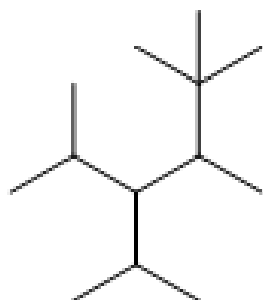
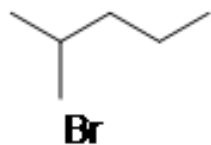


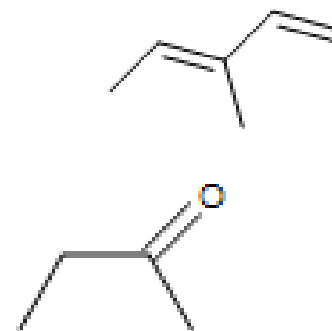
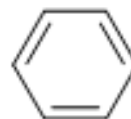
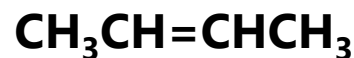
# Como interpretar um espectro de Infravermelho?

**Passo zero: Calcular o grau de insaturação da molécula (se souber a fórmula molecular)**

## Moléculas saturadas



## Moléculas insaturadas



$$GI = \frac{2C + 2 + N - H - X}{2}$$

C, N, H, X nº de átomos de C, N, H e X (halogéneo), respetivamente

# Como interpretar um espectro de Infravermelho?

## Exemplos:

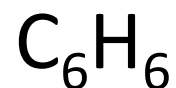
Moléculas saturadas



$$GI = \frac{2*3+2+0-8-0}{2} = 0$$

Não existem ligações duplas nem anéis

Moléculas insaturadas



$$GI = \frac{2*6+2+0-6-0}{2} = 4$$

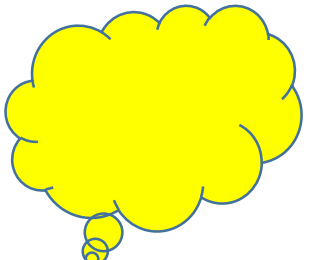
Existem 3 ligações duplas e um anel.

$$GI = \frac{2C + 2 + N - H - X}{2}$$

C, N, H, X nº de átomos de C, N, H e X (halogéneo), respetivamente

# Como interpretar um espectro de Infravermelho?

## Passo 1 – Observar as diferenças



**OBSERVATION**

PUDDLES AND WORMS...

IT MUST HAVE RAINED.

**INFERENCE**

**OBSERVATION**

AN IR BAND OF THIS SIZE AND SHAPE...

PROBABLY THAT FUNCTIONAL GROUP.

**INFERENCE**

ALL IR BANDS ARE EQUAL, BUT SOME ARE MORE EQUAL THAN OTHERS.

# Passo 2 – Observar as frequências de grupos mas por ordem de *poder interpretativo*

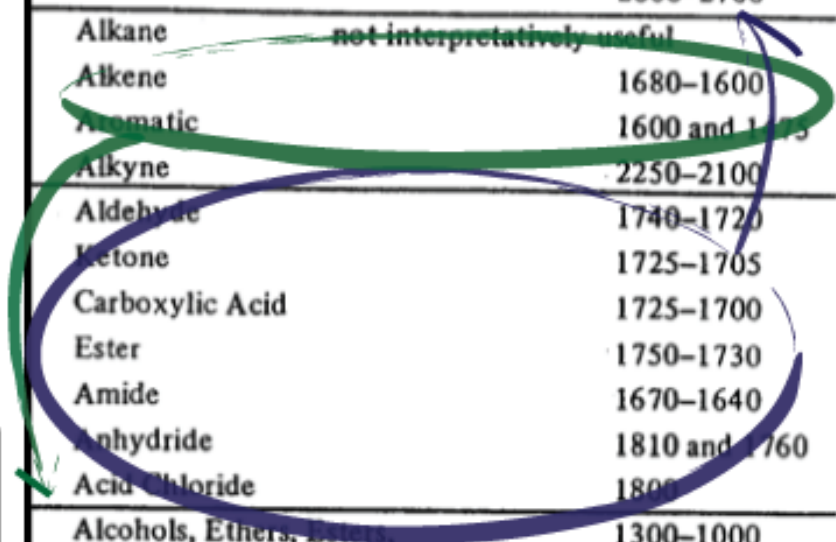


Alkyne (stretch)	ca. 3300	ca. 3.4
Aldehyde	2900–2800	3.45
	2800–2700	3.57
Alkane	not interpretatively useful	
Alkene	1680–1600	5.95
Aromatic	1600 and 1475	6.25
Alkyne	2250–2100	4.44
Aldehyde	1740–1720	5.75
Ketone	1725–1705	5.80
Carboxylic Acid	1725–1700	5.80
Ester	1750–1730	5.71
Amide	1670–1640	6.00
Anhydride	1810 and 1760	5.52
Acid Chloride	1800	5.56
Alcohols, Ethers, Esters, Carboxylic Acids, Anhydrides	1300–1000	7.69

INSTEAD, LET'S ARRANGE THEM BY THEIR **INTERPRETIVE POWER.**

Alkyne (stretch)	ca. 3300
Aldehyde	2900–2800
	2800–2700
Alkane	not interpretatively useful
Alkene	1680–1600
Aromatic	1600 and 1475
Alkyne	2250–2100
Aldehyde	1740–1720
Ketone	1725–1705
Carboxylic Acid	1725–1700
Ester	1750–1730
Amide	1670–1640
Anhydride	1810 and 1760
Acid Chloride	1800
Alcohols, Ethers, Esters, Carboxylic Acids, Anhydrides	1300–1000
Alcohols, Phenols	

MOVING DOWN THE CHART ONE AT A TIME, MATCHING BANDS AS YOU GO, IS NOT A USEFUL STRATEGY.



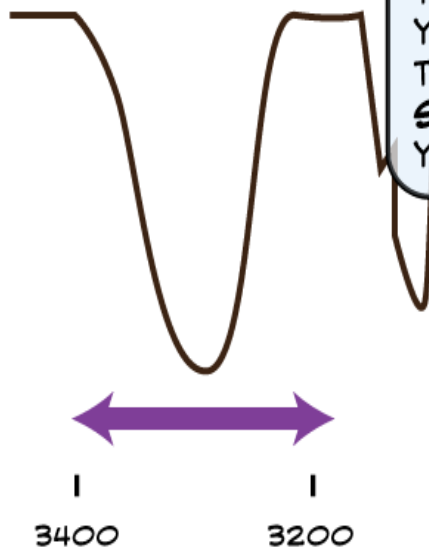
# Passo 3– Observar *as formas das bandas* ( $3400\text{ cm}^{-1}$ a $3200\text{ cm}^{-1}$ )

Zona chave

Forma das bandas

THIS IS THE FIRST REGION YOU SHOULD LOOK AT, AND THERE ARE 4 DIFFERENT **SHAPES** OF BANDS THAT YOU MAY SEE HERE.

...AND IF YOU DON'T SEE ANY BAND HERE, YOU MOST LIKELY DON'T HAVE ANY OF THESE FUNCTIONAL GROUPS (FG)



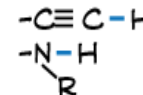
A SMOOTH TONGUE MEANS AN **ALCOHOL**.



VAMPIRE FANGS MEANS A **PRIMARY AMINE**...



ONE KNOCK-OUT FANG MEANS A **2° AMINE**, OR A **TERMINAL ALKYNE**.



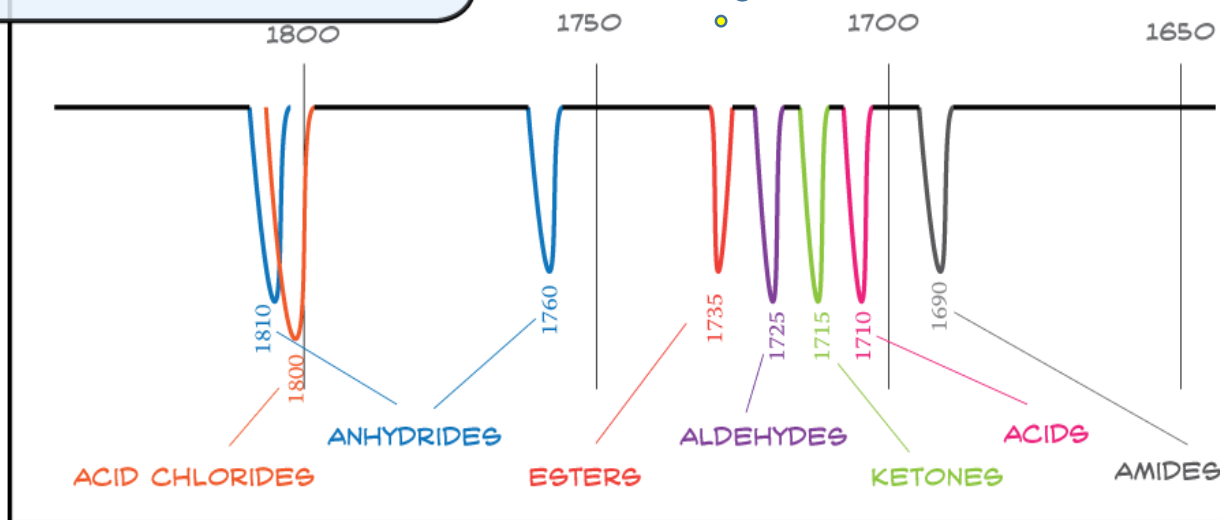
HAIRY BEARD IS A SIGN FOR A **CARBOXYLIC ACID**.



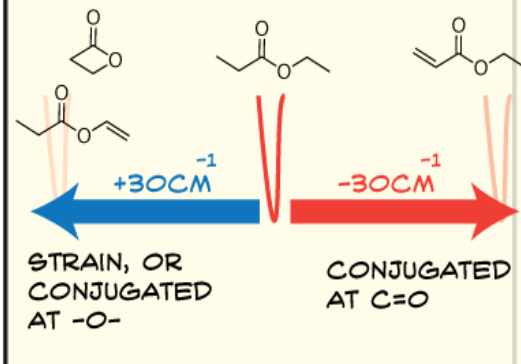
# Passo 4 – Observar algumas localizações exatas para cada grupo funcional

Localizações exatas

IN THE C=O REGION, IT'S NOT THE SHAPE, BUT THE EXACT **LOCATION** THAT REVEALS THE IDENTITY OF THE FG.



NOTE THAT THE EXACT POSITION DEPENDS ON THE SURROUNDING ENVIRONMENT:



# C=O

## Passo 4 – Observar algumas localizações exatas

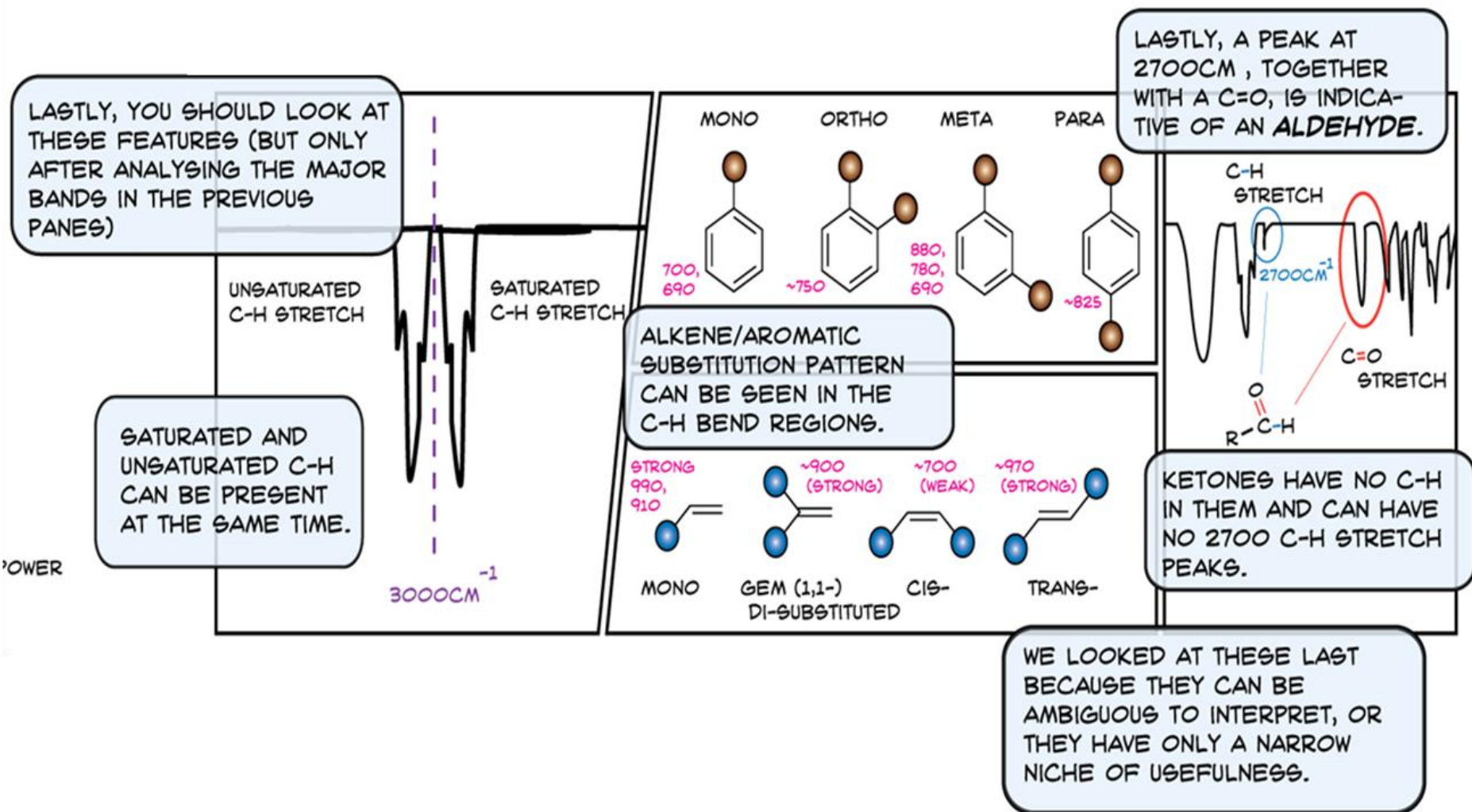
AT  $\sim 2200\text{CM}^{-1}$ , WE  
FIND **TRIPLE**  
**BONDS:**  
 $\text{C}\equiv\text{C}$ , AND  
 $\text{C}\equiv\text{N}$



USUALLY SHARP  
(CAN BE  
SMALLISH)

HINT: USE  $3300\text{CM}^{-1}$  TO  
DISTINGUISH TERMINAL  
AND INTERNAL ALKYNES.

# Passo 5 – Observar algumas localizações exatas



Usar as tabelas com as frequências de grupo à disposição

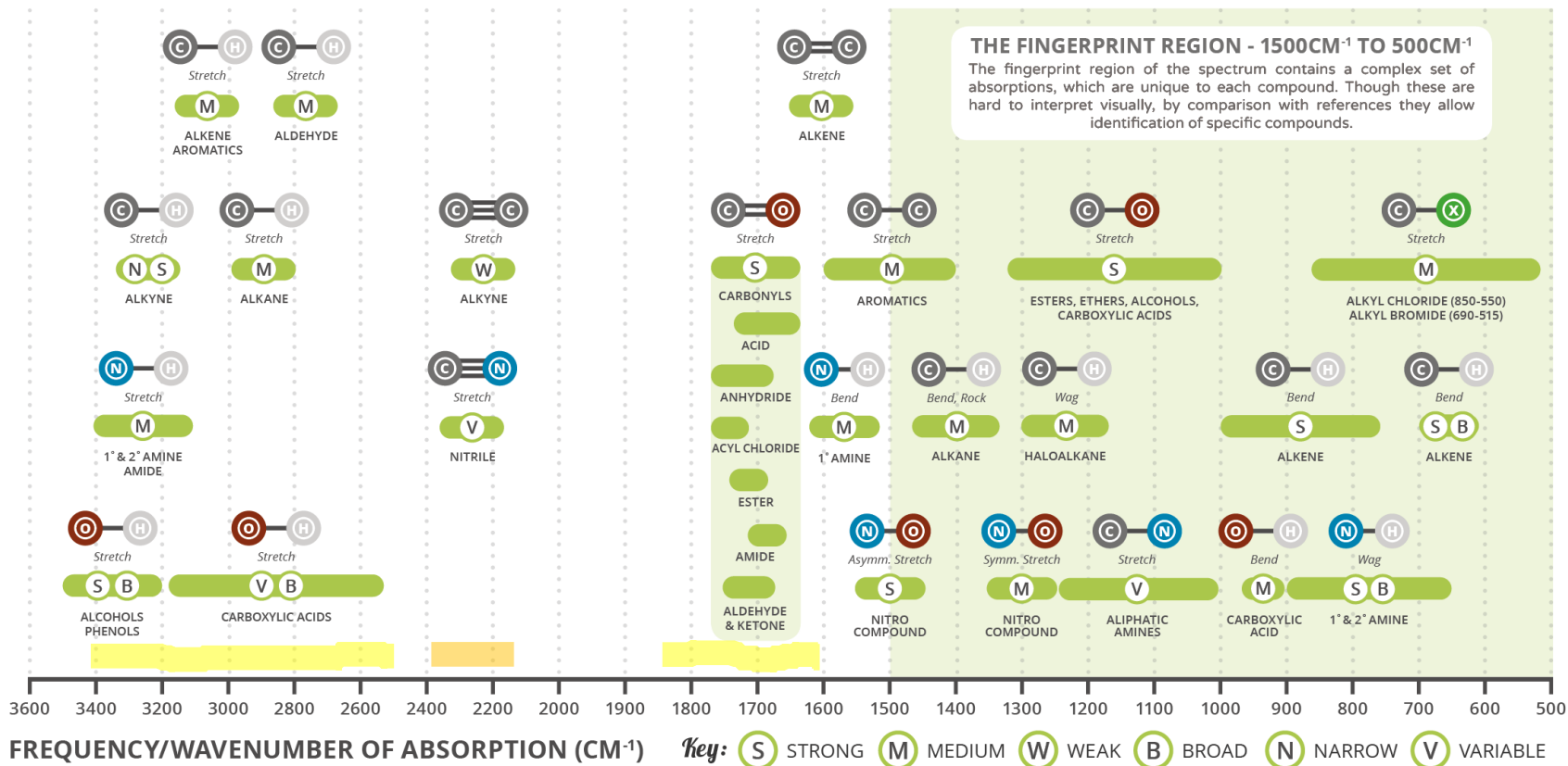


## Algumas considerações importantes:

- i) As frequências de estiramento são mais elevadas do que as correspondentes de deformação angular (é mais fácil deformer uma ligação do que alongar ou comprimir a mesma).
  
- ii) Ligações de um átomo ao hidrogénio apresentam maiores valores de frequência de estiramento do que as mesmas ligadas a átomos mais pesados.
  
- iii) Ligações triplas apresentam maiores frequências de estiramento do que as duplas e estas maiores do que as ligações simples (except para ligações com o hidrogénio).

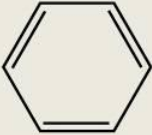
# ANALYTICAL CHEMISTRY - INFRARED SPECTROSCOPY

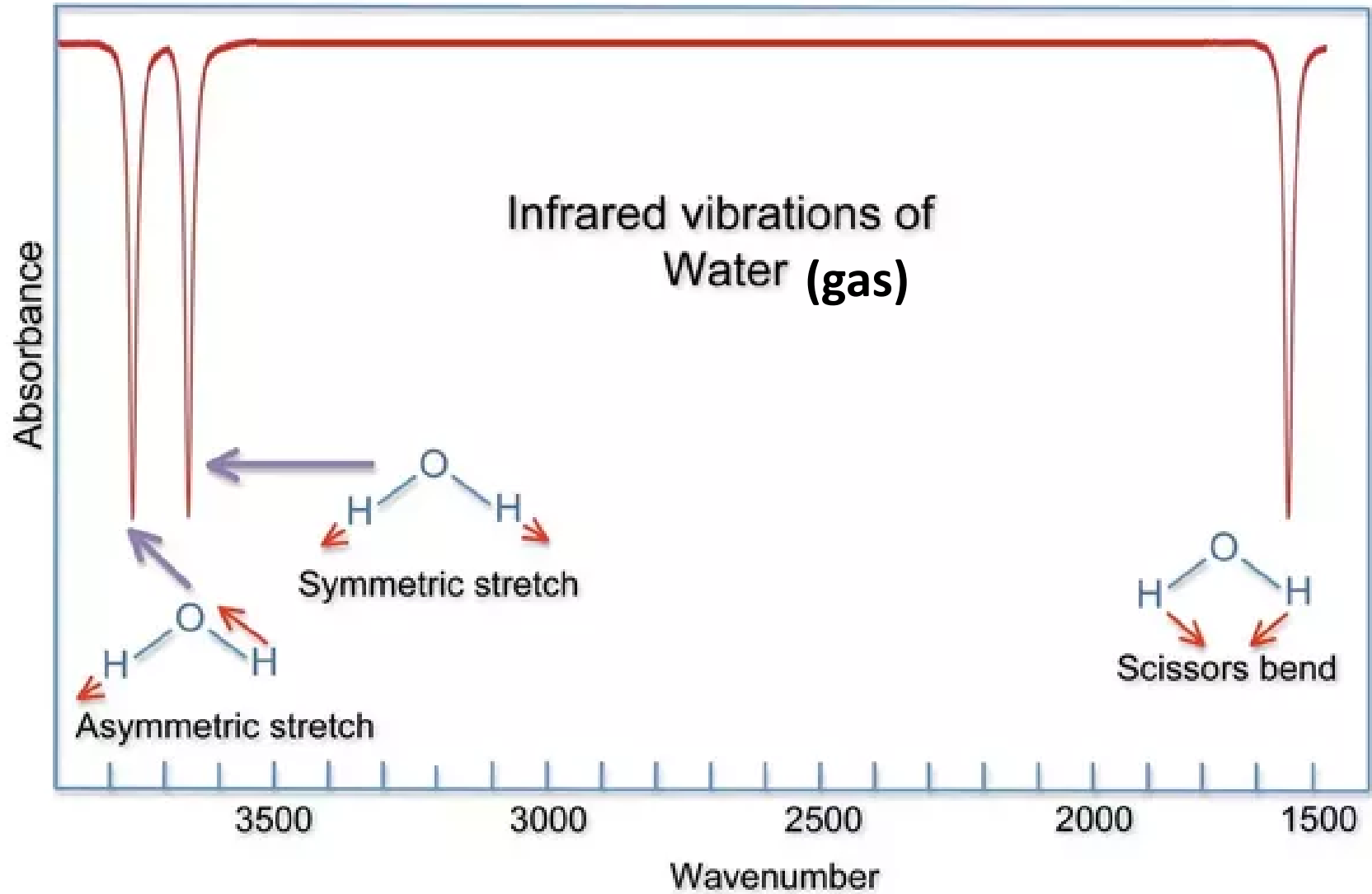
Commonly referred to as IR spectroscopy, this technique allows chemists to identify characteristic groups of atoms (functional groups) present in molecules.



Infrared frequencies make up a portion of the electromagnetic spectrum. If a range of infrared frequencies are shone through an organic compound, some of the frequencies are absorbed by the chemical bonds within the compound. Different chemical bonds absorb different frequencies of infrared radiation. There are a number of characteristic absorptions which allow functional groups (the parts of a compound which give it its particular reactivity) to be identified. This graphic shows a number of these absorptions.

**Table 13.4** Important IR Stretching Frequencies

Type of bond	Wavenumber (cm <sup>-1</sup> )	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium



# ***Branco* (Background) num espectro de FT-IR (transformada de Fourier de Infravermelho) E as moléculas de O<sub>2</sub>???**

**São inativas no IV, não há variação do momento dipolar!  
As moléculas diatómicas homonucleares não absorvem no IV**

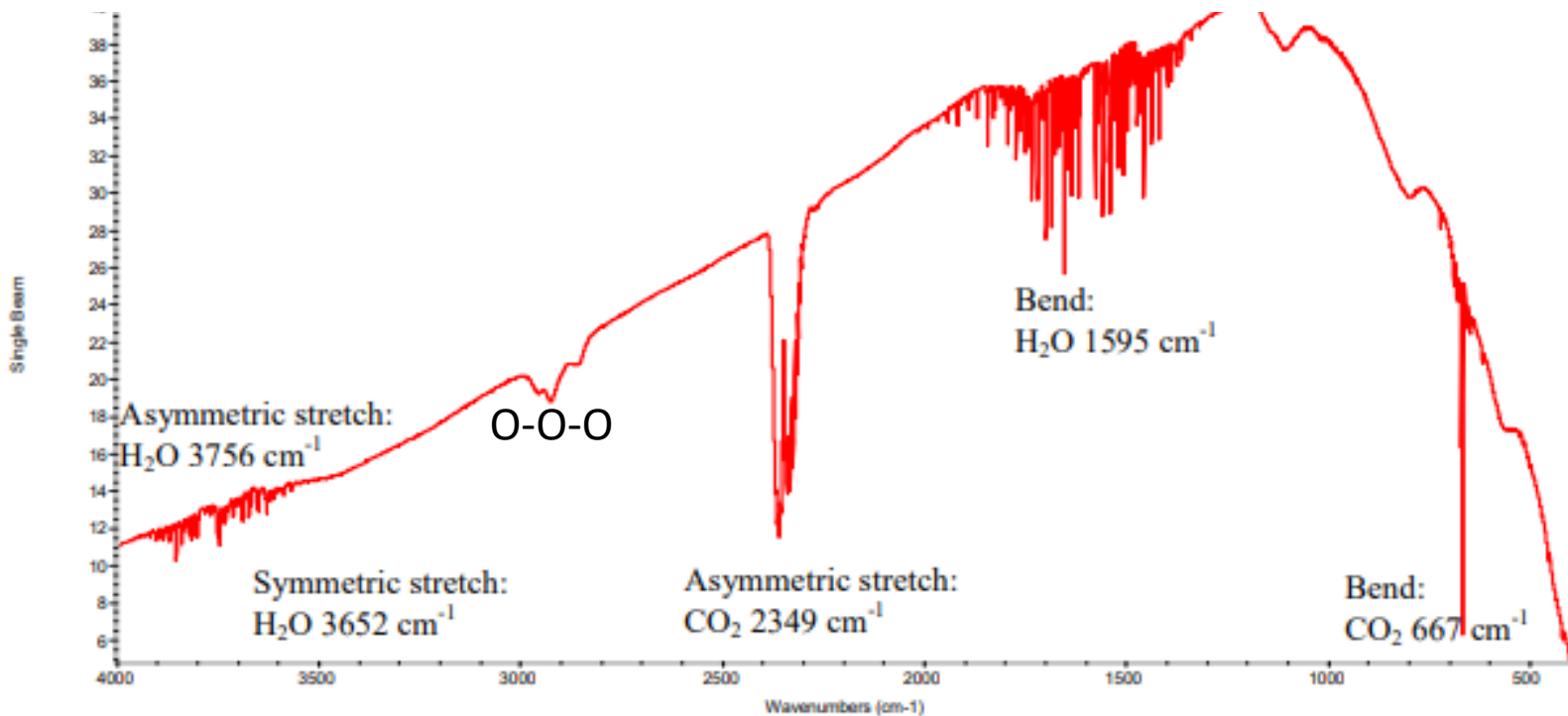
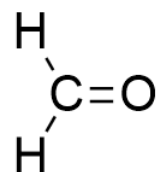


Figure 2. The Infrared spectrum of air. This spectrum is the background scan from an FT-IR spectrometer.

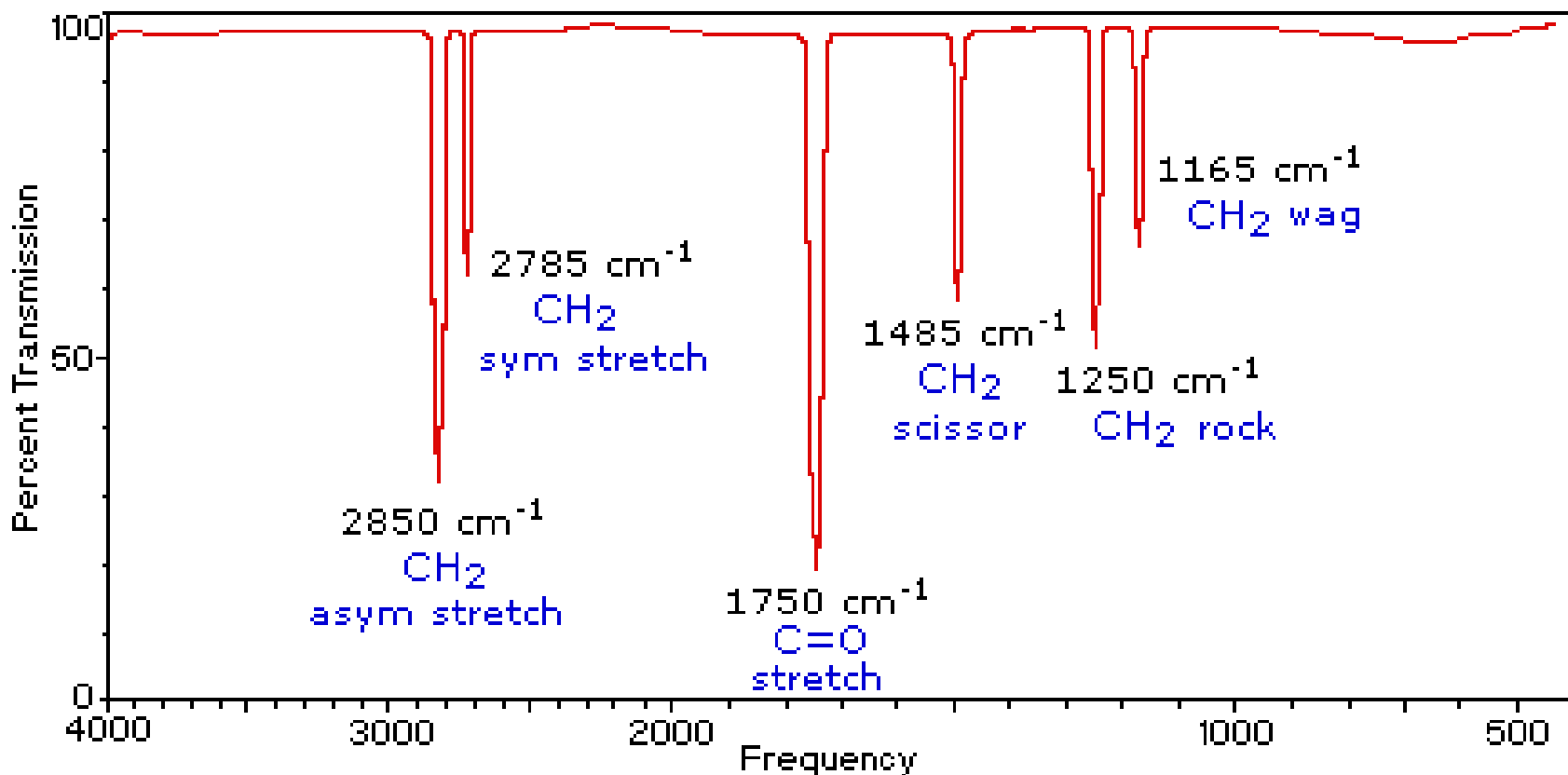
# Análise Estrutural IV – Análise Qualitativa

Frequências de grupo estão associadas a certos grupos funcionais

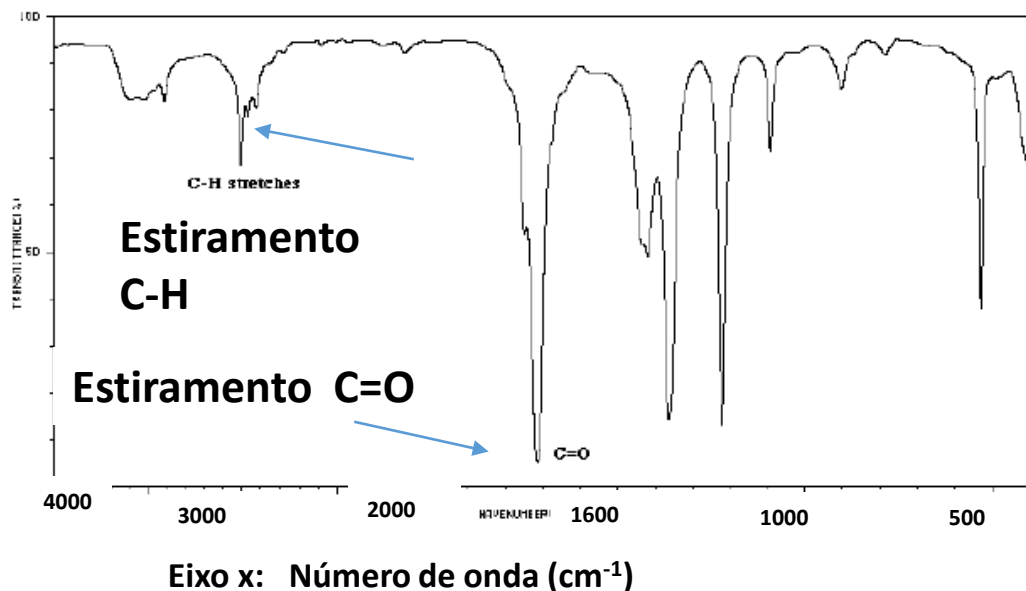


$$\text{MNV} = 3N - 3 - 3 = 12 - 6 = 6$$

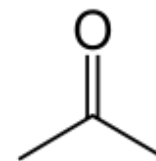
## Gas Phase Infrared Spectrum of Formaldehyde, $\text{H}_2\text{C}=\text{O}$



# Espectros infravermelho: Intensidade da banda



acetona



**Polaridade das ligações e a intensidade das bandas:**

**C-H : (eletronegatividade,  $\Delta EN = 0,4$  )**

**C=O : (eletronegatividade,  $\Delta EN = 1,0$ )**

**>  $\Delta EN \Rightarrow$  > intensidade da banda**

## Table of IR Absorptions

<i>Functional Group</i>	<i>Characteristic Absorption(s)</i> ( $\text{cm}^{-1}$ )	<i>Notes</i>
Alkyl C-H Stretch	2950 - 2850 (m or s)	Alkane C-H bonds are fairly ubiquitous and therefore usually less useful in determining structure.
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)	Absorption peaks above $3000 \text{ cm}^{-1}$ are frequently diagnostic of unsaturation
Alkynyl C-H Stretch Alkynyl C $\equiv$ C Stretch	~3300 (s) 2260 - 2100 (v)	
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)	
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)	See " <a href="#">Free vs. Hydrogen-Bonded Hydroxyl Groups</a> " in the <a href="#">Introduction to IR Spectra</a> for more information
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)	
Amine N-H Stretch	3500 - 3300 (m)	Primary amines produce two N-H stretch absorptions, secondary amides only one, and tertiary none.
Nitrile C $\equiv$ N Stretch	2260 - 2220 (m)	
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)	The carbonyl stretching absorption is one of the strongest IR absorptions, and is very useful in structure determination as one can determine both the number of carbonyl groups (assuming peaks do not overlap) but also an estimation of which types.
Amide N-H Stretch	3700 - 3500 (m)	As with amines, an amide produces zero to two N-H absorptions depending on its type.

*All figures are for the typical case only -- signal positions and intensities may vary depending on the particular bond environment.*

<https://webspectra.chem.ucla.edu//irtable.html>



# Guia IV

# FIVE ZONES

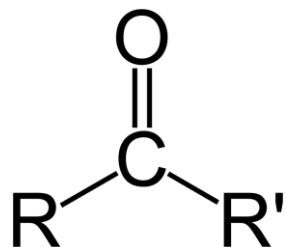
- Each zone has a characteristic frequency and in each zone specific bonds have very specific peak intensities. Looking at the peak determines what functional group is present.

## Characteristic Stretching Frequencies: The Five Zones (Table)

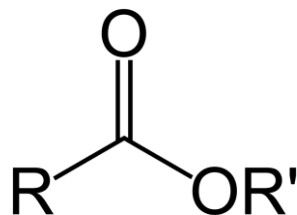
Bond	Stretching Frequency ( $\text{cm}^{-1}$ )	Intensity and Shape
<b>ZONE 1: 3700-3200 <math>\text{cm}^{-1}</math></b>		
Alcohol O-H	3650-3200 $\text{cm}^{-1}$	Usually strong and broad
<b>Alkyne</b> $\text{C}\equiv\text{H}$	3340-3250	Usually strong and sharp
<b>Amine or Amide</b> N-H	3500-3200	Medium; often broad
<b>ZONE 2: 3200-2700 <math>\text{cm}^{-1}</math></b>		
Aryl or Vinyl $\text{sp}^2$ C-H	3100-3000	Variable
Alkyl $\text{sp}^3$ C-H	2960-2850	Variable
<b>Aldehyde</b>	~2900 and ~2700	Medium; two peaks
<b>Carboxylic Acid</b> O-H	3000-2500	Usually strong; very broad
<b>ZONE 3: 2300-2000 <math>\text{cm}^{-1}</math></b>		
<b>Alkyne</b> $\text{C}\equiv\text{C}$	2260-2000	Variable and sharp
Nitrile $\text{C}\equiv\text{N}$	2260-2220	Variable and sharp
<b>ZONE 4: 1850-1650 <math>\text{cm}^{-1}</math></b>		
Ketone $\text{C}=\text{O}$	1750-1705	Strong
Ester $\text{C}=\text{O}$	1750-1735	Strong
<b>Aldehyde</b> $\text{C}=\text{O}$	1740-1720	Strong
<b>Carboxylic Acid</b> $\text{C}=\text{O}$	1725-1700	Strong
<b>Amide</b> $\text{C}=\text{O}$	1690-1650	Strong
<b>ZONE 5: 1680-1450 <math>\text{cm}^{-1}</math></b>		
Alkene $\text{C}=\text{C}$	1680-1620	Variable
Benzene Ring $\text{C}=\text{C}$	~1600 and ~1500	~1600 often has 2 peaks

**Attention:** The functional group **BOLDED** are the ones that appear in more than one zone.

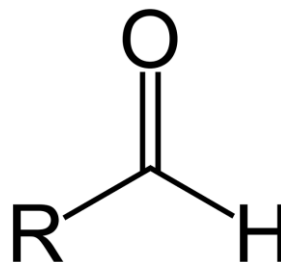
# Functional Groups 😊: Here's a quick recap of some functional groups in case you forgot.



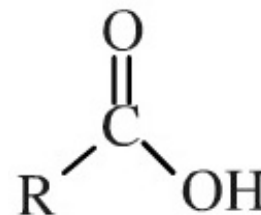
Cetona



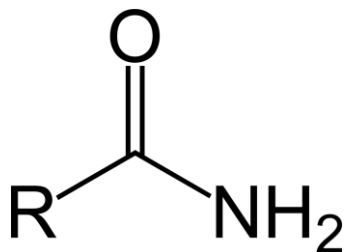
Èster



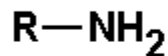
aldeído



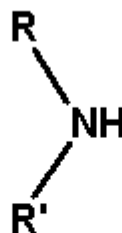
Ácido carboxílico



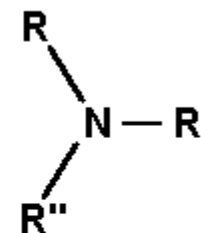
amida



amina  
primária



amina  
secundária



amina  
terciária

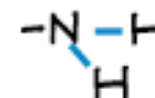
# Tricks for Identifying the Zones



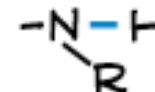
A SMOOTH TONGUE  
MEANS AN **ALCOHOL**.



VAMPIRE FANGS MEANS  
A **PRIMARY AMINE**...



ONE KNOCK-OUT FANG  
MEANS A **2° AMINE**,  
OR A **TERMINAL ALKYNE**.



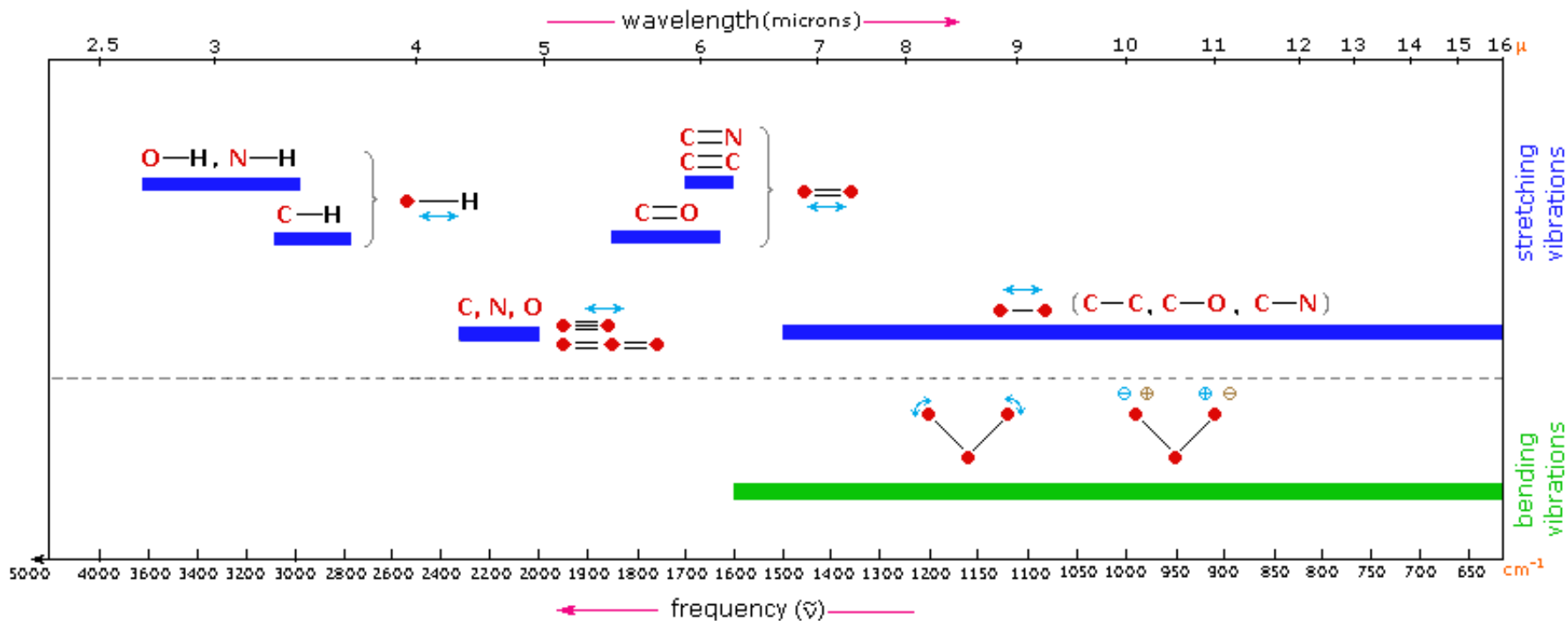
HAIRY BEARD IS A SIGN FOR  
A **CARBOXYLIC ACID**.



## Some General Trends:

- i)** Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)
- ii)** Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.
- iii)** Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds.  
(Except for bonds to hydrogen).

The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. Note that the blue colored sections above the dashed line refer to **stretching vibrations**, and the green colored band below the line encompasses **bending vibrations**. The complexity of infrared spectra in the 1450 to 600  $\text{cm}^{-1}$  region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption bands in the 4000 to 1450  $\text{cm}^{-1}$  region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.



## Typical Infrared Absorption Frequencies

Functional Class	Stretching Vibrations			Bending Vibrations		
	Range (cm <sup>-1</sup> )	Intensity	Assignment	Range (cm <sup>-1</sup> )	Intensity	Assignment
<b>Alkanes</b>	2850-3000	str	CH <sub>3</sub> , CH <sub>2</sub> & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH <sub>2</sub> & CH <sub>3</sub> deformation CH <sub>3</sub> deformation CH <sub>2</sub> rocking
<b>Alkenes</b>	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH <sub>2</sub> (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH <sub>2</sub> (out-of-plane bending) cis-RCH=CHR
<b>Alkynes</b>	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
<b>Arenes</b>	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
<b>Alcohols &amp; Phenols</b>	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
<b>Amines</b>	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str var	NH <sub>2</sub> scissoring (1°-amines) NH <sub>2</sub> & N-H wagging (shifts on H-bonding)
<b>Aldehydes &amp; Ketones</b>	2690-2840(2 bands) 1720-1740 1710-1720  1690 1675 1745 1780	med str str  str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone)  aryl ketone α, β-unsaturation cyclopentanone cyclobutanone	1350-1360 1400-1450 1100	str str med	α-CH <sub>3</sub> bending α-CH <sub>2</sub> bending C-C-C bending
<b>Carboxylic Acids &amp; Derivatives</b>	2500-3300 (acids) overlap 1705-1720 (acids) 1210-1320 (acids)  1785-1815 ( acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300 1630-1695(amides)	str str med-str  str str str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks)  C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395-1440    1590-1650 1500-1560	med    med med	C-O-H bending    N-H (1;-amide) II band N-H (2;-amide) II band
<b>Nitriles</b>	2240-2260	med	C≡N (sharp)			
<b>Isocyanates, Isothiocyanates, Diimides, Azides &amp; Ketenes</b>	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N <sub>3</sub> , C=C=O			

## Other Functional Groups

Infrared absorption data for some functional groups not listed in the preceding table are given below. Most of the absorptions cited are associated with stretching vibrations. Standard abbreviations (str = strong, wk = weak, brd = broad & shp = sharp) are used to describe the absorption bands.

Functional Class	Characteristic Absorptions
<b>Sulfur Functions</b>	
S-H thiols	2550-2600 $\text{cm}^{-1}$ (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)
C=S thiocarbonyl	1050-1200 (str)
S=O sulfoxide sulfone sulfonic acid sulfonyl chloride sulfate	1030-1060 (str) 1325 $\pm$ 25 (as) & 1140 $\pm$ 20 (s) (both str) 1345 (str) 1365 $\pm$ 5 (as) & 1180 $\pm$ 10 (s) (both str) 1350-1450 (str)
<b>Phosphorous Functions</b>	
P-H phosphine	2280-2440 $\text{cm}^{-1}$ (med & shp) 950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)
P=O phosphine oxide phosphonate phosphate phosphoramidate	1100-1200 (str) 1230-1260 (str) 1100-1200 (str) 1200-1275 (str)
<b>Silicon Functions</b>	
Si-H silane	2100-2360 $\text{cm}^{-1}$ (str)
Si-OR	1000-11000 (str & brd)
Si-CH <sub>3</sub>	1250 $\pm$ 10 (str & shp)
<b>Oxidized Nitrogen Functions</b>	
=NOH oxime O-H (stretch) C=N N-O	3550-3600 $\text{cm}^{-1}$ (str) 1665 $\pm$ 15 945 $\pm$ 15
N-O amine oxide aliphatic aromatic	960 $\pm$ 20 1250 $\pm$ 50
N=O nitroso nitro	1550 $\pm$ 50 (str) 1530 $\pm$ 20 (as) & 1350 $\pm$ 30 (s)