تفريغ تحليل آلي

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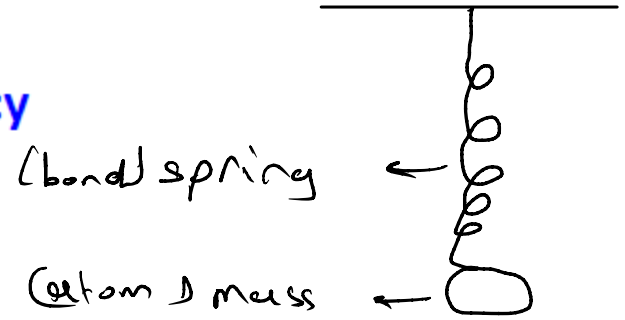
Seul Academy

لجان الدُّفعات

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

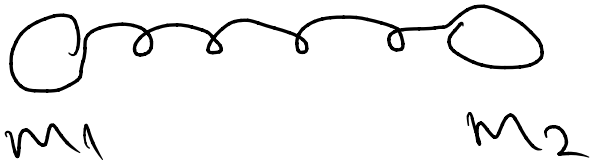
- The equation may be modified to describe the behavior of a system consisting of two masses m_1 and m_2 connected by a spring.
- it is only necessary to substitute the reduced mass μ for the single mass m, where

← وزن الذرتين المرتبطتان مع هذا spring او bond

* اقل molecule تكون من 2 atoms.

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

← بعوضها بدل m في القانون



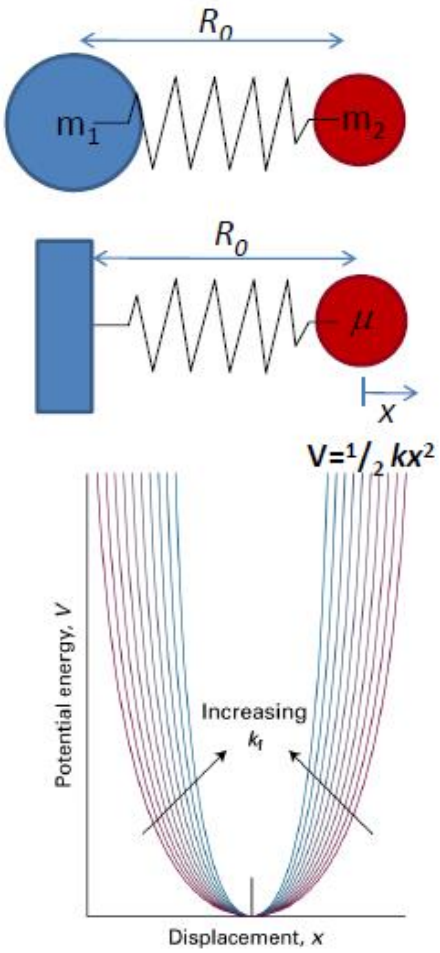
The equation may be modified to describe the behavior of a system consisting of two masses m_1 and m_2 connected by a spring. Here, it is only necessary to substitute the reduced mass μ for the single mass m where

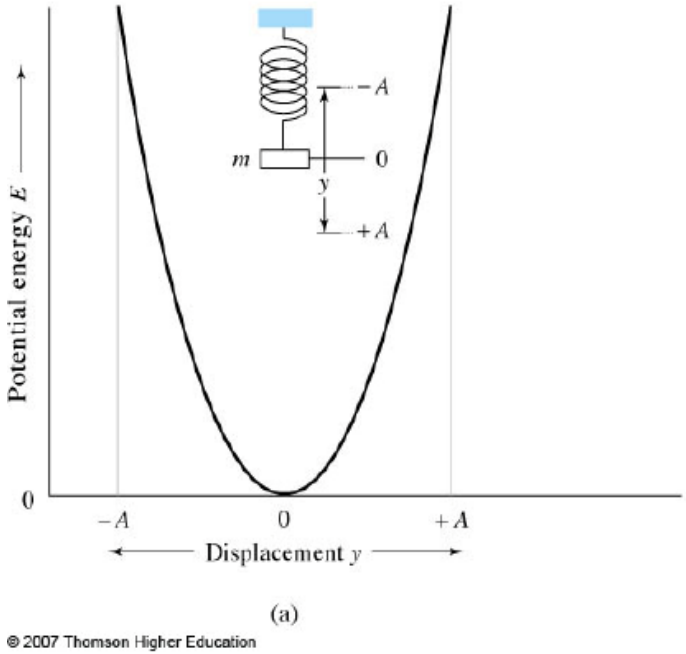
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

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

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

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





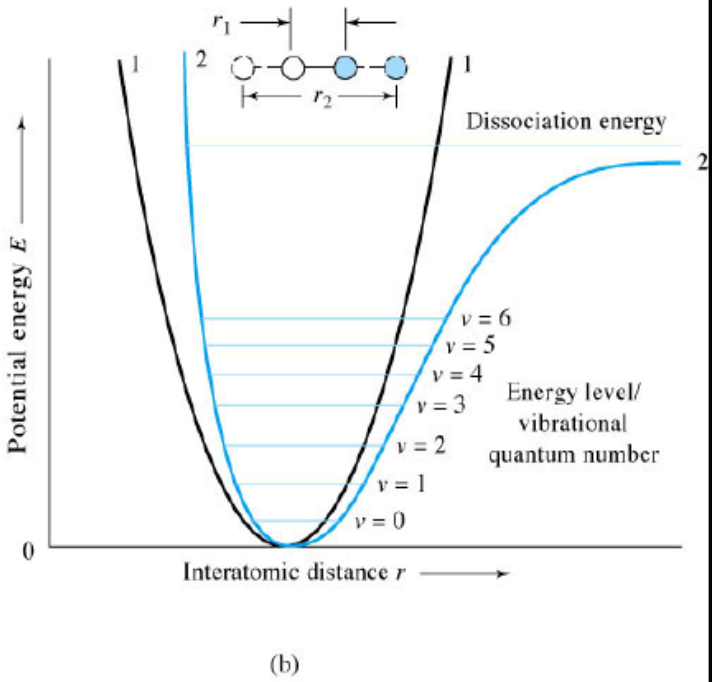


FIGURE 16-3 Potential-energy diagrams. (a) harmonic oscillator. (b) Curve 1, harmonic oscillator; curve 2, anharmonic motion.

- **Quantum Treatment of Vibrations**

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

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

The radiation in wavenumbers,

$\bar{\nu} = \frac{1}{\lambda}$, $\lambda = \frac{c}{\nu} \rightarrow \bar{\nu} = \frac{\nu}{c} \rightarrow \nu = c.\bar{\nu} \rightarrow \bar{\nu} = \frac{\nu}{c}$

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

Where, ν 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).

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.

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:

1 mole → 6×10^{23} atom mW C = 12 g mW O = 16 g

double

k = 1×10^3

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

= 2×10^{-26} kg

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

And the reduced mass μ is given by:

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

$$= 1.1 \times 10^{-26} \text{ kg}$$

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

1×10^3

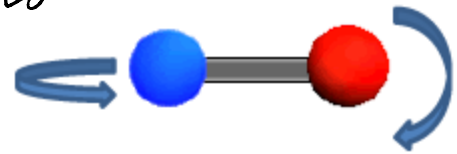
wavenumber = $$\overline{\nu}_m = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12}\sqrt{\frac{k}{\mu}} = 1.6 \times 10^3 \text{ cm}^{-1} = 1600 \text{ cm}^{-1}$$

$\approx 1.1 \times 10^{-26}$

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

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

نظرية تستخدم لتحديد الشكل الهندسي للمركب في الفراغ (linear or not)

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

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:

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.

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.

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

How many vibrational modes?

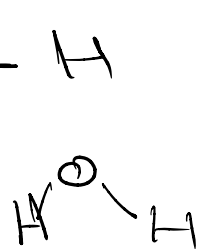
2 atoms (H_2) - 1 vibration (~~stretch~~ ν)

3 atoms (H_2O) - 3 vibrations (~~ν_s, ν_{as}, σ~~)

3 atoms (CO_2) - 4 vibrations (~~ν_s, ν_{as}, σ, ω~~)

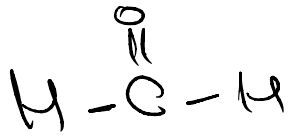
4 atoms (H_2CO) - 6 vibrations (~~ν_s, ν_{as}, σ, ω, ρ(CH_2) ν(C=O)~~)

H – H linear



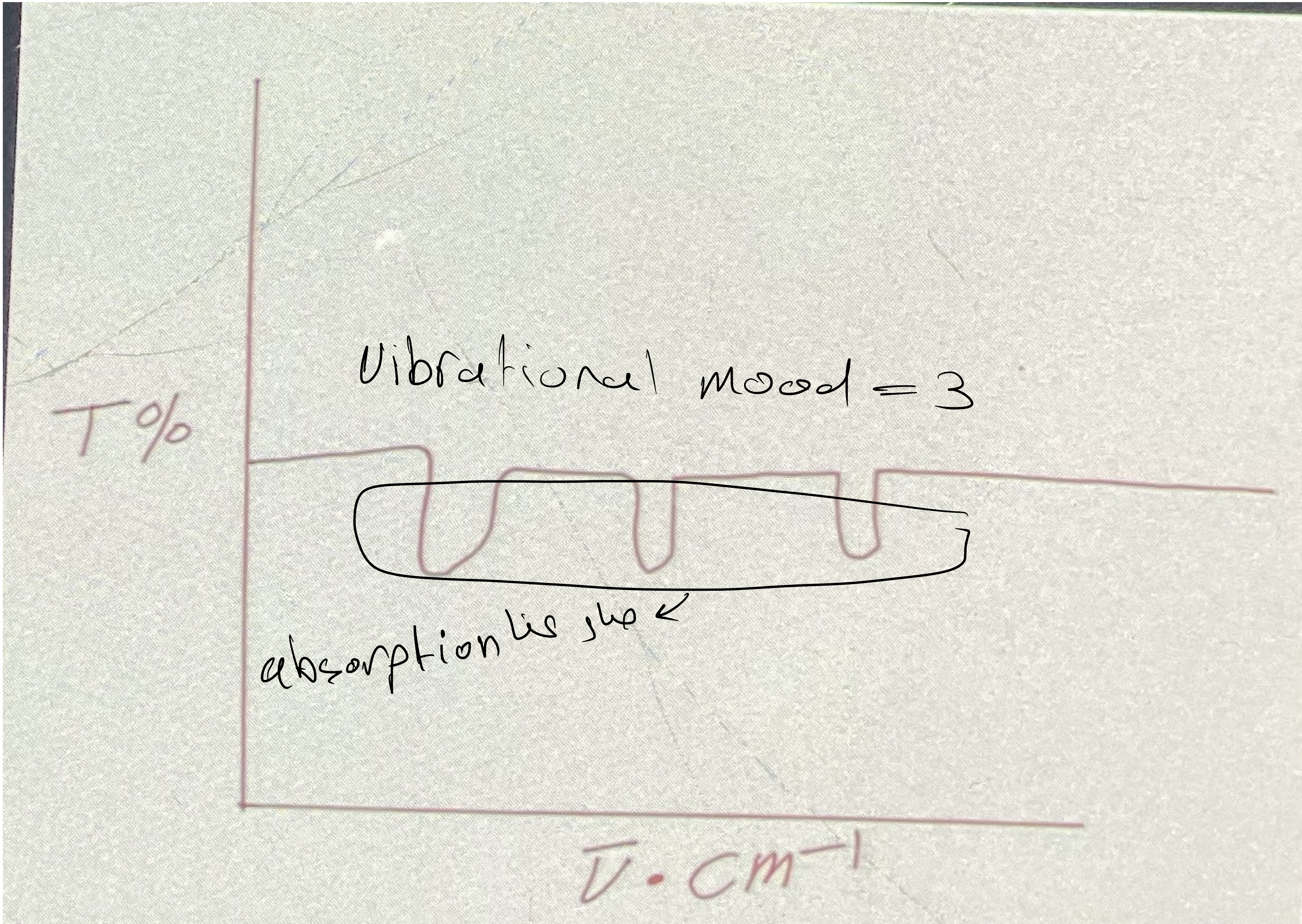
nonlinear

O = C = O linear



nonlinear

Vibrational mood بظهرها في IR spectrum على شكل peaks.



Factors Influence the Normal Modes

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

(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

- More peaks → بنلاحظ peaks اكثر من المتوقع

(1) Overtone

(2) Combination bands

Fundamental Peaks and Overtones

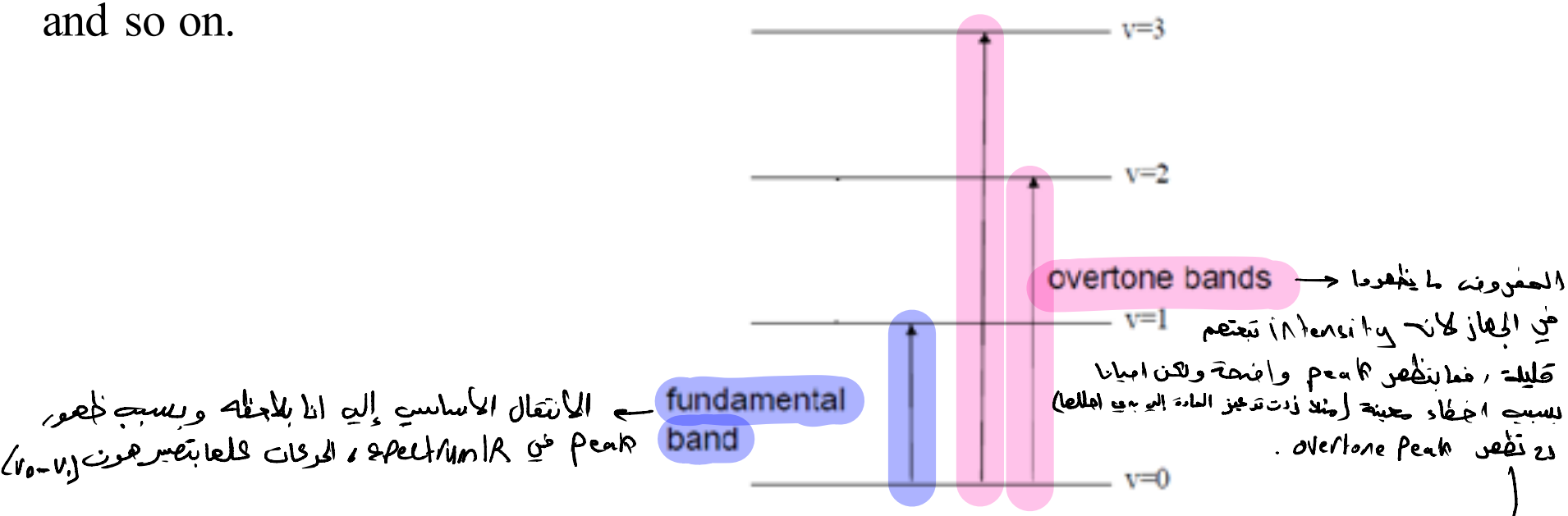
Fundamental transition:

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.

* الأنا overtone و Fundamental band.

Coupling modes:

* اذا overtone ظهرت في peak رح تعمل coupling
مع FP فيجمعوا مع بعض و ينتجوا frequency جديدة تظهر على
شكل peak زيادة عن إلي حاسبينها.

- 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.
  (new peak = Fundamental band + overtone; FP + overtone)

- 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

→ or wavenumber

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

C–H

3000 cm^{-1}

C–C

1200 cm^{-1}

2. Stronger bonds vibrate faster than weaker bonds.

* قلنا قبل انه الـ single bond اعلى wavenumber ولكن كانت الحركات فيها H مثل N–H, O–H, X–H, C–H ولكن عندما تقارن C–C في جميع انواع الروابط نجد أن single bond لها اقل wavenumber.

C≡C

2200 cm^{-1}

> 1600

C=C

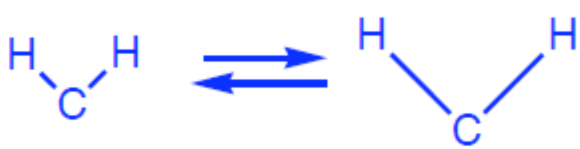
1660 cm^{-1}

< 160

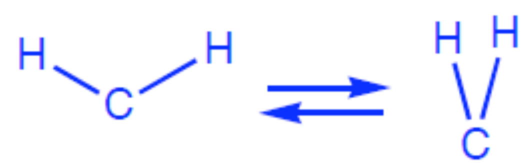
C–C

1200 cm^{-1}

3. Stretching vibrations are faster than bending vibrations



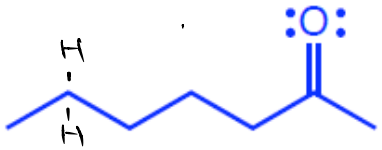
2920 cm^{-1}



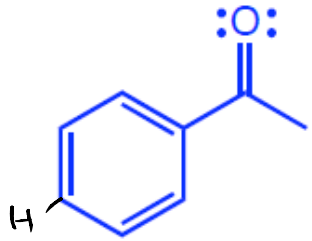
1380 cm^{-1}

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.

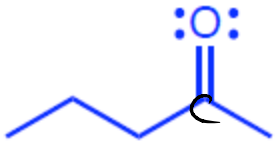


lots of C-H bonds
large absorption



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

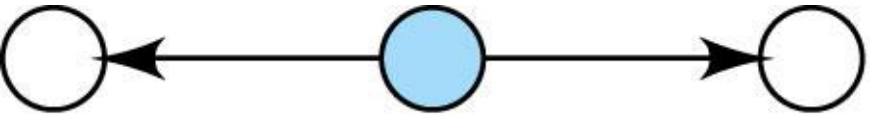
Let us consider the infrared spectrum of carbon dioxide. If no coupling occurred between the two C=O bonds, an absorption peak would be expected at the same wavenumber as the peak for the C=O stretching vibration in an aliphatic ketone (about 1700 cm^{-1}). Experimentally, carbon dioxide exhibits two 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.

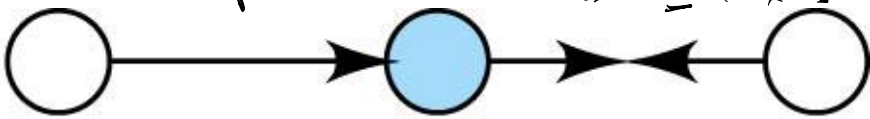
The remaining two vibrational modes of carbon dioxide involve bending scissoring. The two bending vibrations are the resolved components at 90 deg to one another of the bending motion in all possible planes around the bond axis. The two vibrations are identical in energy and thus produce a single peak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

كلها بتحسب vibrational mood لل CO_2 بطلع 4 واحد symmetric
stretching 2 بتنحسب و ٣ بظهرو بس ال ٢ بظهر عنا 2 peaks لـ (2330, 667)

لانه هنا Vibrational is Identical وهاي وحده من الاسباب
إلي بخلي بظهر عدد Peak اقل من المتوقع



Symmetric

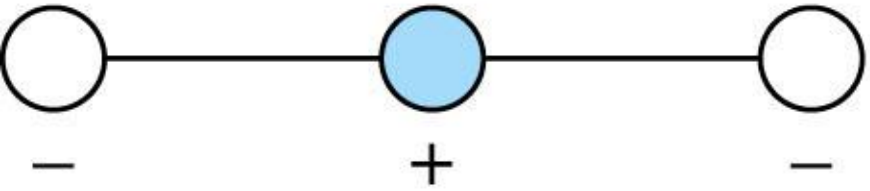


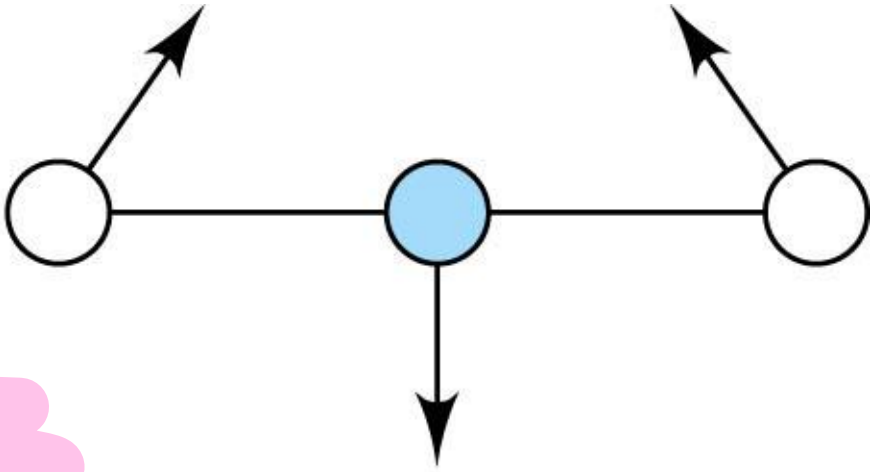
Asymmetric

2330

Inactive

Stretching





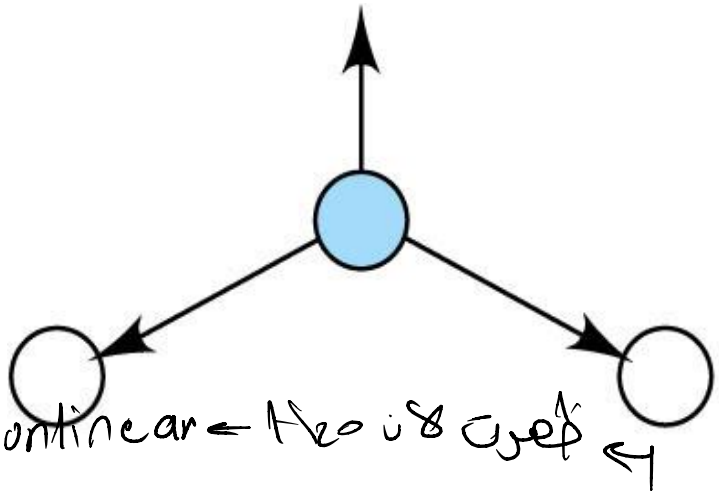
BBT

Bending

H_2O molecule

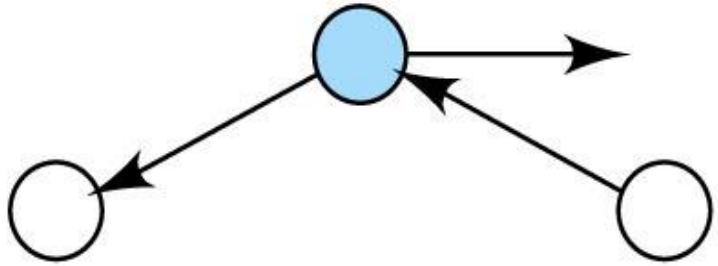
Triatomic molecule such as water, sulfur dioxide, or nitrogen dioxide have 3 x 3 – 6 = 3 vibrational modes. The central atom is not in line with the other two, a symmetric stretching vibration will produce a change in dipole and will thus be responsible for infrared absorption. Stretching peaks at 3650 (symmetric) and 3760 (asymmetric) 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}.

scissoring (bending)

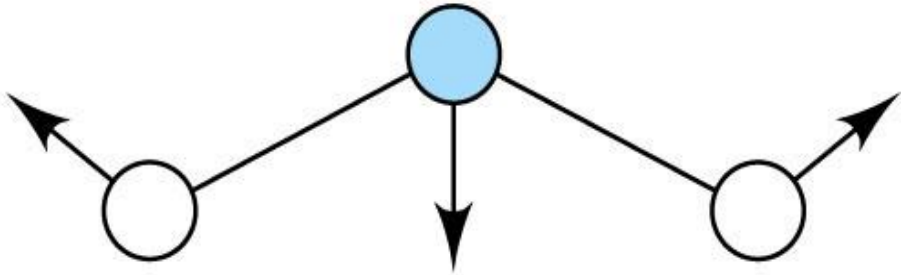


nonlinear ← H2O is bent ↵

Symmetric stretching 3650



Asymmetric stretching 3760



Scissoring 1595

INFRARED SOURCES

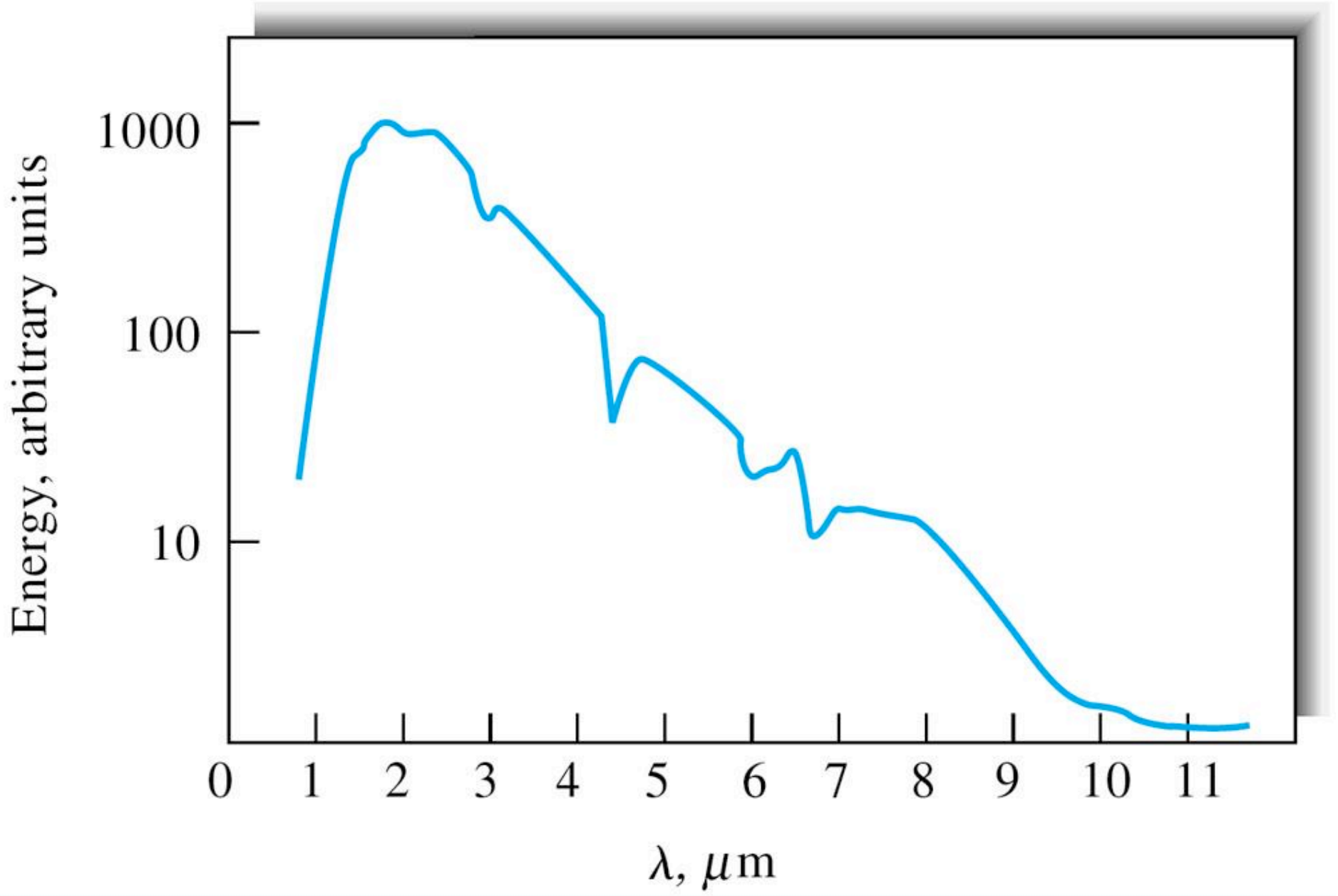
- **Sources**

  مادة صلبة خاملة

  Infrared sources consist of an inert solid that is heated electrically to a temperature between 1500 and 2200 K. Continuum 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.

* صفيحة او اسطوانة من البلاتين او الرصاص ,يشعها عن طريق الكهرباء والتسخين ينتج حرارة بمقدار (1200-2200)K إلى يعطي (5000-5000)cm' وهذا Davenumber



- **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 ($\lambda > 50\ \mu m$), 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}.

قابل للتعديل ←

- **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