تفريغ تحليل آلي

اسم الموضوع: *Infrared spectrometery*

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للهِ نَمضي والحَياةُ مُخيفةٌ
واللهُ يحفظُ مَن إليهِ يَسيرُ

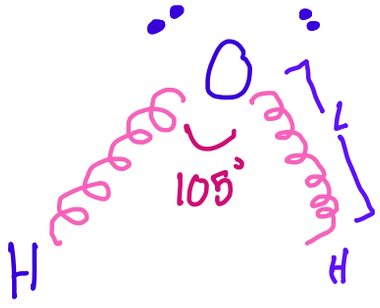
Seul Academy

لجان الدفعات

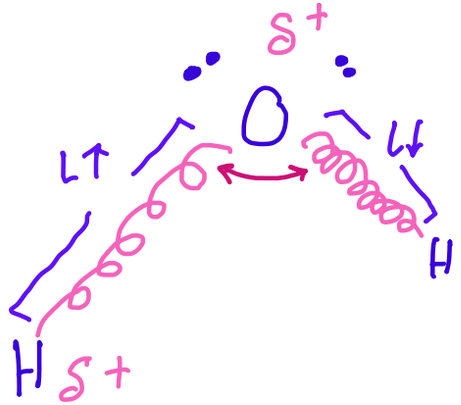
Chapter 16
An Introduction to Infrared Spectrometry

only Qualitative

Covalent كل التعامل مع روابط



بالوضع الطبيعي ← استعطت عليها موجة IR

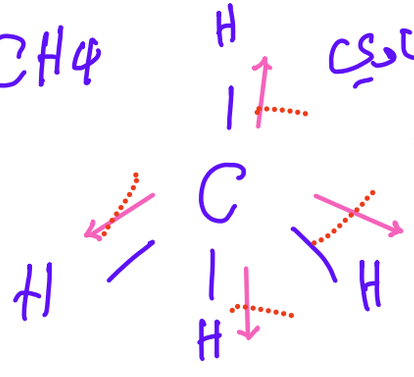


← Stretching حول الرابطة (بيزداد وبنقص)

← Bending مقدار الزاوية يتغير

← بنتج اختلاف بتوزيع الشحنة بتعطي Dibole of molecule

CH_4



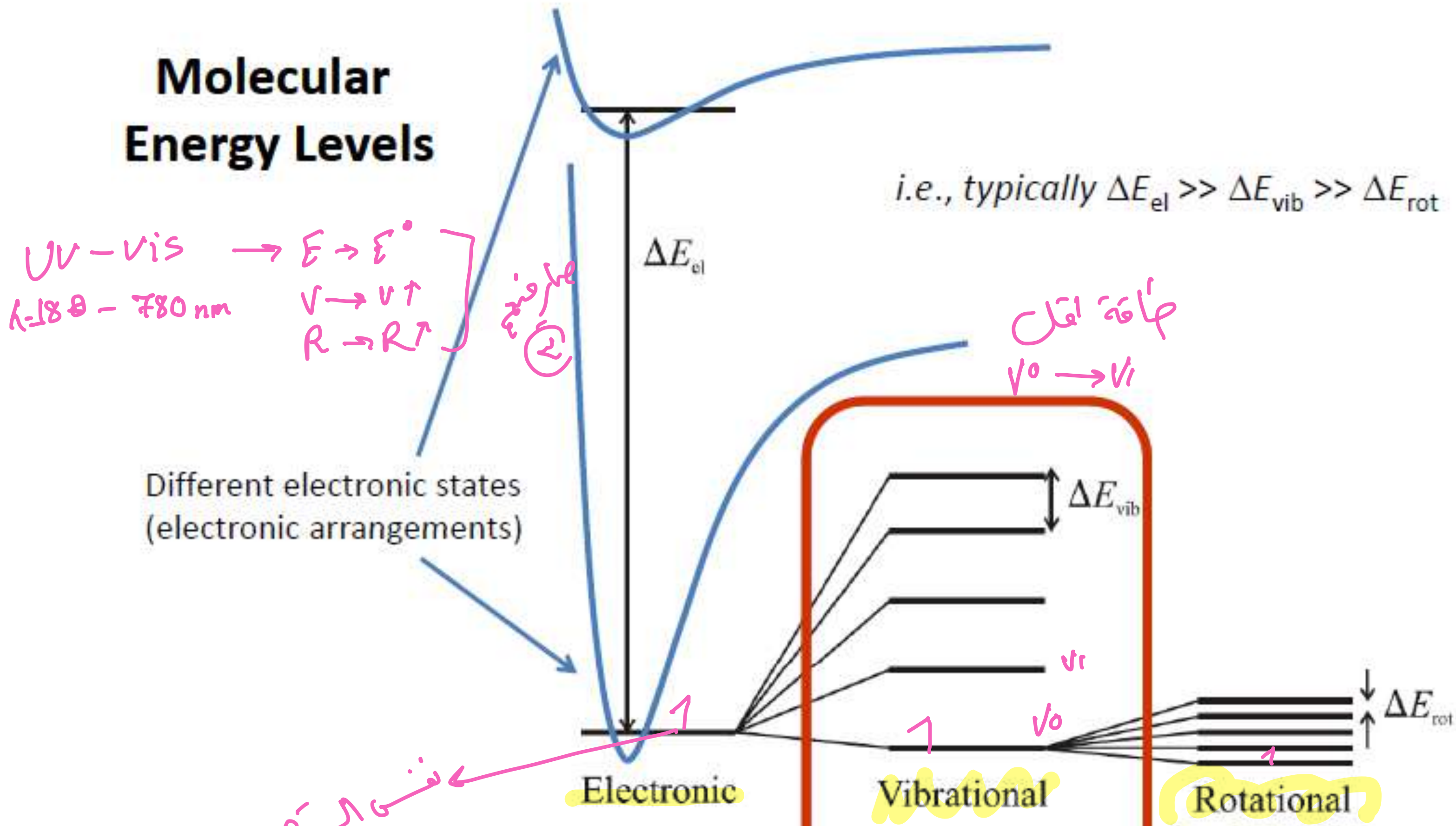
مقدار السحب متساوي ومتعاكس بالاتجاه فكل وحدة بتلغي اللي قبالها

Symmetrical molecule

← لا يمكن تحليل IR

IR Spectrometry ← بعد احلله باستخدام

Molecular Energy Levels



i.e., typically $\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$

	Electronic	Vibrational	Rotational
$\Delta E \approx$	$2 \times 10^4 - 10^5$ cm^{-1}	$10^2 - 5 \times 10^3$ cm^{-1}	3 – 300 GHz (0.1 – 10 cm^{-1})
Transitions at $\lambda \approx$	500 – 100 nm	100 µm – 2 µm	10 cm – 1 mm
	Vis – UV	infrared	microwave

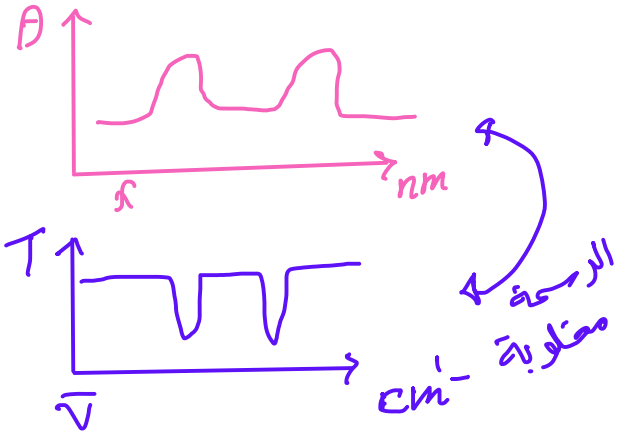
$E^0 \to E^*$ · $V^0 \to V^*$ · $R^0 \to R^*$

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

التي سنتكلم عليه

$\lambda = 180 - 780$ nm UV vis → Wavelength



$\bar{\nu} = 4000 - 200\ cm^{-1}$ IR → Wavenumber

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}

بالأجهزة الحديثة

$A \propto \frac{1}{T}$

إذا زاد C ← A يزيد
T يقل

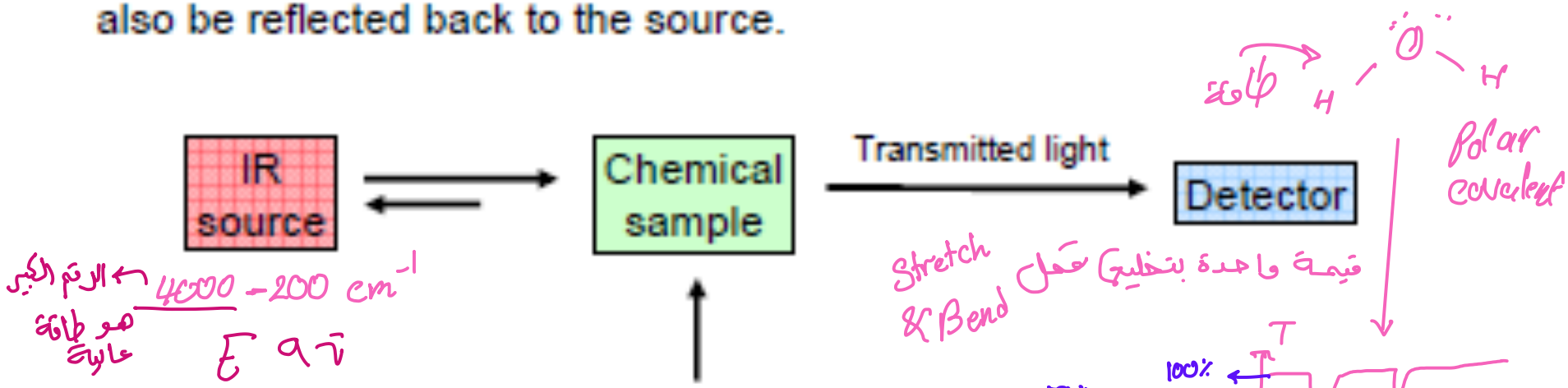
إذا زاد (A) فالضوء الخارج (T) قليل

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.

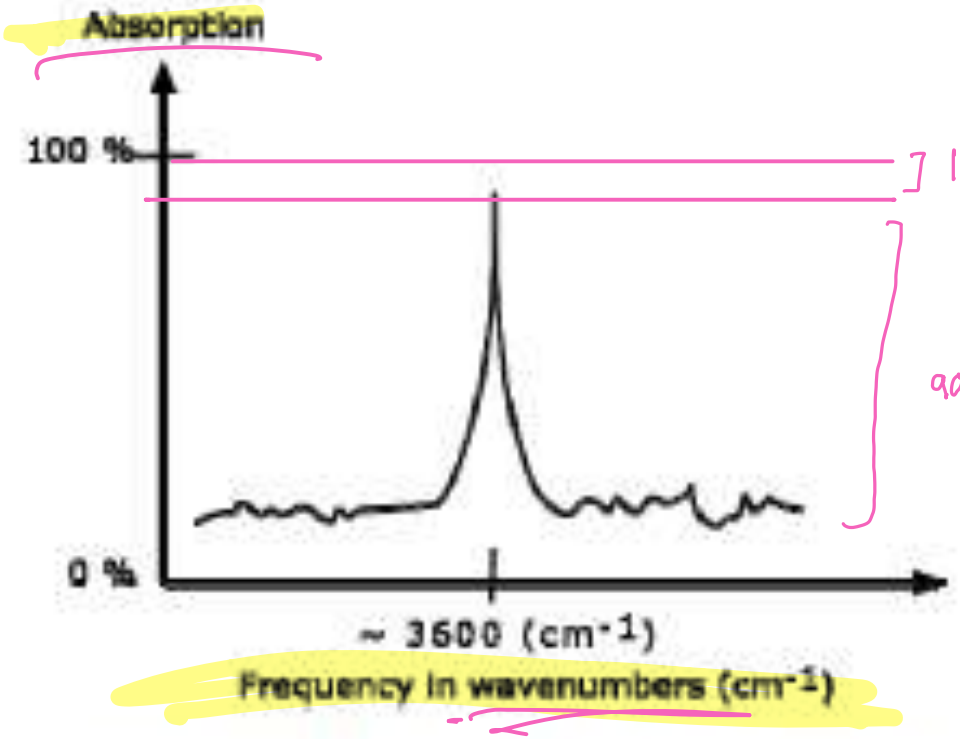


From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

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

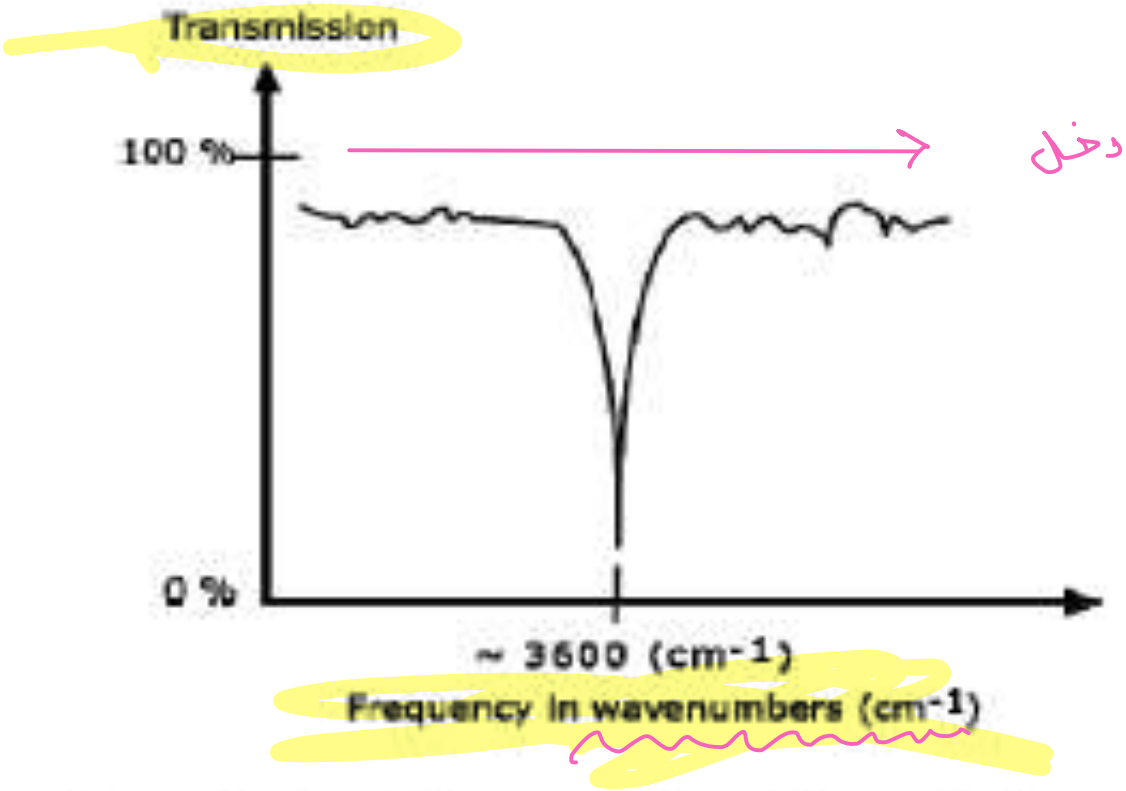
AN IR SPECTRUM IN ABSORPTION MODE

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.

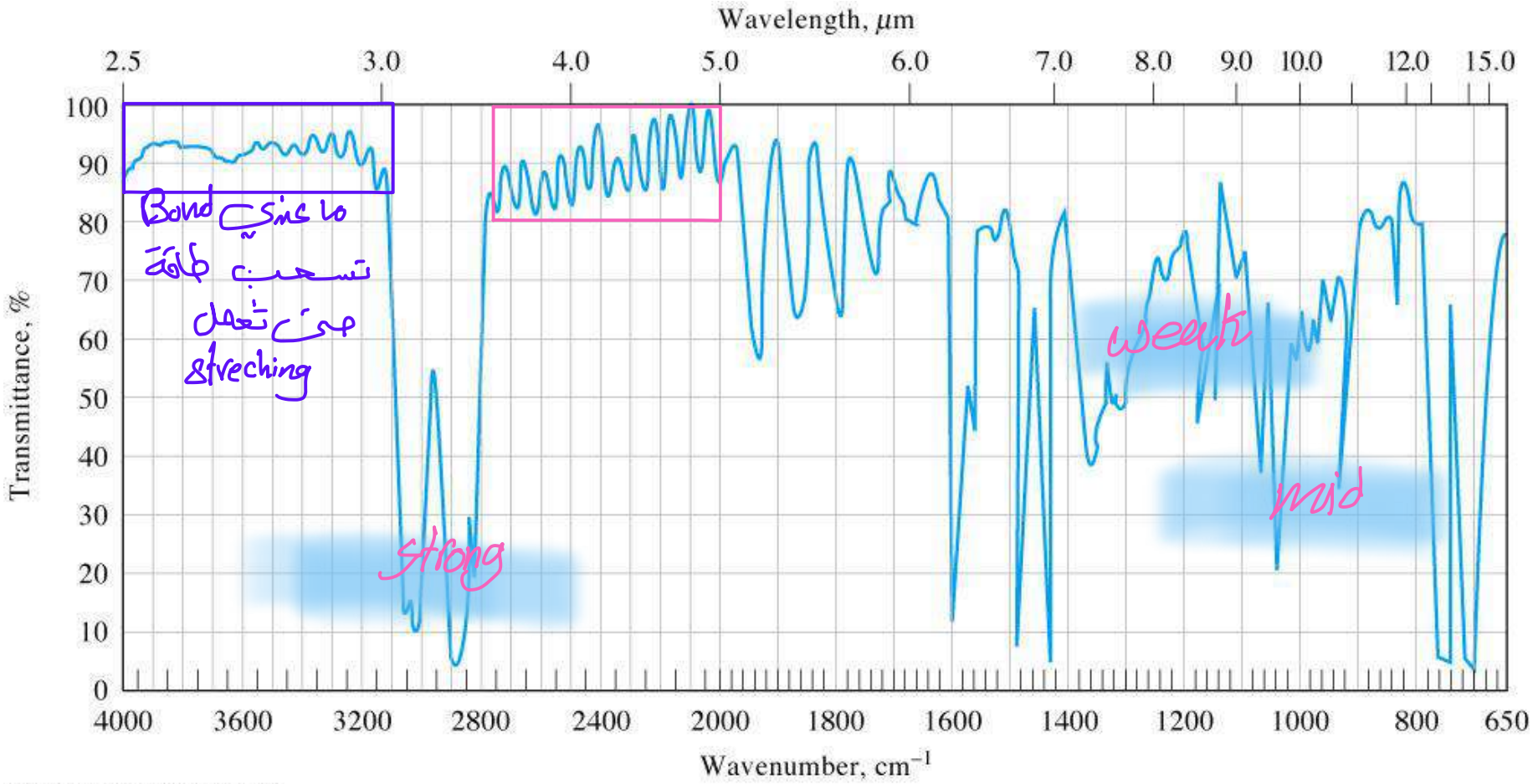
AN IR SPECTRUM IN TRANSMISSION MODE



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.

Stretching

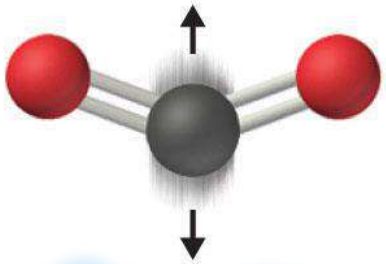
Bending



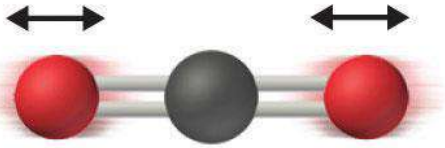
↑ $\bar{\nu}$ ←

↑ E ←

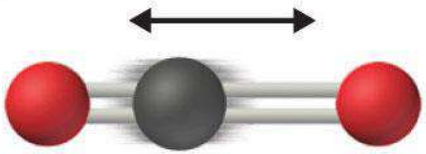
Molecular Vibration, Rotation and Translation motion



bending

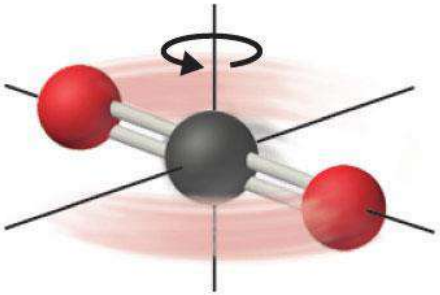


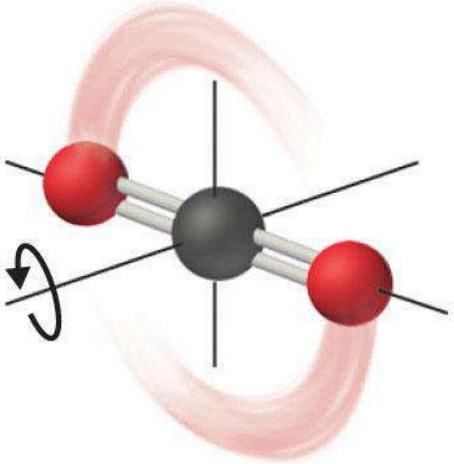
symmetric stretching



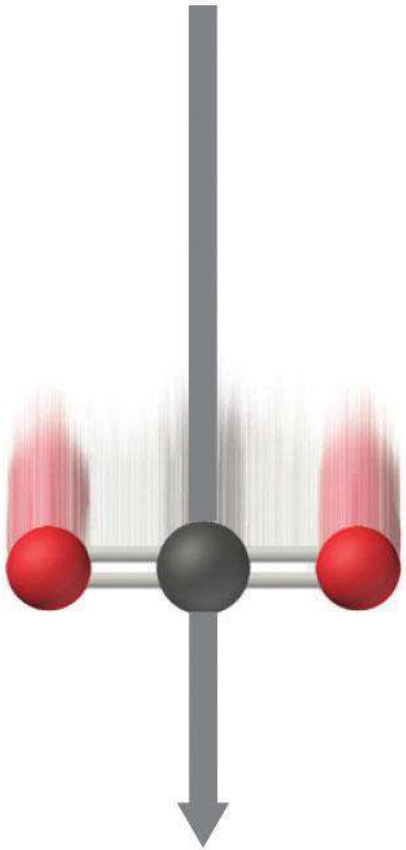
asymmetric stretching

vibrational motion





rotational motion



translational motion

الحركة الظاهرة باد IR

اي حركة ما بتعمل Dipole

ما بيشوفها بالجهاز

Dipole Changes During Vibrations

Infrared radiation is not energetic enough to bring about electronic transitions. Absorption of infrared radiation is thus confined largely to molecular species that have small energy differences between various vibrational and rotational states.

Homomolecule
كل الـ atoms فيه متشابهين

$O_2 \rightarrow O=O$
$H_2 \rightarrow H-H$

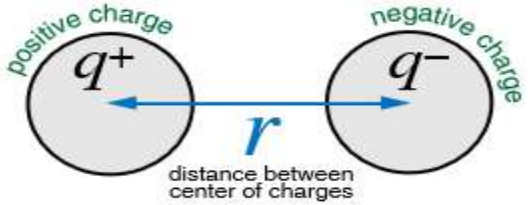
Dipole ما بيعمل حتى لو بعدوا عن بعض ما بينتج عليهم δ^- , δ^+

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

Dipole moment $= \mu = qr$

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

Molecules with permanent dipole moments (μ) are IR active

$H^{\delta+}-Cl^{\delta-}$ → IR

HCl, H_2O, NO

IR active

Polar covalent

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.

استخدمت الملح لان IR مابتقرأه

1% of Sample ← covalent + {99% KBr} in morter → to fine Powder

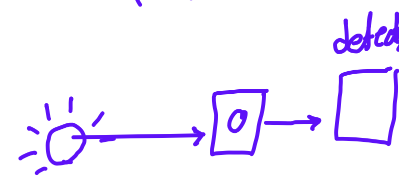
لما ينضغط بعمل lens → وبمسك العينة

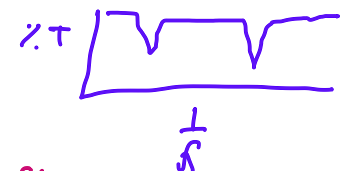
compreser → lens

بحطها بال holder

4000 – 500 cm^{-1}

detector





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

CO_2 → لا يمكن تحليلها « السبب في السلايدات التحت »

NaCl ← هو أملاح مشحون شحنة كاملة (مش δ)

+ ما في Covalent Bond ← ما في حركة Stretch أو Bend

والي ماسك Na^+ مع Cl^-

Ionic Bond → Attractivness

→ Dipole-Dipole الأملاح رغم انه فيها

لا يمكن تحليلها لأنه ما في Covalent

فبستخدمها as a carrier (KBr)

$\Delta E = h\nu$

There are three types of molecular transitions that occur in IR

a) **Rotational transitions**

- **When an asymmetric molecule rotates about its center of mass, the dipole moment seems to fluctuate.**
- **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.**

b) **Vibrational-rotational transitions**

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

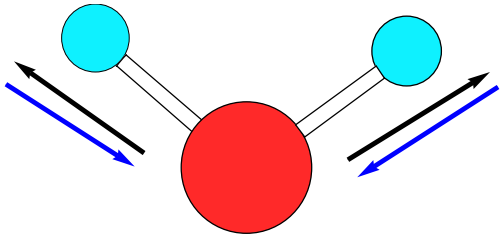
c) **Vibrational transitions**

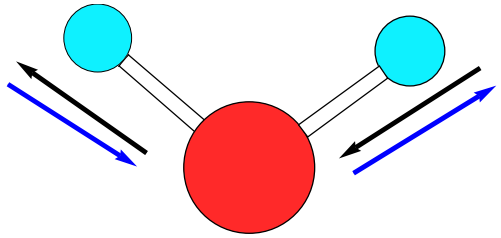
- **The most important transitions observed in qualitative mid-IR spectroscopy.**
- **$\bar{\nu}$ = 13,000 – 675 cm^{-1} (0.78 – 15 μm)**

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

Stretch: change in bond length

E Stretching > E Bending





E Symmetric stretch < E Antisymmetric stretch

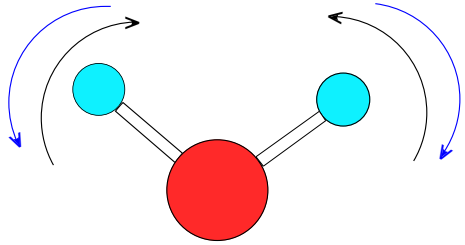
اتجاه الحركة نفسه ← (يبعدوا مع بعض ويرجعوا مع بعض)

ν_s

ν_{as} ← مش نفس اتجاه الحركة

وحدة بتطول والتانية بتقصر

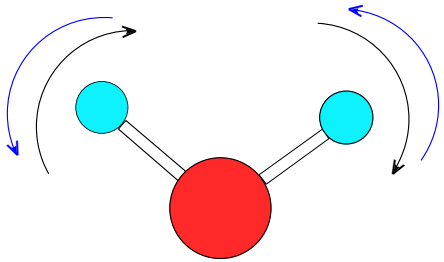
Bend: change in bond angle



Scissoring

مثل حركة المقص

ρ



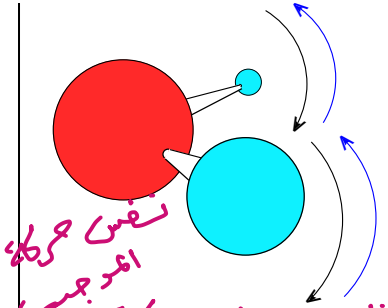
Rocking

σ

مع اتجاه الحركة على مستوى واحد

in-plane bend

عكس اتجاه الحركة على مستوى واحد



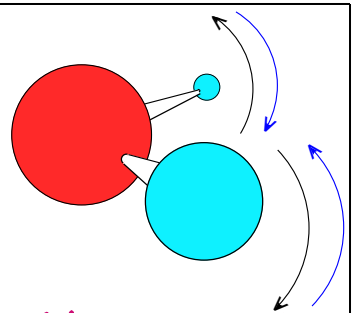
نفس حركة اللوجيحة

نفس اتجاه الحركة

wagging

ليست على نفس المستوى

ω



عكس اتجاه الحركة

twisting

ليست على نفس المستوى

τ

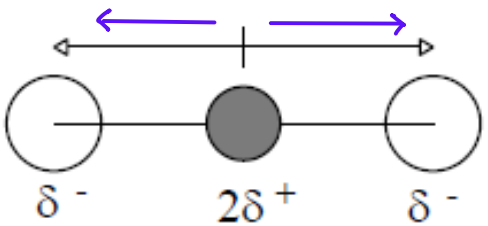
out-of-plane bend

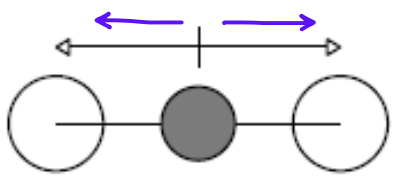
$\bar{\nu}_{Asym} > \bar{\nu}_{Sym} >> \bar{\nu}_{Bending}$

Only some modes may be IR active: Symmatric molecule

Example CO_2 O=C=O linear

Symmetric Stretching :- Not Active



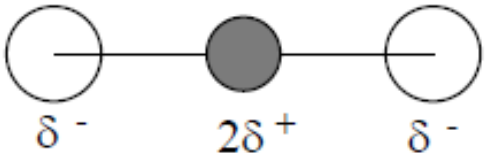


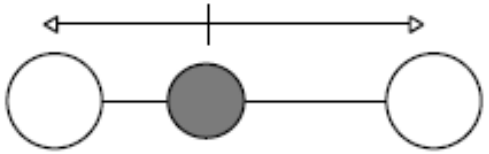
No net dipole moment change

مقدار السحب متساوى ومتعاكس بالاتجاه فبيلغوا بعظ وما بيعمل Dipole فهو مش Active

Asymmetric Stretching :- Active

وحدة انضغطت والثانية انسحبت بشوفها بالـ IR

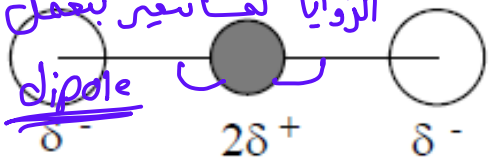


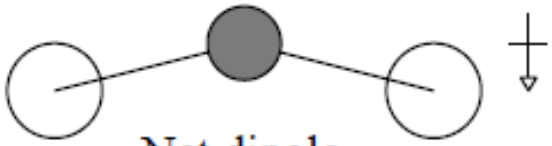


Net dipole moment change

Bending :- Active

الزوايا لما تتغير بتعمل dipole





Net dipole moment change

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

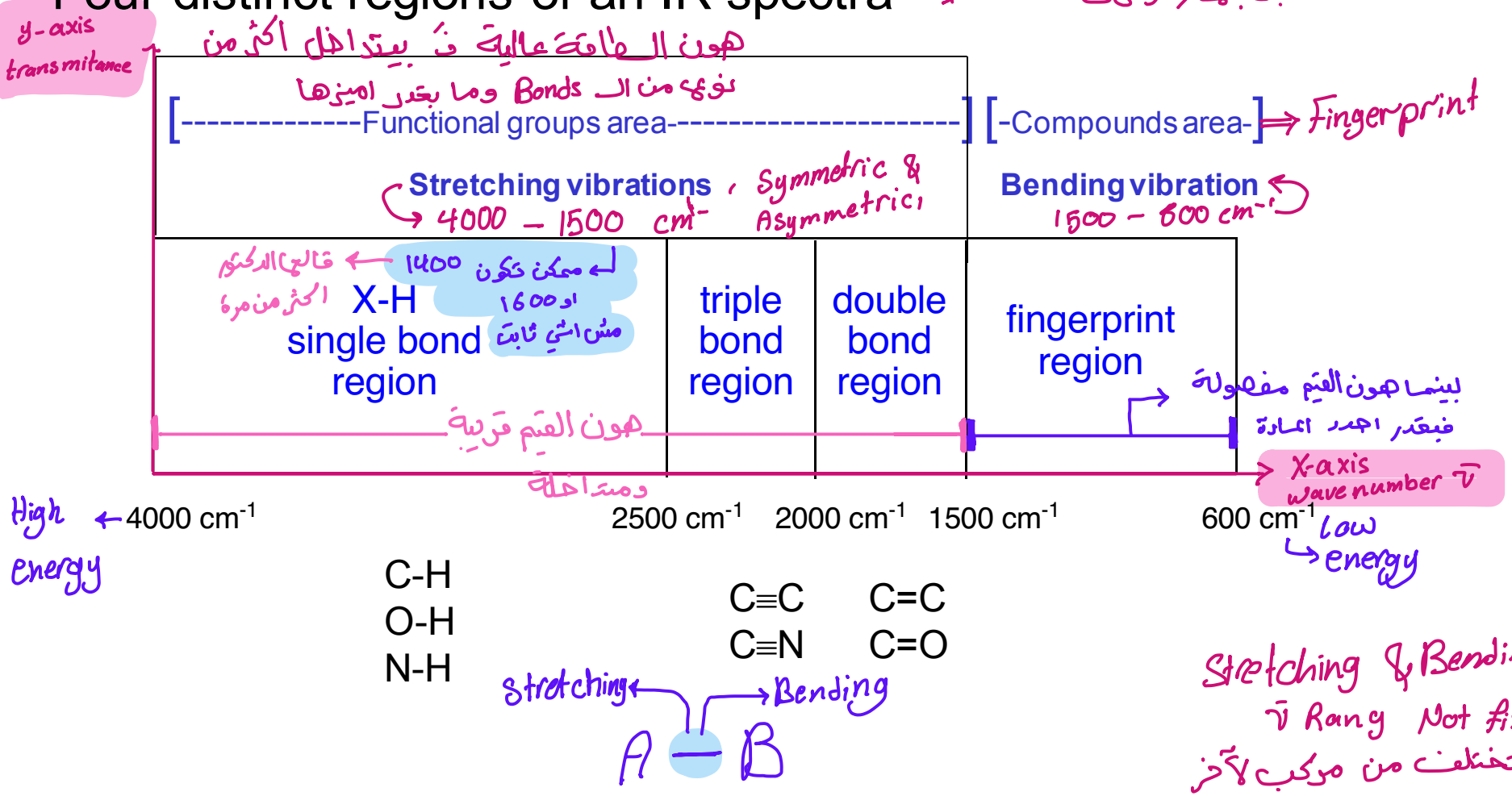
(Qualitative) حسب نوع المادة

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

نحضر العينة بنفس الطريقة ← ونحطها بالجهاز وننزل الـ IR waves

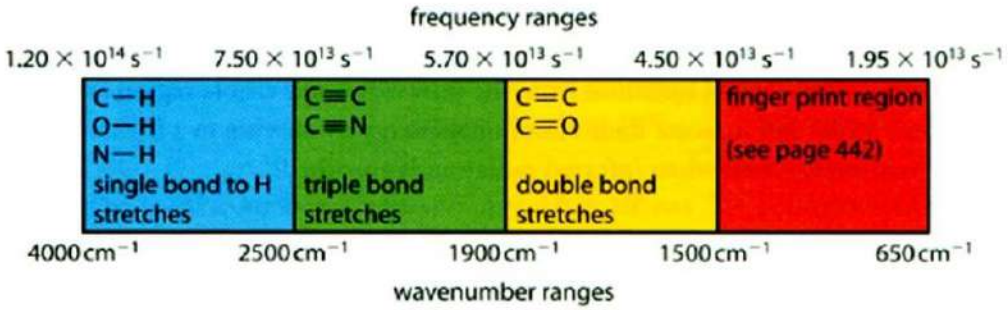
Four distinct regions of an IR spectra



C-H
O-H
N-H

C≡C C=C
C≡N C=O

Stretching & Bending
ν̄ Rang Not fixed
وتختلف من مركب لآخر

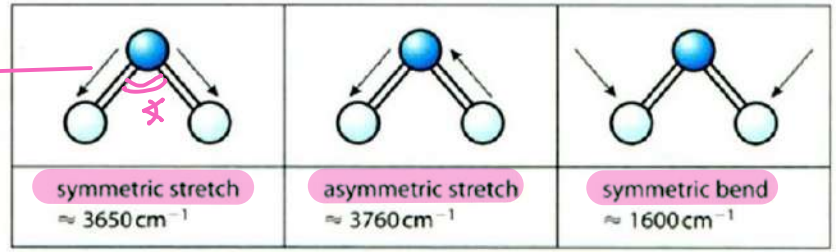


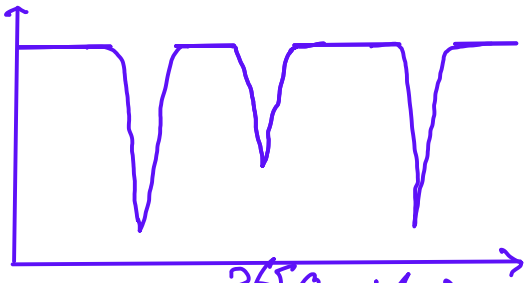
Stretching and bending in a polyatomic molecule

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.

H_2O $\nu asy > \nu sym > Bending$

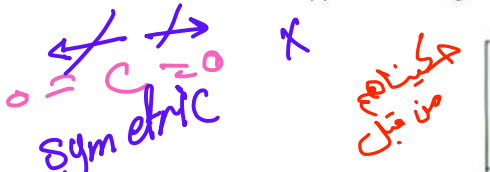
الزاوية Bent ≈ 105

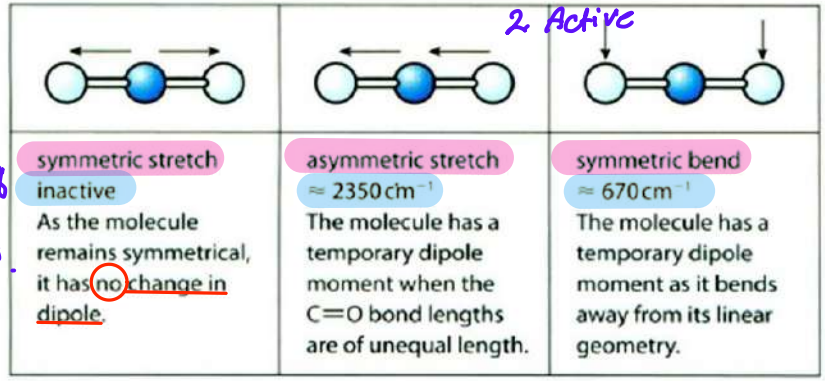


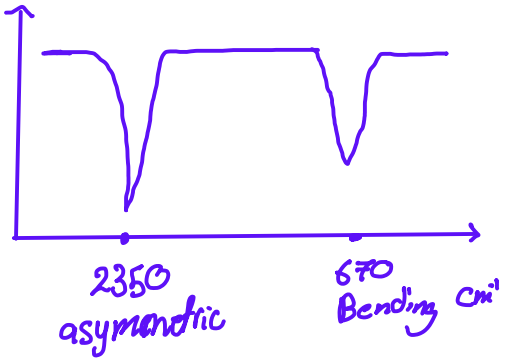


For a symmetrical linear molecule such as carbon dioxide, there are also three modes of vibration. However, the symmetric stretch is IR inactive as it produces no change in dipole moment. The dipoles of both C=O bonds are equal and opposite throughout the vibration.

CO_2 فعليا عنده 3 حركات لكن فقط 2 Active



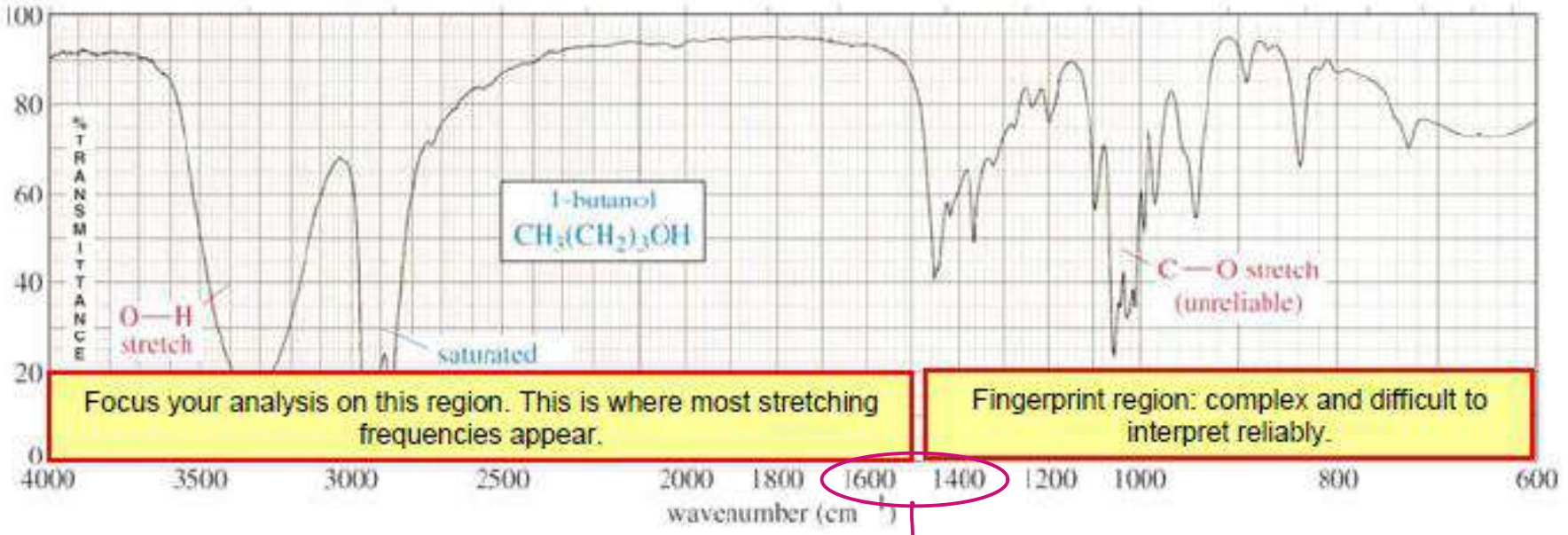




stretching

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}.



كل molecule الها حالة

Bending Rang الخاصية

يبدأ من 1600 - 1400 بهاى المنطقة

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.

من حسابات نظرية وعملية

مافي فيه حفظ

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}

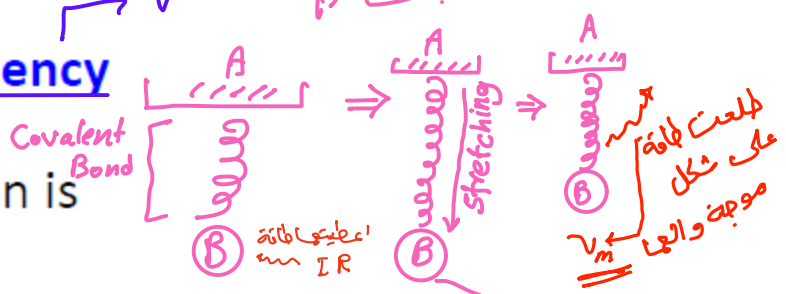
sp^3 -C-H 2850 - 2950 cm^{-1}

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

sp ≡C-H 3310 - 3320 cm^{-1}

الحسابات نظرية

Harmonic Oscillator Vibrational Frequency



The natural frequency of the oscillation is

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

ν_m = natural frequency

m = mass of the attached body

k = force constant of the spring

- The equation may be modified to describe the behavior of a system consisting of two masses m_1 and m_2 connected by a spring.
- it is only necessary to substitute the reduced mass μ for the single mass m, where

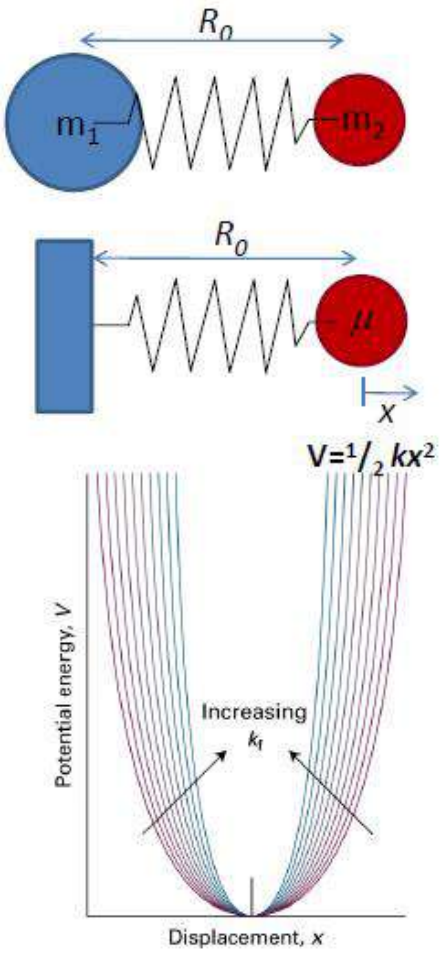
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

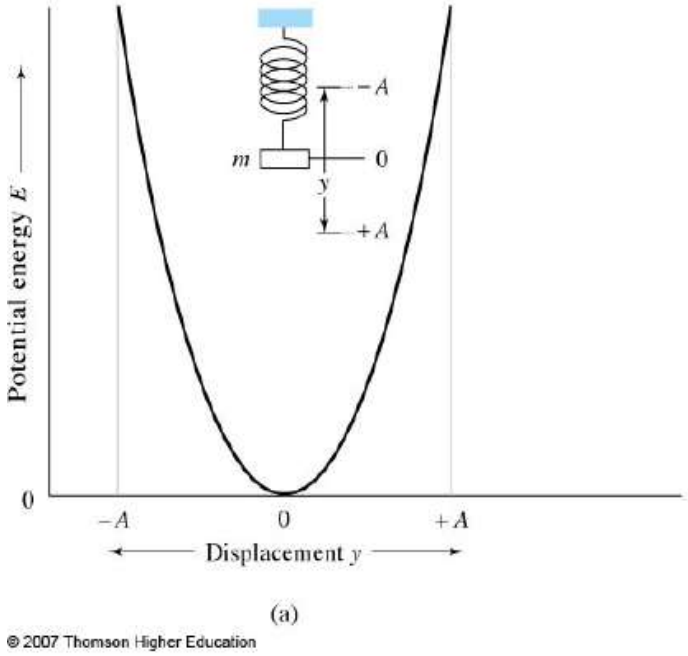
The equation may be modified to describe the behavior of a system consisting of two masses m_1 and m_2 connected by a spring. Here, it is only necessary to substitute the reduced mass μ for the single mass m where

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

Thus, the vibrational frequency for such a system is given by

$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k(m_1 + m_2)}{m_1 \quad m_2}}$$





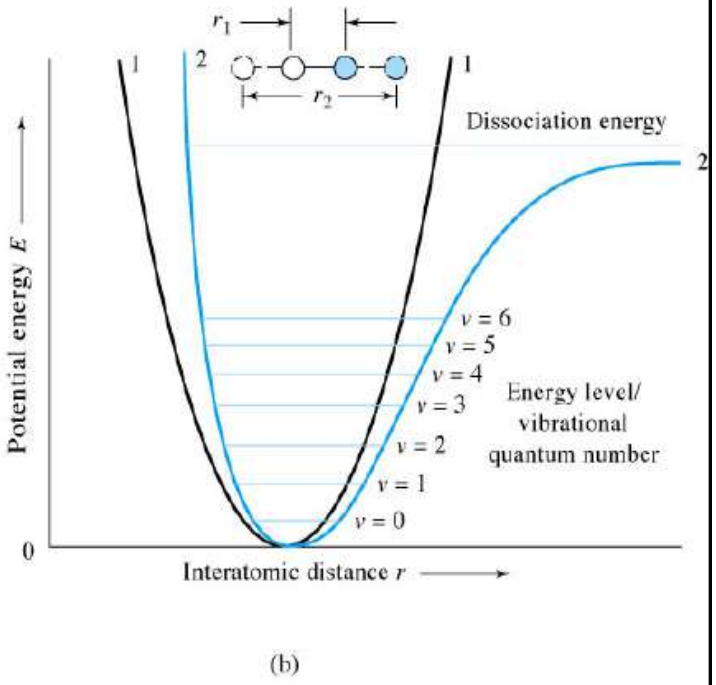


FIGURE 16-3 Potential-energy diagrams. (a) harmonic oscillator. (b) Curve 1, harmonic oscillator; curve 2, anharmonic motion.

- **Quantum Treatment of Vibrations**

ثابت بلانك

$$\Delta E = h\nu_m = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$E_{radiation} = h\nu = \Delta E = h\nu_m = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

The radiation in wavenumbers,

$c = \nu * f$

$f = \frac{c}{\nu}$

$\bar{\nu} = \frac{1}{f} = \frac{\nu}{c}$, $c = 3\times10^{8}$ m/s

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

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3\times10^{-12}\sqrt{\frac{k}{\mu}}$$

only

Where, $\tilde{\nu}$ is the wavenumber of an absorption peak in cm^{-1}, k is the force constant for the bond in newtons per meter (N/m), c is the velocity of light in cm/s, and the reduced mass μ has units of kg. k has been found to lie in the range between 3×10^2 and 8×10^2 N/m for most single bonds, with 5×10^2 serving as a reasonable average value. Double and triple bonds are found by this same means to have force constants of about two and three times this value (1×10^3 and 1.5×10^3, respectively).

$K_\sigma = 5 \times 10^2$ N/m

$K_{\sigma,\pi} = 2 * K_\sigma = 2 \times 5 \times 10^2 = 10^3$ N/m

$K_{\sigma,\pi} = 3 K_\sigma = 1.5 \times 10^3$ N/m

فرضنا انه $2\sigma = \pi$ و الـ $3\sigma \equiv$

The radiation in wavenumbers

$$\Delta E = h\nu_m = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

$C = \lambda \times \nu \Rightarrow \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{C}$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12}\sqrt{\frac{k}{\mu}}$$

$\Rightarrow V_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

ν : wavenumber of an absorption peak in cm^{-1}

k: the force constant for the bond in newtons per meter (N/m)

C: the velocity of light in cm/s

μ: the reduced mass has in kg.

الوحدات مهمة

k: in the range between 3×10^2 and 8×10^2 N/m for most single bonds, with 5×10^2 serving as a reasonable average value. Double and triple bonds are found by this same means to have force constants of about two and three times this value (1×10^3 and 1.5×10^3 , respectively).

Example:

Calculate the approximate wavenumber and wavelength of the fundamental absorption peak due to the stretching vibration of a carbonyl group C=O

Solution:

mass = molar mass * Avocado number

عدد افوكادرو

Mass of C is m1 = 12 x 10^{-3} kg/mol / 6 x 10^{23} atom/mol

= 2 x 10^{-26} kg

Mass of O is m2 = 16 x 10^{-3} / 6 x 10^{23} = 2.7 x 10^{-26} kg

And the reduced mass μ is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$ = (2 x 10^{-26}) x (2.7 x 10^{-26}) / (2 + 2.7) x 10^{-26}

mass C mass O

= 1.1 x 10^{-26} kg

As noted earlier, the force constant for the typical double bond is about 1 x 10^3 N/m. substituting this value and μ into

wavenumber =

$$\overline{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12}\sqrt{\frac{k}{\mu}}$$

ثابتة

10^3 / $1.1 * 10^{-26}$

= 1.6 x10^3 cm^{-1}

And the stretching band is found experimentally to be in the region of 1600 to 1800 cm^{-1}

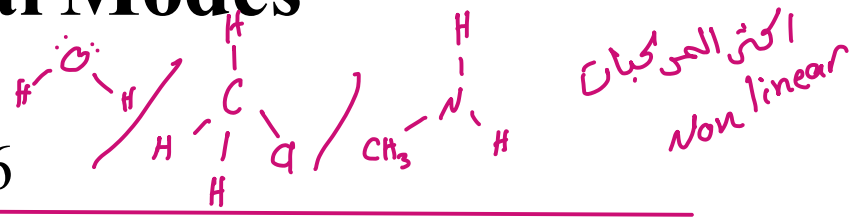
$E = \frac{h}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$ 10^3 N/m

ممكن يطلب الطاقة

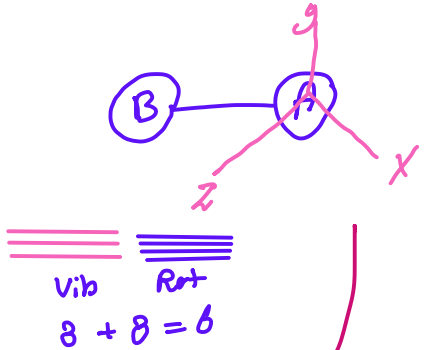
$\frac{\nu}{c} = \frac{1}{\lambda}$

Vibrational Modes

- Number of possible modes
  - Nonlinear molecule: 3N – 6
  - Linear molecule: 3N – 5



- 3 degrees of freedom – i.e., 3 coordinates in space
- 3 translations and 3 rotations account for 6 motions of molecule
- Rotation about center bond in linear molecule is indistinguishable



- Remaining degrees of motion represent vibrational motion (i.e., number of vibrations within the molecule)

Calculate Number of Vibrational Modes

The degrees of vibrational modes for linear molecules can be calculated using the formula:

$$3n - 5 \text{-----(1)}$$

The degrees of freedom for nonlinear molecules can be calculated using the formula:

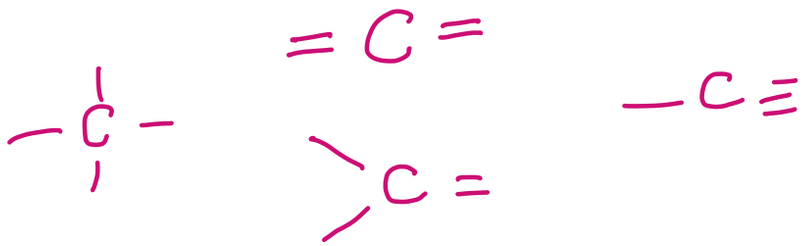
$$3n - 6 \text{-----(2)}$$

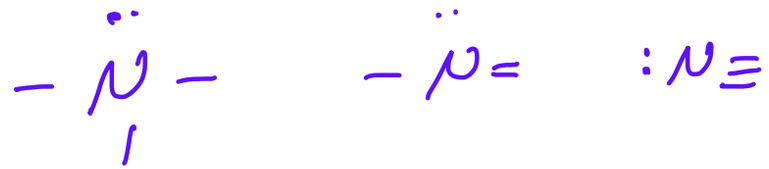
n is equal to the number of atoms within the molecule of interest.

The following procedure should be followed when trying to calculate the number of vibrational modes:

1- Determine if the molecule is linear or nonlinear (i.e. Draw out molecule using VSEPR). If linear, use Equation 1. If nonlinear, use Equation 2

2- Calculate how many atoms are in your molecule. This is your *n* value. Plug in your *n* value and solve.

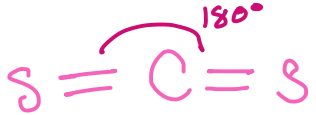




$X = F , Cl , Br , I$

$-X$

4 Bonds بعمل ← 4 = 0 تكافؤ ←



Example 1: CS_2

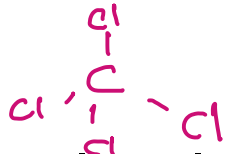
An example of a linear molecule would be CS_2. There are a total of 3 atoms in this molecule. Therefore, to calculate the number of vibrational modes, it would be:

حتى لو مش Active وطلب اني احسبه بحسب ال theory

theory → ✓

Practical = ✗

3(3)-5 = 4 vibrational modes.



Example 2: CCl_4

CCl_4 is a nonlinear molecule. In this molecule, there are a total of 5 atoms. $3N-6$ $N=5$

Therefore, there are 3(5)-6 = 9 vibrational modes.

Example 2: H_2O

H_2O is a nonlinear molecule. In this molecule, there are a total of 3 atoms. $3N-6$ $N=3$

Therefore, there are 3(3)-6 = 3 vibrational modes.

حكيناهم من قبل ورسمنا صورة من الـ Spectrum

expected theoratical

How many vibrational modes?

H — H

N = 2

3 * 2 − 5 = 1 Practical = 0

2 atoms (H_2) - 1 vibration (stretch ν)

---

3 atoms (H_2O) - 3 vibrations (ν_s, ν_{as}, σ) → Σ = line

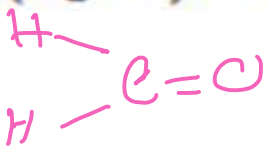
---

3 atoms (CO_2) - 4 vibrations (ν_s, ν_{as}, σ, ω) → Σ = line N = 3

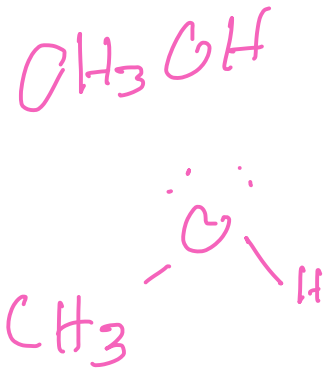
Active

---

4 atoms (H_2CO) - 6 vibrations (ν_s, ν_{as}, σ, ω, ρ(CH_2) ν(C=O))



3 * 4 − 6 = 6



Factors Influence the Normal Modes

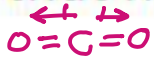
لما حسبت Theory اعطاني 5 حركات بينما الPractical اعطاني فقط 3

Four factors tend to produce fewer experimental peaks than would be expected from the theoretical number of normal modes. (1) the symmetry of the molecules is such that no change in dipole results from a particular vibration; (2) the energies of two or more vibrations are identical or nearly identical; (3) the absorption intensity is so low as to be undetectable by ordinary means; or the vibrational energy is in a wavelength region beyond the range of the instrument

Fewer and more experimental peaks than calculated

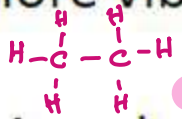
- Fewer peaks (Theory Peaks >)

(1) the symmetry of the molecules is such that no change in dipole results from a particular vibration



(2) the energies of two or more vibrations are identical or nearly identical

C_2H_6



δ(C-H) وحدة Peak على شكل 6 Bonds جمع لكن بظهروا

(3) the absorption intensity is so low as to be undetectable by ordinary means

بكون الـ Peak ضعيفة فبعملها ، بكون موجودة عمليًا لكن لاتحب

ضعيف Intensity

- More peaks (Theory Peaks < Practical Peaks)
  - (1) Overtone
  - (2) Combination bands

Fundamental Peaks and Overtones

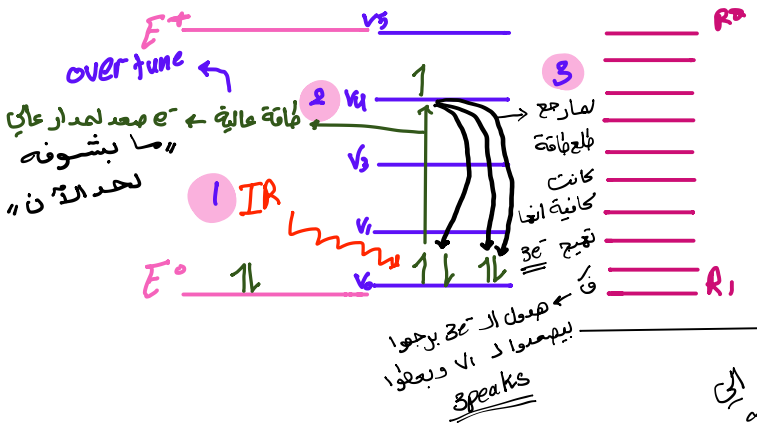
Fundamental transition:

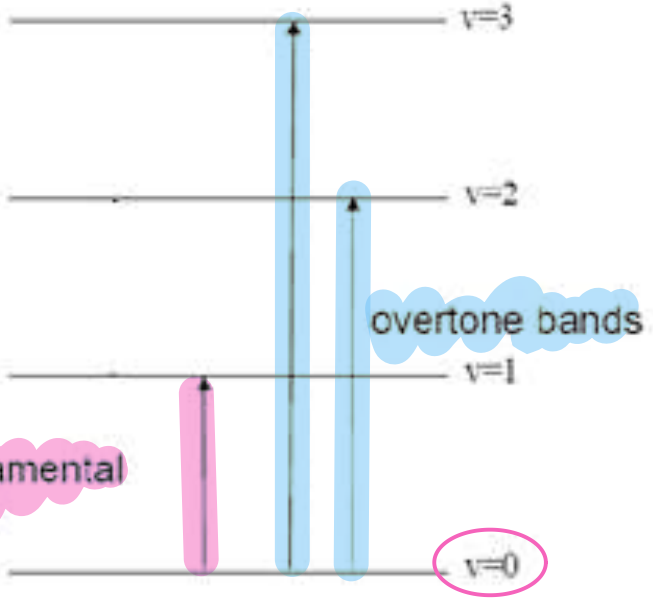
The excitation from the ground state V_0 to the first excited state V_1 is called the fundamental transition. It is the most likely transition to occur.

Fundamental absorption bands are strong compared with other bands that may appear in the spectrum due to overtone, combination, and difference bands.

Overtone bands:

Result from excitation from the ground state to higher energy states V_2 , V_3 , and so on.





- If the fundamental absorption occurs at frequency ν, the overtones will appear at about 2ν, 3ν, and so on.
- Overtones are weak bands and may not be observed under real experimental conditions.

Coupling modes:

- Vibrating atoms may interact with each other. Two vibrational frequencies may couple to produce a new frequency $\nu_3 = \nu_1 + \nu_2$. The band at ν_3 is called a combination band.

- If two frequencies couple such that $\nu_3 = \nu_1 - \nu_2$, the band is called a difference band.

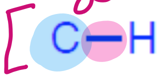
- Not all possible combinations and differences occur.

Factors that affect the frequency of light absorbed

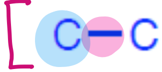
1. Bonds which have one lighter and one heavier atom vibrate faster than bonds which have two heavier atoms.

اعطيت نفس الطاقة

كل ما كان الفرق بين الـ masses كبير كل ما الطاقة عالية



3000 cm^{-1}



1200 cm^{-1}

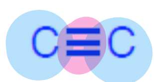
طرفين ثقال او متساويين → قليل $\bar{\nu}$

* طرف خفيف ← ν عالي، يرجع بسرعة
* طرفين ثقال ← ν ضعيف، يرجع ببطء

أنواع ذرات مختلفة، الرابطة σ

2. Stronger bonds vibrate faster than weaker bonds.

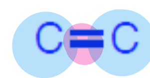
ثبت أنواع الذرات
غير أنواع الروابط



2200 cm^{-1}

C ≡ N

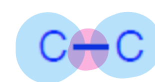
>



1660 cm^{-1}

C = N

>



1200 cm^{-1}

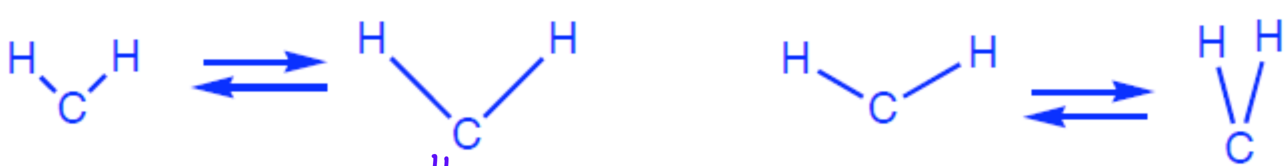
C − N، الفرق بين الكتل قليل ← طاقة قليلة

الجدول الدوري: H; B C N O X

③ C−N, C−Cl ①, ④ C−H, C−O ②

من اقل طاقة إلى اعلى طاقة

3. Stretching vibrations are faster than bending vibrations



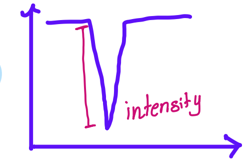
2920 cm^{-1} 1380 cm^{-1}

E asymmetric > E symmetric > Bending

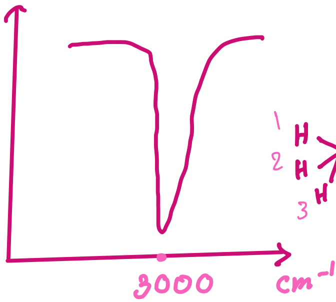
اهتم بنوع الـ Vibration

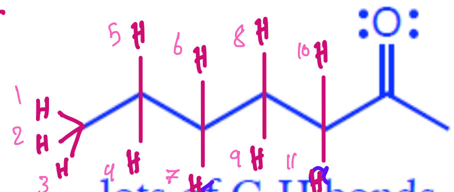
[Stretching بده طاقة عالية → بجدد الطاقة بسرعة → ν اعلى] والعكس Bending

Factors that affect the amount of light that is absorbed

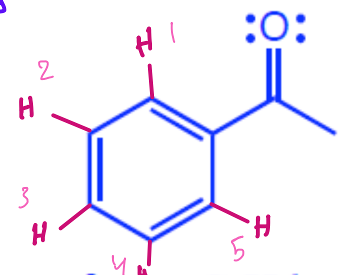


1. If there are many C-H bonds in a molecule absorbing light at the same frequency, the band will be much larger than if there are only a few.

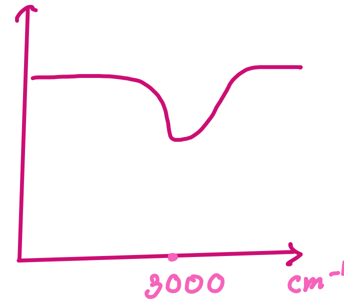




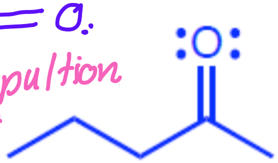
lots of C-H bonds
large absorption

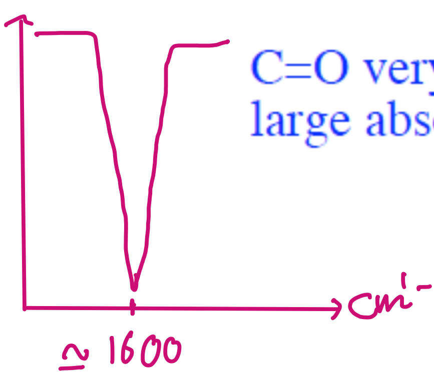


fewer C-H bonds
smaller absorption



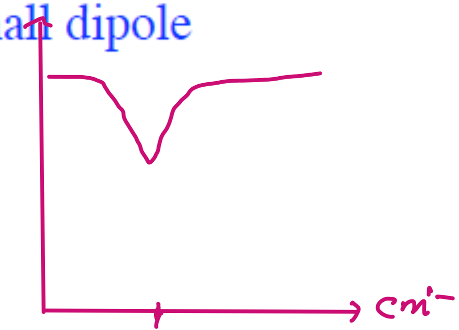
2. Strength of the dipole - bonds which have a strong dipole moment will absorb light more strongly than those which have a weaker dipole moment.





C=O very polar, strong dipole
large absorption

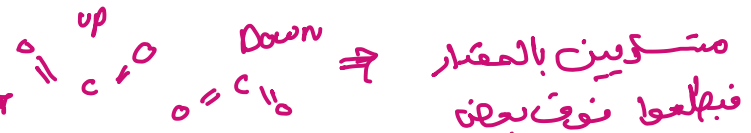
C=C nonpolar, small dipole
small absorption



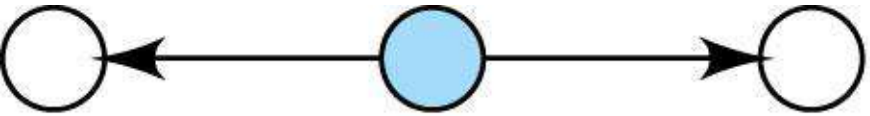
CO_2 Molecule

Let us consider the infrared spectrum of carbon dioxide. If no coupling occurred between the two C=O bonds, an absorption peak would be expected at the same wavenumber as the peak for the C=O stretching vibration in an aliphatic ketone (about 1700 cm^{-1}). Experimentally, carbon dioxide exhibits two absorption peaks, the one at 2330 cm^{-1} and the other at 667 cm^{-1}. Carbon dioxide is a linear molecule and thus has 3 x 3 – 5 = 4 normal modes. Two stretching vibrations are possible. The symmetric vibration causes no change in dipole. Thus, the symmetric vibration is infrared inactive.

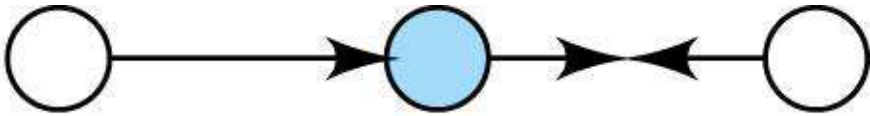
The asymmetric vibration produce a change in dipole moments, so absorption at 2330 cm^{-1} results.



The remaining two vibrational modes of carbon dioxide involve scissoring. The two bending vibrations are the resolved components at 90 deg to one another of the bending motion in all possible planes around the bond axis. The two vibrations are identical in energy and thus produce a single peak at 667 cm^{-1}.

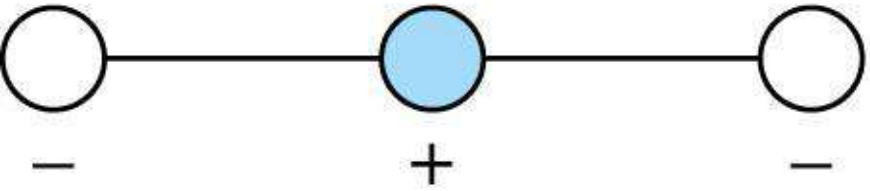


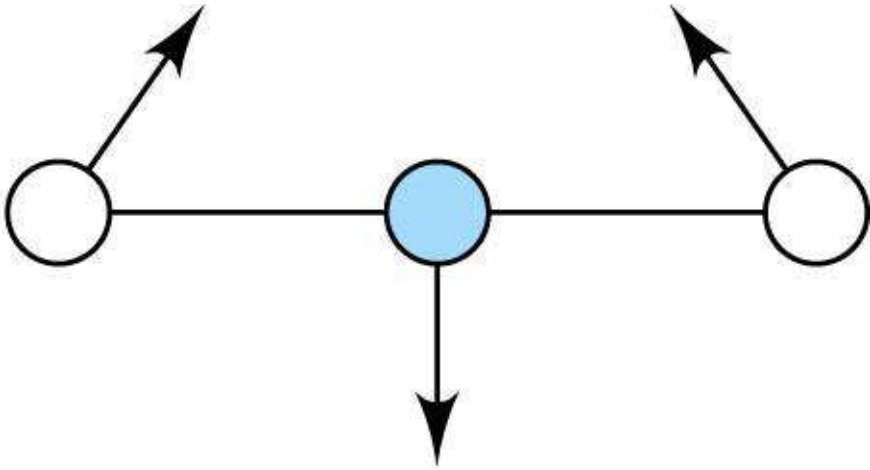
Symmetric



Asymmetric

Stretching

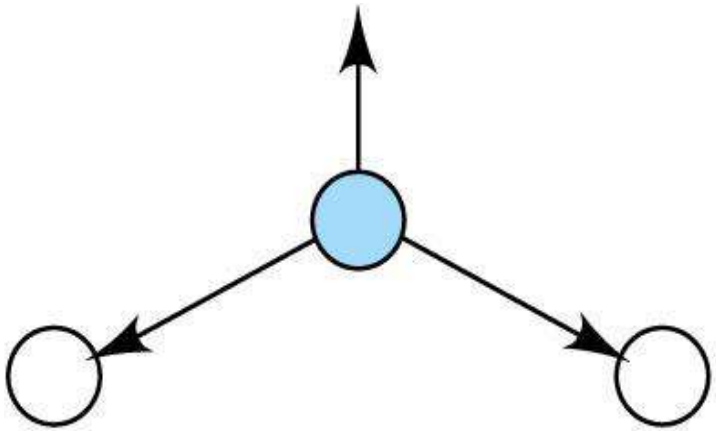




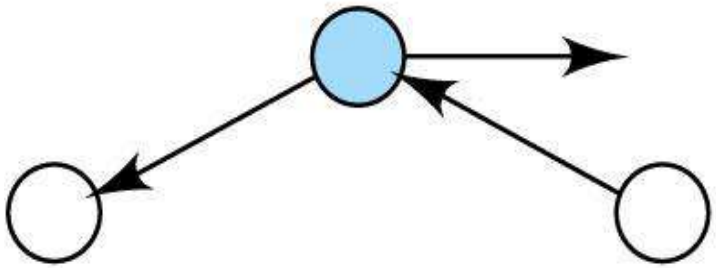
Bending

H_2O molecule

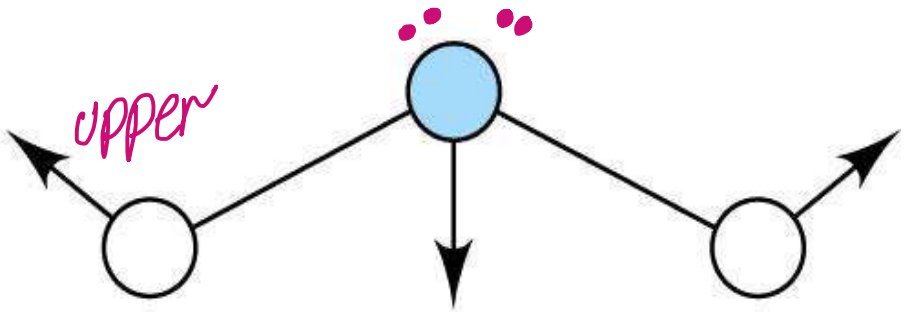
Triatomic molecule such as water, sulfur dioxide, or nitrogen dioxide have 3 x 3 – 6 = 3 vibrational modes. The central atom is not in line with the other two, a symmetric stretching vibration will produce a change in dipole and will thus be responsible for infrared absorption. Stretching peaks at 3650 and 3760 cm^{-1} appear in the infrared spectrum for the symmetric and asymmetric vibrations of the water molecule. There is only one component to the scissoring vibration for this nonlinear molecule. For water, the bending vibration cause absorption at 1595 cm^{-1}.



Symmetric stretching

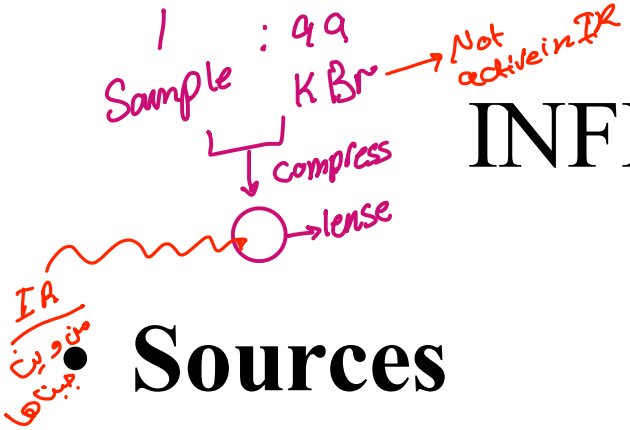


Asymmetric stretching



Scissoring

Bending



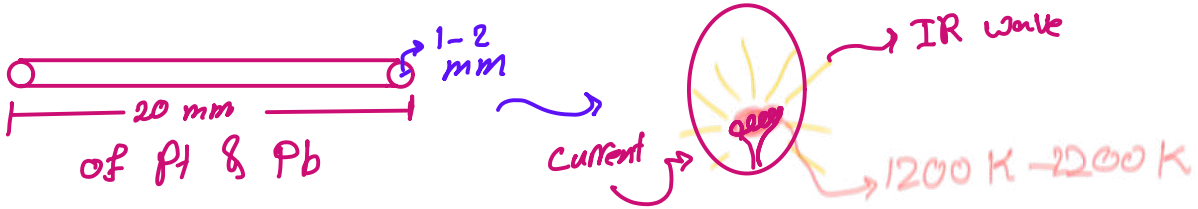
INFRARED SOURCES

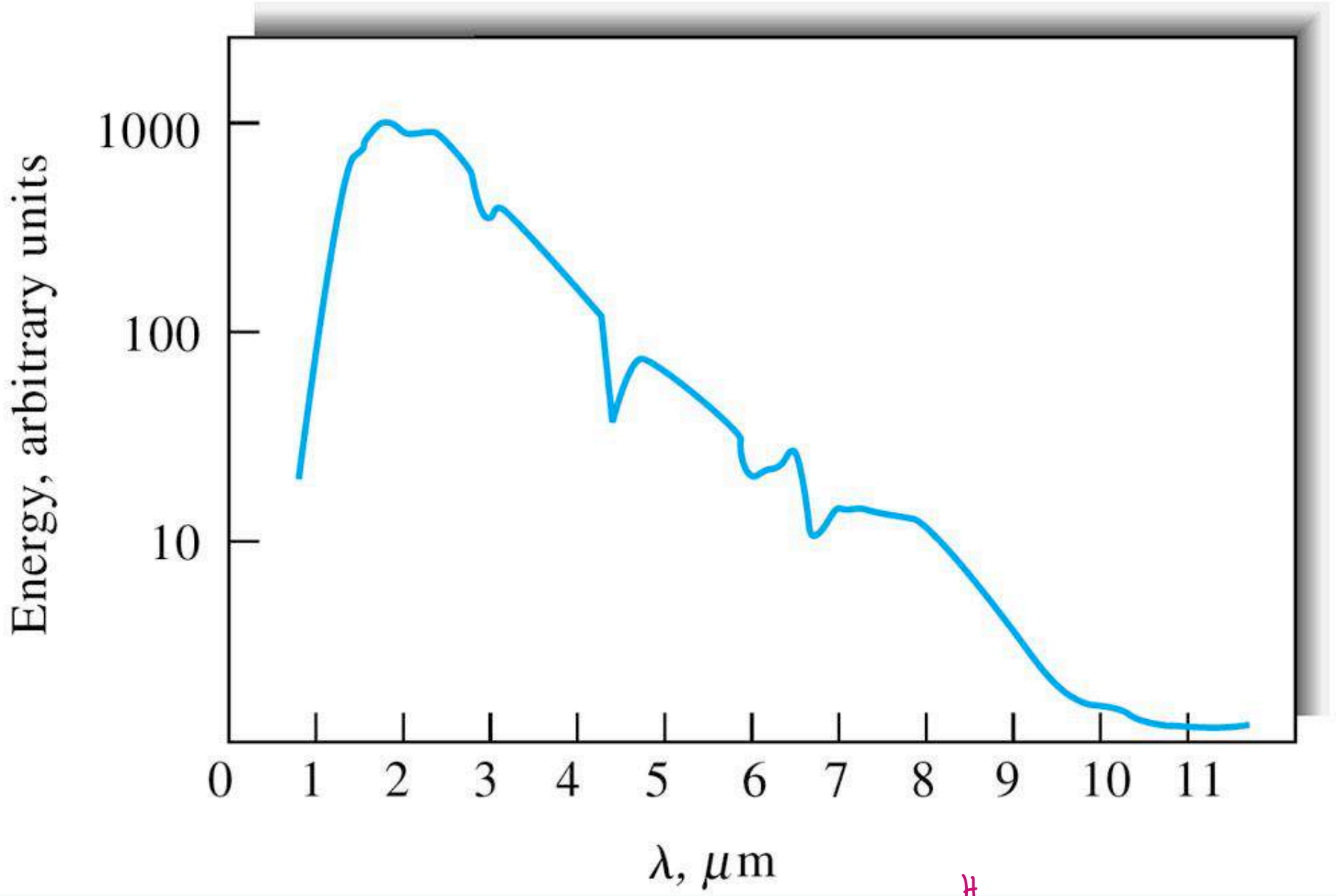
4000 – 650 cm^{-1}
- 500 الاحدث
- 200 احدث وأغلى

Sources

Infrared sources consist of an inert solid that is heated electrically to a temperature between 1500 and 2200 K. Continuum (متصل) radiation approximating that of a blackbody results. The maximum radiant intensity at these temperatures occurs between 5000 to 5900 cm^{-1}.

- **The Nernst Glower:** The Nernst glower is composed of rare earth oxides formed into a cylinder having a diameter of 1 to 2 mm and a length of perhaps 20 mm. Platinum leads are sealed to the ends of the cylinder to permit electrical connection to what amounts to a resistive heating element. As current is passed through the device, temperature between 1200 K and 2200 K result.

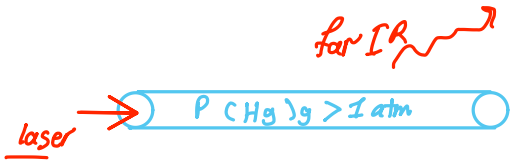




- **The Globar Source:** A Globar is a silicon carbide rod, usually about 50 mm in length and 5 mm in diameter. It also is electrically heated (1300 to 1500 K). Spectral energies of the Globar and the Nernst glower are comparable except in the region below 5μm, where the Globar provides a significantly greater output.

- **Incandescent Wire Source:** A source of somewhat lower intensity but longer life than the Globar or Nernst glower is a tightly wound spiral of nichrome wire heated to about 1100 K by an electrical current.

- **The Mercury Arc**: For the far-infrared region of the spectrum ($\lambda > 50$ μm), none of the thermal sources just described provides sufficient radiant power for convenient detection. Here, a high-pressure mercury arc is used. This device consists of a quartz-jacketed tube containing mercury vapor at a pressure greater than one atmosphere. Passage of electricity through the vapor forms an internal plasma source that provides continuum radiation in the far-infrared region.



- **The Tungsten Filament Lamp**: An ordinary tungsten filament lamp is a convenient source for the near-infrared region of 4000 to 12,800 cm^{-1}.

- **The Carbon Dioxide Laser Source**: A tunable carbon dioxide laser is used as an infrared source for monitoring the concentrations of certain atmospheric pollutants and for determining absorbing species in aqueous solutions. A carbon dioxide laser produces a band of radiation in the 900 to 1100 cm^{-1} range.

Sources

Nernst Glower	heated rare earth oxide rod (~1500 K)	1-10 μm
Globar	heated SiC rod (~1500 K)	1-10 μm
W filament lamp	1100 K	0.78-2.5 μm
Hg arc lamp	plasma	>50 μm
CO_2 laser	stimulated emission lines	9-11 μm