تفريغ تحليل آلي

اسم الموضوع: IR

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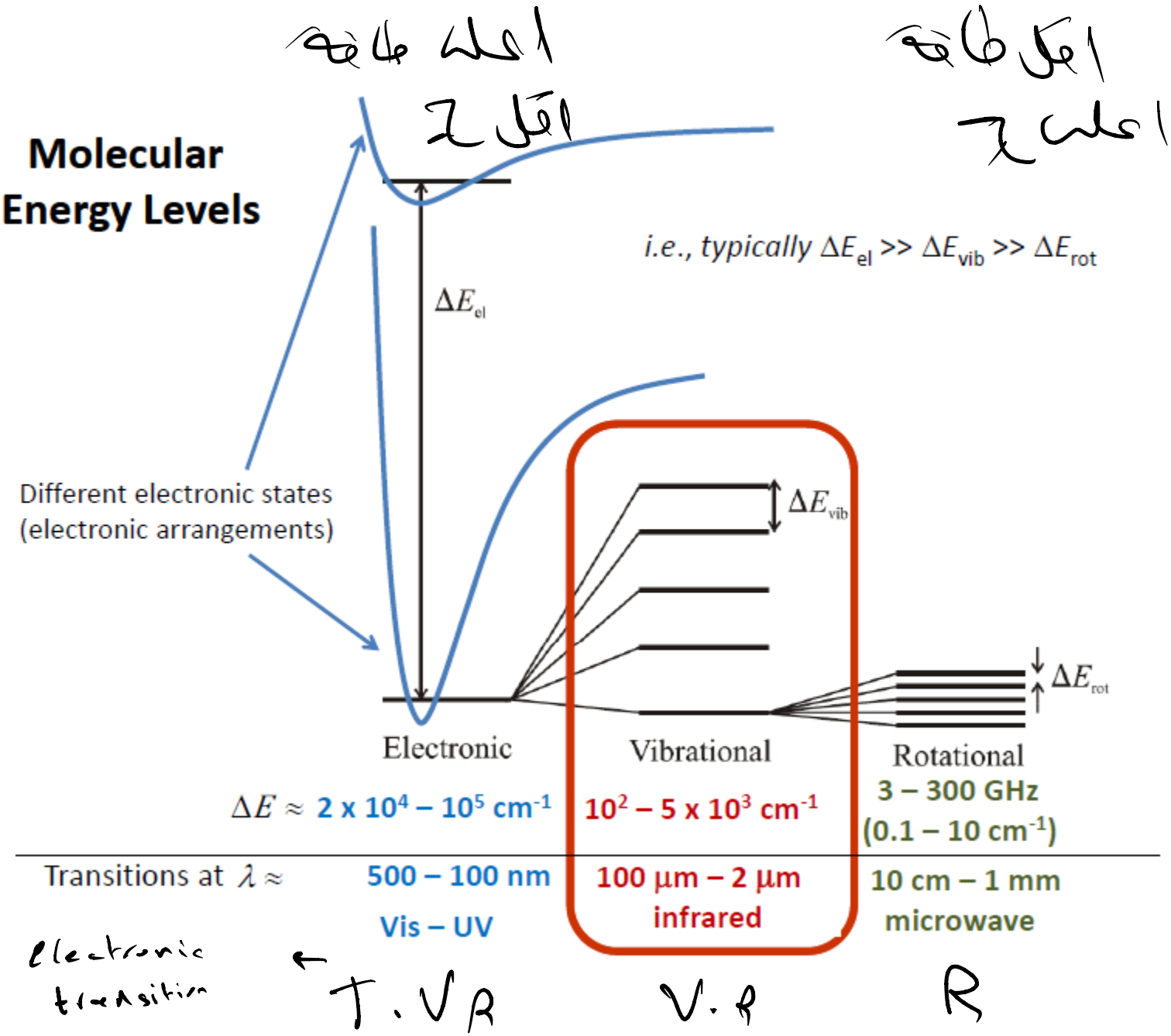
Seul Academy

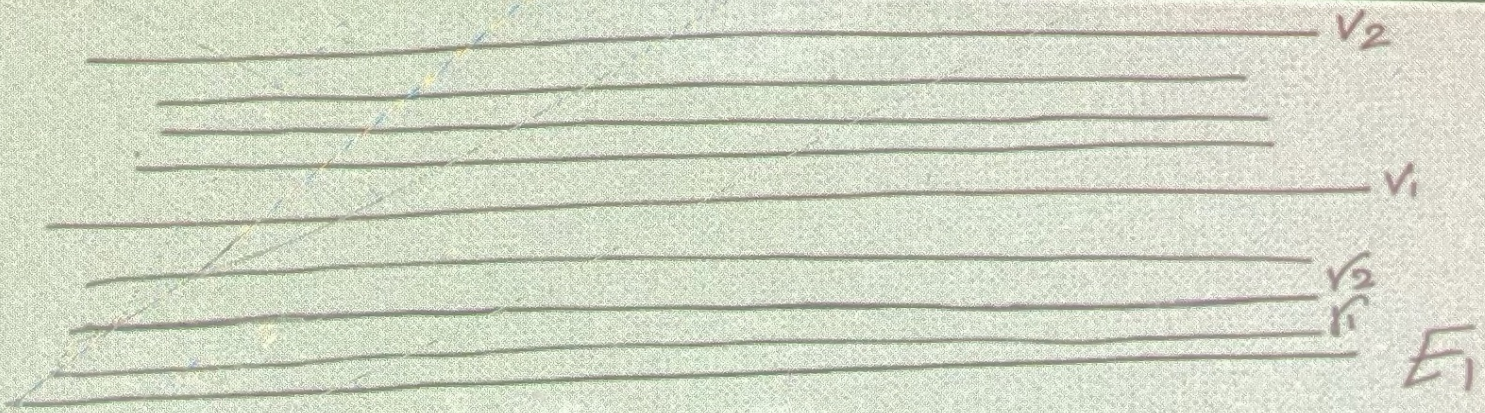
لجان الدفعات

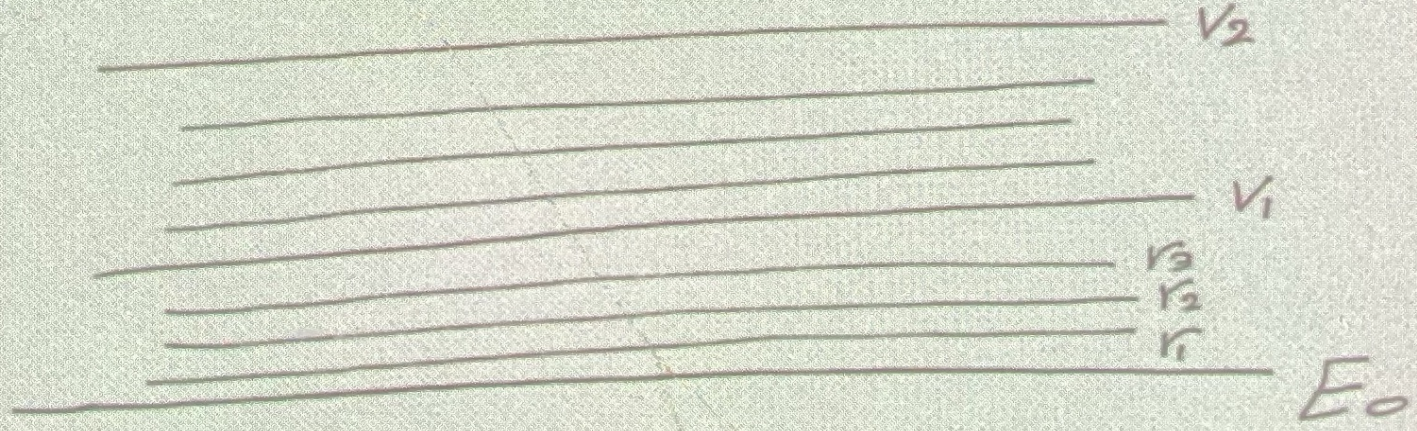
Chapter 16
An Introduction to Infrared Spectrometry

UV radiation يؤثر على Covalent bond

Ionic bond يؤثر على Flame


Molecular Energy Levels
i.e., typically $\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$
ΔE_{el}
Different electronic states (electronic arrangements)
ΔE_{vib}
ΔE_{rot}
Electronic
Vibrational
Rotational
$\Delta E \approx$ 2 x 10^4 – 10^5 cm^{-1}
10^2 – 5 x 10^3 cm^{-1}
3 – 300 GHz
(0.1 – 10 cm^{-1})
Transitions at $\lambda \approx$
500 – 100 nm
Vis – UV
100 µm – 2 µm
infrared
10 cm – 1 mm
microwave
Electronic transition
T.V.R
V.R
R





ex:

	microwave	middle IR	Near UV
Photons	468,000 nm,	11000 nm,	250 nm
	300000 - 10^9	9000 - 30000	100 - 350

The infrared region of the spectrum encompasses radiation with wavenumbers ranging from about 12,800- 10 cm^{-1} or wavelengths from 0.78 to 1000 μm. The infrared spectrum is divided into **near-, mid-,** and **far-**infrared radiation.

Region	Energy (kJ/mol)	Wavenumber (cm^{-1})	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

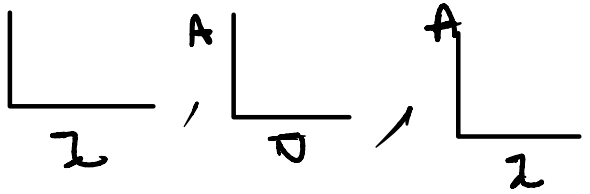
$$\bar{\nu} = \frac{1}{\lambda}$$

TABLE 16-1 IR Spectral Regions

Region	Wavelengths (λ), μm	Wavenumbers ($\bar{\nu}$), cm^{-1}	Frequencies (ν), Hz
Near	0.78 to 2.5	12800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

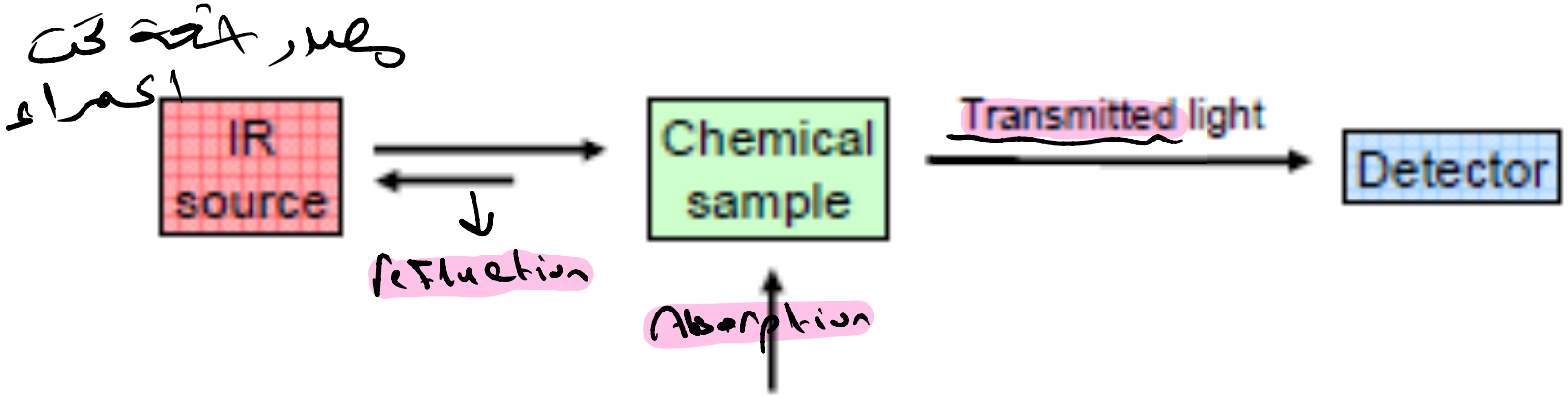
THEORY OF INFRARED ABSORPTION SPECTROMETRY

The ordinate is linear in transmittance. The abscissa is linear in wavenumbers with units of reciprocal centimeters. Modern instruments utilize a microcomputer capable of producing a variety of other output formats, such as transmittance versus wavelength and absorbance versus wavenumber or wavelength.



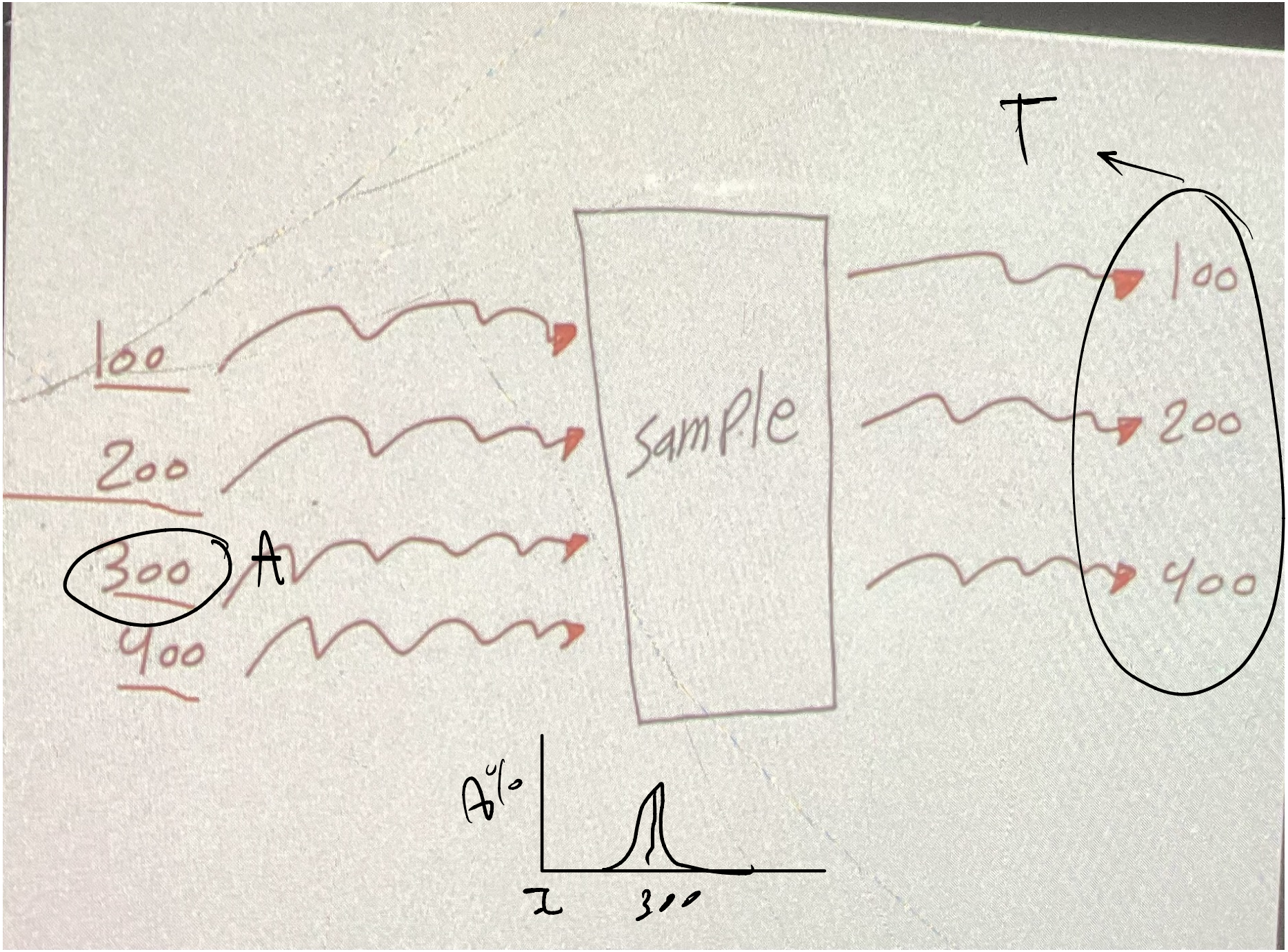
TRANSMISSION vs. ABSORPTION

When a chemical sample is exposed to the action of IR LIGHT, it can **absorb** some frequencies and **transmit** the rest. Some of the light can also be reflected back to the source.



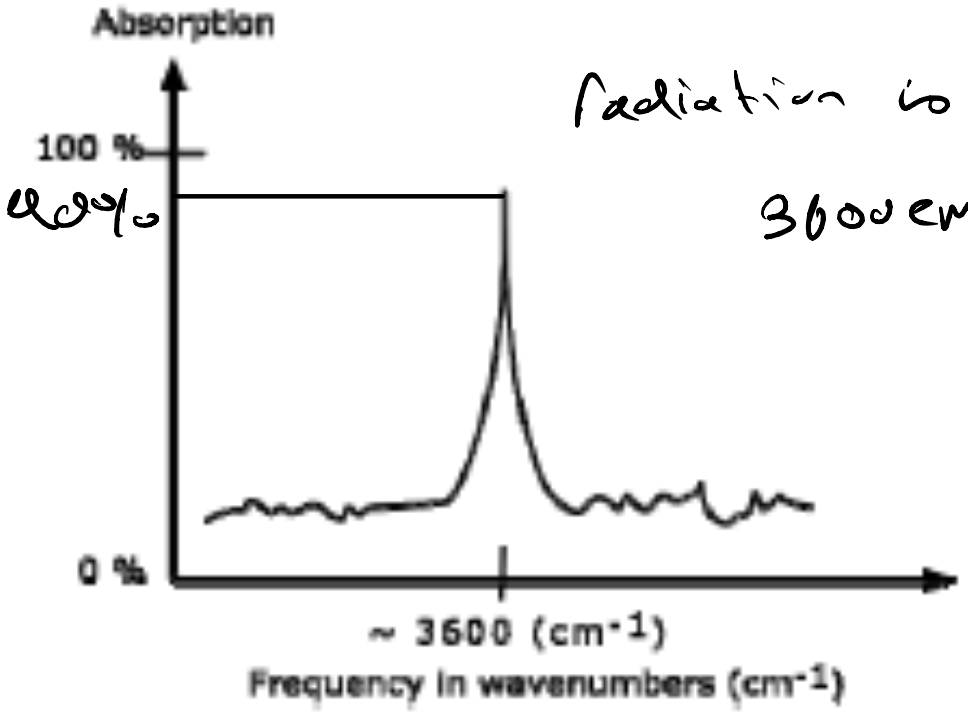
From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies. →


T
100
200
300
400
A
sample
100
200
400
A%
I
300

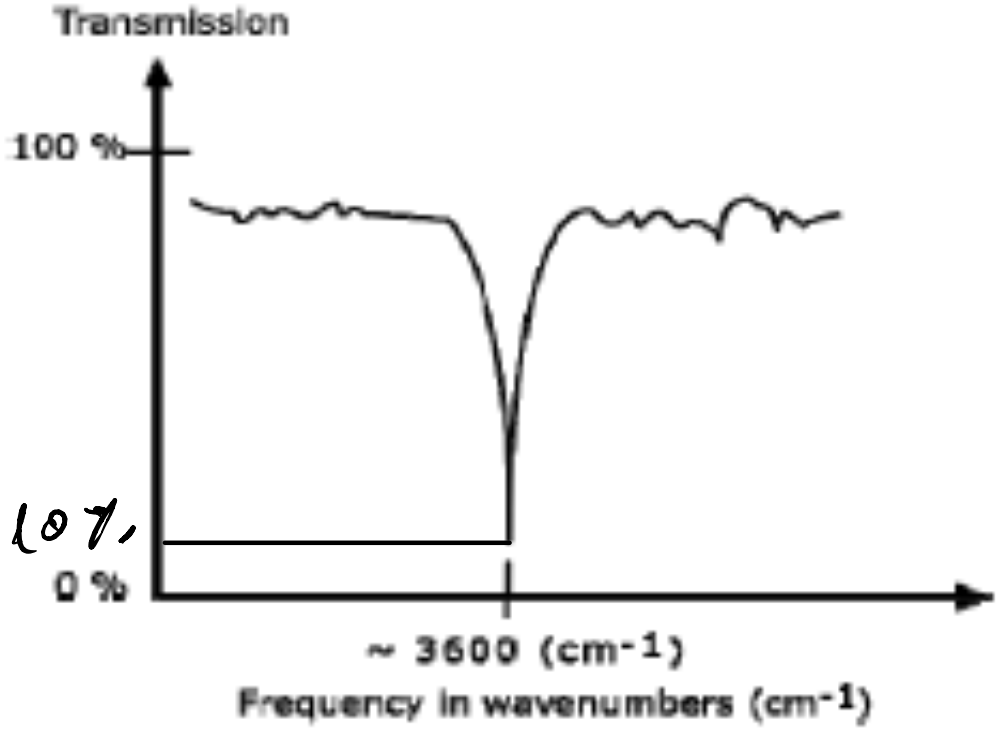
AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the *x*-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the *y*-axis in percentage units.



The graph above shows a spectrum in **absorption** mode.

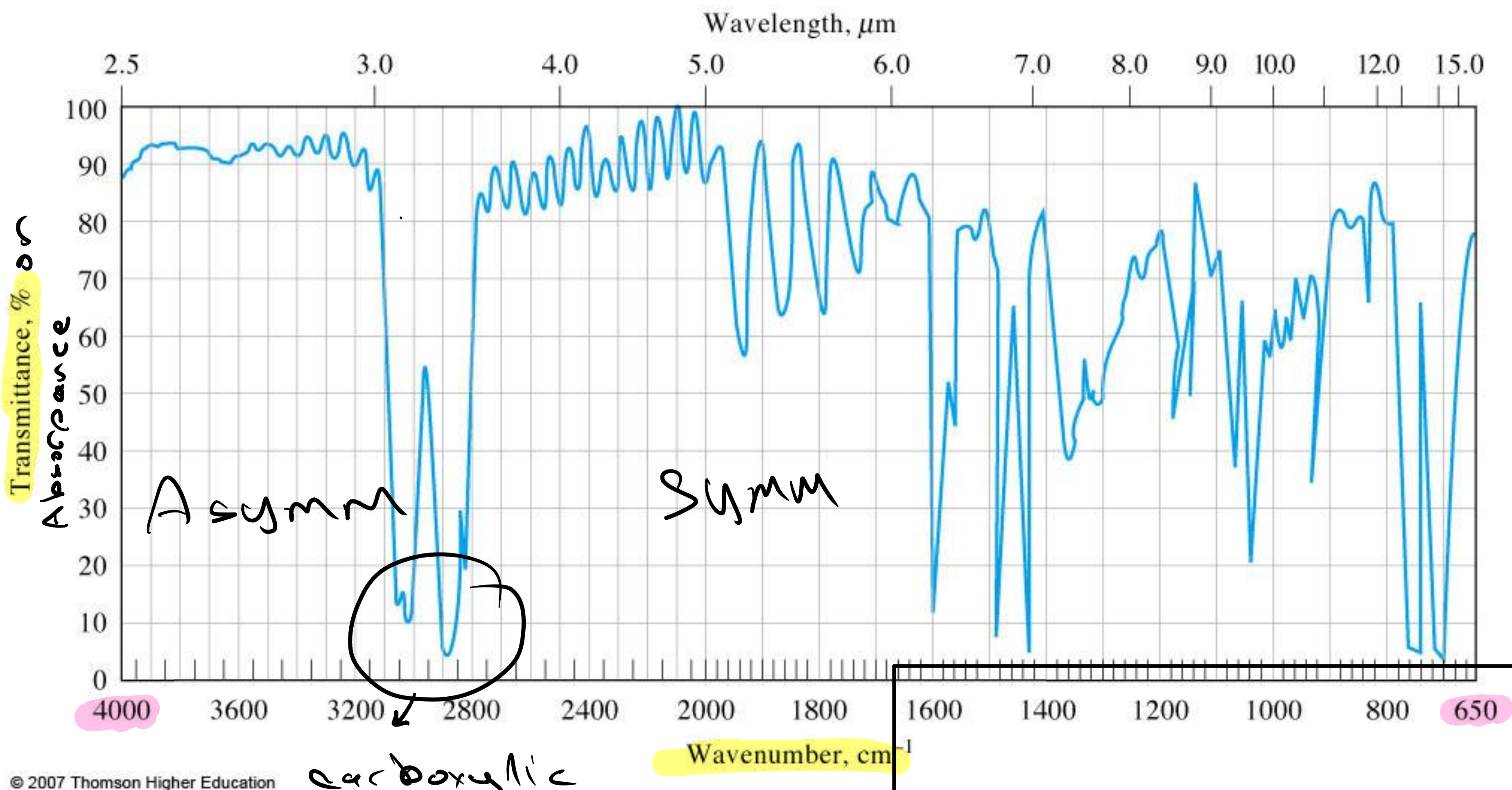
AN IR SPECTRUM IN TRANSMISSION MODE



The graph above shows a spectrum in **transmission** mode.
This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

هون IR استخدمناه عشان اعرف ال molecule (qualitative

(quantitative ل UV & Fluorol



carboxylic acid O-H

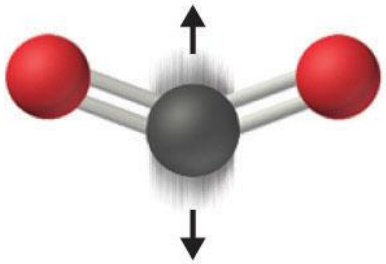
تحت 1600 بيكون stretching

binding

$\bar{\nu}$ middle IR → (4000-500) cm^{-1}

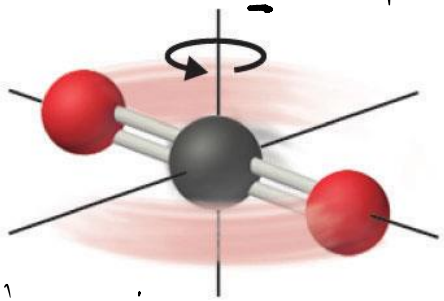
	C=C	1500, 1600	
Alcohol	O – H	3200 – 3640 (broad)	The shape of alcohol O – H peak is a smooth tongue 
	C – O	1050 – 1275	
Ether	C – O	1050 – 1275	
Alkyl halide	C – Cl	600 – 800	
	C – Br	500 – 600	
Amine	N – H	3300 – 3500	The shape of primary amine N – H peak is vampire fangs 
	C – N	1030 – 1230	The shape of secondary amine N – H peak is one fang 
Carbonyl		Generally 1670 – 1780	
	C=O in carboxylic acid	1712	
	C=O in aldehyde	1705 – 1730	
	C=O in ketone	1690 – 1750	
	C=O in ester	1735 or 1715	
Carboxyl	O – H	2500 – 3100	The shape of carboxylic acid O – H peak is a hairy beard 
	C=O	1712	

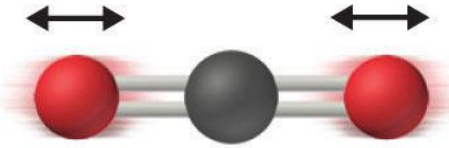
Molecular Vibration, Rotation and Translation motion



bending → Molecule داية تغير

دوران أفقي

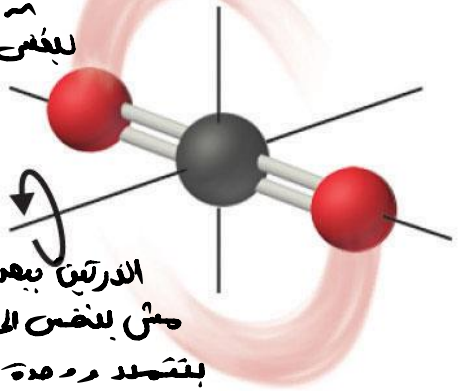


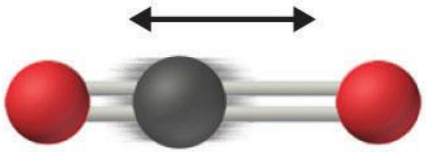


symmetric stretching

الذرتين يبعدوا عن center مايس بنفس المقدار

دوران عامودي



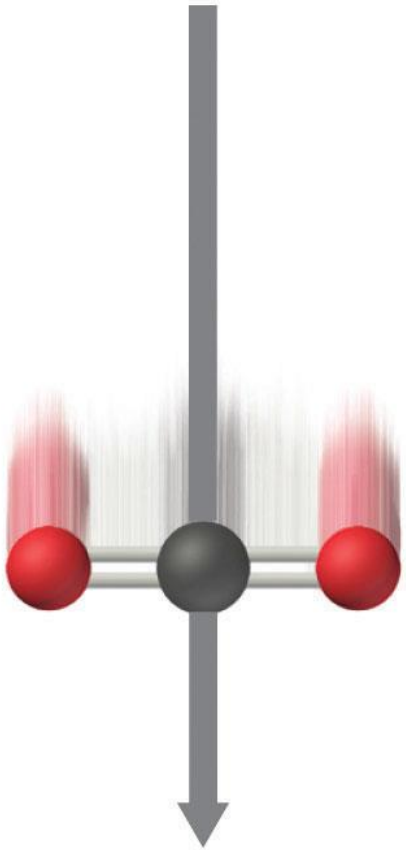


asymmetric stretching

الذرتين يبعدوا عن بعض مش بنفس المقدار لزوجة بتتحدد وحدة بتتغلص

vibrational motion

rotational motion



translational motion

بسبب زيادة الطاقة الحركية للجزيء وانتقالها من مكان إلى مكان بتصير غالبا في (liquid + gas)

اعلى احتاج طاقة stretching ★

من bending

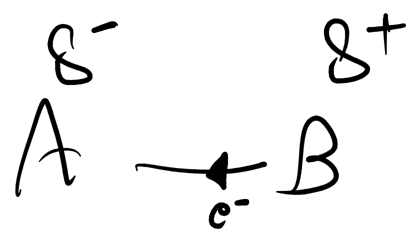
بسبب فرق electronegativity بين الذرات في المركب
لـ الطريقة الي بشتغل عليها IR)

Dipole Changes During Vibrations

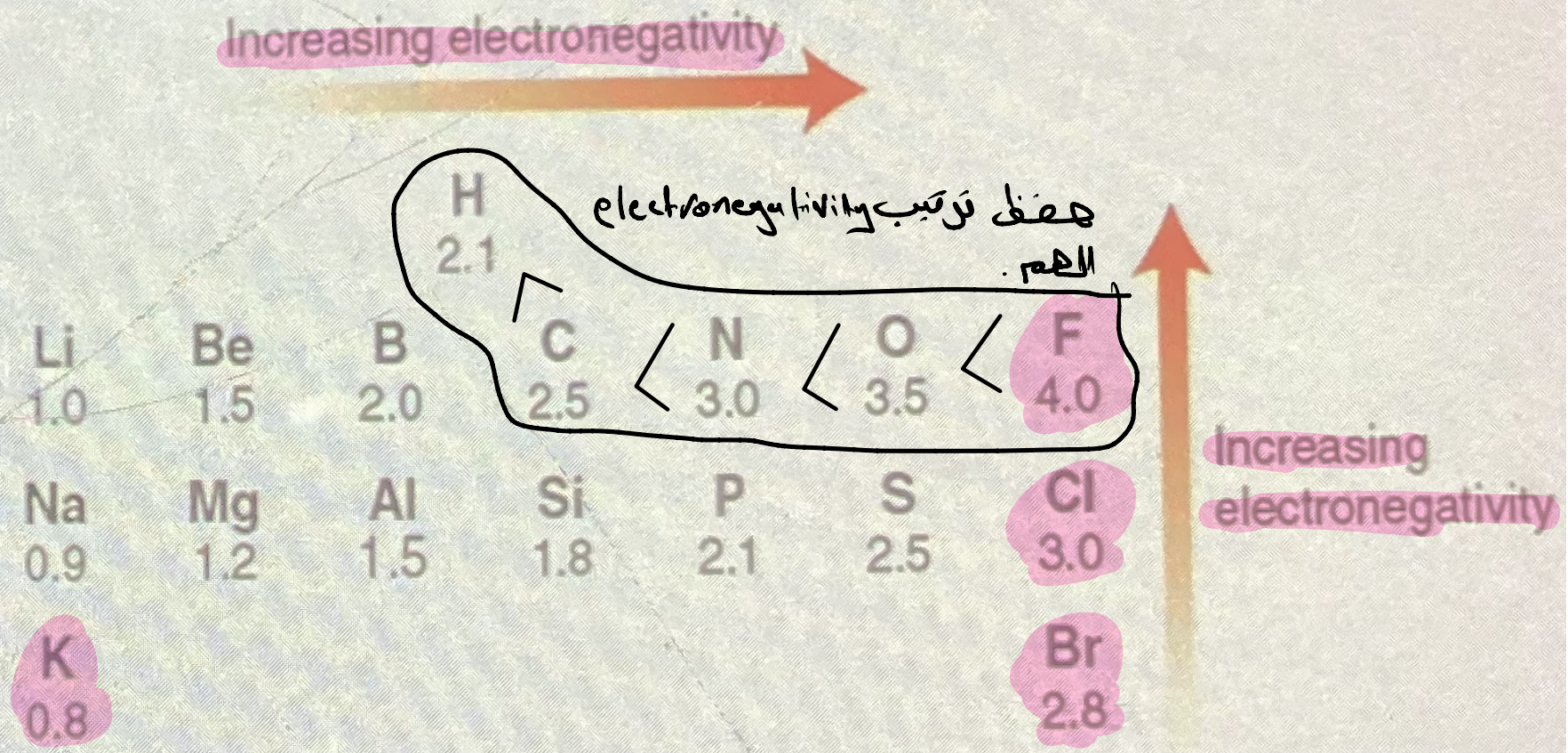
Infrared radiation is not energetic enough to bring about electronic transitions.

بس UV/Visible الي بعملوا طاقة كافية عشان يعملوا electronic transitions

Absorption of infrared radiation is thus confined largely to molecular species that have small energy differences between various vibrational and rotational states.



as electronegativity A > B



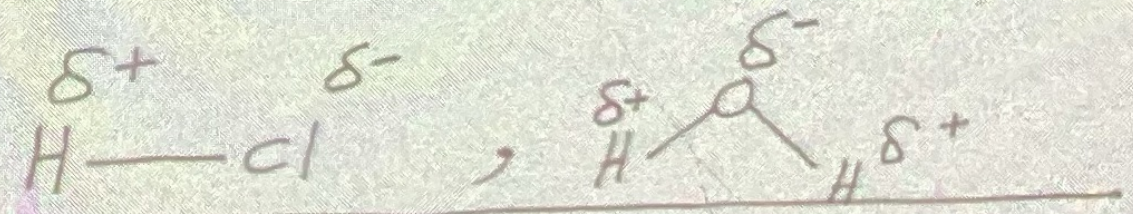
* F ← electronegativity اعلى

* K ← electronegativity اقل

* شرطين لحدوث الـ IR absorbance

1- الـ molecule لازم يكون عندها فرق في الـ (electronegativity) بين الـ atoms اللي مكونين الـ molecule

2- بالتالي لازم يكون عندها Dipole moment بتتغير مع تسليط IR radiation وحدوث الـ stretching والـ bending



$$\mu = q * r$$

- μ: علامة طردية
- q: ثابت لكل atom
- r: متغير بسبب الـ vibrational motion

2- أن تتوافق الـ frequency الـ IR radiation بـ frequency الـ molecule بـ rotation و الـ vibration الازم لحدوث الـ

(=) double bond ⟶ 1600 – 2000 cm^{-1}

(≡) triple bond ⟶ 2000 – 2500 cm^{-1}

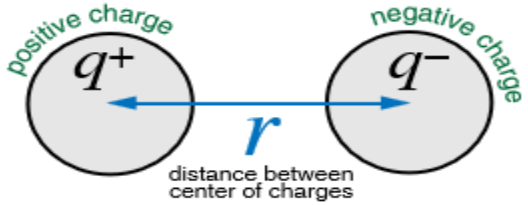
(–) single bond ⟶ 2500 – 4000 cm^{-1}

In order for IR absorbance to occur two conditions must be met:

1. A molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion.

The dipole moments is determined by the magnitude of the charge difference and the distance between the two centers of charge.

No net change in dipole moment occurs during the vibration or rotation of homonuclear species such as O_2, N_2, or Cl_2; consequently, such compounds cannot absorb in the infrared.



$$\mu = q \cdot r$$

dipole moment — separated charge — distance between

المسافة بين الذرتين

Dipole moment $= \mu = qr$

1 debye $= 3.336 \times 10^{-30}$ **Cm**

Molecules with permanent dipole moments (μ) are IR active

$H^{\delta+}-Cl^{\delta-}$ →

HCl, H_2O, NO

IR active

O – O

No dipole moment

Atoms, O_2, H_2, Cl_2

IR inactive

2. If the frequency of the radiation matches the natural frequency of the vibration (or rotation), the IR photon is absorbed and the amplitude of the vibration increases.

* كلما زادت فرق electronegativity بين الذرتين، بتزيد dipole moment

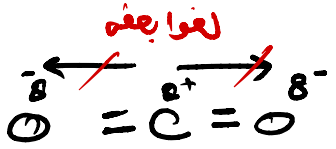
C - H اقل

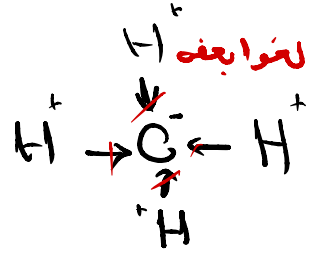
H - F اعلى

Dipole Moments of Specific Molecules

Molecule	μ (debye)
H_2O	1.85
HF	1.91
HCl	1.08
HBr	0.80
HI	0.42
CO	0.12
CO_2	0
NH_3	1.47
PH_3	0.58
AsH_3	0.20
CH_4	0
NaCl	9.00

→ dipole وحدة قياس moment





IR radiation بالعكس بالعكس Ionic bond

بس مطولة عشان يبين انه فرق الشحنات بين Natcl كبير و dipole moment عالية.

$\Delta E = h\nu$

There are three types of molecular transitions that occur in IR

a) **Rotational transitions** → الجهاز ما بلاقطها او ما بدخلها

- **When an asymmetric molecule rotates about its center of mass, the dipole moment seems to fluctuate.** تذبذب
  → For IA
- **ΔE for these transitions correspond to $\bar{\nu} < 100\ cm^{-1}$**

- **Quite low energy, show up as sharp lines that subdivide vibrational peaks in gas phase spectra.** → IR spectrum بالسبكترم ح يظهروا على شكل خطوط حادة بين الـ vibrational beaks العالية

b) **Vibrational-rotational transitions** → الجهاز بعللهم filter لانهم complex ولربوا القراءات

- **complex transitions that arise from changes in the molecular dipole moment due to the combination of a bond vibration and molecular rotation.**

c) **Vibrational transitions** → الجهاز بس يدخل Vibration فقط

- **The most important transitions observed in qualitative mid-IR spectroscopy.**
- **$\bar{\nu} = 13{,}000 - 675\ cm^{-1}$ (0.78 – 15 μm)**

- **Vibrational Transitions:** Vibrational energy levels are quantized, and for most molecules the energy differences between quantum states correspond to the mid-infrared region.

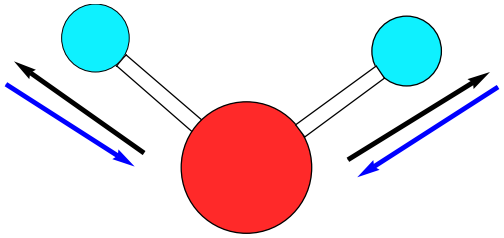
* الطاقة الحتاجة عشان يصير عندك
transition تكون محاطة بـ طاقة
mid-IR

- **Types of Molecular Vibrations:** Vibrations fall into the basic categories of stretching and bending. A **stretching** vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms. **Bending** vibrations are characterized by a change in the angle between two bonds and are of four types: **scissoring**, **rocking**, **wagging**, and **twisting**.

المسافة بين atoms تقصر

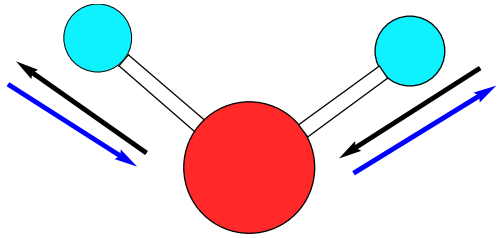
↑ النوع اللي بتغير بين الروابط bending

Stretch: change in bond length تغير في الطول



Symmetric stretch

ν_s ثاني اكبر مقدار طاقة

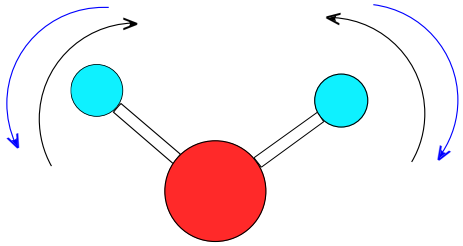


Antisymmetric stretch

ν_{as} اكبر مقدار طاقة

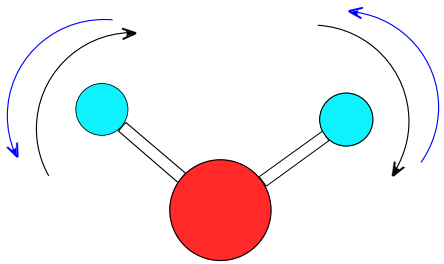
اقل مقدار طاقة

Bend: change in bond angle تغير في الزاوية



Scissoring

ρ

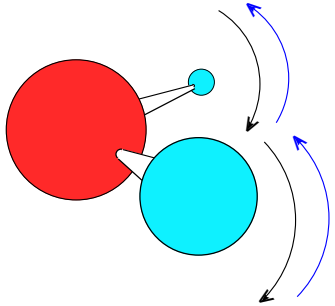


Rocking

σ

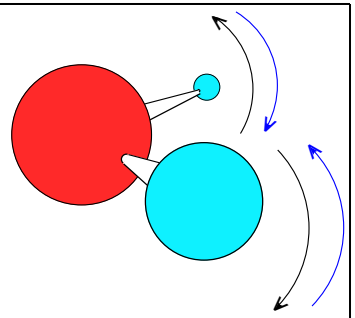
in-plane bend

نفس المستوى



wagging

ω



twisting

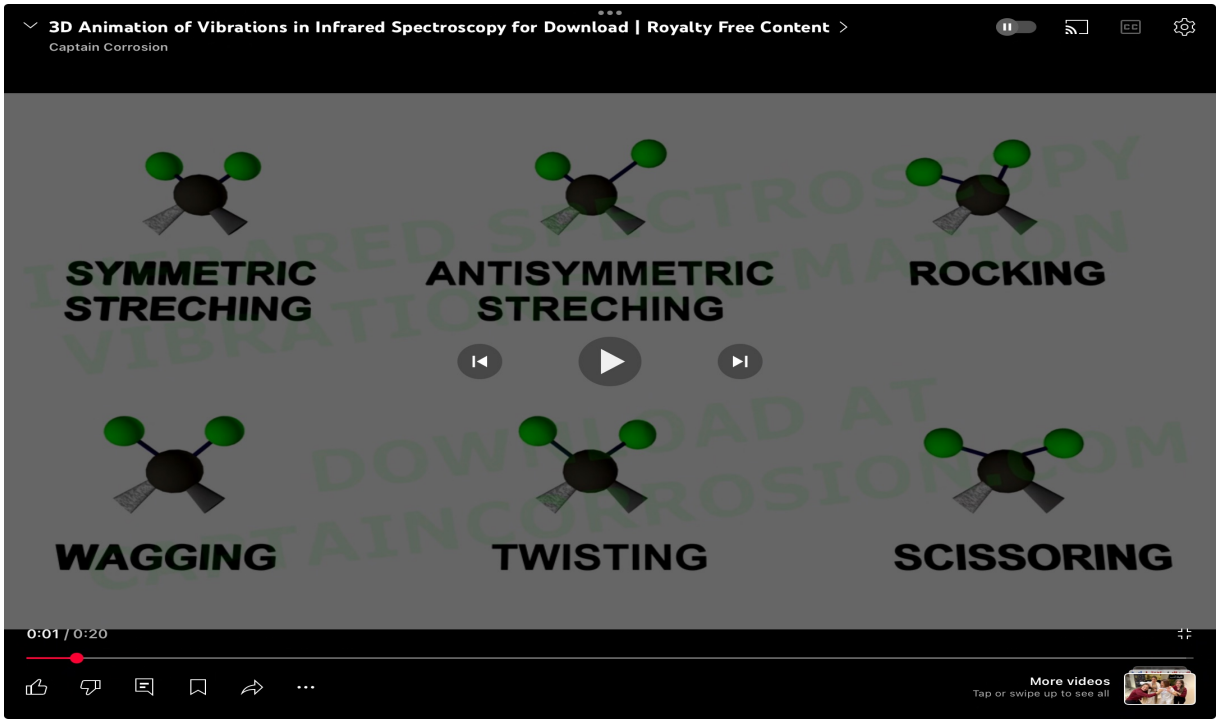
τ

out-of-plane bend

$\bar{\nu}_{Asym} > \bar{\nu}_{Sym} >> \bar{\nu}_{Bending}$

IR spectroscopy فيديوهات توضيحية لانواع *

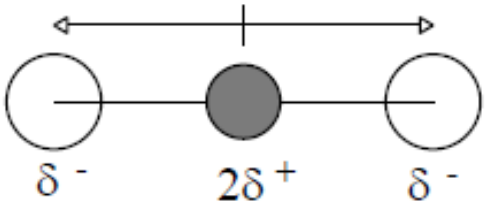
https://youtu.be/1PQqDfJKXvA?si=idU6vuhzvjLVuBfy

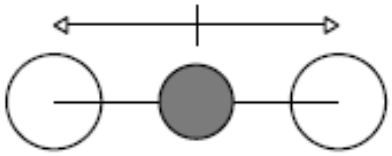


https://youtu.be/ZWwLCnuYRys?si=piUZblN1-ujYuaDp

Only some modes may be IR active:

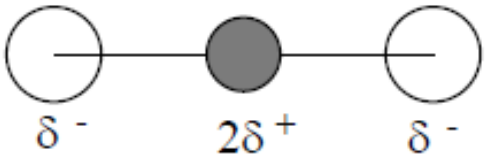
Example CO_2 O=C=O linear

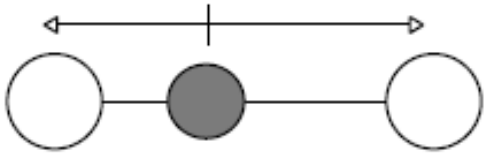




No net dipole moment change

Symmetric stretching

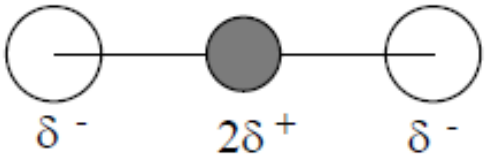


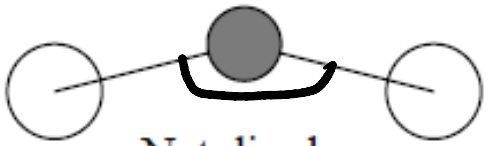


Net dipole moment change

Asymmetric stretching

Water مثل





Net dipole moment change

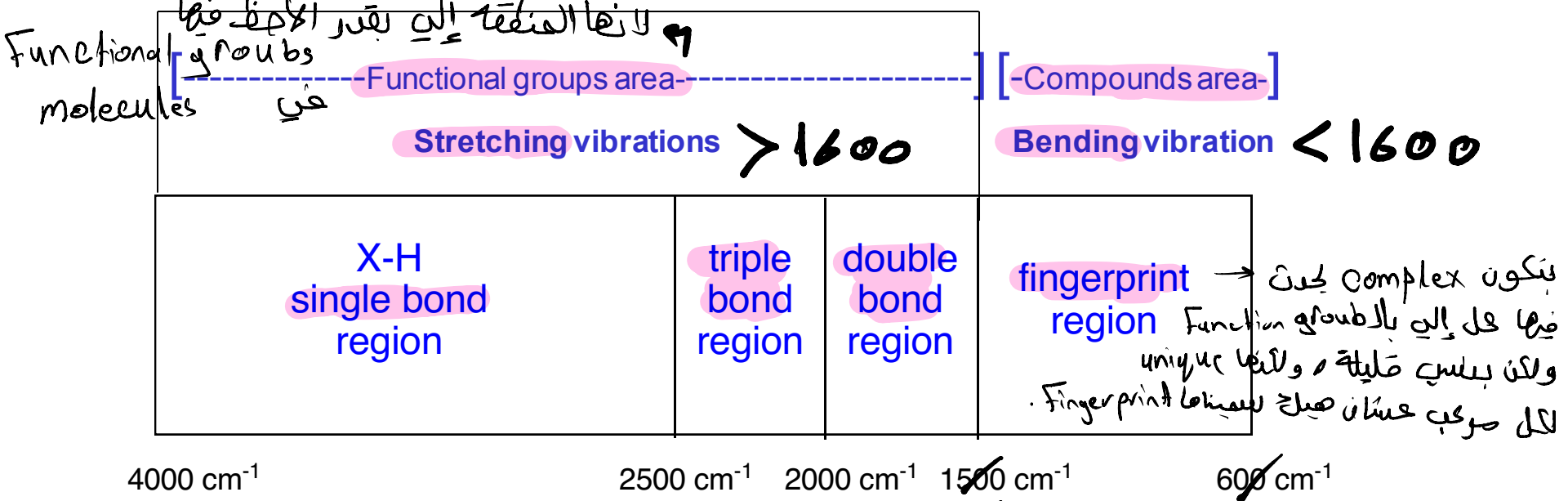
Bending

ν_s not IR active ν_{as}, bend IR active

Interpretation of an Infrared Spectra:

organic molecules contain many atoms. As a result, there are many stretching and bending modes- IR spectra have many absorption bands

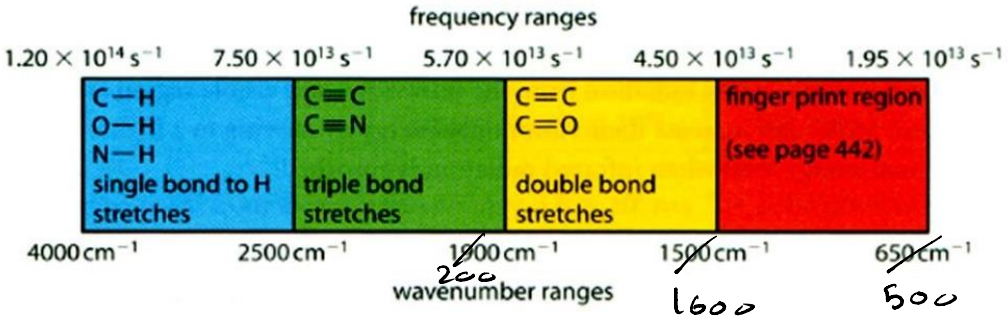
Four distinct regions of an IR spectra



C-H
O-H
N-H

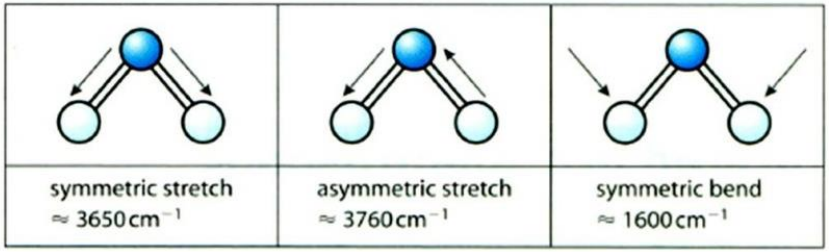
C≡C C=C
C≡N C=O

$\lambda = \frac{1}{\text{wave number}}$

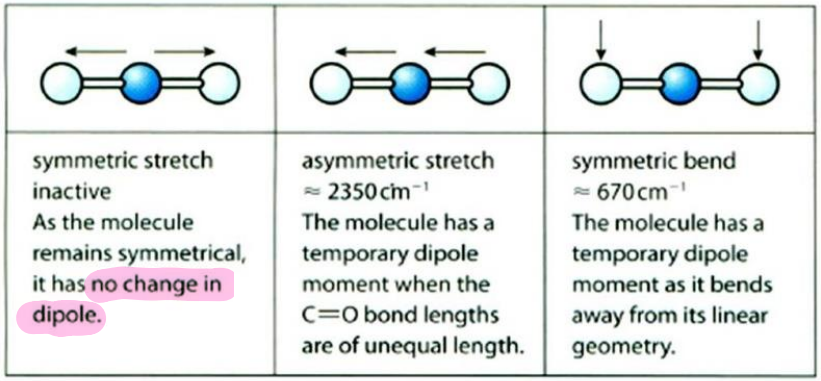


Stretching and bending in a polyatomic molecule

In a polyatomic molecule such as water, it is more correct to consider the molecule as a whole stretching and bending rather than the individual bonds. Water, for example, can vibrate at three fundamental frequencies as shown below. As each of the three modes of vibration results in a change in dipole of the molecule, they can be detected with IR spectroscopy.

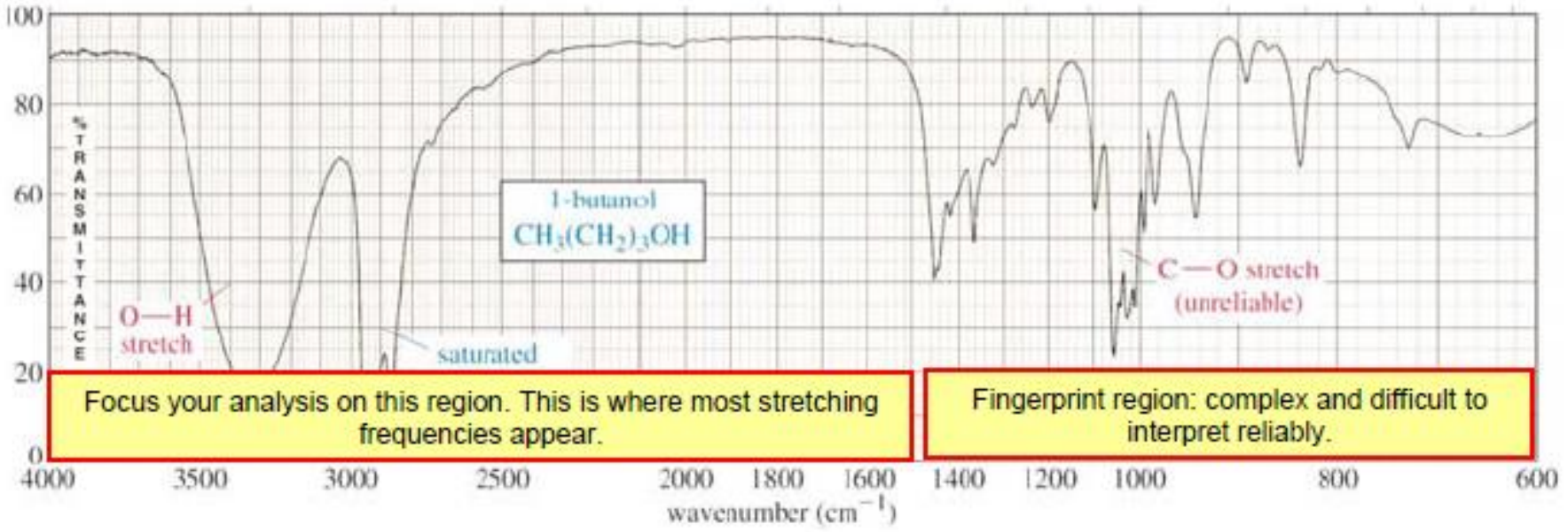


For a symmetrical linear molecule such as carbon dioxide, there are also three modes of vibration. However, the symmetric stretch is IR inactive as it produces no change in dipole moment. The dipoles of both C=O bonds are equal and opposite throughout the vibration.



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}.



Fingerprint region (600 - 1500 cm^{-1})- low energy single bond stretching and bending modes. The fingerprint region is unique for any given organic compound. However, there are few diagnostic absorptions.

Double-bond regions (1500 - 2000 cm^{-1})

C=C 1620 - 1680 cm^{-1}

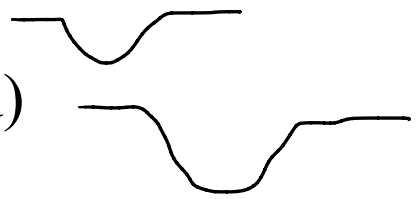
C=O 1680 - 1790 cm^{-1}

Triple-bond region: (2000 - 2500 cm^{-1})

C≡C 2100 - 2200 cm^{-1} (weak, often not observed)

C≡N 2240 - 2280 cm^{-1}

X-H Single-bond region (2500 - 4000 cm^{-1})



O-H 3200 - 3600 cm^{-1} (broad)

CO-OH 2500-3600 cm^{-1} (very broad)

N-H 3350 - 3500 cm^{-1}

C-H 2800 - 3300 cm^{-1}

sp^3 -C-H 2850 - 2950 cm^{-1}

sp^2 =C-H 3000 - 3100 cm^{-1}

sp ≡C-H 3310 - 3320 cm^{-1}