mathbf{n_H}$: number of hydrogen atoms,

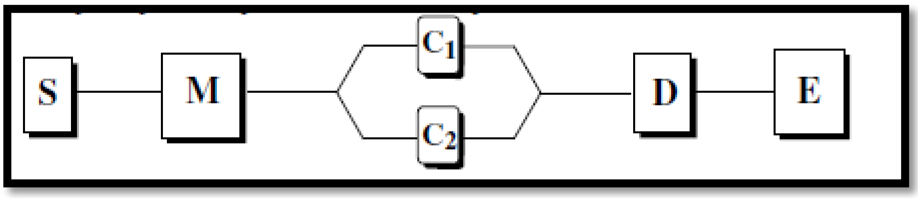
$\mathbf{n_N}$: number of nitrogen atoms (or other trivalent elements like phosphorus),

$\mathbf{n_O}$: number of oxygen atoms (or other divalent elements like sulfur),

$\mathbf{n_X}$: number of halogen atoms.

10. Equipment

The basic schematic of an IR spectrometer is as follows:



- **S (Source):** The source can be a **Globar** (a silicon carbide rod heated to approximately 1300 °C, with maximum energy around 5300 cm^{-1}) or a **Nernst** filament (a mixture of zirconium, yttrium, and thorium oxides in a thin tube heated to 1900 °C, with maximum energy around 7100 cm^{-1}).
- **M (Monochromator):** A prism or grating used to separate wavelengths.

C_1 and C_2 (Cells): Reference and sample cells, respectively, made from materials transparent to IR radiation (e.g., **NaCl** or **KBr**).

D (Detector): Converts radiant energy into thermal or electrical energy.

E (Recording System): Captures and records the spectrum.

10.1. SAMPLE PRESENTATION

It is possible to analyze solid, liquid, or gaseous samples.

10.1.1. Solids

Solids can be dissolved in a solvent or mixed with anhydrous potassium bromide (KBr). The resulting powder is then subjected to high pressure using a press to form a pellet. Alternatively, the solid can be suspended in liquid paraffin (e.g., nujol).

Typically, pellets are made by mixing 0.2% to 2% of the sample (in powder form) with **KBr**, which is transparent to IR radiation between **4000 cm^{-1}** and **700 cm^{-1}.** The mixture is finely ground in a mortar to ensure homogeneity before being pressed into a mold.

10.1.2. Liquids

Liquids can be analyzed in pure form or in solution.

For pure liquids, the cells used have thicknesses ranging from **0.005 mm** to **0.1 mm**, while for solutions; the thickness is between **0.1 mm** and **1 mm**.

Low-viscosity, volatile liquids are introduced into a closed cell with a determined thickness, whereas high-viscosity, low-volatility liquids are placed between two KBr or NaCl plates.

10.1.3. Gases

Gases are introduced into a larger cell than those used for liquids.

10.2. CHOICE OF SOLVENTS

In IR techniques, it is essential to use rigorously **anhydrous solvents**. Water should be avoided as it can dissolve the cells, which are made of alkali halides such as **NaCl** or **KCl**.

Additionally, the solvents used should have the simplest possible structure to minimize interference with the identification of the analyte. Commonly used solvents include chloroform, carbon tetrachloride (CCl_4), and carbon disulfide (CS_2).