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Third year fundamental chemistry

Course molecular spectroscopy

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How can I use this manuscript?

This manuscript is considered a summary of the course on molecular spectroscopy for the third year of fundamental chemistry. Furthermore the physics students can benefit from it. Since this manuscript is considered a basic concept, its readers must be instructed on how to use it. To facilitate its use, knowledge must be in group theory and determining the group of a molecule at first glance. This saves a lot of time and effort, as students find it difficult to determine symmetry elements and the symmetry operation. They cannot determine the vibration modes and this is the key of the first step, so more time and effort must be allocated. The basic idea of this manuscript is a prelude to understanding spectroscopy theoretically and reading the spectrum. Likewise, this summary must be read more than once to carefully understand how to link the results obtained in the laboratory with the theoretical hypotheses, and the student's effort remains the main key.

Units

quantity	Symbol	value and units
speed of light	c	$2,99792458 \times 10^8 \text{ ms}^{-1}$
plank constat	h	$6,626068 \times 10^{-34} \text{ Js}$
avogadro constant	$N_A$	$6,02214199 \times 10^{23} \text{ mol}^{-1}$
boltzman constant	k	$1,3806503 \times 10^{-23} \text{ JK}^{-1}$

Useful Conversion Factors

Unit	$\text{cm}^{-1}$	MHz	kJ	Ev	$\text{kJmol}^{-1}$
------	------------------	-----	----	----	---------------------

<b>1 cm<sup>-1</sup></b>	<b>1</b>	<b>29979.25</b>	<b>1. 98945 10<sup>-26</sup></b>	<b>1. 23984 10<sup>-4</sup></b>	<b>1. 19627 10<sup>-2</sup></b>
<b>1 MHz</b>	<b>3. 335 10<sup>-5</sup></b>	<b>1</b>	<b>6. 6208 10<sup>-5</sup></b>	<b>4. 13567 10<sup>-9</sup></b>	<b>3. 99031 10<sup>-7</sup></b>
<b>1kJ</b>	<b>5. 034 10<sup>25</sup></b>	<b>1. 50919 10<sup>30</sup></b>	<b>1</b>	<b>6. 24151 10<sup>21</sup></b>	<b>6. 02214 10<sup>23</sup></b>
<b>1eV</b>	<b>8065. 54</b>	<b>2. 41799 10<sup>8</sup></b>	<b>1. 60218 10<sup>-22</sup></b>	<b>1</b>	<b>96. 485</b>
<b>1kJmol<sup>-1</sup></b>	<b>83. 5925</b>	<b>2. 50607 10<sup>6</sup></b>	<b>1. 66054 10<sup>-24</sup></b>	<b>1. 03643 10<sup>-2</sup></b>	<b>1</b>

## Metric conversions

<b>SI SYMBOL</b>	<b>Si prefix</b>	<b>Factor power</b>	<b>Factor language</b>
<b>Y</b>	<b>yotta</b>	<b>10<sup>24</sup></b>	<b>septillion</b>
<b>Z</b>	<b>zetta</b>	<b>10<sup>21</sup></b>	<b>sextillion</b>
<b>E</b>	<b>exa</b>	<b>10<sup>18</sup></b>	<b>quintillion</b>
<b>P</b>	<b>peta</b>	<b>10<sup>15</sup></b>	<b>quadrillion</b>
<b>T</b>	<b>tera</b>	<b>10<sup>15</sup></b>	<b>trillion</b>
<b>G</b>	<b>giga</b>	<b>10<sup>9</sup></b>	<b>billion</b>
<b>M</b>	<b>mega</b>	<b>10<sup>6</sup></b>	<b>million</b>
<b>k</b>	<b>kilo</b>	<b>10<sup>3</sup></b>	<b>thousand</b>
<b>h</b>	<b>hecto</b>	<b>10<sup>2</sup></b>	<b>hundred</b>
<b>da</b>	<b>deca</b>	<b>10</b>	<b>ten</b>
		<b>1</b>	<b>one</b>
<b>d</b>	<b>deci</b>	<b>10<sup>-1</sup></b>	<b>tenth</b>
<b>c</b>	<b>centi</b>	<b>10<sup>-2</sup></b>	<b>hundredth</b>
<b>m</b>	<b>mili</b>	<b>10<sup>-3</sup></b>	<b>thousandth</b>
<b>μ</b>	<b>micro</b>	<b>10<sup>-6</sup></b>	<b>millionth</b>
<b>n</b>	<b>nano</b>	<b>10<sup>-9</sup></b>	<b>billionth</b>
<b>p</b>	<b>pico</b>	<b>10<sup>-12</sup></b>	<b>trillionth</b>
<b>f</b>	<b>femto</b>	<b>10<sup>-15</sup></b>	<b>quadrillionth</b>
<b>a</b>	<b>atto</b>	<b>10<sup>-18</sup></b>	<b>quintillionth</b>
<b>z</b>	<b>zepto</b>	<b>10<sup>-21</sup></b>	<b>sextillionth</b>
<b>y</b>	<b>yocto</b>	<b>10<sup>-24</sup></b>	<b>septillionth</b>

## **general Introduction**

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. It provides valuable information about the structure, composition, and dynamics of molecules.

Group theory plays a crucial role in understanding spectroscopy, particularly in molecular spectroscopy.

In molecular spectroscopy, molecules are often classified based on their symmetry properties. Group theory provides a systematic way to analyze and predict these properties. Here is how group theory intersects with spectroscopy:

1. **Symmetry Elements and Operations:** Group theory helps in identifying the symmetry elements and operations present in a molecule. Symmetry elements include rotation axes, reflection planes, inversion centers, and improper rotation axes. These elements determine the symmetry of a molecule.
2. **Point Groups:** Group theory categorizes molecules into point groups based on their symmetry elements. Each point group represents a set of symmetry operations that leave the molecule unchanged. These point groups are fundamental to understanding the selection rules for spectroscopic transitions.
3. **Selection Rules:** Group theory provides selection rules for different spectroscopic techniques, such as infrared (IR), Raman, electronic, and nuclear magnetic resonance (NMR) spectroscopy. These rules dictate which transitions are allowed or forbidden based on the symmetry properties of the molecule and the selection rules for the particular spectroscopic method.
4. **Vibrational Spectroscopy:** In IR and Raman spectroscopy, molecules absorb or scatter light due to vibrational motions. Group

theory helps in predicting the number of vibrational modes and their symmetries. It also explains the intensity and polarization of spectral peaks.. In Raman spectroscopy, the spectrum represents the intensity of scattered light as a function of the energy shift from the incident light. The Raman spectrum typically consists of peaks corresponding to vibrational modes of the molecule. In IR spectroscopy, the spectrum represents the absorption of infrared light by the sample molecule as a function of the wavenumber (or frequency) of the incident light. The IR spectrum consists of peaks corresponding to specific vibrational modes of the molecule.

5.

In rotation-vibration spectroscopy, the rotational motion of a molecule can affect its vibrational energy levels, and vice versa. This coupling leads to the appearance of rotation-vibration transitions in the molecular spectra. The transitions correspond to changes in both rotational and vibrational energy levels, resulting in more complex spectra compared to pure rotational or vibrational spectra.

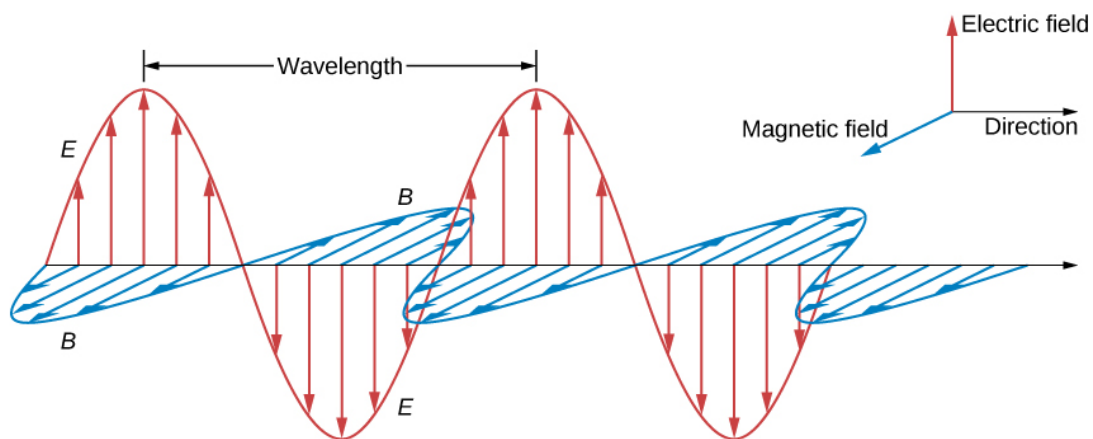
In microwave spectroscopy, molecules undergo rotational transitions, where the energy levels associated with the rotational motion change due to absorption or emission of microwave radiation. These transitions occur when the energy of the microwave radiation matches the energy difference between rotational levels in the molecule.

In UV-visible spectroscopy, molecules absorb light energy, promoting electrons from their ground state to higher energy levels. The absorption of light by a molecule depends on its electronic structure and the energy of the incident photons. Different molecules absorb light at different wavelengths, leading to characteristic absorption spectra that provide information about the molecular structure, concentration, and chemical environment

## Chapter I

## Electromagnetic waves

**An electromagnetic wave contains an electric field and a magnetic field oscillating at the same frequency. These two fields, perpendicular to each other, propagate in a medium in an orthogonal direction(Ishimaru 2017)**



**Electromagnetic radiation and characterized by its frequency, its wavelength or its wave number.**

$$\vartheta = \frac{1}{T}$$

**$T$  Periodic in seconde**

**$\vartheta$  Frequency in Hertz**

$$\lambda = cT = \frac{c}{\vartheta}$$

**Wave lenght in  $cm$**

**$c$  speed of light**

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

Wave number in  $cm^{-1}$

The energy is given by the expression

$$E = h\nu$$

$h$  planck constant

example

show the transfer between units joule to cm and  $cm^{-1}$

$$E = h\nu = hc \frac{1}{\lambda} = hc\bar{\nu}$$

$$\lambda = \frac{6,62606876 \cdot 10^{-34} Js * 2,99792458 \cdot 10^8 * 100 \frac{cm}{m} ms^{-1}}{1J}$$
$$= 19.8644544 \cdot 10^{-24} cm$$

$$\bar{\nu} = 0,05034118 \cdot 10^{24} = 5.034118 \cdot 10^{25} cm^{-1}$$

$$1J \rightarrow 19.8644544 \cdot 10^{-24} cm$$

$$1J \rightarrow 5.034118 \cdot 10^{25} cm^{-1}$$

show the transfer between units joule to Hertz  $s^{-1}$

$kJmol^{-1}$	Ev	kJ	MHz	$cm^{-1}$	Unit
$1.19627 \cdot 10^{-2}$	$1.23984 \cdot 10^{-4}$	$1.98945 \cdot 10^{-26}$	29979.25	1	$1 cm^{-1}$
$3.99031 \cdot 10^{-7}$	$4.13567 \cdot 10^{-9}$	$6.6208 \cdot 10^{-5}$	1	$3.335 \cdot 10^{-5}$	1 MHz
$6.02214 \cdot 10^{23}$	$6.24151 \cdot 10^{21}$	1	$1.50919 \cdot 10^{30}$	$5.034 \cdot 10^{25}$	1kJ
96.485	1	$1.60218 \cdot 10^{-22}$	$2.41799 \cdot 10^8$	8065.54	1eV
1	$1.03643 \cdot 10^{-2}$	$1.66054 \cdot 10^{-24}$	$2.50607 \cdot 10^6$	83.5925	$1kJmol^{-1}$

$$E = h\nu = hc \frac{1}{\lambda} = hc\bar{\nu}$$

$$\frac{1E}{h} = c\bar{\nu} = \frac{1J}{6,62606876 \cdot 10^{-34} Js} = 0.15091905 \cdot 10^{34} s^{-1}$$

$$1E \rightarrow 0.15091905 \cdot 10^{34} s^{-1}$$

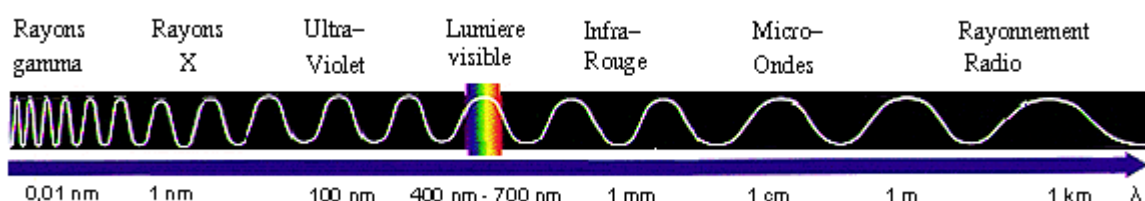
$$= \frac{10^3 \text{ kJ}}{6,626068 \text{ } 76 \text{ } 10^{-34} \text{ Js}} = 1.5091905 \text{ } 10^{35} \text{ } 10^{-5} \text{ Ms}^{-1}$$

$$= 1.5091905 \text{ } 10^{30} \text{ Ms}^{-1}$$

$$1 \text{ cm}^{-1} \rightarrow 1.98945 \text{ } 10^{-26} * 6.02310^{23} \text{ mol}^{-1} = 1.19627 \text{ } 10^{-2} \text{ kJ/mole}$$

Ray-matter interaction

**Molecular spectroscopy may be defined as the study of the interaction of electromagnetic ray waves and matter. actually only a narrow window of all electromagnetic waves, which include gamma, x-rays, ultraviolet, infrared, radio waves, etc. study of the interaction of electromagnetic ray waves and matter. To answer this question, you should know that visible light is in fact only a narrow window of all electromagnetic waves, which include gamma rays, X, ultraviolet, infrared, radio waves, etc.. (Bahnemann and Patrocínio 2022)**



## Electromagnetic spectrum

An elementary particle (atom, ion or molecule) can only exist in certain quantized energy states. In the case of a molecule, the total energy is considered to be the sum of the terms:

$$E = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}} + E_{\text{spin}}$$

The orders of ascending magnitude are very different:  $E_e > E_{\text{vib-rot}} >$

$$E_v \gg E_r \gg E_s.$$

The levels of electronic energy, vibration, vib-rotational and rotation are represented by a diagram in which each level is schematized by a horizontal line and characterized by a set of quantum numbers  $n$ ,

$\nu$  and  $J$  connected respectively to the electronic, vibrational and rotational movements of the molecule. (Dobbs 2013)

Example

By how many kilojoules per mole is the energy of oxygen increased when it absorbs ultraviolet radiation with a wavelength of  $147 \text{ nm}$  how much the energy of  $\text{CO}_2$  increased when it absorbs infrared radiation with wavenumber of  $2300 \text{ cm}^{-1}$

$$\Delta E = h\nu = h \frac{c}{\lambda}$$

$$= 6,62606876 \cdot 10^{-34} \text{ Js} \left[ \frac{2,99792458 \cdot 10^8 \frac{\text{m}}{\text{s}}}{147 \text{ nm} \cdot 10^{-9} \frac{\text{m}}{\text{nm}}} \right]$$

$$= 0.13513234 \cdot 10^{-18} \text{ J/molecules}$$

$$0.13513234 \cdot 10^{-18} \frac{\text{J}}{\text{molecules}} \cdot 6.02214199 \cdot 10^{23} \text{ molecules mol}^{-1}$$

$$= 814 \cdot 10^3 \text{ J/mol}$$

For  $\text{CO}_2$  the energy is increased

$$6,62606876 \cdot 10^{-34} \text{ Js} \cdot 2,99792458 \cdot 10^8 \frac{\text{m}}{\text{s}} \cdot 2300 \text{ cm}^{-1} \cdot 100 \text{ cm m}^{-1}$$

$$= 4.6 \cdot 10^{-20} \text{ J/molecule}$$

Infrared absorption increases the amplitude of the vibration of  $\text{CO}_2$  bonds but the UV is enough energy to break the  $\text{O}=\text{O}$  bond.

## Intensity measurement

The absorbing species of the sample determines the intensity with which the incident radiation  $I_0$  is absorbed. In the visible domain, the unit responsible for coloring is called the chromophore. The incident radiation  $I_0$  and the intensity of the emerging radiation  $I$ , after having traveled a distance  $l$  from a homogeneous sample of molar concentration  $M$  is given by the (Robinson 1996);

$$A = \log \frac{1}{T} = \log \frac{I_0}{I} = \epsilon M l$$

$A$  Absorbance (optic density)

$\epsilon$  Molar Absorption Coefficient (Molar Extinction Coefficient)

$M$  molar Concentration

$T$  Transmittance

### Validity of the Beer-Lambert law

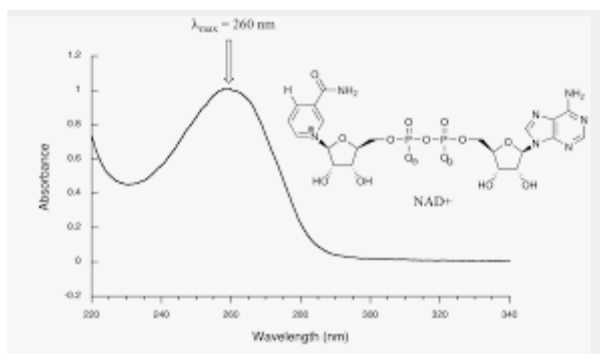
- Monochromatic light
- Low concentrations the points are rectilinear
- The solution must be neither fluorescent nor heterogeneous (bubbles, precipitate, colloidal...)
- The solution is not the site of a photochemical reaction

### additivity of absorbance

If the solution to be studied contains several absorbing species, the absorbance measured at a given wavelength is the sum of absorbances of the species taken separately, provided that the latter do not interact with each other. It is noted that if the sample is green it is possible to have two yellow and blue species remains to be checked on chromatographic paper

## Absorption Spectrum

The graphical recording - made by a device called a spectrophotometer of the amount of radiation absorbed or transmitted by a substance as a function of wavelength (nm), frequency or wave number gives the absorption spectrum of the substance. According to a representation in absorbance or in transmittance, we have the following appearances: The position of the absorption maximum of a band corresponds to the wavelength of the radiation which caused the electronic transition between the occupied orbital and another vacant.  $\lambda_{\text{max}}$  Corresponds to the maximum absorption.



We use the complementary colour to determine the colour of the sample

The human eye is able to “see” light in the wavelength range 400-700 nm (nanometer or  $10^{-9}$  m). To the human eye, wavelength appears as colour, as shown in the following table

When we see an object as purple, in fact it absorbs light in the “green” region of the spectrum: only blue and red wavelengths reach the eye, which we experience as the purple colour

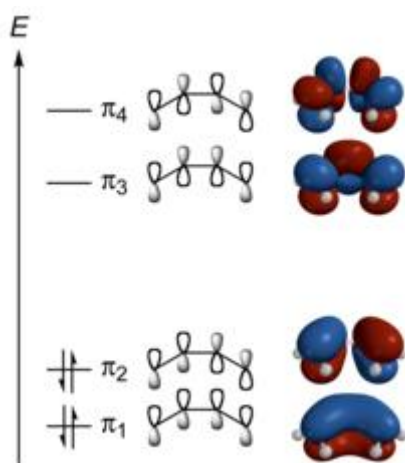
Table correlation between –wavelength colour and (Hollas and Chemistry 2002)

Wave length	Colour	Complementary colour
400-430	Violet	Yellow Green
430-490	Blue	Yellow
490-550	Green	Purple
550-590	Yellow	Blue

590-630	Orange	Green-blue
630-700	Red	Blue-green

## Molecular orbitals

The linear combination of atomic orbitals results in molecular orbitals, if we take the case of butadiene we have four molecular orbital electrons  $P_z$  this combination gives four molecular orbitals HOMO, HOMO-1, LUMO and LUMO+1, Which are mathematical functions describing the wave behaviour of an electron in a molecule.(Sharma 1981)



From the energetic point of view, the electronic gap represents the energy difference between the occupied orbital and the energy of a vacant orbital

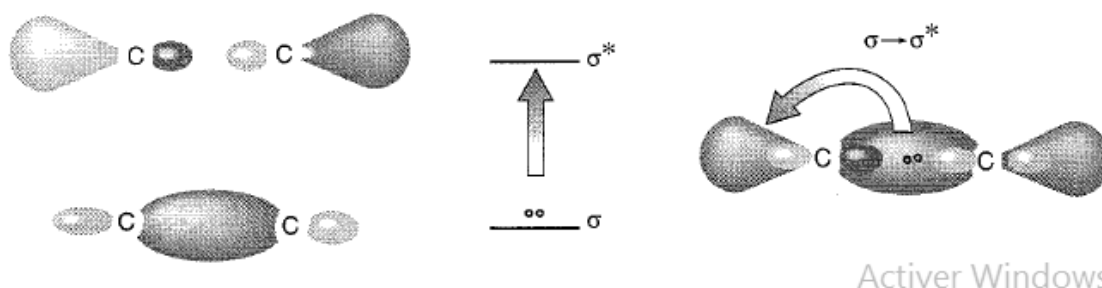
$$E_{gap} = E_{LUMO} - E_{HOMO}$$

In other words, it represents the energy (of absorption) that must be given to an electron of the occupied orbital so that it moves towards the vacant orbital, the latter becomes a new frontier orbital HOMO thus we obtain an electronic transition Of type  $\pi \rightarrow \pi^*$ , The other vibration effects on the bond, the rot-vibration, the vibration and the rotation also take place since the quantum energy of transitions of these effects are

low.

## Alkanes (Hirayama 1967)

, which contain only  $\sigma$  bonds (C–C and C–H single bonds), the only possible electronic transition is the  $\sigma \rightarrow \sigma^*$  transition:.



$$\sigma \rightarrow \sigma^*; \lambda_{max} < 150nm (UV \text{ lointain})$$

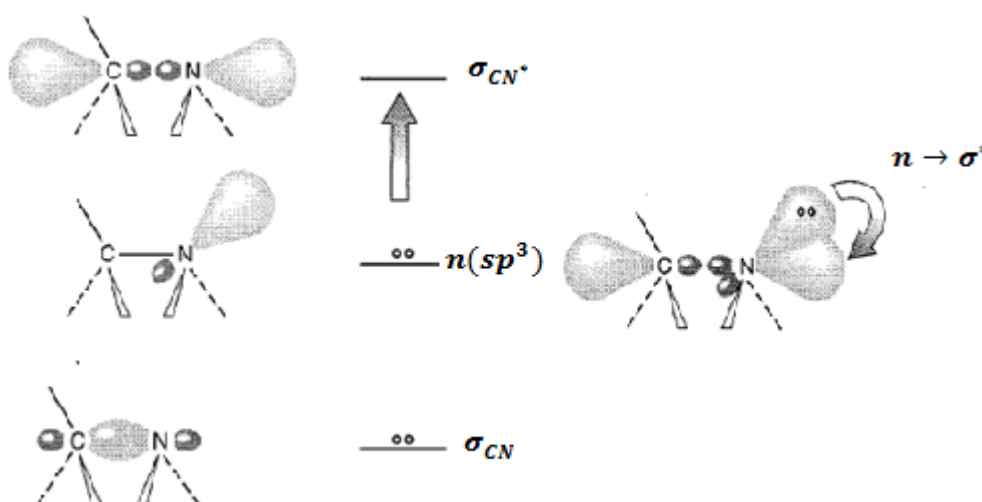
Methane 125 nm

Ethane 135 nm

Cyclopropane 190 nm

When a hydrogen atom is replaced by a nitrile group, the nitrogen atom introduces a lone pair of electrons. This makes an additional electronic transition possible — the  $n \rightarrow \pi^*$  transition — in addition to the  $\sigma \rightarrow \sigma^*$  transition

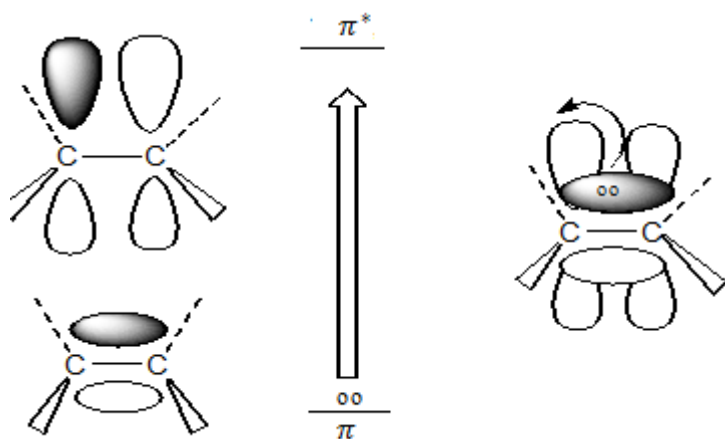
$$n \rightarrow \sigma^*; 150nm < \lambda_{max} < 250nm$$



**“ $n \rightarrow \sigma^*$  transitions also occur from the lone pairs( free doublet) on heteroatoms such as oxygen and sulfur, as in alcohols, ethers, and sulfur-containing compounds. However, the exact energies of these transitions vary slightly from one compound to another, mainly due to differences in electronegativity.**

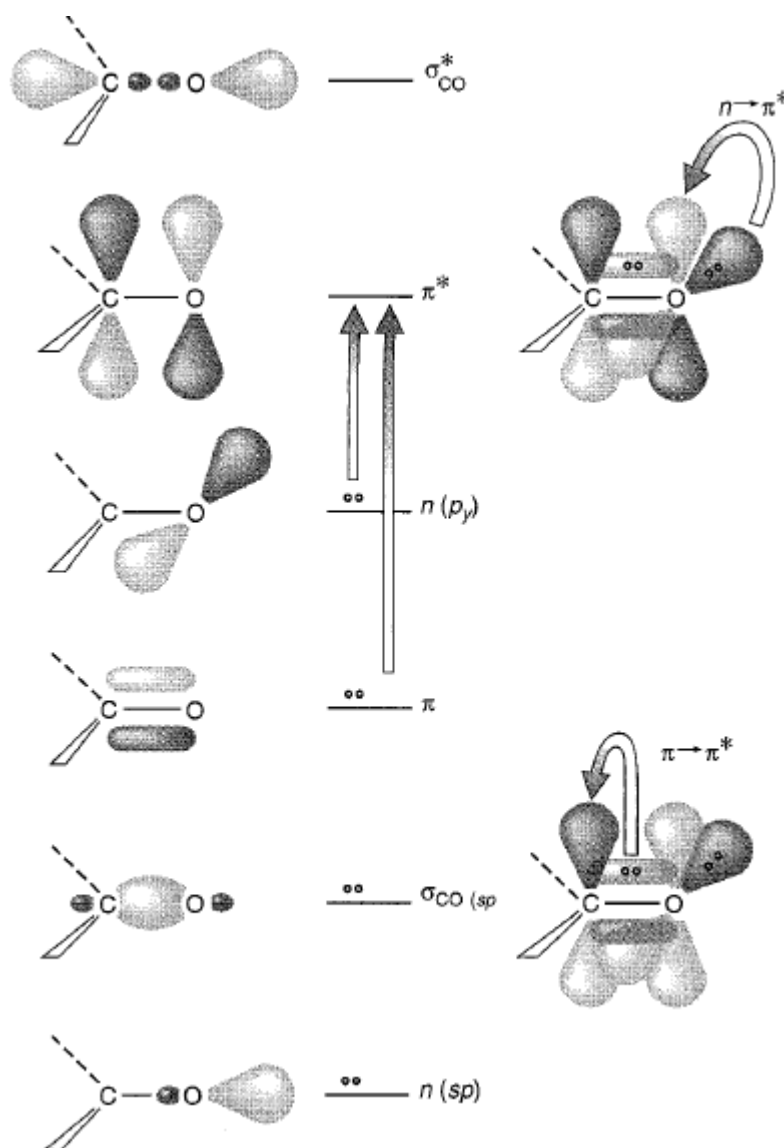
### Alkenes and alkynes

**“Unsaturated compounds, characterized by the presence of  $\pi$  bonds, also undergo relatively high-energy transitions. However, their absorption positions are highly sensitive to substitution, which influences the electronic cloud. For example, alkynes absorb around 170 nm, while alkenes absorb near 175 nm.”.**



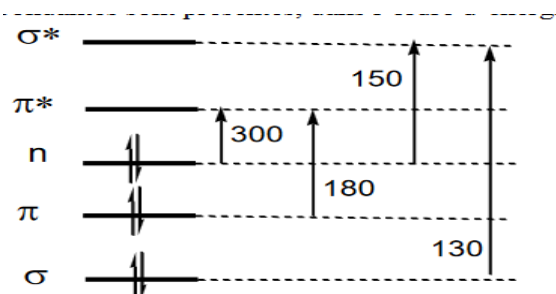
### The carbonyl compound

**The unsaturated compounds containing an oxygen are the most important and the most extensively studied.**



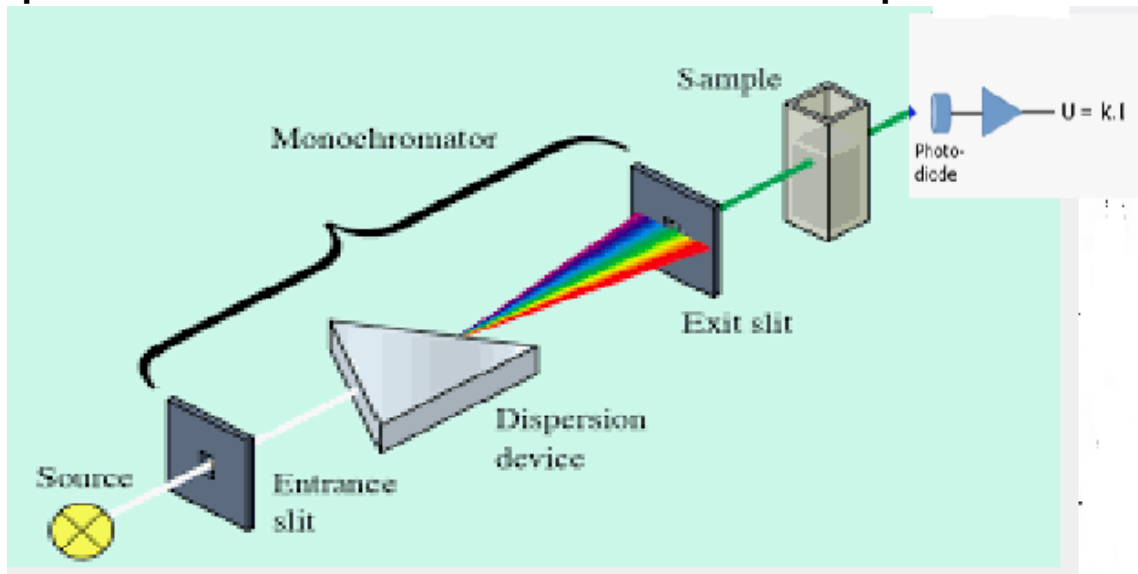
## amines and Alcohols

absorb in the range of 175-200 nm. While organic thiols and sulfides absorb between 200 and 220 nm. Most of the absorption is below the cutoff points for common solvents, so they are not observed in solution spectra. The figure illustrates an  $n \rightarrow \sigma^*$  transition for an amine. The excitation of unbound electrons at the anti-bonding orbital is shown on the right (Pavia, Lampman et al. 2014)



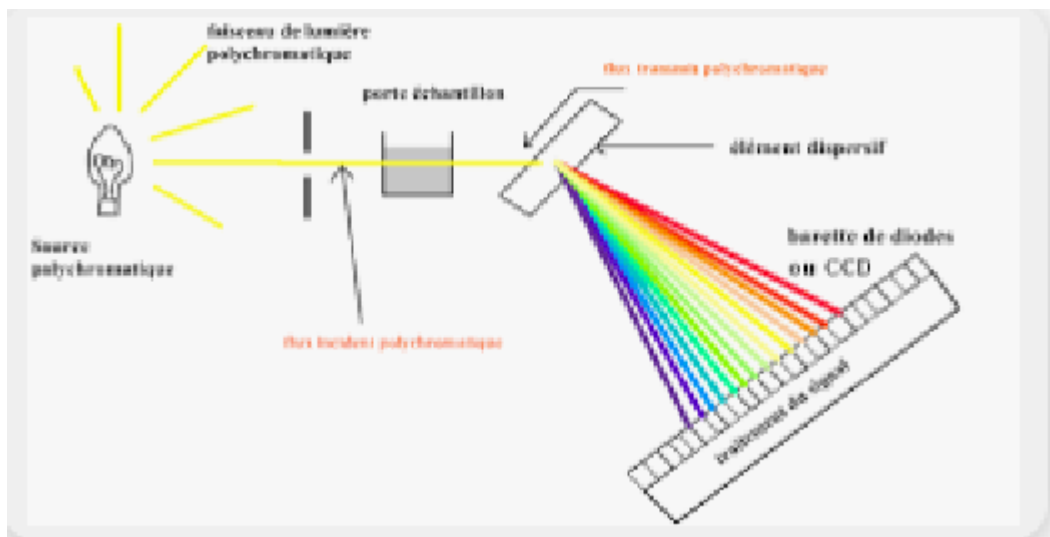
## Apparatus

A beam of polychromatic light is passed through a monochromator for the purpose of selecting a single spectral band. This monochromatic radiation passes through the sample carried by a quartz cell where a material does not show absorption in the



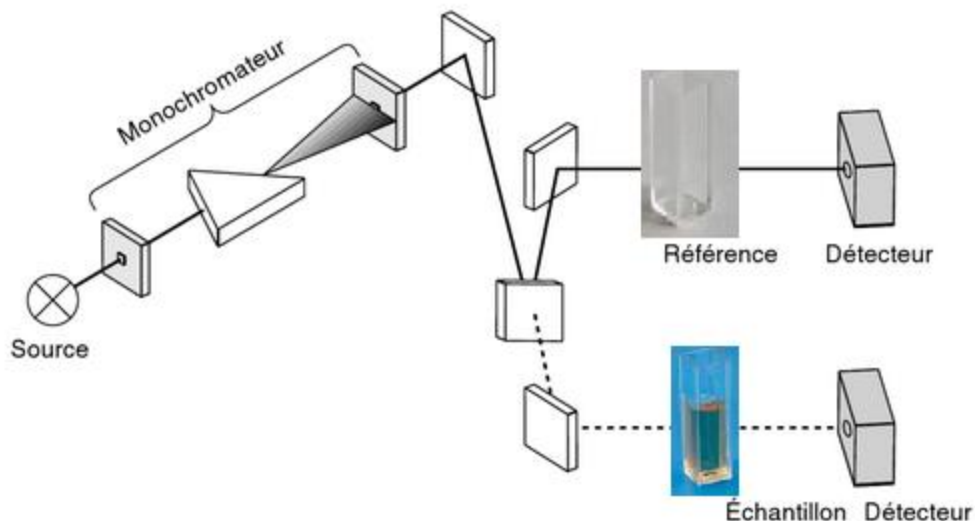
spectral analysis range and the beam will end up in the detector. (Clark, Frost and Russell 1993)

Unlike a conventional detector in which the receiver is capable of analyzing only one wavelength at a time, the diode array UV detector, made up of many photosensitive miniature diodes, is capable of analyzing a wide range of wavelengths simultaneously





## Double beam spectrophotometers



**The light beam passes through the sample carrying measuring cell and the reference cell or the blank and test simultaneously, there are photometers that contain a single detector.(Kenkel 2002)**

## Quantitative analysis

### Determination of the acidity of molecules

**A quantity of the target substance is dissolved in buffered solutions at different pH Then measure the absorbance of the different solutions and we will have a reading table The two ends of the pH we measure the absorbance  $d_i$  for the ionized molecule at low pH and the absorbance  $d_n$  of the non-ionized molecule at high pH,  $d$  and the reading at tapped pH Then we calculate  $pK_a$  by the formula**

$$pK_a = pH + \log\left(\frac{d_i - d}{d - d_n}\right)$$

Determination of sample concentrations

**We draw calibration curves of the compound, the slope represents the molar absorption coefficients. It is enough to read the absorbance of the compound in another sample to determine its unknown concentration.**

Light scattering spectroscopy

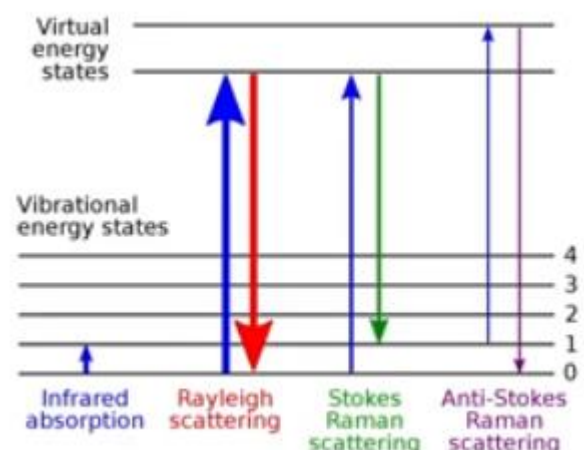
Raman scattering is the inelastic scattering of a photon by a medium. The fact that scattering is inelastic implies that there is an exchange of energy between the incident photon and the molecule via vibrational excitation or, in the solid state, the creation or annihilation of an optical phonon. Thus, the scattered light does not have the same wavelength as the incident light. Two cases can be distinguished:

**Stokes shift:**

**Light is red-shifted (longer wavelength, lower energy) with vibrational excitation or creation of a phonon. The name Stokes recalls the physicist George Stokes who demonstrated in 1852 that fluorescence involves a red shift.**

**Anti-Stokes shift:**

**Light is blue-shifted (shorter wavelength, greater energy) with vibrational decay or phonon absorption. If there is no energy exchange between the molecule and the incident photon, then the scattering is elastic and the wavelength of the scattered photon is not shifted. This is called Rayleigh scattering. (Placzek and Laboratory 1959)**



The wavelength shift depends on the material and is characteristic of it: it does not depend on the excitation wavelength, which makes it possible to analyze the chemical composition of a sample from the way in which it scatters light

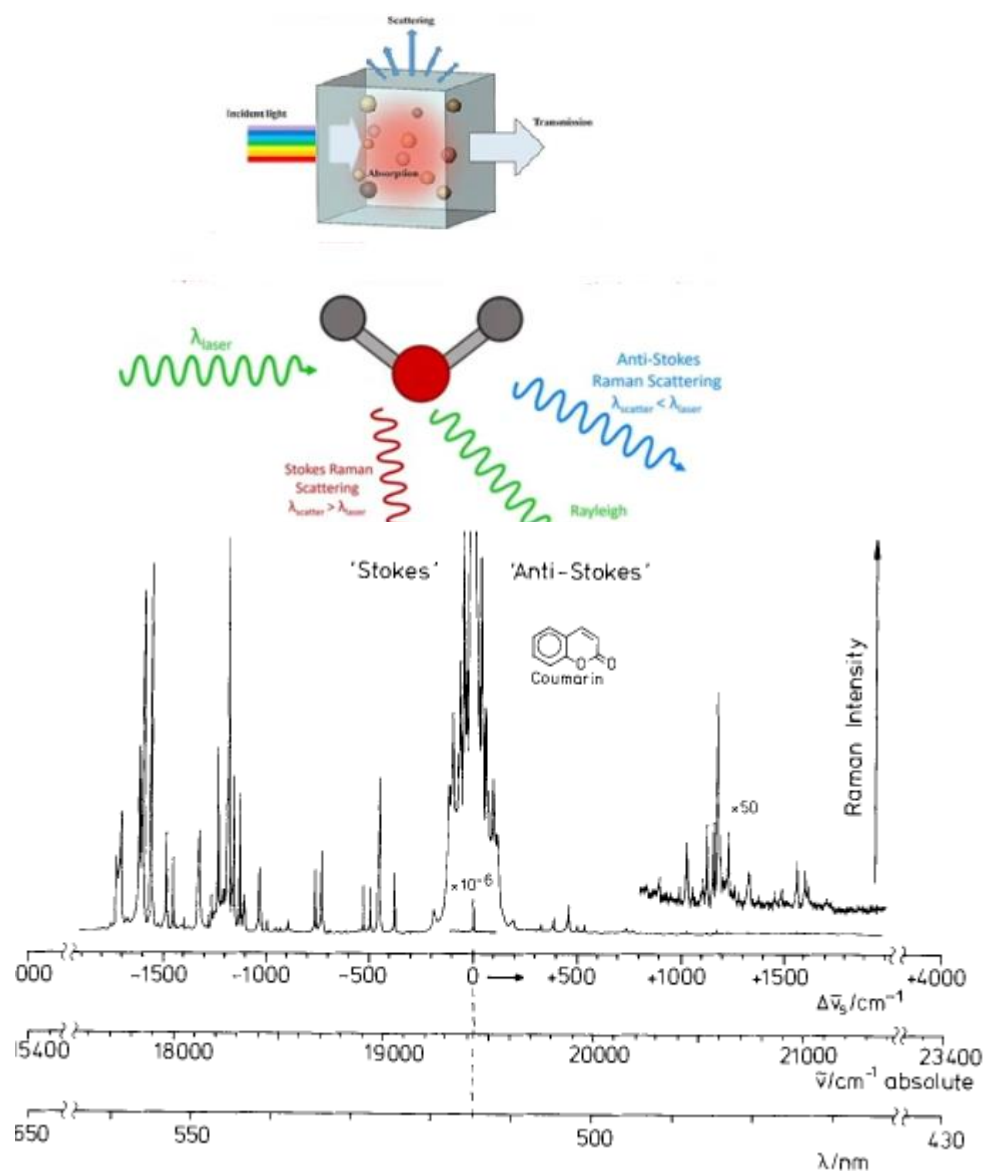


fig :Raman spectrum of coumarin

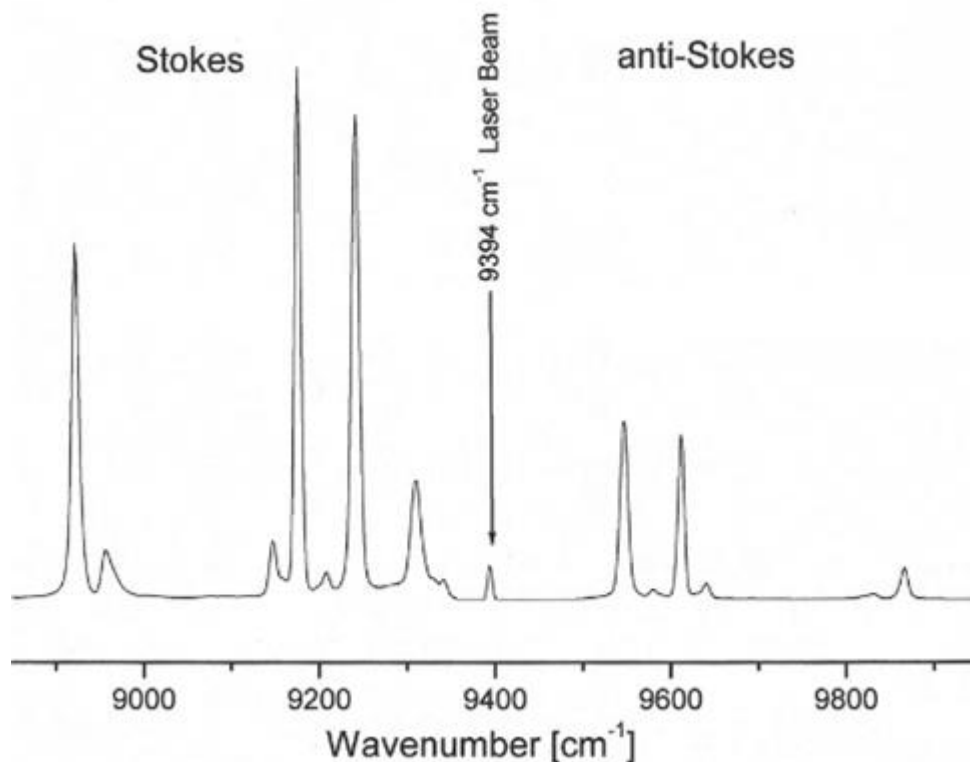


Fig: the stokes and antistokes raman spectrum of sulfur at 1064nm

#### Raman spectroscopy instruments

Modern, compact Raman spectrometers have several basic components, including a laser beam that serves as an excitation source to induce Raman scattering. Modern Raman instruments emitting waves of standard length (532, 785, 830 and 1064 nm) are usually equipped with semiconductor lasers. Lasers emitting shorter waves have larger transverse Raman scattering sections. The signal is therefore stronger, but the incidence of fluorescence is also higher. This is why many Raman systems are equipped with a 785 nm laser. The laser energy is directed to the sample and then collected by fiber optic cables. A slit or edge filter eliminates Rayleigh and anti-Stokes scattering. The remaining Stokes scattered light is transmitted to a scattering element, usually a holographic grid. A CCD detector captures the light to generate the Raman spectrum. Raman scattering generates a weak signal

## Exercises

### Ex1

Determine the types possible transitions of the following molecules

Class	transition	$\lambda_{max}(nm)$	$\log \epsilon$	Class	transition	$\lambda_{max}(nm)$	$\log \epsilon$
R-OH		180	2.5	R-NO <sub>2</sub>		271	1.0
R-O-R		180	3.5	R-CHO		190	2.0
R-NH <sub>2</sub>		190	3.5			290	1.0
R-SH		210	3.0	R <sub>2</sub> CO		180	3.0
R <sub>2</sub> C=CR <sub>2</sub>		172	3.0			280	1.5
R-C≡C-R		170	3.0	RCOOH		205	1.5
R-C≡N		160	<1.0	RCOO R'		205	1.5
R-N=N-R		340	<1.0	RCONH <sub>2</sub>		210	1.5

### Ex2

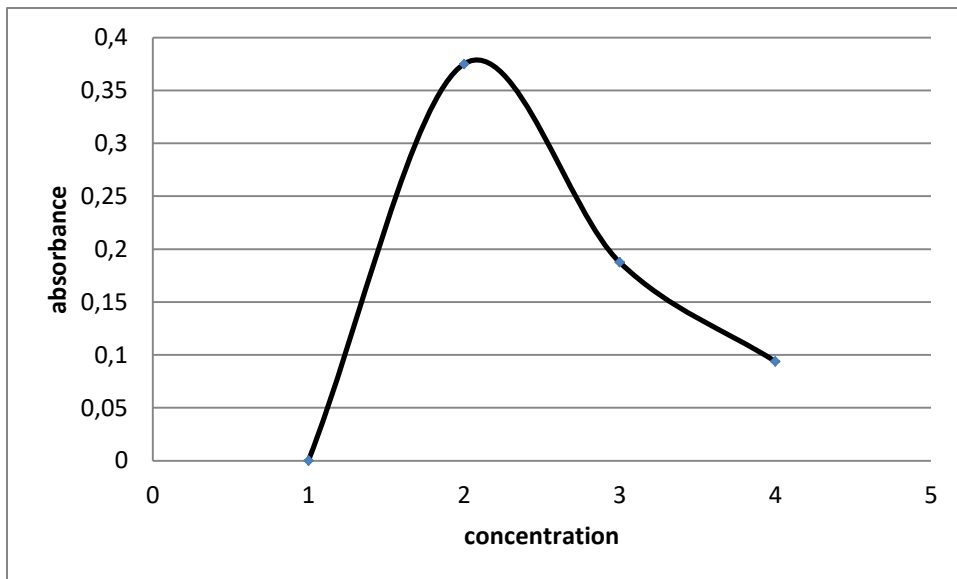
the absorbance readings for a series of solutions after the stock solution has been diluted to a specified concentration

Concentration g/l	abs
0.5	0.75
0,25	0,375
0,125	0,1875
0,075	0,09375

Is the Beer-Lambert law verified?

Determines the concentration from the reading 0.665?

Can the concentration be deduced from the 2.500 reading?



the abs and concentration must be a line thus the Beer-Lambert law is not verified

we can't give the concentration for the reading  $\text{abs}=0.665$  due to outlier value

for  $\text{abs}=2.2$  we can't read the concentration for this value is out the domain of validity.

### Exercise3:

a solution containing two compounds A and B Their molar masses are respectively  $M_A=200 \text{ g/mol}$  and  $M_B=400 \text{ g/mol}$ . In the solution, the concentration of compound A is  $0.05 \text{ g/l}$  and that of B is  $0.06 \text{ g/l}$ . The molar extinction coefficients are:

for A :  $\epsilon_{500} = 500 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$  , :  $\epsilon_{450} = 1000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$

for B :  $\epsilon_{500} = 2000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$  , :  $\epsilon_{450} = 3000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ .

The thickness of the tank is  $1 \text{ cm}$ . What will be the absorbance of the solution at two wavelengths:  $500\text{nm}$  and  $450\text{nm}$ ?

### Exercise 4 :

1. Calculate the  $\epsilon_{\text{max}}$  of a compound whose maximum absorption (A) is 1.2. The cell length L is  $1 \text{ cm}$ , the concentration is  $1.9 \text{ mg per } 25 \text{ ml}$  of solution and the molecular mass of the compound is  $100 \text{ g/mol}$ .

2. Calculate the molar absorption coefficient of a solution of concentration  $10^{-4}$  M, placed in a 2 cm optical cells , with  $I_0 = 85,4$  et  $I = 20,3$

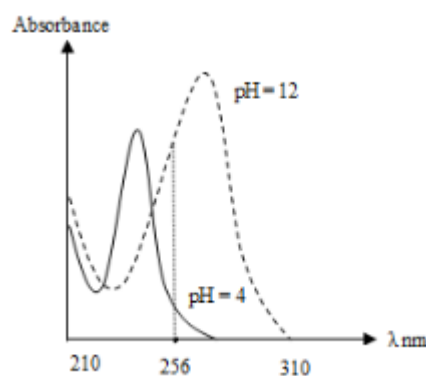
Ex5 :

An aqueous solution of potassium permanganate ( $c = 1.28 \times 10^{-4}$  mol/l) has a transmittance of 0.5 at 525 nm, if a cell with a 10 mm optical path is used. To. Calculate the molar absorption coefficient of permanganate for this wavelength

b. If the concentration is doubled, calculate the absorbance and transmittance of the new solution ?

Ex6 :

Determination of the pKa of paracetamol by UV spectrophotometry. To do this, prepare 100 ml of a  $10^{-3}$  M solution of paracetamol in distilled water. (Solution S). Two 1/10 dilutions of solution S are carried out: - Solution SA: Dilution with an acid buffer solution (pH= 4). - SB solution: Dilution with a basic buffer solution (pH= 12). The UV absorption spectra of the SA and SB solutions are plotted between 210 and 360 nm. Buffer solutions do not absorb in this area.



Figure

UV absorption spectra of SA and SB solutions.

1. From the chemical formula say why the spectrophotometric determination of the pKa is possible in the case of paracetamol
2. Explain the difference in the appearance of the 2 spectra - The absorbances of the SA and SB solutions measured at 256 nm are:  $A_A = 0.688$   $A_B = 1.080$  - The SA and SB solutions are mixed in defined proportions. The solution obtained SM has a pH=9.80 and its absorbance A measured at 256 nm is equal to 0.920.

### 3) Calculate the pKa of paracetamol :

Ex

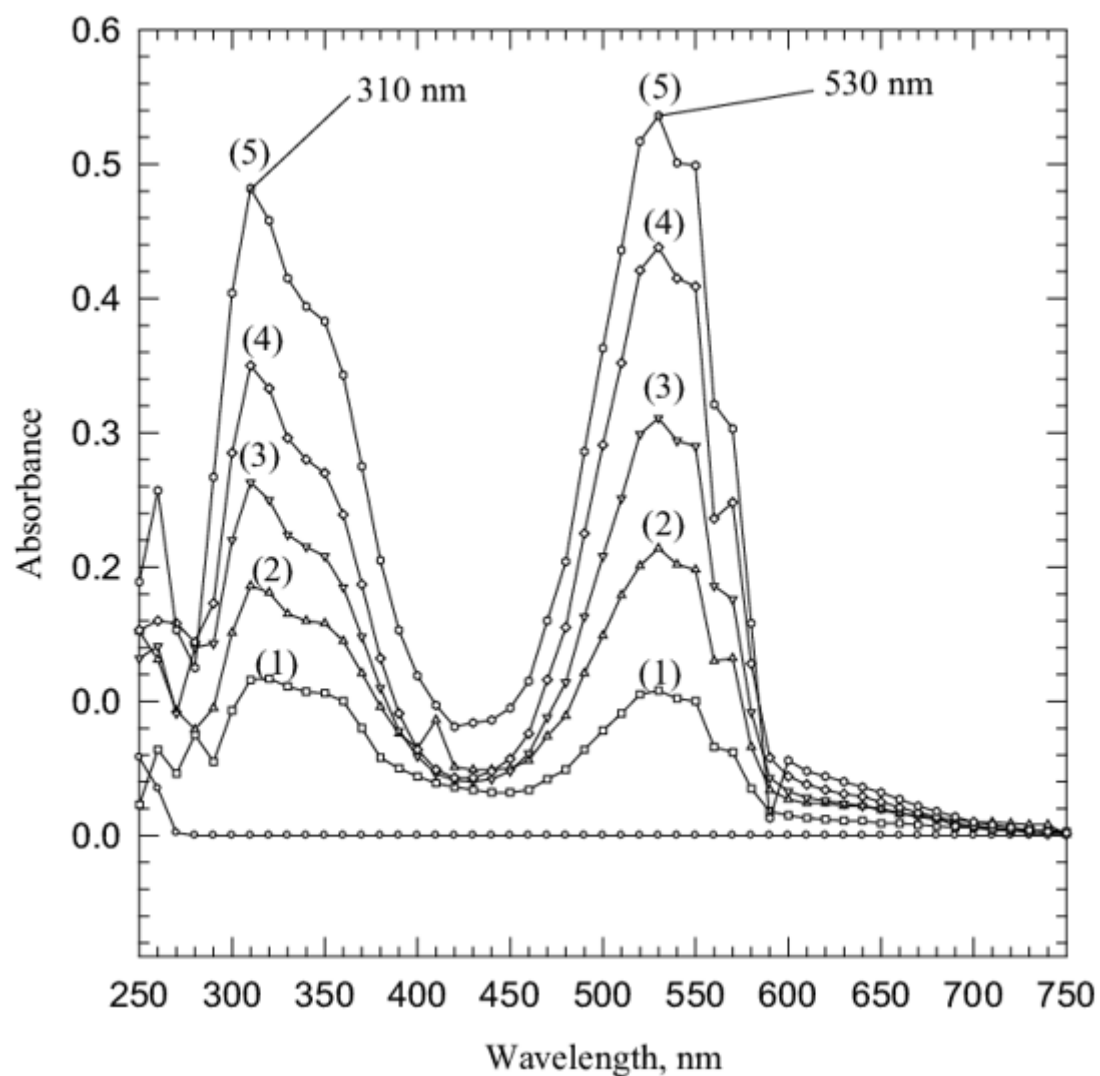
the following spectrum is the  $\text{KMnO}_4$  spectrum

#### 1-determine the colour of permanganate ?

Table correlation between wavelength , colour, and complementary colour

Wavelength, nm	colour	Complementary colour
400-430	violet	Yellow-green
430-490	blue	yellow
490-550	green	purple
550-590	yellow	blue
590-630	orange	Green-blue
630-700	red	Lue-green

#### 2-determine $\lambda_{\max}$ ?



**Fill in the table with the appropriate values**

Spectrum	absorbance	concentration
1		
2		
3		
4		
5		

## Chapter II

Reminder

In mathematics, if we have an even function and we want to draw the curve of it, we just have to draw one part and the other part is obtained by symmetry, with respect to the ordinate axis. If the function is odd it accepts the origin as a point of symmetry. Molecules are like mathematical functions but with specificities related to the nature of chemical bonds and molecular orbitals. Looking at the structures of chemical compounds and after extrapolation, each symmetry operation corresponds to a symmetry element that defines the operation, In general practice we distinguish five types of operation:

- (i) E, Identity Operation
- (ii)  $C_n^M$ , Proper Rotation about an axis
- (iii), Reflection through a plane
- (iv) i, Inversion through a center
- (v)  $S_n^M$ , Rotation about an axis followed by reflection through a plane perpendicular to that axis.

$\sigma_h$  - Horizontal Plane which is perpendicular to the Principal Axis of Rotation (i.e. Axis with highest value of n). If no principal axis exists  $\sigma_h$  is defined as the molecular plane.  $\sigma_v$  or  $\sigma_d$  - Vertical Plane which contains the Principal Axis of Rotation and is perpendicular to a  $\sigma_h$  plane, if it exists. When both  $\sigma_v$  and  $\sigma_d$  planes are present, the  $\sigma_v$  planes contain the greater number of atoms, the  $\sigma_d$  planes contain bond angle bisectors. If only one type of vertical plane is present,  $\sigma_v$  or  $\sigma_d$  may be used depending on the total symmetry of the molecule. (Jaffé and Orchin 2002, Moore, Chemistry and University 2002)

In practice, inversion involves taking every atom to the center – and out the same distance in the same direction on the other side.

Definition: a symmetry operation on an object A is an operation that lets object A unchanged. Definition: each symmetry operation

**corresponds to a symmetry element which defines the operation.**

### Symmetry classes

Symmetry elements of the same kind are called symmetry classes these symmetry classes represent a point subgroup of symmetry because they had the same property (internal operation .....).

### Character table

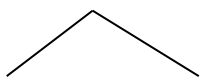
For each group it assigned a character table that summarizes the behaviour of all of the possible irreducible representations of a group under each of the symmetry operations of the group(Joshi 1997)

### Example

**Consider the water molecule  $H_2O$**

- 1- determine the elements of symmetry**
- 2- symmetry classes**
- 3- the point group of symmetry**
- 4- write the character for this group**

**To succeed in determining the elements of symmetry and the point group of symmetry it is necessary to draw the molecule taking into account the theory of the repulsions of the electronic pairs. Then first we look for the main axis of symmetry if there are several axes, it will be of higher index. For the molecule  $A_2B$**



**So the higher order axis is  $C^2$  of the orientation counter-clockwise**  
**We also observe a mirror carrying the main axis and  $\sigma'_{yz}$  in our case on which sleeps the molecule.**

- 1- The plane (mirror) carrying the molecule is noted  $\sigma$**
- 2- E (do nothing).**
- 2-the symmetry classes are three classes**
- 3 - The symmetry point group is  $C_{2V}$**

#### 4- The character table is

$C_{2v}$	$E$	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_z$	$yz$

### Matrix

#### Definition :

An  $m \times n$  matrix is an array of numbers with  $m$  rows and  $n$  columns. The numbers that make up the matrix are called the elements of the matrix (or also the coefficients). A matrix with  $m$  rows and  $n$  columns is said to be a matrix of order  $(m, n)$  or of dimension  $m \times n$ . The set of  $n$  matrices with  $m$  rows and  $n$  columns with real coefficients is denoted  $M_{m,n}(\mathbb{R})$ .

#### matrix products

**matrix product** Let  $A$  be an  $m \times p$  matrix and  $B$  a  $p \times n$  matrix. We can perform the product of a matrix with  $m$  rows and  $p$  columns by a matrix with  $p$  rows and  $n$  columns. We call product  $A \times B$  the matrix of dimension  $m \times n$  obtained by multiplying each row of  $A$  by each column of  $B$ . More precisely, the coefficient of the  $i$ th row and the  $j$ th column of  $A \times B$  is obtained by multiplying the  $i$ th row of  $A$  by the  $j$ th column of  $B$ . (Johnston 2021)

**Example** By a number

$$3 * \begin{pmatrix} 1 & -2 \\ 0 & 2 \end{pmatrix} = \begin{pmatrix} 3 & -6 \\ 0 & 6 \end{pmatrix}$$

**By a vector**

$$\begin{pmatrix} 1 & -2 \\ 0 & 2 \end{pmatrix} * \begin{pmatrix} 3 \\ 4 \end{pmatrix} = \begin{pmatrix} 1 * 3 + (-2) * 4 \\ 0 * 3 + 2 * 4 \end{pmatrix} = \begin{pmatrix} -3 \\ 8 \end{pmatrix}$$

**By a square matrix**

$$\begin{pmatrix} 1 & -2 \\ 0 & 2 \end{pmatrix} * \begin{pmatrix} 3 & 4 \\ -3 & 5 \end{pmatrix} = \begin{pmatrix} 1 * 3 + (-2) * (-3) & 1 * 4 + (-2) * (5) \\ (0) * 3 + (2) * (-3) & (0) * 4 + (2) * (5) \end{pmatrix} \\ = \begin{pmatrix} 9 & -6 \\ -6 & 10 \end{pmatrix}$$

**By a non-square matrix**

$$\begin{pmatrix} 1 & -2 \\ 0 & 2 \end{pmatrix} * \begin{pmatrix} 3 & -1 & 4 \\ 5 & 6 & 7 \end{pmatrix} \\ = \begin{pmatrix} 3 * 1 - 2 * 5 & 1 * (-1) + (-2) * 6 & 1 * 4 - 2 * 7 \\ 0 * 3 + 2 * 5 & 0 * (-1) + 2 * 6 & 0 * 4 + 7 * 2 \end{pmatrix} \\ = \begin{pmatrix} -7 & -13 & -10 \\ 10 & 12 & 14 \end{pmatrix}$$

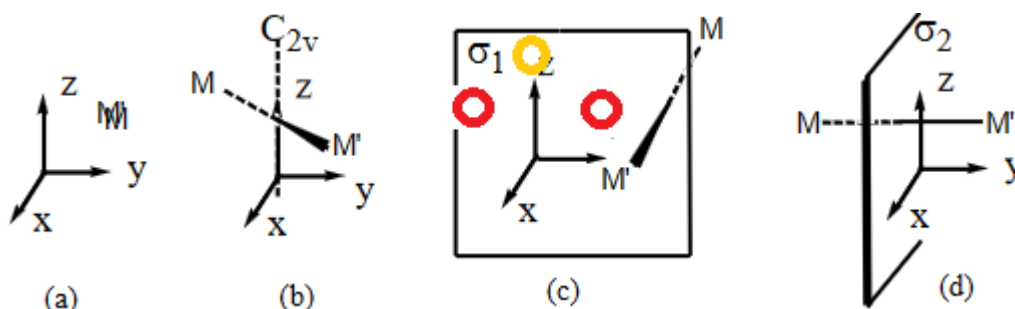
## Transform matrices

**A transformation matrix represents how a vector or basis function changes under a symmetry operation.**

## Transfer matrix for the water molecule

**To form the transfer matrix, each atom has an orthonormal system**

**The *zy* plane carries the three atoms the product of the vector matrix by the coordinates of the atoms which are always taken by**



**port to the identity. Give the vector matrix of the symmetry operation this result is called transfer matrix.(Tsukerblat 2006)**

**We can write in matrix form for the identity  $E$  which leaves the molecule unchanged**

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} & a_{18} & a_{19} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} & a_{27} & a_{28} & a_{29} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} & a_{37} & a_{38} & a_{39} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} & a_{47} & a_{48} & a_{49} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} & a_{57} & a_{58} & a_{59} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} & a_{67} & a_{68} & a_{69} \\ a_{71} & a_{72} & a_{73} & a_{74} & a_{75} & a_{76} & a_{77} & a_{78} & a_{79} \\ a_{81} & a_{82} & a_{83} & a_{84} & a_{85} & a_{86} & a_{87} & a_{88} & a_{89} \\ a_{91} & a_{92} & a_{93} & a_{11} & a_{95} & a_{86} & a_{97} & a_{98} & a_{99} \end{bmatrix} \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

The product give

$$\begin{bmatrix} x_0 a_{11} + x_0 a_{12} + z_0 a_{13} + x_1 a_{14} + y_1 a_{15} + z_1 a_{16} + x_2 a_{17} + y_2 a_{18} + z_2 a_{19} = 1 * x_0 \\ x_0 a_{21} + y_0 a_{22} + z_0 a_{23} + x_1 a_{24} + y_1 a_{25} + z_1 a_{26} + x_2 a_{27} + y_2 a_{28} + z_2 a_{29} = 1 * y_0 \\ x_0 a_{31} + y_0 a_{32} + z_0 a_{33} + x_1 a_{34} + y_1 a_{35} + z_1 a_{36} + x_2 a_{37} + y_2 a_{38} + z_2 a_{39} = 1 * z_0 \\ x_0 a_{41} + y_0 a_{42} + z_0 a_{43} + x_1 a_{44} + y_1 a_{45} + z_1 a_{46} + x_2 a_{47} + y_2 a_{48} + z_2 a_{49} = 1 * x_1 \\ x_0 a_{51} + y_0 a_{52} + z_0 a_{53} + x_1 a_{54} + y_1 a_{56} + z_1 a_{57} + x_2 a_{58} + y_2 a_{58} + z_2 a_{59} = 1 * y_1 \\ x_0 a_{61} + y_0 a_{62} + z_0 a_{63} + x_1 a_{64} + y_1 a_{65} + z_1 a_{66} + x_2 a_{67} + y_2 a_{68} + z_2 a_{69} = 1 * z_1 \\ x_0 a_{71} + y_0 a_{72} + z_0 a_{73} + x_1 a_{74} + y_1 a_{75} + z_1 a_{76} + x_2 a_{77} + y_2 a_{78} + z_2 a_{79} = 1 * x_2 \\ x_0 a_{81} + y_0 a_{82} + z_0 a_{83} + x_1 a_{84} + y_1 a_{85} + z_1 a_{86} + x_2 a_{87} + y_2 a_{88} + z_2 a_{89} = 1 * y_2 \\ x_0 a_{91} + y_0 a_{92} + z_0 a_{93} + x_1 a_{94} + y_1 a_{95} + z_1 a_{96} + x_2 a_{97} + y_2 a_{98} + z_2 a_{99} = 1 * z_2 \end{bmatrix}$$

This can be reduced to

$$\begin{bmatrix} 1x_{o_{11}} + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = 1*x_0 \\ 0 + 1y_{o_{22}} + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = 1*y_0 \\ 0 + 0 + 1z_{o_{22}} + 0 + 0 + 0 + 0 + 0 + 0 + 0 = 1*z_0 \\ 0 + 0 + 0 + 1x_1 + 0 + 0 + 0 + 0 + 0 + 0 = 1*x_1 \\ 0 + 0 + 0 + 0 + 1y_1 + 0 + 0 + 0 + 0 + 0 = 1*y_1 \\ 0 + 0 + 0 + 0 + 0 + 1z_1 + 0 + 0 + 0 + 0 = 1*z_1 \\ 0 + 0 + 0 + 0 + 0 + 0 + 1x_{2_{11}} + 0 + 0 + 0 = 1*x_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1y_{2_{11}} + 0 + 0 = 1*y_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1z_{2_{11}} + 0 = 1*z_2 \end{bmatrix} \Rightarrow \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

The general expression can be written as;

$$\begin{pmatrix} \text{New} \\ \text{coordinates} \end{pmatrix} = \begin{pmatrix} \text{transformation} \\ \text{matrix} \end{pmatrix} \begin{pmatrix} \text{Old} \\ \text{coordinates} \end{pmatrix} = \begin{pmatrix} \text{New in terms} \\ \text{of old} \end{pmatrix}$$

Instead to write a matrix of 9\*9 we can simply reduce the expression to

$$\begin{pmatrix} (M) & (0) & (0) \\ (0) & (M) & (0) \\ (0) & (0) & (M) \end{pmatrix} M = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

**Matrix for  $C_2$**

First write the transformation of the operation symmetry, undergo by the element  $C_2$

$$\begin{pmatrix} O \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} \\ H_1 \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \\ H_2 \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \end{pmatrix} C_2 \begin{pmatrix} O \begin{pmatrix} -x_0 \\ -y_0 \\ z_0 \end{pmatrix} \\ H_2 \begin{pmatrix} -x_1 \\ -y_1 \\ z_1 \end{pmatrix} \\ H_1 \begin{pmatrix} -x_2 \\ -y_2 \\ z_2 \end{pmatrix} \end{pmatrix}$$

The matrix can be written as

$$[GM]^* \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} -x_0 \\ -y_0 \\ +1z_0 \\ -x_2 \\ -y_2 \\ +1z_2 \\ -x_1 \\ -y_1 \\ +1z_1 \end{bmatrix}$$

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} & a_{18} & a_{19} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} & a_{27} & a_{28} & a_{29} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} & a_{37} & a_{38} & a_{39} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} & a_{47} & a_{48} & a_{49} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} & a_{57} & a_{58} & a_{59} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} & a_{67} & a_{68} & a_{69} \\ a_{71} & a_{72} & a_{73} & a_{74} & a_{75} & a_{76} & a_{77} & a_{78} & a_{79} \\ a_{81} & a_{82} & a_{83} & a_{84} & a_{85} & a_{86} & a_{87} & a_{88} & a_{89} \\ a_{91} & a_{92} & a_{93} & a_{94} & a_{95} & a_{96} & a_{97} & a_{98} & a_{99} \end{bmatrix} \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} -x_0 \\ -y_0 \\ -1z_0 \\ -x_2 \\ -1y_2 \\ +1z_2 \\ -x_1 \\ -1y_1 \\ +1z_1 \end{bmatrix}$$

The matrix Product gives

**Trace is**  $\chi(R) = -1$  = unshifted atom . the matrix trace  $[M]$  it called the contribution

$$\left[ \begin{array}{l} -1x_0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1 * x_0 \\ 0 - 1y_0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1 * y_0 \\ 0 + 0 + 1z_0 + 0 + 0 + 0 + 0 + 0 + 0 = 1 * z_0 \\ 0 + 0 + 0 + 0 + 0 + 0 - 1x_2 + 0 + 0 = -1 * x_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 - 1y_2 + 0 = -1 * y_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1z_2 = 1 * z_2 \\ 0 + 0 + 0 + -1x_1 + 0 + 0 + 0 + 0 + 0 = -1 * x_1 \\ 0 + 0 + 0 + 0 - 1y_1 + 0 + 0 + 0 + 0 = -1 * y_1 \\ 0 + 0 + 0 + 0 + 0 + 1z_1 + 0 + 0 + 0 = 1 * z_1 \end{array} \right] \Rightarrow \left[ \begin{array}{cccccccccc} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array} \right]$$

**Trace of the matrix  $\chi(R) = -1 = 1_{unchanged} * -1_{contribution}$**

**Matrix for plan  $\sigma_{v(xz)}$**

First write the transformation of the operation symmetry, undergo by the element  $\sigma_{v(xz)}$

$$\begin{pmatrix} O \begin{Bmatrix} x_0 \\ y_0 \\ z_0 \end{Bmatrix} & O \begin{Bmatrix} 1x_0 \\ -1y_0 \\ z_0 \end{Bmatrix} \\ H_1 \begin{Bmatrix} x_1 \\ y_2 \\ z_2 \end{Bmatrix} \frac{\sigma_{v(xz)}}{H_2} \begin{Bmatrix} 1x_1 \\ -1y_2 \\ z_2 \end{Bmatrix} \\ H_2 \begin{Bmatrix} x_2 \\ y_2 \\ z_2 \end{Bmatrix} & H_1 \begin{Bmatrix} 1x_2 \\ -1y_2 \\ z_2 \end{Bmatrix} \end{pmatrix}$$

The matrix can be written as

$$[GM]^* \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} x_0 \\ -y_0 \\ +1z_0 \\ x_2 \\ -y_2 \\ +1z_2 \\ x_1 \\ -y_1 \\ +1z_1 \end{bmatrix}$$

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} & a_{18} & a_{19} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} & a_{27} & a_{28} & a_{29} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} & a_{37} & a_{38} & a_{39} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} & a_{47} & a_{48} & a_{49} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} & a_{57} & a_{58} & a_{59} \\ a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66} & a_{67} & a_{68} & a_{69} \\ a_{71} & a_{72} & a_{73} & a_{74} & a_{75} & a_{76} & a_{77} & a_{78} & a_{79} \\ a_{81} & a_{82} & a_{83} & a_{84} & a_{85} & a_{86} & a_{87} & a_{88} & a_{89} \\ a_{91} & a_{92} & a_{93} & a_{11} & a_{95} & a_{86} & a_{97} & a_{98} & a_{99} \end{bmatrix} \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} +1x_0 \\ -1y_0 \\ -1z_0 \\ 1x_2 \\ -1y_2 \\ +1z_2 \\ 1x_1 \\ -1y_1 \\ +1z_1 \end{bmatrix}$$

The matrix Product gives

**Trace is**  $\chi(R) = 1$  =unshifted atom . the matrix trace  $[M]$  it called the contribution

$$\begin{bmatrix} +1x_o + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1*x_0 \\ 0 - 1y_o + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1*y_0 \\ 0 + 0 + 1z_o + 0 + 0 + 0 + 0 + 0 + 0 = 1*z_0 \\ 0 + 0 + 0 + 0 + 0 + 0 + 1x_2 + 0 + 0 = -1*x_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 - 1y_2 + 0 = -1*y_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1z_2 = 1*z_2 \\ 0 + 0 + 0 + 1x_1 + 0 + 0 + 0 + 0 + 0 = -1*x_1 \\ 0 + 0 + 0 + 0 - 1y_1 + 0 + 0 + 0 + 0 = -1*y_1 \\ 0 + 0 + 0 + 0 + 0 + 1z_1 + 0 + 0 + 0 = 1*z_1 \end{bmatrix} \Rightarrow \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$$\begin{bmatrix} +1x_o + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1*x_0 \\ 0 - 1y_o + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1*y_0 \\ 0 + 0 + 1z_o + 0 + 0 + 0 + 0 + 0 + 0 = 1*z_0 \\ 0 + 0 + 0 + 0 + 0 + 0 + 1x_2 + 0 + 0 = -1*x_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 - 1y_2 + 0 = -1*y_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1z_2 = 1*z_2 \\ 0 + 0 + 0 + 1x_1 + 0 + 0 + 0 + 0 + 0 = -1*x_1 \\ 0 + 0 + 0 + 0 - 1y_1 + 0 + 0 + 0 + 0 = -1*y_1 \\ 0 + 0 + 0 + 0 + 0 + 1z_1 + 0 + 0 + 0 = 1*z_1 \end{bmatrix} \Rightarrow \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

**Trace of the matrix  $\chi(\mathbf{r}) = \mathbf{1} = 1_{\text{unchanged}} * 1_{\text{contribution}}$**

transfert matrix of the plan  $\sigma'_{v(yz)}$

**The element  $\sigma'_{v(yz)}$  affect only the coordinates thus  $x_0$  become  $-1x_0$  for oxygen atome.  $y_0$  remain unchanged and the same for  $z_0$ . We extend the effect to hydrogen atoms we get the expression .**

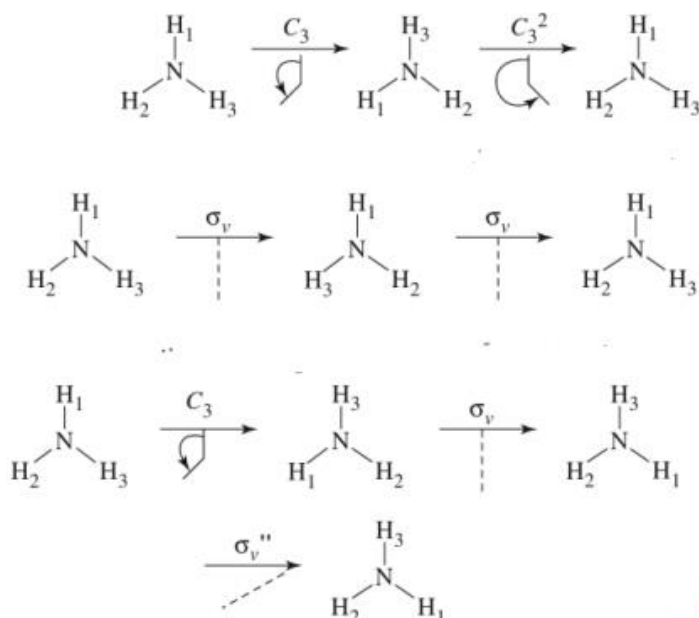
$$\begin{cases} O \begin{cases} x_0 \\ y_0 \\ z_0 \end{cases} \\ H_1 \begin{cases} x_1 \\ y_2 \\ z_2 \end{cases} \\ H_2 \begin{cases} x_2 \\ y_2 \\ z_2 \end{cases} \end{cases} \rightarrow \begin{cases} O \begin{cases} -1x_0 \\ 1y_0 \\ z_0 \end{cases} \\ H_1 \begin{cases} -1x_1 \\ 1y_2 \\ z_2 \end{cases} \\ H_2 \begin{cases} -1x_2 \\ 1y_2 \\ z_2 \end{cases} \end{cases}$$

The transform matrix is

$$\begin{bmatrix} -1x_{011} + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = 1*x_0 \\ 0 + 1y_{022} + 0 + 0 + 0 + 0 + 0 + 0 + 0 = 1*y_0 \\ 0 + 0 + 1z_{022} + 0 + 0 + 0 + 0 + 0 + 0 = 1*z_0 \\ 0 + 0 + 0 + -1x_1 + 0 + 0 + 0 + 0 + 0 = 1*x_1 \\ 0 + 0 + 0 + 0 + 1y_1 + 0 + 0 + 0 + 0 = 1*y_1 \\ 0 + 0 + 0 + 0 + 0 + 1z_1 + 0 + 0 + 0 = 1*z_1 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + -1x_2 + 0 + 0 = 1*x_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1y_{211} + 0 = 1*y_2 \\ 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 1z_{211} = 1*z_2 \end{bmatrix} \Rightarrow \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_0 \\ y_0 \\ z_0 \\ x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} -x_0 \\ y_0 \\ z_0 \\ -x_1 \\ y_1 \\ z_1 \\ -x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

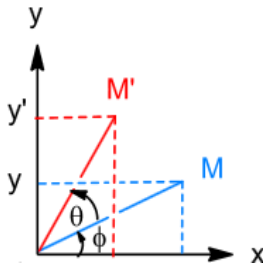
The Trace of the matrix is  $\chi(R) = 3$

Transformation matrices for the symmetry group  $C_{3v}$



## Rotation transform Matrix

The Operation by the element  $C_3$  cannot be represented by a “fully” diagonal matrix; at best, if we take the axis of symmetry for the z axis, it always presents a block of dimension 2. In fact, each  $x'$  and  $y'$  coordinate of a point  $M'$  transformed from any point  $M (x, y)$  is a linear combination of  $x$  and  $y$ . The matrix  $C_3$  in Fig is deduced from the rotation matrix of an angle  $\theta$  around  $Oz$  (Reddy 2007)



The point  $M$  being transformed into  $M'$  by a rotation of  $\theta$  around  $O$ , we look for the expression coordinates  $(x', y')$  as a function of  $(x, y)$ . We set  $OM = OM' = r$ . The plan is oriented as above: angles are counted positively counter clockwise of a watch (trigonometric direction). We have

$$\begin{aligned}x &= r \cos \varphi \\y &= r \sin \varphi\end{aligned}$$

these coordinates which are transformed by rotation by  $\theta$  to the new coordinates which are :

$$\begin{aligned}x' &= r \cos (\varphi + \theta) = r (\cos \varphi \cos \theta - \sin \varphi \sin \theta) = x \cos \theta - y \sin \theta \\y' &= r \sin (\varphi + \theta) = r (\sin \theta \cos \varphi + \sin \varphi \cos \theta) = x \sin \theta + y \cos \theta\end{aligned}$$

It can be given in matrix form:

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

**For a rotation in three-dimensional space around Oz,  $z' = z$  and the transformation matrix is**

$$C_{n(z)} = M = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \chi(\mathbb{R}) = 1 + 2\cos\theta$$

**For the improper rotation the projection according to z gives an irreducible representation -1 so we can write**

$$S_{n(z)} = M = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix} \chi(k) = -1 + 2\cos\theta$$

$$\mathbf{C}_{n(x)} = \begin{bmatrix} 1 & 0 & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & -\sin\theta & \cos\theta \end{bmatrix} \chi(\mathbf{R}) = 1 + 2\cos\theta$$

$$C_{n(y)} = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix} \chi(\mathbb{R}) = \mathbf{1} + 2\cos\theta$$

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \chi(\mathbb{R}) = -3$$

The groups  $O_h$  and  $T_d$  have irreducible third-order representations (third-order degeneracy) It is symbolized by T. The identity character  $\chi(E)$  is always take the value 2 in the doubly degenerate RIs for E and value 3 in the triple-degenerate RIs T.

### Identity Transfer Matrix E

For the symmetry element E the atoms are immobile so the coordinate matrix is diagonal we can write for the symmetry operation which results from the application of the symmetry element identity the transfer matrix can be given as

$$\begin{aligned}
 N &\xrightarrow{E} N \\
 H_1 &\xrightarrow{E} H_1 \\
 H_2 &\xrightarrow{E} H_2 \\
 H_3 &\xrightarrow{E} H_3
 \end{aligned}$$

$$\begin{bmatrix}
 a_{11} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & a_{112} \\
 \cdot & \cdot & & & & & & & & & & & \cdot \\
 \cdot & & \cdot & & & & & & & & & & \cdot \\
 \cdot & & & \cdot & & & & & & & & & \cdot \\
 \cdot & & & & \cdot & & & & & & & & \cdot \\
 \cdot & & & & & a_{66} & a_{67} & & & & & & a_{612} \\
 \cdot & & & & & \cdot & & & & & & & \cdot \\
 \cdot & & & & & & \cdot & & & & & & \cdot \\
 \cdot & & & & & & & \cdot & & & & & \cdot \\
 \cdot & & & & & & & & \cdot & & & & \cdot \\
 \cdot & & & & & & & & & \cdot & & & \cdot \\
 a_{121} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & a_{1212}
 \end{bmatrix}
 \begin{bmatrix}
 x_N \\
 y_N \\
 z_N \\
 x_{H1} \\
 y_{H1} \\
 z_{H1} \\
 x_{H2} \\
 y_{H2} \\
 z_{H2} \\
 x_{H3} \\
 y_{H3} \\
 z_{H3}
 \end{bmatrix}
 =
 \begin{bmatrix}
 x_N \\
 y_N \\
 z_N \\
 x_{H1} \\
 y_{H1} \\
 z_{H1} \\
 x_{H2} \\
 y_{H2} \\
 z_{H2} \\
 x_{H3} \\
 y_{H3} \\
 z_{H3}
 \end{bmatrix}$$

The matrix expression can simplified to

$M$	$[0]$	$[0]$	$[0]$	$X$
				$Y$
				$Z$
$[0]$	$M$	$[0]$	$[0]$	$X1$
				$Y1$
				$Z1$
$[0]$	$[0]$	$M$	$[0]$	$X2$
				$Y2$
				$Z2$
$[0]$	$[0]$	$[0]$	$M$	$X3$
				$Y3$
				$Z3$

$$M = \begin{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & 0 \\ 0 & 0 & 1 \end{bmatrix} \chi(R)$$

$= 3$

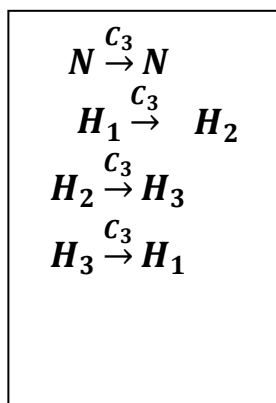
The trace of global matrix is :

$$\chi(R) = 3 * 4 = 12$$

Rotation axis transfer matrix  $C_3$

The symmetry operation obtained by the application of the higher order axis of rotation Leaves only the nitrogen atom unshifted because it carries the nitrogen atom while H1 moves to the place of H2 and H2 moves to the place of H3 hence:

And For xyz coordinates



$$\begin{array}{l} N \left\{ \begin{array}{l} X \\ Y \\ Z \end{array} \right\} \xrightarrow{C_3} N \left\{ \begin{array}{l} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x + \frac{1}{2}y \\ Z \end{array} \right. \\ H_1 \left\{ \begin{array}{l} X \\ Y \\ Z \end{array} \right\} \xrightarrow{C_3} H_2 \left\{ \begin{array}{l} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x + \frac{1}{2}y \\ Z \end{array} \right. \\ H_2 \left\{ \begin{array}{l} X \\ Y \\ Z \end{array} \right\} \xrightarrow{C_3} H_3 \left\{ \begin{array}{l} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x + \frac{1}{2}y \\ 0Z \end{array} \right. \\ H_3 \left\{ \begin{array}{l} X \\ Y \\ Z \end{array} \right\} \xrightarrow{C_3} H_1 \left\{ \begin{array}{l} -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x + \frac{1}{2}y \\ Z \end{array} \right. \end{array} \quad \theta = 120^\circ$$

To obtain the transformation matrix for the C<sub>3</sub> axis, it is enough to move the coordinate matrix of the atom H1 towards the third line. We do the same way for the rest of the hydrogen atoms. Hence the matrix trace

$$\chi(R) = 3 * 1 = 3$$

[N]				X Y z
	[H <sub>1</sub> ] ↓		↑	X1 Y1 Z1 ↓
		[H <sub>2</sub> ] ↓		X2 Y2 Z2 ↓
			[H <sub>3</sub> ] ↑	X3 Y3 Z3 ↓

And the matrix becomes (the last column represents the result of the passage))

[M]	[0]	[0]	[0]	X Y z
[0]	[0]	[M]	[0]	X 2 Y 2 Z 2
[0]	[0]	[0]	[M]	X 3 Y 3 Z 3
[0]	[M]	[0]	[0]	X 1 Y 1 Z 1

The axis of rotation transfer matrix  $C_3^2$

The axis of rotation carries the nitrogen atom we can write

$$\begin{aligned}
 N \begin{Bmatrix} X \\ Y \\ Z \end{Bmatrix} &\xrightarrow{C_3^2} N \begin{Bmatrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{Bmatrix} \\
 H_1 \begin{Bmatrix} X \\ Y \\ Z \end{Bmatrix} &\xrightarrow{C_3^2} H_3 \begin{Bmatrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{Bmatrix} \\
 H_2 \begin{Bmatrix} X \\ Y \\ Z \end{Bmatrix} &\xrightarrow{C_3^2} H_1 \begin{Bmatrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{Bmatrix} \\
 H_3 \begin{Bmatrix} X \\ Y \\ Z \end{Bmatrix} &\xrightarrow{C_3^2} H_2 \begin{Bmatrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{Bmatrix}
 \end{aligned}
 \quad \text{avec } \theta = 120^\circ + 120^\circ$$

These transformations can be translated into a matrix and therefore the matrix can be written in the expression:

$$\begin{aligned}
& a_{11}x_N + a_{11}y_N + a_{11}z_N + 0+0+0+0+0+0+0+0+0+0 = -1/2 x_N - \sqrt{3}/2 y_N = \underline{x_N} \\
& a_{21}x_N + a_{22}y_N + a_{23}z_N + 0+0+0+0+0+0+0+0+0+0+0+0 = \sqrt{3}/2 x_N - 1/2 y_N = \underline{y_N} \\
& a_{31}x_N + a_{32}y_N + a_{33}z_N + 0+0+0+0+0+0+0+0+0+0+0+0 = 0+0+1z_N + 0 = \underline{z_N} \\
& 0+0+0+0+0+0+0 + a_{47}x_{H_2} + a_{48}y_{H_2} + a_{49}z_{H_2} + 0+0+0+0+0+0 = -1/2 x_{H_2} - \sqrt{3}/2 y_{H_2} \\
& 0+0+0+0+0+0+0 + a_{57}x_{H_2} + a_{58}y_{H_2} + a_{59}z_{H_2} + 0+0+0+0+0+0 = \sqrt{3}/2 x_{H_2} - 1/2 y_{H_2} \\
& 0+0+0+0+0+0+0 + a_{67}x_{H_2} + a_{68}y_{H_2} + a_{69}z_{H_2} + 0+0+0+0+0+0 = 0+0+1z_{H_2} \\
& 0+0+0+0+0+0+0+0+0+0+0+0+0+0 + a_{47}x_{H_3} + a_{511}y_{H_3} + a_{412}z_{H_3} = -1/2 x_{H_3} - \sqrt{3}/2 y_{H_3} \\
& 0+0+0+0+0+0+0+0+0+0+0+0+0+0 + a_{57}x_{H_3} + a_{511}y_{H_3} + a_{512}z_{H_3} = \sqrt{3}/2 x_{H_3} - 1/2 y_{H_3} \\
& 0+0+0+0+0+0+0+0+0+0+0+0+0+0 + a_{610}x_{H_3} + a_{611}y_{H_3} + a_{612}z_{H_3} = 0+0+1z_{H_3} \\
& 0+0+0+0 + a_{74}x_{H_1} + a_{75}y_{H_1} + a_{76}z_{H_1} + 0+0+0+0+0+0 = -1/2 x_{H_1} - \sqrt{3}/2 y_{H_1} \\
& 0+0+0+0 + a_{84}x_{H_1} + a_{85}y_{H_1} + a_{86}z_{H_1} + 0+0+0 = \sqrt{3}/2 x_{H_1} - 1/2 y_{H_1} \\
& 0+0+0+0 + a_{94}x_{H_1} + a_{95}y_{H_1} + a_{96}z_{H_1} + 0+0+0 = 0+0+0 + z_{H_1}
\end{aligned}$$

The mirror  $\sigma_v$

The reflection operation by the element plan  $\sigma_v$  carrying the atom H1 bearing the axis  $\overrightarrow{Ox}\sigma_{V(xz)}$  thus  $\sigma_v[x, y, z] \rightarrow [x, -y, z]$

$$\begin{array}{l}
 N \begin{cases} X \\ Y \xrightarrow{\sigma_v} N \\ Z \end{cases} \begin{cases} X \\ -Y \\ Z \end{cases} \\
 H_1 \begin{cases} X \\ Y \xrightarrow{\sigma_v} H_1 \\ Z \end{cases} \begin{cases} X \\ -Y \\ 1Z \end{cases} \\
 H_2 \begin{cases} X \\ Y \xrightarrow{\sigma_v} H_3 \\ Z \end{cases} \begin{cases} X \\ -Y \\ 1Z \end{cases} \\
 H_3 \begin{cases} X \\ Y \xrightarrow{\sigma_v} H_2 \\ Z \end{cases} \begin{cases} X \\ -Y \\ 1Z \end{cases}
 \end{array}
 \begin{pmatrix} (M) & (0) & (0) & (0) & N \\ (0) & (M) & (0) & (0) & H1 \\ (0) & (0) & (0) & (M) & H3 \\ (0) & (0) & (M) & (0) & H2 \end{pmatrix}
 (M) \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Taking these transformations into consideration, the transformation matrix can then be written in the expression:

$$1x_N + 0y_N + 0z_N + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = x_N$$

$$0x_N + -1y_N + 0z_N + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = -1y_N$$

$$0x_N + 0y_N + 1z_N + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 = 1z_N$$

$$0+0+0+0+0+0+0+0+0+0+0+0+0+1x_{H_3}+0y_{H_3}+0z_{H_3}=1x_{H_3}$$

$$0+0+0+0+0+0+0+0+0+0+0+0+0+0+0x_{H_3}-1y_{H_3}+0z_{H_3}=-y_{H_3}$$

$$0+0+0+0+0+0+0+0+0+0+0+0+0+0x_{H_3}+0y_{H_3}+1z_{H_3}=1z_{H_3}$$

$$0+0+0+0+0+0-x_{H_2}+a_{48}y_{H_2}+a_{49}z_{H_2}+0+0+0+0+0+0=-1x_{H_2}$$

$$0+0+0+0+0+0+0+0x_{H_2}-1y_{H_2}+0z_{H_2}+0+0+0+0+0+0=y_{H_2}$$

$$0+0+0+0+0+0+0+0x_{H_2}+0y_{H_2}+1z_{H_2}+0+0+0+0+0+0=0+0+1z_{H_2}$$

$$0+0+0+1x_{H1}-a_{75}y_{H1}+0z_{H1}+0+0+0+0+0+0=-1x_{H1}$$

$$0+0+0+0x_{H_1}+{-1}y_{H_1}+1z_{H_1}+0+0+0+0 \quad 0 \quad 0=-1y_{H_1}$$

$$0+0+0+0x_{H_1}+0y_{H_1}+1z_{H_1}+0+0+0+0 \quad 0 \quad 0 = z_{H_1}$$

**For the mirror  $\sigma_v$  passing it containing H2**

**This plane carries the main axis of rotation and divides the angle**

$[M]$	$[0]$	$[0]$	$[0]$	X Y z
$[0]$	$[0]$	$[0]$	$[M]$	X1 Y1 Z1
$[0]$	$[0]$	$[M]$	$[0]$	X2 Y2 Z2
$[0]$	$[M]$	$[0]$	$[0]$	X3 Y3 Z3

$$\begin{aligned}
N \left\{ \begin{matrix} X \\ Y \\ Z \end{matrix} \right\} \xrightarrow{\sigma_v''} N \left\{ \begin{matrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ 0Z \end{matrix} \right\} \\
H_1 \left\{ \begin{matrix} X \\ Y \\ Z \end{matrix} \right\} \xrightarrow{\sigma_v''} H_3 \left\{ \begin{matrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{matrix} \right\} \\
H_2 \left\{ \begin{matrix} X \\ Y \\ 0Z \end{matrix} \right\} \xrightarrow{\sigma_v''} H_2 \left\{ \begin{matrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{matrix} \right\} \\
H_3 \left\{ \begin{matrix} X \\ Y \\ Z \end{matrix} \right\} \xrightarrow{\sigma_v''} H_1 \left\{ \begin{matrix} -\frac{1}{2}x + \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2}y - 1/2x \\ Z \end{matrix} \right\}
\end{aligned}$$

$$\begin{bmatrix} -1/2 & +\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

between  $o_y$  and  $o_x$ . By projection, it can be written

The plan  $\sigma'_v$

This plan carrying H3

$$\begin{aligned}
 N \begin{cases} X \\ Y \rightarrow N \\ Z \end{cases} \sigma'_v & \begin{cases} -\frac{1}{2}x + \sqrt{3}/2 \\ +\frac{\sqrt{3}}{2}y + 1/2x \\ Z \end{cases} \\
 H_1 \begin{cases} X \\ Y \rightarrow H_2 \\ Z \end{cases} \sigma'_v & \begin{cases} -\frac{1}{2}x + \sqrt{3}/2 \\ +\frac{\sqrt{3}}{2}y + 1/2x \\ Z \end{cases} \\
 H_2 \begin{cases} X \\ Y \rightarrow H_1 \\ Z \end{cases} \sigma'_v & \begin{cases} -\frac{1}{2}x + \sqrt{3}/2 \\ +\frac{\sqrt{3}}{2}y + 1/2x \\ Z \end{cases} \\
 H_3 \begin{cases} X \\ Y \rightarrow H_3 \\ Z \end{cases} \sigma'_v & \begin{cases} -\frac{1}{2}x + \sqrt{3}/2 \\ +\frac{\sqrt{3}}{2}y + 1/2x \\ Z \end{cases}
 \end{aligned}$$

$[M]$	$[0]$	$[0]$	$[0]$	X
				Y
				Z
				X2
$[0]$	$[0]$	$[M]$	$[0]$	Y2
				Z2
				X1
$[0]$	$[M]$	$[0]$	$[0]$	Y1
				Z1
				X3
$[0]$	$[0]$	$[0]$	$[M]$	Y3
				Z3

$$[M] = \begin{bmatrix} -1/2 & +\sqrt{3}/2 & 0 \\ +\sqrt{3}/2 & +1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

And as a result

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} C_3 = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$C_3^2 = \begin{pmatrix} -1/2 & 1/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Transformation matrices and construction of character tables

**The irreducible trace of the transfer matrices of the symmetry elements are grouped in tables called character tables in the event of missing representations in fact calls on the great orthogonality theorem.(McClain 2010)**

**Table des caractères pour le groupe  $C_n$  (n=1-6)**

$C_1$	$E$	$h=1$
<b>A</b>	<b>1</b>	

$C_2$	<b>E</b>	$C_2$	$h=2$	
<b>A</b>	<b>1</b>	<b>1</b>	$z, R_z$	$x^2, y^2, z^2, xy$
<b>B</b>	<b>1</b>	<b>-1</b>	$x, y, R_y, R_x$	$xz, yz$

Mulliken's symbols

Symbol	Property
A	symmetric with respect to rotation around the principal

---

B	<b>rotational axis (one dimensional representations) anti-symmetric with respect to rotation around the principal rotational axis (one dimensional representations)</b>
E	<b>degenerate (German: entartet; two dimensional representations, e.g. in systems with higher order principal axes)</b>
subscript 1	<b>symmetric with respect to a vertical mirror plane perpendicular to the principal axis</b>
subscript 2	<b>anti-symmetric with respect to a vertical mirror plane perpendicular to the principal axis</b>
subscript g	<b>symmetric with respect to a center of symmetry (German: "gerade")</b>
subscript u	<b>anti-symmetric with respect to a center of symmetry (German: "ungerade")</b>
prime (')	<b>symmetric with respect to a mirror plane horizontal to the principal rotational axis</b>
double prime (")	<b>anti-symmetric with respect to a mirror plane horizontal to the principal rotational axis</b>

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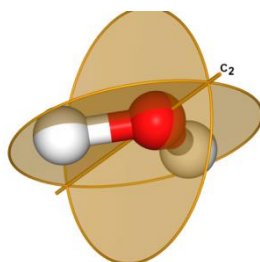
## **T triple degenerate**

### **The normal vibration modes (Willock 2009)**

vibrations in molecules comprise changes in bond lengths and/or bond angles and dihedral angles. An N-atomic molecule has  $3N$  degrees of freedom since each atom needs three coordinates to define its position completely. Three of these are independent degrees of translational motion in the three directions. Three others comprise rotational motion, leaving a total of  $3N - 6$  vibrational degrees of freedom. However, linear molecules have only two rotational degrees of freedom since rotation about the internuclear axis has zero moment of inertia. This leaves  $3N - 5$  vibrational degrees of freedom for linear molecules.

Molecules possessing a dipole moment manifest interactions with radiation of variable energy ranging from lower intensity sweeping the domain of so-called infrared molecular oscillation ( $400\text{cm}^{-1} - 4000\text{cm}^{-1}$ ), nevertheless molecules which do not possess a dipole moment and for these molecules to exhibit an interaction which means creating a temporary dipole moment the system in this case the molecule is excited by a constant energy thus the electronic cloud is polarized the molecules interact with the radiation and oscillate due to the temporary dipole moment appear , we will therefore have an absorption spectrum called RAMAN spectrum.

### Application to the water molecule



For the calculation procedure we are interested in unchanged atoms which do not undergo a change of place which gives, hence the trace of the transfer matrix of molecule for all the xyz coordinates of the system to be studied mathematically by multiplying the unchanged atoms by their contribution (the trace of the matrix M of the three coordinates). What is translated by the table

$C_{2v}$	$E$	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$
Unshifted atoms	3	1	1	3
Contribution	3	-1	1	1
$\Gamma_{3n}$	9	-1	1	3

The character table of the group  $C_{2v}$  the last line is the irreducible representation  $\chi_{irr}$

$C_{2v}$	<b>1E</b>	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	$h = 4$	
$A_1$	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>z</b>	$x^2, y^2, z^2$
$A_2$	<b>1</b>	<b>1</b>	<b>-1</b>	<b>-1</b>	$R_z$	$xy$
$B_1$	<b>1</b>	<b>-1</b>	<b>1</b>	<b>-1</b>	$x, R_y$	$xz$
$B_2$	<b>1</b>	<b>-1</b>	<b>-1</b>	<b>1</b>	$y, R_x$	$yz$
$\Gamma_{3n}$	9	-1	1	3		

repetition of<sub>i</sub>

$$= \frac{1}{h} \left( \left( \sum (\text{number of operations of the class}) * \chi_{irr} * \chi_{ri} \right) \right)$$

h is the sum of the elements of the classes here it is 4.

$$A_1 = \frac{1}{4} (\textcolor{red}{1} * \textcolor{blue}{1} * 9 + 1 * 1 * (-1) + 1 * 1 * 1 + 1 * 1 * 3) = 3$$

$$A_2 = \frac{1}{4} (1 * 1 * 9 + 1 * 1 * (-1) + (-1) * 1 * 1 + (-1) * 1 * 3) = 1$$

$$B_1 = \frac{1}{4} (1 * 1 * 9 + 1 * (-1) * (-1) + 1 * 1 * 1 + (-1) * 1 * 3) = 2$$

$$B_2 = \frac{1}{4} (1 * 1 * 9 + 1 * (-1) * (-1) + (-1) * 1 * 1 + (1) * 1 * 3) = 3$$

$$\Gamma_{3n} = 9 = 3A_1 + 1A_2 + 2B_1 + 3B_2$$

This represents all possible movements' vibrations translations and rotations therefore

$$\Gamma_{3n} = \Gamma_{vib} + \Gamma_{trans} + \Gamma_{Rot}$$

$$\Gamma_{Rot} = A_2 + B_1 + B_2, \Gamma_{Trans} = A_1 + B_1 + B_2$$

$$\Gamma_{vib} = 3A_1 + 1A_2 + 2B_1 + 3B_2 - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2)$$

$$\Gamma_{vib} = 2A_1 + B_2$$

Hence the number of vibration modes for nonlinear molecules

$$\Gamma_{vib} = \Gamma_{3n} - 6$$

$$\Gamma_{vib} = \Gamma_{3n} - 5 \text{ for linear molecules}$$

$A_1$  Has a character of a quadratic term  $xy$  and translation terms so it is both actives in RAMAN and Infrared.

$B_2$  Has a character of a quadratic term  $yz$  and translation term  $y$ , it is active both in RAMAN and in IR. So for infrared transition to take place

$$I_i = \int \Phi_0 \mu_i \Phi_f d\tau \quad i = x, y \text{ or } z \text{ for transition } \Phi_0 \rightarrow \Phi_f$$

Where  $\mu$  is the dipole moment vector of the molecule. If this integral is non-zero, the transition will give rise to an infrared absorption line: we say that it is active infrared. If, however,  $I = 0$ , the particular infrared transition is prohibited. The dipole moment vector  $\mu$  can be resolved along three orthogonal axes. The integral can be written in the form

$$\Phi_0 \begin{pmatrix} x \\ y \\ z \end{pmatrix} \Phi_f$$

We now form the direct products, where  $\Phi_0$  covers  $A_1$ , et  $\Phi_f$  covers  $A_2$  ou  $B_2$  for the symmetry  $A_1$ , we have

$$A_1 \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} A_1$$

Which leads to

$$A_1 B_1 A_1 = B_1$$

$$A_1 B_2 A_1 = B_2$$

$$A_1 A_1 A_1 = A_1$$

For the symmetry  $B_2$

$$A_1 \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} B_2$$

This leads to

$$A_1 B_1 B_2 = A_2$$

$$A_1 B_2 B_2 = A_1$$

$$A_1 A_1 B_2 = B_2$$

The result shows that there is one or more symmetry along x,y or z so the vibration modes are active in infrared.

For the Raman transition

$$I_i = \int \Phi_0 \alpha_{ij} \Phi_f d\tau$$

$$\begin{bmatrix} \alpha_{x^2} \\ \alpha_{y^2} \\ \alpha_{z^2} \\ \alpha_{xy} \\ \alpha_{yz} \\ \alpha_{zx} \end{bmatrix}$$

We can write

$$\begin{aligned} A_1 A_1 A_1(B_2) &= A_1(B_2) \\ A_1 A_2 A_1(B_2) &= A_2(B_1) \\ A_1 B_1 A_1(B_2) &= B_1(A_2) \\ A_1 B_2 A_1(B_2) &= B_2(A_1) \end{aligned}$$

Since A1 and B2 have quadratic terms they also have lines on the RAMAN spectrum

The lines appear at

$$\left\{ \begin{array}{l} A_1(\text{symmetric stretching}) 3650 \text{ cm}^{-1} \\ B_2(\text{asymmetric stretching}) 3760 \text{ cm}^{-1} \\ A_2(\text{bending scissoring}) 1600 \text{ cm}^{-1} \end{array} \right.$$

Asymmetric lines appear in more energetic zones than symmetrical lines; deformation lines are the least energetic.

Representation of modes on the character table

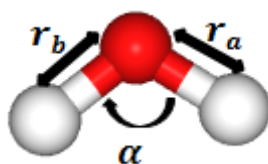
The number of normal modes is the number of degrees of freedom, which was discussed previously using Cartesian coordinates. We consider next the symmetry of the normal modes, taking the water molecule as an illustrative example. The vibrations of symmetry-related atoms are related one to the other, so that the normal modes may be given symmetry labels, such as A1 and E. we considered the  $\Gamma_{3n}$  representation for the water molecule. From the three sets of orthogonal axes, one set emanating from each atom, we constructed four 9 x 9 matrices to represent the actions of the symmetry operations of the point group  $C_{2v}$  on each atom of the molecule, and developed the representation:

$\Gamma_{3n}$	9	-1	1	3
---------------	---	----	---	---

it follows that the (three) vibrational modes correspond to the sum  $\Gamma_{vib} = 2A_1 + B_2$ . We note that the number of modes corresponds to the total dimensionality of the irreducible representations for vibration.

### internal coordinates

We need next to associate the irreducible representations of the normal modes with the internal coordinates of the water molecule. In relation to Figure



, we choose these coordinates to be the vectors  $r_a$ . And  $r_b$  along the O-H bonds, and  $\alpha$ . for the angle H-O-H. Using these internal coordinates as a basis, we generate the representation (Cotton 1991)

$C_{2v}$	$1E$	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	$h = 4$	
$\Gamma_r$	2	0	0	2		
$\Gamma_\alpha$	1	1	1	1		

$C_{2v}$	$1E$	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	$h = 4$	
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$
$\Gamma_r$	2	0	0	2		
$\Gamma_\alpha$	1	1	1	1		

$$A_1 = \frac{1}{4} (1 * 1 * 2 + 1 * 0 * (1) + 0 * 1 * 1 + 1 * 1 * 2) = 1$$

$$A_2 = \frac{1}{4} (1 * 1 * 2 + 1 * 0 * (1) + (-1) * 0 * 1 + (-1) * 1 * 2) = 0$$

$$B_1 = \frac{1}{4}(1 * 1 * 2 + 1 * 0 * (-1) + (1) * 0 * 1 + (-1) * 1 * 2) = 0$$

$$B_2 = \frac{1}{4}(1 * 1 * 2 + 1 * (0) * (-1) + (-1) * 1 * 1 + (1) * 1 * 2) = 1$$

$$\Gamma_r = A_1 + B_2$$

$$A_1 = \frac{1}{4}(\textcolor{red}{1} * \textcolor{blue}{1} * 1 + 1 * 1 * (1) + 1 * 1 * 1 + 1 * 1 * 1) = 1$$

$$A_2 = \frac{1}{4}(1 * 1 * 1 + 1 * 1 * (1) + (-1) * 1 * 1 + (-1) * 1 * 1) = 0$$

$$B_1 = \frac{1}{4}(1 * 1 * 1 + 1 * 1 * (1) + (-1) * 1 * 1 + (-1) * 1 * 1) = 0$$



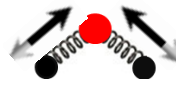









$$B_2 = \frac{1}{4}(1 * 1 * 1 + 1 * (1) * (-1) + (-1) * 1 * 1 + (1) * 1 * 1) = 0$$

$$\Gamma_r = A_1$$

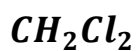
$A_1$	1	1	1	1		
$\Gamma_\alpha$	1	1	1	1		

$A_1$	1	1	1	1		
$B_2$	1	-1	-1	1		
$\Gamma_r$	2	0	0	1		

And this lead to three modes two stretch and one mode angular deformation scissoring

$C_{2v}$	$\textcolor{red}{1}E$	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$		
$Q_1$	 1	 1	 1	 1	$A_1$	
$Q_2$	 1	 -1	 -1	 1	$B_2$	
$Q_3$	 1	 1	 1	 1	$A_1$	

Example



$C_{2v}$	<b>1E</b>	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	linear functions,	quadratic	cubic
					rotations	functions	functions
<b>A<sub>1</sub></b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>z</b>	<b>x<sup>2</sup>, y<sup>2</sup>, z<sup>2</sup></b>	<b>z<sup>3</sup>, x<sup>2</sup>z, y<sup>2</sup>z</b>
<b>A<sub>2</sub></b>	<b>1</b>	<b>1</b>	<b>-1</b>	<b>-1</b>	<b>R<sub>z</sub></b>	<b>xy</b>	<b>xyz</b>
<b>B<sub>1</sub></b>	<b>1</b>	<b>-1</b>	<b>1</b>	<b>-1</b>	<b>x, R<sub>y</sub></b>	<b>xz</b>	<b>xz<sup>2</sup>, x<sup>3</sup>, xy<sup>2</sup></b>
<b>B<sub>2</sub></b>	<b>1</b>	<b>-1</b>	<b>-1</b>	<b>1</b>	<b>y, R<sub>x</sub></b>	<b>yz</b>	<b>yz<sup>2</sup>, y<sup>3</sup>, x<sup>2</sup>y</b>
<b>inch</b>	<b>5</b>	<b>1</b>	<b>3</b>	<b>3</b>			
<b>cont</b>	<b>3</b>	<b>-1</b>	<b>1</b>	<b>1</b>			
<b><math>\Gamma_{3N}</math></b>	<b>15</b>	<b>-1</b>	<b>3</b>	<b>3</b>			

<b>15</b>	<b>-1</b>	<b>3</b>	<b>3</b>	<b>=<math>\Sigma</math>/4=5</b>
<b>15</b>	<b>-1</b>	<b>-3</b>	<b>-3</b>	<b>2</b>
<b>15</b>	<b>1</b>	<b>3</b>	<b>-3</b>	<b>4</b>
<b>15</b>	<b>1</b>	<b>-3</b>	<b>3</b>	<b>4</b>

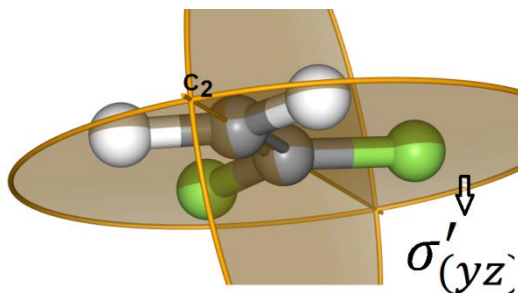
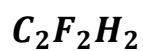
$$\Gamma_{3n} = 5A_1 + A_2 2 + B_1 4 + B_2 4$$

$$\Gamma_{Rot} = A_2 + B_1 + B_2, \Gamma_{Trans} = A_1 + B_1 + B_2$$

$$\Gamma_{vib} = 4A_1 + A_2 + 2B_1 + 2B_2$$

$$4A_1 + 2B_1 + 2B_2 \text{ IRA}$$

$$4A_1 + A_2 + 2B_1 + 2B_2 \text{ RA}$$



$C_{2v}$	<b>1E</b>	$C_2$	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	linear functions, rotations	quadratic functions	cubic functions
$A_1$	1	1	1	1	z	$x^2, y^2, z^2$	$z^3, x^2z, y^2z$
$A_2$	1	1	-1	-1	$R_z$	xy	xyz
$B_1$	1	-1	1	-1	x, $R_y$	xz	$xz^2, x^3, xy^2$
$B_2$	1	-1	-1	1	y, $R_x$	yz	$yz^2, y^3, x^2y$
inch	6	2	2	6			
cont	3	-1	1	1			
$\Gamma_{3N}$	18	-2	2	6			

Calculation results

18	-2	2	6	6
18	-2	-2	-6	2
18	2	2	-6	4
18	2	-2	6	6

$$\Gamma_{3n} = 6A_1 + 2A_2 + 4B_1 + 6B_2$$

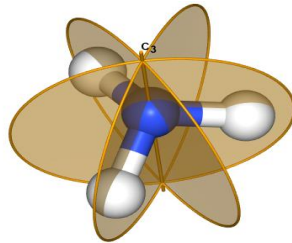
$$\Gamma_{Rot} = A_2 + B_1 + B_2, \Gamma_{Trans} = A_1 + B_1 + B_2$$

$$\Gamma_{vib} = 5A_1 + A_2 + 2B_1 + 4B_2$$

$$5A_1 + 2B_1 + 2B_2 \text{ IRA}$$

$$5A_1 + A_2 + 2B_1 + 4B_2 \text{ RA}$$

Example 2  
the ammonia



molecule  $\text{NH}_3$

$C_{3v}$	E	$2C_3$	$3\sigma_v$
$\Gamma_{3n}$	12	0	2

$$\Gamma_{3n} = 3A_1 + A_2 + 4E = 12 \text{ modes } E \text{ doubly degenerate}$$

$$\Gamma_{trans} = A_1 + E$$

$$\Gamma_{rot} = A_2 + E$$

$$\Gamma_{vib} = 2A_1 + 2E$$

For infrared active modes

*Pour*  $A_1$

$$A_1 \begin{bmatrix} A_1 \\ E \end{bmatrix} A_1$$

Leads to

$$A_1 A_1 A_1 = A_1$$

$$A_1 E A_1 = E$$

for E

$$A_1 \begin{bmatrix} A_1 \\ E \end{bmatrix} E$$

$$A_1 A_1 E = A_1$$

$$A_1 E E = A_1 + A_2 + E$$

the normal vibration modes are activated in infrared and RAMAN at the same time.

The ammonia has 3 bonds lengths and three angles as internal coordinates

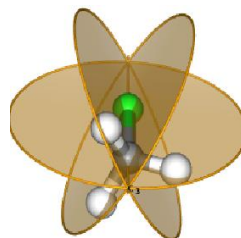
$C_{3v}$	E	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0
$\Gamma_r$	3	0	1
$\Gamma_\alpha$	3	0	1

$A_1$	$1 \cdot 3 \cdot 1$	$1 \cdot 0 \cdot 2$	$1 \cdot 3 \cdot 1/6 = 1$
$A_2$	$1 \cdot 3 \cdot 1$	$1 \cdot 0 \cdot 2$	$1 \cdot 3 \cdot -1/6 = 0$
$E$	$1 \cdot 3 \cdot 2$	$-1 \cdot 0 \cdot 2$	$1 \cdot 3 \cdot 0/6 = 1$

$$\Gamma_r = A_1 + E$$

$$\Gamma_\alpha = A_1 + E$$

$C_{3v}$	E	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0
inch	5	2	3
cont	3	0	1
$\Gamma_{red}$	15	0	3



15	0	9	4
15	0	-9	1
30	0	0	5

$$\Gamma_{3n} = 4A_1 + 1A_2 + 5E$$

$C_{3v}$	E	$2C_3$	$3\sigma_v$	linear functions, rotations	quadratic functions
$A_1$	1	1	1	z	$x^2+y^2, z^2$
$A_2$	1	1	-1	$R_z$	-
E	2	-1	0	(x, y) ( $R_x, R_y$ )	$(x^2-y^2, xy)$ (xz, yz)

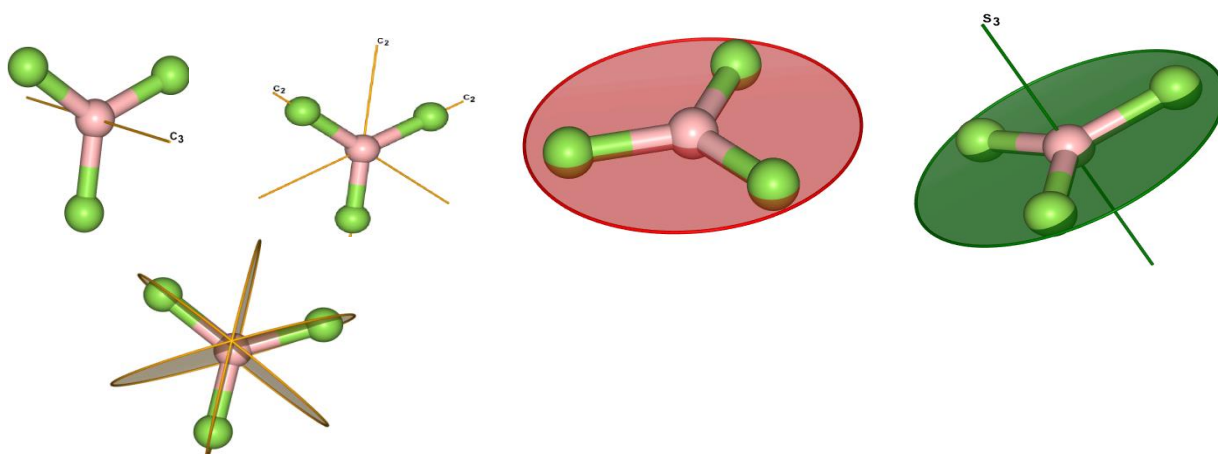
$$\Gamma_{trans} = A_1 + E$$

$$\Gamma_{rot} = A_2 + E$$

$$\Gamma_{vib} = 3A_1 + 3E$$

### Example3

Determine the active vibration modes in Infrared and the normal vibration modes active in RAMAN for the  $BF_3$  molecule (plane molecule)



$D_{3h}$	E	$2C_3 (z)$	$3C'_2$	$\sigma_h(xy)$	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
----------	---	------------	---------	----------------	--------	-------------	-----------------------------	---------------------	-----------------

$A'_1$	+1	+1	+1	+1	+1	+1	-	$x^2+y^2, z^2$	$x(x^2-3y^2)$
$A'_2$	+1	+1	-1	+1	+1	-1	$R_z$	-	$y(3x^2-y^2)$
$E'$	+2	-1	0	+2	-1	0	(x, y)	$(x^2-y^2, xy)$	$(xz^2, yz^2)$ $[x(x^2+y^2), y(x^2+y^2)]$
$A''_1$	+1	+1	+1	-1	-1	-1	-	-	-
$A''_2$	+1	+1	-1	-1	-1	+1	z	-	$z^3, z(x^2+y^2)$
$E''$	+2	-1	0	-2	+1	0	$(R_x, R_y)$	(xz, yz)	$[xyz, z(x^2-y^2)]$
ln	4	1	2	4	1	2			
con	3	0	-1	1	-2	1			
$\Gamma_{3N}$	12	0	-2	4	-2	2			

$D_{3h}$	E	$2C_3(z)$	$3C'_2$	$\sigma_h(xy)$	$2S_3$	$3\sigma_v$	
$A'_1$	[+1*1 2	+1*0* 2	+1* 2*3	+1*1*4	+1*2* 2	+1*3*2]/12	1
$A'_2$	[+1*1 2	+1*0* 2	-1*-2*3	+1*1*4	+1*2* 2	-1*3*2]/12	1
$E'$	+2*12	-1*0*2	0*-2*-3	+2*1*4	-1*2*-2	0*3*2]/12	3
$A''_1$	[+1*1 2	+1*0* 2	+1* 2*3	-1*1*4	-1*2*-2	-1*3*2]/12	0
$A''_2$	[+1*1 2	+1*0* 2	-1*-2*3	-1*1*4	-1*2*-2	+1*3*2]/12	2
$E''$	[+2*1 2	-1*0*2	0*-2*3	-2*1*4	+1*2* 2	0*3*2]/12	1

$$A'_1 = \frac{1}{12} (1 * 1 * 12 + 2 * 1 * 0 + 3 * 1 * -2 + 1 * 1 * 4 + 2 * 1 * -2 + 3 * 1 * 2) = 1$$

$$A'_2 = \frac{1}{12} (1 * 1 * 12 + 2 * 1 * 0 + 3 * -1 * -2 + 1 * 1 * 4 + 2 * 1 * -2 + 3 * -1 * 2) = 1$$

$$E' = \frac{1}{12} ((1 * 2 * 12) + (2 * -1 * 0) + ((-3) * 0 * -2) + (1 * +2 * 4) + (2 * -2 * -1) + 3 * 0 * 2) = 3$$

$$A''1 = \frac{1}{12} (1 * 1 * 12 + 2 * 1 * 0 + 3 * -1 * -2 + 1 * -1 * 4 + 2 * -1 * -2 + 3 * 1 * 2) = 0$$

$$A''2 = \frac{1}{12} (1 * 1 * 12 + 2 * 1 * +3 * -1 * -2 + 1 * -1 * 4 + 2 * -1 * -2 + 3 * 1 * 2) = 2$$

$$\Gamma_{3N} = A'_1 + A'_2 + 3E' + 0A''_1 + 2A''_2 + E''$$

$$\Gamma_{rot} = A'_2 + E'$$

$$\Gamma_{trans} = E' + A''_2$$

$$\Gamma_{vib} = A'_1 + 2E' + A''_2$$

$$RA = A'_1 + 2E'$$

$$IRA = 2E' + A''_2$$

$\sigma_d$  is the vertical symmetry plane also cuts the angle between two axes rotation order 2  $2(C'_2)$  perpendicular to the principal axis, the plane is called dihedral Generally carries fewer atoms

Motion	E	2C <sub>4</sub>	C <sub>2</sub>	2C' <sub>2</sub>	2C <sub>2</sub> » <sub>2</sub>	i	2S <sub>4</sub>	σ <sub>h</sub>	2σ <sub>v</sub>	2σ <sub>d</sub>
$\Gamma_{3n}$	12	0	0	-2	0	0	0	4	2	0

Example

**$MA_5$  belong point group of symmetry  $D_{3h}$**

$D_{3h}$	E	$2C_3(z)$	$3C'_2$	$\sigma_h(xy)$	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions
$A'_1$	+1	+1	+1	+1	+1	+1	-	$x^2+y^2, z^2$
$A'_2$	+1	+1	-1	+1	+1	-1	$R_z$	-
$E'$	+2	-1	0	+2	-1	0	(x, y)	$(x^2-y^2, xy)$
$A''_1$	+1	+1	+1	-1	-1	-1	-	-
$A''_2$	+1	+1	-1	-1	-1	+1	z	-
$E''$	+2	-1	0	-2	+1	0	$(R_x, R_y)$	$(xz, yz)$
unshf	5	3	2	3	1	4		
	3	0	-1	1	-1	1		
$\Gamma_{3n}$	*18	0	-2	4	-2	4		

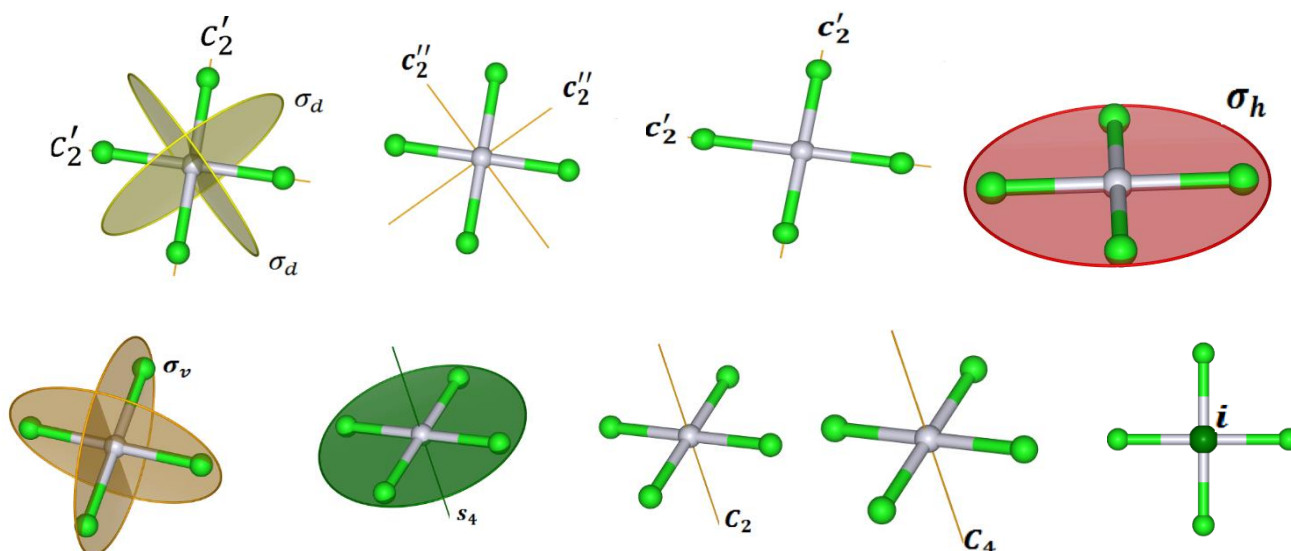
$A'_1$	+1*18	+1*2*0	+1*3*-2	+1*1*4	+1*2*-2	+1*3*4	$\frac{\Sigma}{12} = 2$
$A'_2$	+1*18	+1*2*0	-1*3*-2	+1*1*4	+1*2*-2	-1*3*4	1
$E'$	+2*18	-1*2*0	0*3*-2	+2*1*4	-1*2*-2	0*3*4	4
$A''_1$	+1*18	+1*2*0	+1*3*-2	-1*1*4	-1*2*-2	-1*3*4	0
$A''_2$	+1*18	+1*2*0	-1*3*-2	-1*1*4	-1*2*-2	+1*3*4	3
$E''$	+2*18	-1*2*0	0*3*-2	-2*1*4	+1*2*-2	0*3*4	2

$$\Gamma_{3n} = 2A'_1 + A'_2 + 3A''_2 + 4E' + 2E''$$

$$\Gamma_{vib} = 2A'_1(Ra) + 2A''_2(IRa) + 3E'(Ra, IRa) + E''(Ra)$$

Exemple 4

the  $XeF_4$  molecule The plane  $\sigma_d$  carries the axis  $C'_2$



E	2C <sub>4</sub>	C <sub>2</sub>	2C' <sub>2</sub>	2C <sub>2</sub> » <sub>2</sub>	i	2S <sub>4</sub>	σ <sub>h</sub>	2σ <sub>v</sub>	2σ <sub>d</sub>
15	1	-1	-3	-1	-3	-1	5	3	1

$$A_{1g} = \frac{1}{16} [15 + 2 - 1 - 6 - 2 - 3 - 2 + 5 + 6 + 2] = 1$$

$$A_{2g} = \frac{1}{16} [15 + 2 - 1 + 6 + 2 - 3 - 2 + 5 - 6 - 2] = 1$$

$$B_{1g} = \frac{1}{16} [15 + 2 - 1 - 6 + 2 - 3 + 2 + 5 + 2] = 1$$

$$B_{2g} = 1$$

$$= 1$$

$$= 0$$

$$= 2$$

$$= 0$$

$$= 1$$

$$= 3$$

$$\Gamma_{3n} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

$$\Gamma_{vib} = \Gamma_{3n} - \Gamma_{rot} - \Gamma_{trans} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 3E_u$$

Example 5



The PtCl<sub>6</sub> molecule conforms exactly to the point symmetry group if the two bonds length is greater than that of square planar bonds and we pass from O<sub>h</sub> to D<sub>4h</sub> hence .

$D_{4h}$	E	$2C_4$ (z)	$C_2$	$2C_{2'}$	$2C_{2''}$	i	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	Linear functions, rotations	quadratic functions
$A_{1g}$	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2, z^2$
$A_{2g}$	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	$R_z$	-
$B_{1g}$	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	$x^2-y^2$
$B_{2g}$	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy
$E_g$	+2	0	-2	0	0	+2	0	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$A_{1u}$	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
$A_{2u}$	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
$B_{1u}$	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-
$B_{2u}$	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-
$E_u$	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-
<i>Inch</i>	7	3	3	3	1	1	3	5	5	3		
<i>Contr</i>	3	1	1	-1	-1	-3	-1	1	1	1		
$\Gamma_{3n}$	21	3	-3	-3	-1	-3	-1	5	5	3		

Calcul

$$\Gamma_{3n} = 2A_{1g} + A_{2g} + B_{1g} + B_{2g} + 2E_g + 3A_{2u} + B_{2u} + 4E_u$$

$$\Gamma_{vib} = \Gamma_{3n} - \Gamma_{rot} - \Gamma_{trans} = 2A_{1g} + B_{1g} + B_{2g} + 2A_{2u} + B_{2u} + 3E_u + E_g$$

Infrared

$$A_{1g} \begin{bmatrix} A_{2u} \\ E_u \end{bmatrix} * A_{1g}(B_{1g} + B_{2g}, E_g, A_{2u}, B_{2u}, E_u)$$

$A_{2u}$  et  $E_u$  actives in infrared  
RAMAN

$$A_{1g} \begin{bmatrix} A_{1g} \\ B_{1g} \\ B_{2g} \\ E_g \end{bmatrix} * A_{1g}(B_{1g} + B_{2g}, E_g, A_{2u}, B_{2u}, E_u)$$

$$A_{1g}, B_{1g}, B_{2g}, E_g$$

In case of  $O_h$

$O_h$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4)^2$	i	$6S_4$	$8S_6$	3 $\sigma_h$	6 $\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
$A_{1g}$	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	-
$A_{2g}$	+1	+1	-1	-1	+1	+1	-1	+1	+1	-1	-	-	-
$E_g$	+2	-1	0	0	+2	+2	0	-1	+2	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
$T_{1g}$	+3	0	-1	+1	-1	+3	+1	0	-1	-1	$(R_x, R_y, R_z)$	-	-
$T_{2g}$	+3	0	+1	-1	-1	+3	-1	0	-1	+1	-	$(xz, yz, xy)$	-
$A_{1u}$	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
$A_{2u}$	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1	-	-	xyz
$E_u$	+2	-1	0	0	+2	-2	0	+1	-2	0	-	-	-
$T_{1u}$	+3	0	-1	+1	-1	-3	-1	0	+1	+1	(x, y, z)	-	$(x^3, y^3, z^3)$ $[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$
$T_{2u}$	+3	0	+1	-1	-1	-3	+1	0	+1	-1	-	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$
$\Gamma_{3n}$	21	0	-1	3	-3	-3	-1	0	5	3			

$$\Gamma_{3n}=1A_{1g} +0A_{2g}+1E_g+ 1T_{1g}+0T_{2g}+0A_{1u}+0A_{2u}+0 E_u+3T_{1u}+1T_{2u}1$$

IR active  $T_{1u}$

R active  $A_{1g}$   $E_g$   $T_{2g}$

$T_{2u}$  inactive

$O_h$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{3n}$	21	0	-1	3	-3	-3	-1	0	5	3
$\Gamma_{ptCL}$	6	0	0	2	2	0	0	0	4	2
$\Gamma_{clptCL}$	12	0	2	0	0	0	0	0	4	2

$$\Gamma_{ptCL} = A_{1g} + E_g + T_{1u}$$

$$\Gamma_{clptCL} = A_{1g} + E_g + T_{2g} + T_{1u} + T_{2u}$$

The angular deformation according A1 it impossible to happen geometrically it forbidden but indicate the stretch symmetric or asymmetric thus the mode vibration not observed with internal coordinates .

### Example6 of benzene molecule

$D_{6h}$	E	$2C_6$	$2C_3$	$C_2$	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	$\sigma_h(xy)$	$3\sigma_d$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
$A_{1g}$	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2, z^2$	-
$A_{2g}$	+1	+1	+1	+1	-1	-1	+1	+1	+1	+1	-1	-1	$R_z$	-	-
$B_{1g}$	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	-

<b>B<sub>2g</sub></b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>-1</b>	<b>+1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>-1</b>	<b>+1</b>	-	-	-
<b>E<sub>1g</sub></b>	<b>+2</b>	<b>+1</b>	<b>-1</b>	<b>-2</b>	<b>0</b>	<b>0</b>	<b>+2</b>	<b>+1</b>	<b>-1</b>	<b>-2</b>	<b>0</b>	<b>0</b>	(R <sub>x</sub> , R <sub>y</sub> )	(xz, yz)	-
<b>E<sub>2g</sub></b>	<b>+2</b>	<b>-1</b>	<b>-1</b>	<b>+2</b>	<b>0</b>	<b>0</b>	<b>+2</b>	<b>-1</b>	<b>-1</b>	<b>+2</b>	<b>0</b>	<b>0</b>	-	(x <sup>2</sup> -y <sup>2</sup> , xy)	-
<b>A<sub>1u</sub></b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	-	-	-
<b>A<sub>2u</sub></b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>+1</b>	<b>+1</b>	z	-	z <sup>3</sup> , z(x <sup>2</sup> +y <sup>2</sup> )
<b>B<sub>1u</sub></b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	-	-	x(x <sup>2</sup> -3y <sup>2</sup> )
<b>B<sub>2u</sub></b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>+1</b>	<b>-1</b>	-	-	y(3x <sup>2</sup> -y <sup>2</sup> )
<b>E<sub>1u</sub></b>	<b>+2</b>	<b>+1</b>	<b>-1</b>	<b>-2</b>	<b>0</b>	<b>0</b>	<b>-2</b>	<b>-1</b>	<b>+1</b>	<b>+2</b>	<b>0</b>	<b>0</b>	(x, y)	-	(xz <sup>2</sup> , yz <sup>2</sup> ) [x(x <sup>2</sup> +y <sup>2</sup> ), y(x <sup>2</sup> +y <sup>2</sup> )]
<b>E<sub>2u</sub></b>	<b>+2</b>	<b>-1</b>	<b>-1</b>	<b>+2</b>	<b>0</b>	<b>0</b>	<b>-2</b>	<b>+1</b>	<b>+1</b>	<b>-2</b>	<b>0</b>	<b>0</b>	-	-	[xyz, z(x <sup>2</sup> -y <sup>2</sup> )]
<b>inc h</b>	<b>12</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>4</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>12</b>	<b>0</b>	<b>4</b>			
<b>con t</b>	<b>3</b>	<b>2</b>	<b>0</b>	<b>-1</b>	<b>-1</b>	<b>-1</b>	<b>-3</b>	<b>-2</b>	<b>0</b>	<b>1</b>	<b>1</b>	<b>1</b>			
<b>Γ<sub>3n</sub></b>	<b>36</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>-4</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>12</b>	<b>0</b>	<b>4</b>			

$$\Gamma_{vib} = 2A_{1g} + A_{2g} + 2B_{2g} + E_{1g} + 4E_{2g} + A_{2u} + 2B_{1u} + 2B_{2u} + 3E_{1u} + 2E_{2u}$$

$$\Gamma_{rot} + \Gamma_{trans} = E_{1g} + E_{1u} + A_{2u} + A_{2g}$$

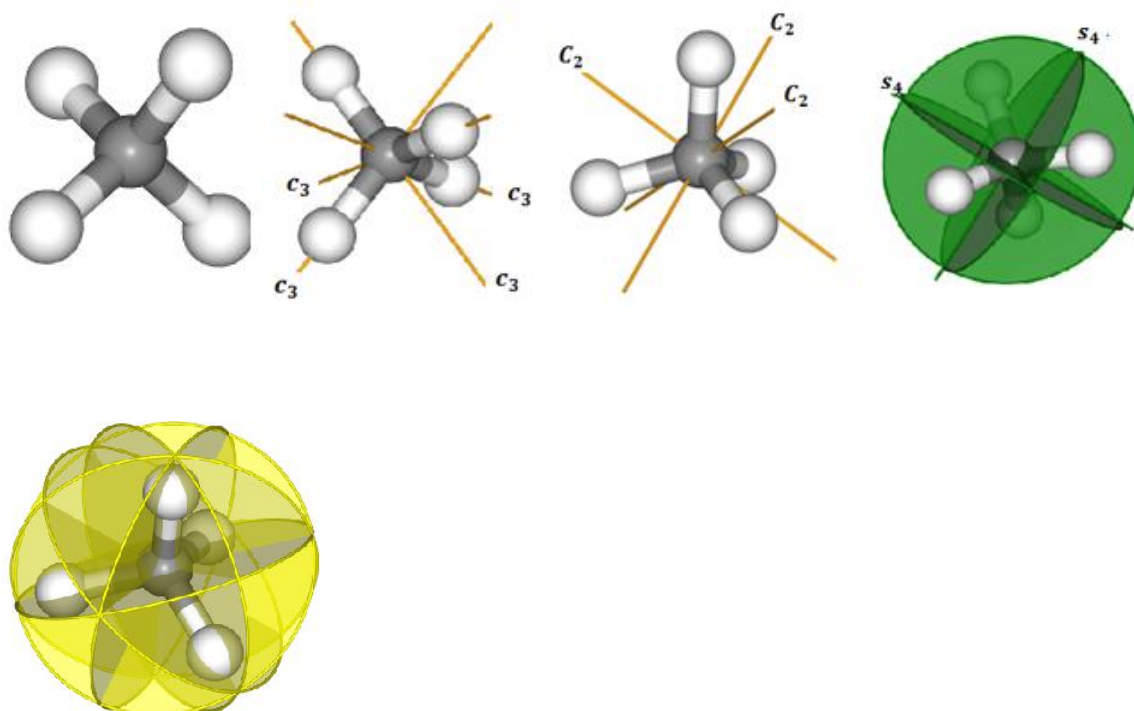
<b>(a<sub>1g</sub>)</b> <b>3206 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>1u</sub>)</b> <b>3195 cm<sup>-1</sup></b> <b>(IR intensity = 0.69)</b> <b>(Raman inactive)</b>	<b>(e<sub>1u</sub>)</b> <b>3195 cm<sup>-1</sup></b> <b>(IR intensity = 0.69)</b> <b>(Raman inactive)</b>	<b>(e<sub>2g</sub>)</b> <b>3187 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>2g</sub>)</b> <b>3187 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>
<b>(b<sub>1u</sub>)</b> <b>3184 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(e<sub>2g</sub>)</b> <b>1767 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>2g</sub>)</b> <b>1767 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>1u</sub>)</b> <b>1579 cm<sup>-1</sup></b> <b>(IR intensity = 0.095)</b> <b>(Raman inactive)</b>	<b>(e<sub>1u</sub>)</b> <b>1579 cm<sup>-1</sup></b> <b>(IR intensity = 0.095)</b> <b>(Raman inactive)</b>
<b>(b<sub>2u</sub>)</b> <b>1366 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(a<sub>2g</sub>)</b> <b>1329 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(a<sub>1g</sub>)</b> <b>1276 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>2g</sub>)</b> <b>1222 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>2g</sub>)</b> <b>1222 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>
<b>(b<sub>2u</sub>)</b> <b>1179 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(e<sub>1u</sub>)</b> <b>1146 cm<sup>-1</sup></b> <b>(IR intensity = 0.0085)</b> <b>(Raman inactive)</b>	<b>(e<sub>1u</sub>)</b> <b>1146 cm<sup>-1</sup></b> <b>(IR intensity = 0.0085)</b> <b>(Raman inactive)</b>	<b>(b<sub>1u</sub>)</b> <b>1028 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(b<sub>2g</sub>)</b> <b>1012 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>
<b>(e<sub>2u</sub>)</b> <b>989 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(e<sub>2u</sub>)</b> <b>989 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(e<sub>1g</sub>)</b> <b>891 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>1g</sub>)</b> <b>891 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(a<sub>2u</sub>)</b> <b>744 cm<sup>-1</sup></b> <b>(IR intensity = 1.0)</b> <b>(Raman inactive)</b>
<b>(e<sub>2g</sub>)</b> <b>648 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(e<sub>2g</sub>)</b> <b>648 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman active)</b>	<b>(b<sub>2g</sub>)</b> <b>618 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(e<sub>2u</sub>)</b> <b>371 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>	<b>(e<sub>2u</sub>)</b> <b>371 cm<sup>-1</sup></b> <b>(IR inactive)</b> <b>(Raman inactive)</b>

It is observed,

In a centrosymmetric molecule no Raman active vibration is also infrared active and no active vibration is also Raman active

Exemple 7

**Methane**



$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Linear functions, rotations	quadratic functions	cubic functions
$A_1$	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	xyz
$A_2$	+1	+1	+1	-1	-1	-	-	-
E	+2	-1	+2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$	-
$T_1$	+3	0	-1	+1	-1	$(R_x, R_y, R_z)$	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2)]$
$T_2$	+3	0	-1	-1	+1	$(x, y, z)$	$(xy, xz, yz)$	$(x^3, y^3, z^3) [x(z^2+y^2),$

								$y(z^2+x^2), z(x^2+y^2)]$
un sh	5	2	1	1	3			
co nt r	3	0	-1	-1	1			
$\Gamma_{3n}$	15	0	-1	-1	3			

$$\Gamma_{3n} = A_1 + E + T_1 + 3T_2$$

Eliminating the translational and rotational components gives

$$\Gamma_{vib} = A_1 + E + 2T_2$$

$A_1 + E$  Raman

$T_2$  Raman and IR

For the contribution of internal coordinates C-H bond lengths and HCH angles

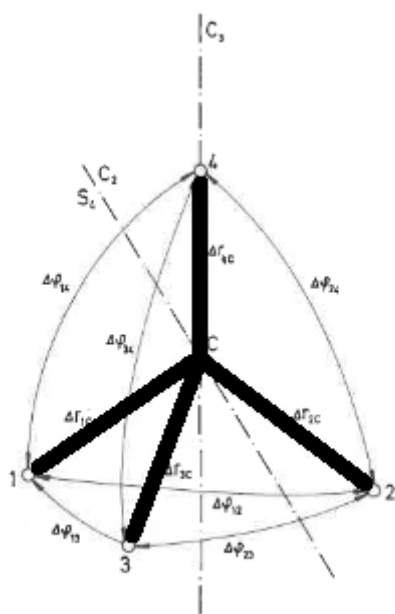
$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{CH}$	4	1	0	0	2
$\Gamma_{HCH}$	6	0	2	0	2

This is easily found to reduce as follows (for band)

$$\Gamma_{CH} = A_1 + T_1$$

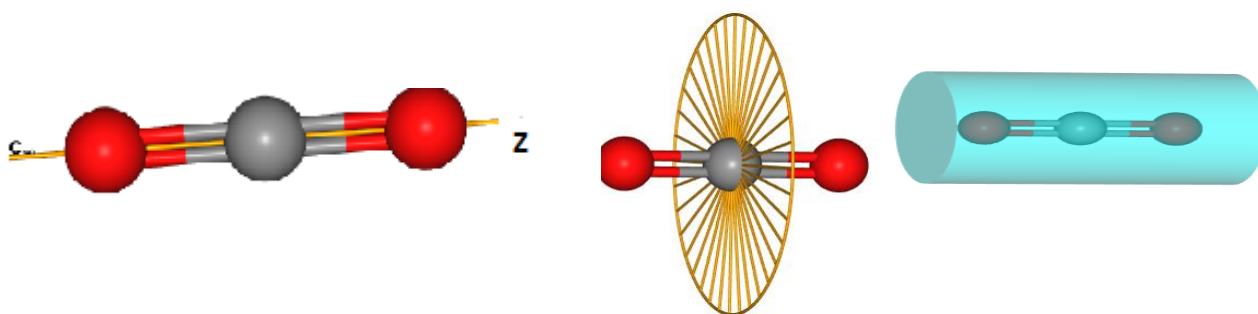
$$\Gamma_{HCH} = A_1 + E + T_2$$

The interbond angles representation for A1 show a symmetric motion but it is not possible that the angular deformation can occur in this manner. The increasing or decreasing in deformation angle arise an reverse effect in other angle hence this motion it is not possible in considered representation the only away to occur is the motion along the bond length (stretched).



Example8 linear molecule CO<sub>2</sub>

The molecule Carbon dioxide belongs to  $D_{\infty h}$



$D_{\infty h}$	E	$2C_{\infty}$	...	$\infty\sigma_v$	i	$2S_{\infty}$	...	$\infty C'_2$	linear functions, rotations	quadratic functions	cubic functions
$A_{1g}=\Sigma_g^+$	+1	+1	...	+1	+1	+1	...	+1	-	$x^2+y^2, z^2$	-
$A_{2g}=\Sigma_g^-$	+1	+1	...	-1	+1	+1	...	-1	$R_z$	-	-
$E_{1g}=\Pi_g$	+2	$+2\cos(\varphi)$	...	0	+2	$-2\cos(\varphi)$	...	0	$(R_x, R_y)$	$(xz, yz)$	-
$E_{2g}=\Delta_g$	+2	$+2\cos(2\varphi)$	...	0	+2	$+2\cos(2\varphi)$	...	0	-	$(x^2-y^2, xy)$	-
$E_{3g}=\Phi_g$	+2	$+2\cos(3\varphi)$	...	0	+2	$-2\cos(3\varphi)$	...	0	-	-	-
$E_{ng}$	+2	$+2\cos(n\varphi)$	...	0	+2	$(-1)^n 2\cos(n\varphi)$	...	0	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-

$A_{1u}=\Sigma_u^+$	+1	+1	...	+1	-1	-1	...	-1	z	-	$z^3, z(x^2+y^2)$
$A_{2u}=\Sigma_u^-$	+1	+1	...	-1	-1	-1	...	+1	-	-	-
$E_{1u}=\Pi_u$	+2	$+2\cos(\varphi)$	...	0	-2	$+2\cos(\varphi)$	...	0	(x, y)	-	$(xz^2, yz^2)$ $[x(x^2+y^2), y(x^2+y^2)]$
$E_{2u}=\Delta_u$	+2	$+2\cos(2\varphi)$	...	0	-2	$-2\cos(2\varphi)$	...	0	-	-	$[xyz, z(x^2-y^2)]$
$E_{3u}=\Phi_u$	+2	$+2\cos(3\varphi)$	...	0	-2	$2\cos(3\varphi)$	...	0	-	-	$[y(3x^2-y^2), x(x^2-3y^2)]$
$E_{nu}$	+2	$+2\cos(n\varphi)$	...	0	-2	$(-1)^{n+1}2\cos(n\varphi)$	...	0	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-
$\Gamma_{3n}$	9	$3+6\cos\varphi$		3	-3	$-1+2\cos\varphi$		-1			

$$\Gamma_{3n} = \Pi_g + \Sigma_g^+ + 2\Pi_u + 2\Sigma_u^+$$

We subtract the representations for translation and rotation; it is worth mentioning that rotation according axis z does not constitute a degree of freedom in linear molecule, in order that

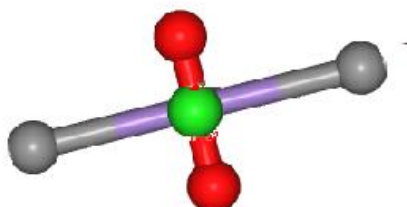
$$\Gamma_{vib} = \Sigma_g^+ + \Pi_u + \Sigma_u^+$$

$\leftarrow O - C - O \rightarrow$  Symmetric stretch  $\bar{\nu} = 1330 \text{ cm}^{-1}$

$\leftarrow O - C \rightarrow -\leftarrow O$  Asymmetric stretch  $\bar{\nu} = 2349 \text{ cm}^{-1}$

$\uparrow O - C \downarrow -O \uparrow$   $\bar{\nu} = 667 \text{ cm}^{-1}$  (Ladd 1998)

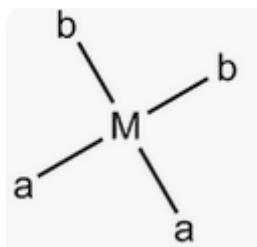
Example  $PTCl_2I_2$



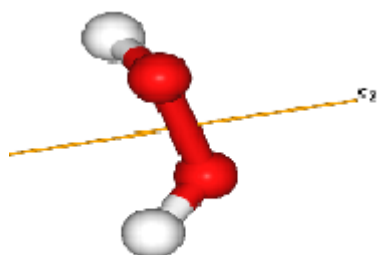
$$2 A_g \oplus 1 B_{1g} \oplus 0 B_{2g} \oplus 0 B_{3g} \oplus 2 B_{1u} \oplus 2 B_{2u} \oplus 2 B_{3u}$$

## Example

$C_{2v}$



## Example $C_2$



$C_2$	E	$C_2$	linear functions, rotations	quadratic functions	cubic functions
A	+1	+1	$z, R_z$	$x^2, y^2, z^2, xy$	$z^3, xyz, y^2z, x^2z$
B	+1	-1	$x, y, R_x, R_y$	$yz, xz$	$xz^2, yz^2, x^2y, xy^2, x^3, y^3$
	4	0			
	3	-1			
	12	0			

\*

$$\Gamma_{3n} = 6A + 6B$$

$$\Gamma_{vib} = 4A + 2B$$

$$\Gamma_{vib} = 4A + 2B$$

$$4A + 2B \text{ RA}$$

$$4A + 2B \text{ IRA}$$

(cis  $C_{2v}$  and trans  $D_{2h}$ )

Solution

$MA_5$  Belongs point group of symmetry  $D_{3h}$

$D_{3h}$	E	$2C_3(z)$	$3C'_2$	$\sigma_h(xy)$	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions
$A'_1$	+1	+1	+1	+1	+1	+1	-	$x^2+y^2, z^2$
$A'_2$	+1	+1	-1	+1	+1	-1	$R_z$	-
$E'$	+2	-1	0	+2	-1	0	(x, y)	$(x^2-y^2, xy)$
$A''_1$	+1	+1	+1	-1	-1	-1	-	-
$A''_2$	+1	+1	-1	-1	-1	+1	z	-
$E''$	+2	-1	0	-2	+1	0	$(R_x, R_y)$	$(xz, yz)$
unshf	5	3	2	3	1	4		
	3	0	-1	1	-1	1		
$\Gamma_{3n}$	*18	0	-2	4	-2	4		

$A'_1$	+1*18	+1*2*0	+1*3*-2	+1*1*4	+1*2*-2	+1*3*4	$\frac{\Sigma}{12} = 2$
$A'_2$	+1*18	+1*2*0	-1*3*-2	+1*1*4	+1*2*-2	-1*3*4	1
$E'$	+2*18	-1*2*0	0*3*-2	+2*1*4	-1*2*-2	0*3*4	4
$A''_1$	+1*18	+1*2*0	+1*3*-2	-1*1*4	-1*2*-2	-1*3*4	0
$A''_2$	+1*18	+1*2*0	-1*3*-2	-1*1*4	-1*2*-2	+1*3*4	3
$E''$	+2*18	-1*2*0	0*3*-2	-2*1*4	+1*2*-2	0*3*4	2

$$\Gamma_{3n} = 2A'_1 + A'_2 + 3A''_1 + 4E' + 2E''$$

$$\Gamma_{vib} = 2A'_1(Ra) + 2A'_2(IRa) + 3E'(Ra, IRa) + E''(Ra)$$

$C_{4v}$	E	$2C_4(z)$	$C_2$	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
$A_1$	+1	+1	+1	+1	+1	z	$x^2+y^2, z^2$	$z^3, z(x^2+y^2)$
$A_2$	+1	+1	+1	-1	-1	$R_z$	-	-
$B_1$	+1	-1	+1	+1	-1	-	$x^2-y^2$	$z(x^2-y^2)$
$B_2$	+1	-1	+1	-1	+1	-	xy	xyz
E	+2	0	-2	0	0	(x, y) $(R_x, R_y)$	(xz, yz)	$(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)$
	18	2	-2	4	2			

$$\Gamma_{3n} = 4A_1 + A_2 + 2B_1 + B_2 + 5E$$

$$\Gamma_{vib} = 3A_1 + B_1 + B_2 + 3E$$

$$\Gamma_{vib} = 3A_1(Ra, IRa) + B_1(Ra) + B_2(Ra) + 3E(Ra, IRa)$$

Table of results

We can summarize the above results in the table

Molecular type	Point group	Description	Reduced representation	$n_R$	$n_P$	$n_I$	$n_C$
<b>MA</b>	$C_{\infty v}$	<b>Linear</b>	$\Sigma^+(R, I)$	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>
<b>MA<sub>2</sub></b>	$D_{\infty v}$	<b>Linear</b>	$\sum_g^+(R) + \sum_u^+(I) + \prod_u(I)$	<b>1</b>	<b>1</b>	<b>2</b>	<b>0</b>
	$C_{2v}$	<b>Bent</b>	$2A_1(R, I) + B_1(R, I)$	<b>3</b>	<b>2</b>	<b>3</b>	<b>3</b>
<b>MAB</b>	$C_{\infty v}$	<b>Linear</b>	$2\Sigma^+(R, I) + \Pi(R, I)$	<b>3</b>	<b>2</b>	<b>3</b>	<b>3</b>
<b>MA<sub>3</sub></b>	$D_{3h}$	<b>Centered equilateral triangle</b>	$A'_1(R) + A''_2(I) + 2E'(R, I)$	<b>3</b>	<b>1</b>	<b>3</b>	<b>2</b>
	$C_{3v}$	<b>Pyramidal</b>	$2A_1(R, I) + 2E(R, I)$	<b>4</b>	<b>2</b>	<b>4</b>	<b>4</b>
<b>MBA<sub>2</sub></b>	$C_{2v}$	<b>Planar Y</b>	$3A_1(R, I) + 2B_1(R, I) + B_2(R, I)$	<b>6</b>	<b>3</b>	<b>6</b>	<b>6</b>
	$C_s$	<b>Pyramidal</b>	$4A'(R, I) + 2A''(R, I)$	<b>6</b>	<b>4</b>	<b>6</b>	<b>6</b>
<b>AM<sub>2</sub>A</b>	$D_{\infty v}$	<b>Linear</b>	$\sum_g^+(R) + \sum_u^+(I) + \prod_g(R) + \prod_u(I)$	<b>3</b>	<b>2</b>	<b>2</b>	<b>0</b>

	$C_{2v}$	Planar cis form	$3A_1(R, I) + A_2(R) + 2B_1(R, I)$	6	3	5	5
	$C_{2h}$	Planar trans form	$3A_g(R) + A_u(I) + 2B_u(I)$	3	3	3	0
$M_2A_2$	$C_{2v}$	Planar Y	$3A_1(R, I) + 2B_1(R, I) + B_2(R, I)$	6	3	6	6
	$C_{2h}$	Non planar twist	$4A(R, I) + 2B(R, I)$	6	4	6	6
$MA_4$	$T_d$	Tetrahedral	$4A_1(R) + E(R) + 2T_2(R, I)$	4	1	2	2
	$D_{4h}$	Square planar	$A_{1g}(R) + B_{1g}(R) + B_{2g}(R) + A_{2u}(I) + B_{2u}(ai) + 3E_u(I)$	3	1	3	0
	$C_{4v}$	Tetragonal pyramid	$2A_1(R, I) + 2B_1(R) + B_2(R) + 2E(R, I)$	7	2	4	4
$M(AB)_4$	$T_d$	Tetrahedral	$2A_1(R) + 2E(R) + 4T_2(R, I) + T_1(ia)$	8	2	4	4
	$D_{4h}$	Square planar	$2A_{1g}(R) + 2A_{2g}(ia) + 2B_{1g}(R) + B_{2g}(R) + 2A_{2u}(I) + B_{1u}(ia) + B_{2u}(ia) + 4E_u(I) + E_g(R)$	7	2	6	0
$M(A)_3B$	$c_{3v}$	Tetrahedral	$3A_1(R, I) + 3E(R, I)$	6	3	6	6
	$c_{2v}$	Planar with $c_2$ axis	$4A_1(R, I) + 3B_1(R, I) + 2B_2(R, I)$	9	4	9	9
	$c_s$	planar	$7A'(R, I) + 2A''(R, I)$	9	7	9	9
$MA_2B_2$	$c_{2v}$	Tetrahedral	$4A_1(R, I) + A_2(R) + 2B_1(R, I) + 2B_2(R, I)$	9	4	8	8
	$D_{2h}$	Trans symmetric planar	$2A_g(R) + B_{1g}(R) + 2B_{1u}(I) + 2B_{2u}(I) + 2B_{3u}(I)$	3	2	6	0
	$c_{2v}$	cis symmetric planar	$4A_1(R, I) + A_2(R) + 3B_1(R, I) + B_2(R, I)$	9	4	8	8
$MA_2(AB)$	$c_s$	planar	$7A'(R, I) + 2A''(R, I)$	9	7	9	9

<b><math>MA_5</math></b>	<b><math>D_{3h}</math></b>	<b>Trigonal bipyramid</b>	$2A'_1(R) + A''_2(I) + 2E'(R, I) + E''(R)$	<b>6</b>	<b>2</b>	<b>5</b>	<b>3</b>
	<b><math>C_{4v}</math></b>	<b>Tetragonal pyramid</b>	$3A_1(R) + 2B_1(R) + B_2(R) + 3E(R, I)$	<b>9</b>	<b>3</b>	<b>6</b>	<b>6</b>
<b>13 <math>MA_4B</math></b>	<b><math>c_{3v}</math></b>	<b>Trigonal bipyramid B axial</b>	$4A_1(R, I) + 4E(R, I)$	<b>8</b>	<b>4</b>	<b>8</b>	<b>8</b>
	<b><math>c_{2v}</math></b>	<b>Trigonal bipyramid B quatorial</b>	$4A_1(R, I) + A_2(R) + 3B_1(R, I) + B_2(R, I)$	<b>12</b>	<b>5</b>	<b>11</b>	<b>11</b>
	<b><math>c_{4v}</math></b>	<b>Tetragonal pyramid</b>	$3A_1(R, I) + 2B_1(R) + B_2(R) + 3E(R, I)$	<b>9</b>	<b>3</b>	<b>6</b>	<b>6</b>
<b>14 <math>MA_3B_2</math></b>	<b><math>D_{3h}</math></b>	<b>Trigonal bipyramid b axial</b>	$2A'_1(R) + A''_2(I) + 3E'(R, I) + E''(R)$	<b>5</b>	<b>2</b>	<b>6</b>	<b>3</b>
	<b><math>C_s</math></b>	<b>Distord trigonal bipyramid</b>	$8A'(R, I) + 4A''(R, I)$	<b>12</b>	<b>8</b>	<b>12</b>	<b>12</b>
	<b><math>c_{2v}</math></b>	<b>Trigonal bipyramid B aquatorial</b>	$5A_1(R, I) + A_2(R) + 3B_1(R, I) + B_2(R, I)$	<b>12</b>	<b>5</b>	<b>11</b>	<b>11</b>
<b>15 <math>A_2M_2A_2</math></b>	<b><math>D_{2h}</math></b>	<b>Symmetric planar</b>	$3A_g(R) + A_u(ia) + 2B_{1g}(R) + B_{1u}(I) + B_{2g}(R) + 2B_{2u}(I) + 2B_{3u}(I)$	<b>6</b>	<b>3</b>	<b>5</b>	<b>0</b>
<b>16 <math>ABM_2AB</math></b>	<b><math>c_{2v}</math></b>	<b>Cis symmetric planar</b>	$5A_1(R, I) + 2A_2(R) + 4B_1(R, I) + B_2(R, I)$	<b>12</b>	<b>5</b>	<b>10</b>	<b>10</b>
	<b><math>C_{2h}</math></b>	<b>transsummetric planar</b>	$5A_g(R) + 2A_u(I) + 2B_u(I) + 4B_u(I)$	<b>6</b>	<b>5</b>	<b>6</b>	<b>0</b>
<b>17 <math>A_2M_2B_2</math></b>	<b><math>c_{2v}</math></b>	<b>Unsymetrmetric planar</b>	$5A_1(R, I) + A_2(R) + 4B_1(R, I) + 2B_2(R, I)$	<b>12</b>	<b>5</b>	<b>11</b>	<b>11</b>
<b>18 <math>MA_6</math></b>	<b><math>O_h</math></b>	<b>Regular octahedron</b>	$A_{1g}(R) + E_g(R) + 2T_{1u}(I) + T_{2g}(R) + T_{2u}(ai)$	<b>3</b>	<b>1</b>	<b>2</b>	<b>0</b>

	$D_{4h}$	Distorted octahedron	$2A_{1g}(R) + B_{1g}(R)$ $+ B_{2g}(R) + 2A_{2u}(I)$ $+ B_{2u}(I) + 3E_{2u}(ia) + E_{2g}(R)$	5	2	5	0
	$D_{6h}$	Plane symmetric	$A_{1g}(R) + B_{1g}(ia)$ $+ B_{2u}(ia) + A_{2u}(I)$ $+ B_{1u}(ia)$ $+ E_{2u}(ia) + 2E_{2g}(R) + 2E_{1u}(I)$	3	1	3	0
$19MA_5B$	$C_{4v}$	Octahedron	$4A_1(R, I) + 2B_1(R) + B_2(R)$ $+ 4E(R, I)$	11	4	8	8
$MA_4B_2$	$D_{4h}$	Trans octahedron	$2A_{1g}(R) + B_{1g}(R)$ $+ B_{2g}(R) + 2A_{2u}(I)$ $+ B_{2u}(ia) + 3E_u(I) + E_g(R)$	5	2	5	0
	$C_{2v}$	Cis octahedron	$6A_1(R, I) + 2A_2(R)$ $+ 4B_1(R, I)$ $+ 3B_2(R, I)$	15	6	13	13
$MA_3B_3$	$C_s$	Octahedron 2B's is in plane	$9A'(R, I) + 6A''(R, I)$	15	9	15	15
	$C_{2v}$	Octahedron 2B's is in plan2	$6A_1(R, I) + A_2(R)$ $+ 4B_1(R, I)$ $+ 4B_2(R, I)$	15	6	14	14
$M(AB)_6$	$O_h$	Regular octaheron	$2A_{1g}(R) + 2E_g(R) + T_{1g}(ia)$ $+ 4T_{1u}(I)$ $+ 2T_{2g}(R)$ $+ 2T_{2u}(ia)$	6	2	4	0
$A_2MA_2MA_2$	$D_{2h}$	Bridget	$4A_g(R) + A_u(ia) + 2B_{1g}(R)$ $+ 3B_{1u}(I)$ $+ 2B_{2g}(R)$ $+ 2B_{2u}(I)$ $+ 3B_{3u}(I)$ $+ B_{3g}(I)$	9	4	8	0

R=RAMAN, I infrared, ia inactive

## Types of vibration in molecule

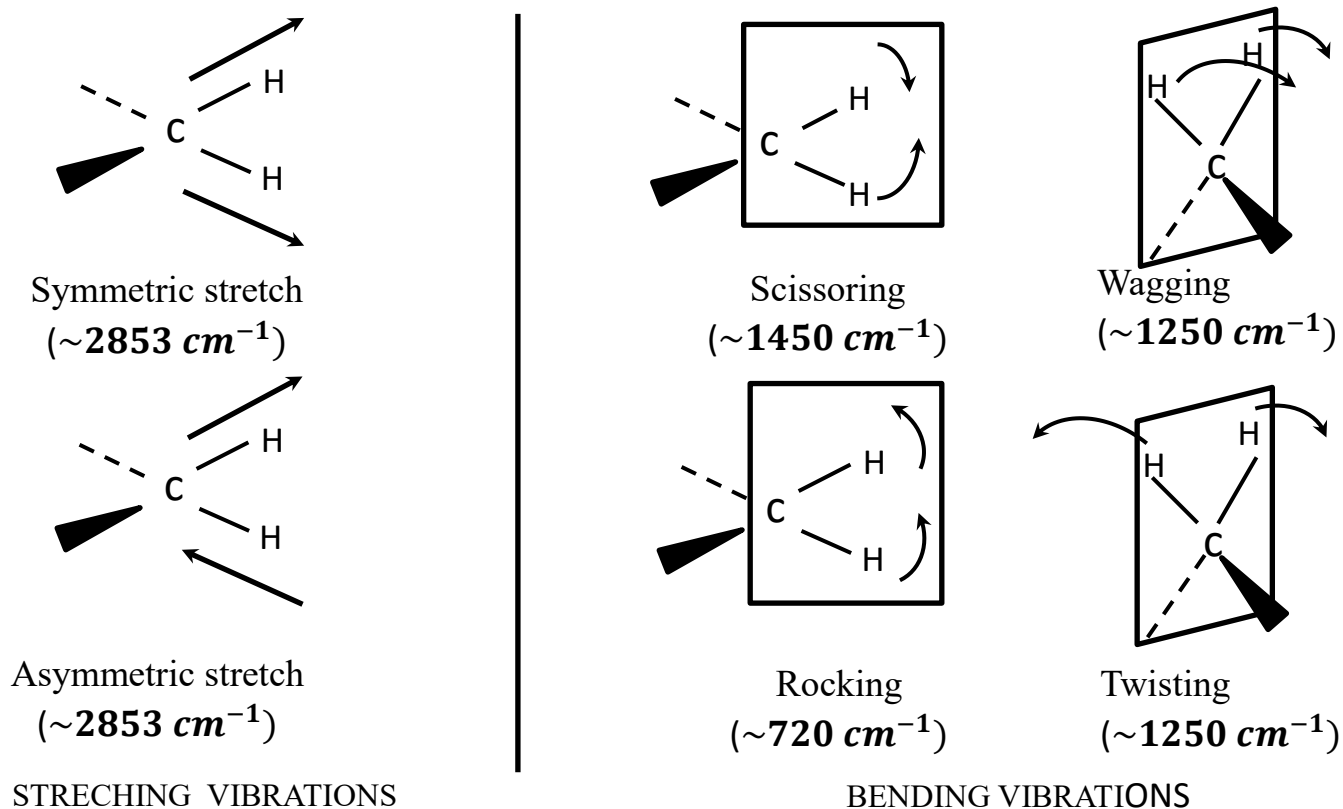
A molecule can vibrate in many ways, and each way is called a *vibrational mode*. For molecules with N number of atoms, linear molecules have  $3N - 5$  degrees of vibrational modes, whereas nonlinear molecules have  $3N - 6$  degrees of vibrational modes (also called vibrational degrees of freedom)

The atoms in a  $\text{CH}_2\text{X}_2$  group, commonly found in organic compounds and where X can represent any other atom, can vibrate in nine different ways. Molecular vibrations fall into two main categories: stretching or bending. The stretching vibration entails a change in the inter-atomic distance along the bond axis, whereas in bending vibrations the bond lengths remain constant, but the bond angles change. Six of these vibrations involve Only the  $\text{CH}_2$  portion, hence the Types of molecular vibrations :symmetric stretching and antisymmetric stretching with highest energy ,the bending vibration in plan scissoring rocking with lower energy ,out of plan wagging and twisting . Stretching absorptions

Usually stretching produce stronger peaks than bending in the infrared spectrum; however, bending absorptions can be useful in differentiating similar types of bonds. (Scheinmann 2013)

## Infrared band shapes

**Infrared band shapes come in various forms. Two of the most common are narrow and broad. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother(El-Azazy, Al-Saad and El-Shafie 2023)**



**Fig: Types of molecular vibrations: (a) Stretching vibrations and (b) bending vibrations.**

Exercises

Ex

Complete the table bellow

Symmetry element		Symmetry operation	
Symbol	Description	Symbol	Description
$E$ or $I$	Identify	$\hat{E}$	No change
	(x,y)		(x,y)
$C_n$	n-fold axis of symmetry	$\hat{C}_n$	One or several rotation about the axis by an angle $\frac{2\pi}{n}$
	(x,y)		(.....,.....)

$\sigma$	Plan of symmetry	$\hat{\sigma}$	Reflection in a plane
	(x,y)		(.....,.....)
$i$	Centre of symmetry Inversion centre	$\hat{i}$	Inversion of all atoms through a centre (i) or reflection through the centre
	(x,y)		(.....,.....)
$S_n$	n-fold rotation – reflection axis of symmetry	$\hat{S}_n$	rotation about the axis by an angle $\frac{2\pi}{n}$ followed by reflection in the plane perpendicular to the rotation axis
	(x,y)		(.....,.....)

### Exercise1

What means selection rules?

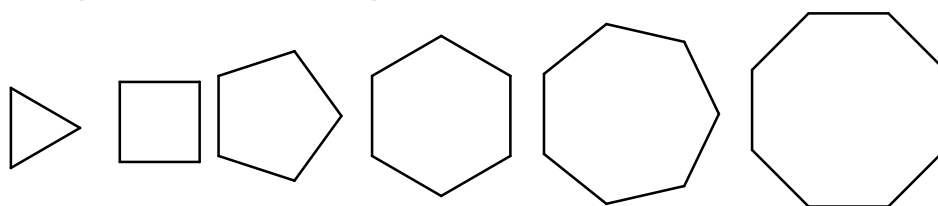
### Exercise2

Represent the symmetry operation of the improper axis  $S_4$  ?

### Exercise 3

Use the multiplication of symmetry elements, write the matrix product and deduce the transfer matrix?

We give the following skeletons



Determine the symmetry elements of each structure and the point symmetry group of the first four structures?

Determine the infrared active and Raman active modes vibration

Give the number of symmetry classes of each point symmetry group?

Determine the number of changed and unchanged atoms?

Exercise4

Determine a, b, c? Use orthogonally theorem

$C_{3v}$	E	$2C_3$	$3\sigma_v$
$\Gamma_1$	1	1	1
$\Gamma_2$	1	a	b
$\Gamma_3$	2	c	d

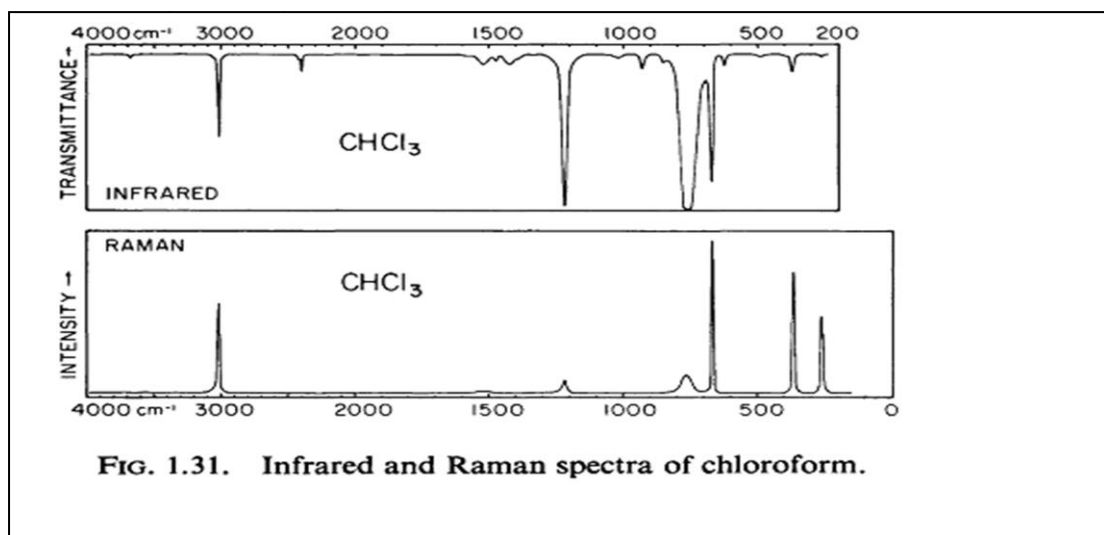
Ex

Why generally, k can be assumed to be  $5 \times 10^2$  N/m for single bonds (e.g., C–H, O–H),  $1 \times 10^3$  N/m for double bonds (e.g., C=O, C=C), and  $1.5 \times 10^3$  N/m for triple bonds (e.g., C≡N, C≡C)

## ChapterIII

## Vibration spectroscopy

We obtain the following two spectra



The fundamental question is how we are going to relate the energy of the incident radiation to the molecule! That is to say the effect of energy on the molecule or the matter ray interaction. We will treat the problem in the same way that Bohr treated the hydrogen spectrum, we ask the question what type of rethinking manifests the molecule in the energy domain considered, in wave number ( $4000 \text{ cm}^{-1}$  to  $200 \text{ cm}^{-1}$ ), we know that in the visible UV domain we have electronic transitions. , nevertheless in the domain considered the energy is low so that it can't produce electronic transitions and interacts in this way, which suggests that this energy is not linked to electronic transitions, they are therefore excluded, so it is necessary seek to link the transitions to other phenomena, namely vibrations, rotations or vibro-rotational phenomena depending on the state of the sample.

### Molecular oscillation (Raman and Infrared)

## Harmonic Oscillator

### For a single mass

A harmonic oscillator is any physical system whose evolution over time is described by a sinusoidal function. Thus The treatment consists of considering the chemical bond equivalent to a spring of recovery force  $f : f = -k(R - R_e)$

The name comes from the relationship between the recovery force experienced by atoms when a bond is stretched to the magnitude of the elongation.

$k$ ; is the spring stiffness constant and the negative sign indicates that the direction of the force and that of the displacement are opposite.

The greater the slope of the potential (the stiffer the bond), the higher the force constant.). Deformations of molecules by bending generally have lower force constants than elongations.

$$V = \frac{1}{2}k(R - R_e)^2 = \frac{1}{2}k(x)^2$$

We obtain by comparison

$$\left[ \frac{d^2V}{dx^2} \right]_0 = k$$

We have also

$$kx = m \frac{d^2x}{dt^2}$$

Which give

$$m \frac{d^2x}{dt^2} + kx = 0$$
$$m\ddot{x} + kx = 0$$

This equation admits as a solution

$$x(t) = C_1 \sin \omega t + C_2 \cos \omega t \text{ avec } \omega = \sqrt{\frac{k}{m}}$$

We have the boundry conditions

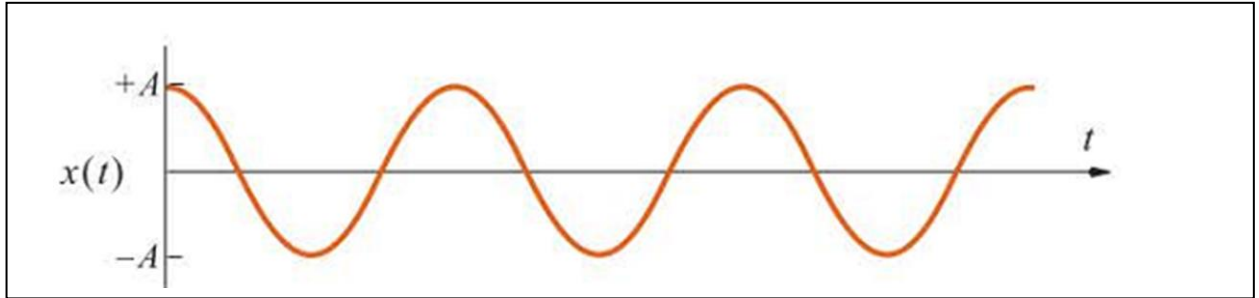
$$x(0) = A$$

$$\left(\frac{dx}{dt}\right)_{t=0} = 0 = C_1 \omega$$

The solution

$$x(t) = C_2 \cos \omega t$$

$C_2$  Is the amplitude of the wave (Wellner 2012)



$$-\frac{h^2}{m} \frac{d^2 \Psi_{vib}}{dx^2} + \left(E - \frac{1}{2} k x^2\right) \Psi_{vib} = 0;$$

Harmonic Oscillator (two masses)

For two masses we can write the Lagrangians

$$m_1 \ddot{x}_1 + k x_1 = 0$$

$$m_2 \ddot{x}_2 + k x_2 = 0$$

The solutions in this case are

$$x_1(t) = A_1 \cos(2\pi \nu t + \varphi)$$

$$x_2(t) = A_2 \cos(2\pi \nu t + \varphi)$$

The system frequency  $\nu$  and which must be the same for both masses

$$\ddot{x}_1 = -4\pi^2 \nu^2 A_1 \cos(2\pi \nu t + \varphi)$$

$$\ddot{x}_2 = -4\pi^2 \nu^2 A_2 \cos(2\pi \nu t + \varphi)$$

It gives

$$(4\pi^2 \nu^2 m_1 + k) A_1 - k A_2 = 0$$

$$k A_1 + (-4\pi^2 \nu^2 m_2 + k) A_2 = 0$$

The determinant

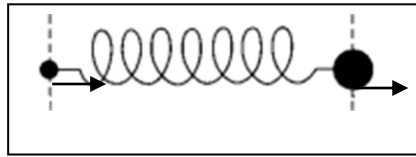
$$\begin{vmatrix} 4\pi^2 \nu^2 m_1 + k & -k \\ -k & -4\pi^2 \nu^2 m_2 + k \end{vmatrix} = 0$$

We obtain

$$(4\pi^2 \nu^2)^2 m_1 m_2 - 4\pi^2 \nu^2 k (m_1 + m_2) + k^2 - k^2 = 0$$

The solutions are

$v = 0$  and if  $x_1 = x_2$  this motion is translation



The second solution is

$$etv = \omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ avec } \mu = m_{eff} = \frac{m_1 m_2}{m_1 + m_2}$$

We can give the Schrödinger equation:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \Psi_{vib}}{dq^2} + \left( E - \frac{1}{2} k q^2 \right) \Psi_{vib} = 0; q = x_2 - x_1$$

Solving this equation gives

$$E_v = \left( v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}; \text{ quantum numbers } v = 0, 1, 2..$$

$$\Delta E_v = \left( v + \frac{1}{2} \right) h \omega_{osc} \text{ in joule with } \omega_{osc} = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \text{ in Hz; } \bar{\omega}_{osc} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2} \text{ in cm}^{-1}$$

$$\text{Avec } \Delta v = \mp 1$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \rightarrow \mu = \frac{m_1 * m_2}{m_1 + m_2} = m_{eff}; \text{ Reduced mass}$$

1 Dyne is equal to  $10^{-5}$  Newton measurement unit in the system CGS

$\omega = \left( \frac{k}{\mu} \right)^{1/2}$ ; is the circular frequency of the oscillator in radians per second.

Energy levels

$$E_0 = \left( 0 + \frac{1}{2} \right) h \omega_{osc} = \frac{1}{2} h \omega_{osc}$$

$$E_1 = \left( 1 + \frac{1}{2} \right) h \omega_{osc} = \frac{3}{2} h \omega_{osc}$$

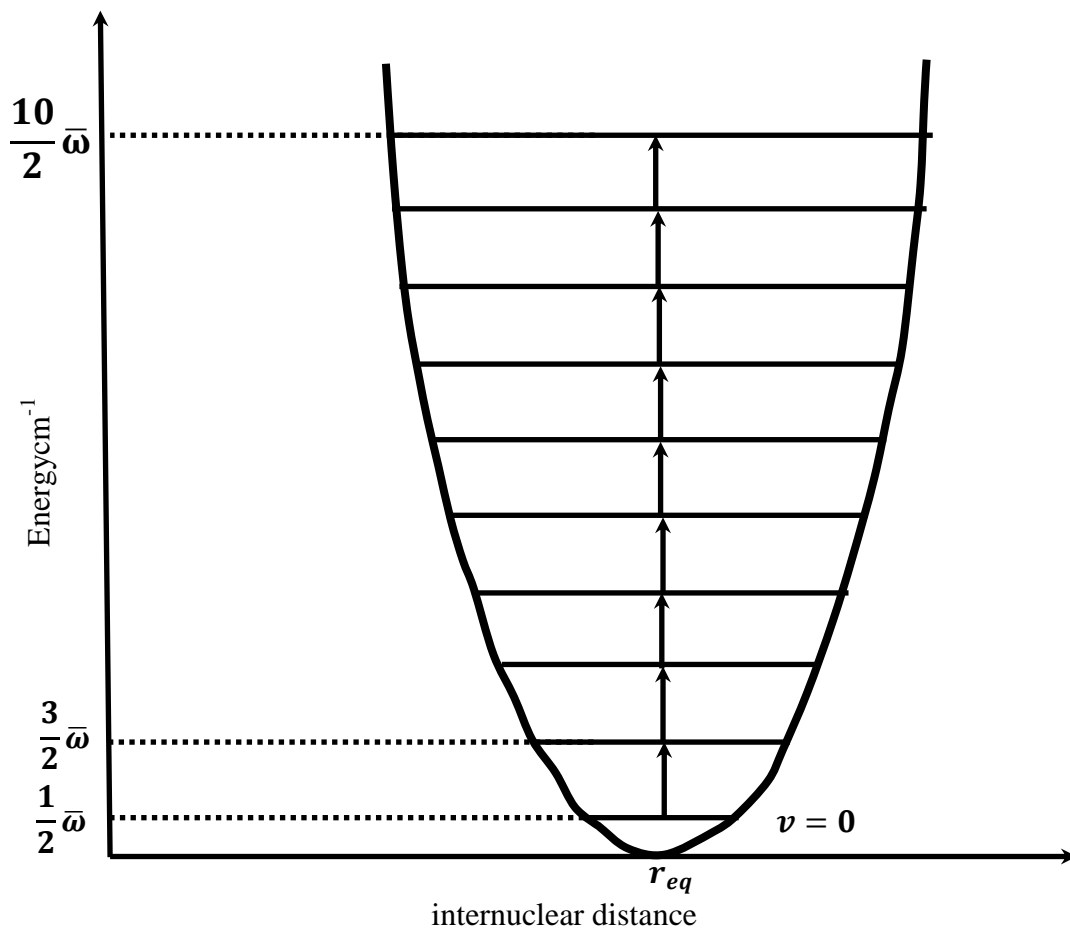
$$E_2 = \left( 2 + \frac{1}{2} \right) h \omega_{osc} = \frac{5}{2} h \omega_{osc}$$

$$E_3 = \left(3 + \frac{1}{2}\right) h\omega_{osc} = \frac{7}{2} h\omega_{osc}$$

$$E_4 = \left(4 + \frac{1}{2}\right) h\omega_{osc} = \frac{9}{2} h\omega_{osc}$$

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \bar{\omega}_{osc} \text{ en } cm^{-1}$$

$$\varepsilon_0 = \frac{E_v}{hc} = \left(0 + \frac{1}{2}\right) \bar{\omega}_{osc} = \left(\frac{1}{2}\right) \bar{\omega}_{osc} cm^{-1}$$



The transition energy (absorption or emission) takes place if there is interaction of the molecular vibration with the radiation. This is possible if the molecule has a dipole moment (for infrared) if the molecule does not have a polar moment. We use Raman spectroscopy and we will polarize

the electron cloud to reveal the dipole moment. It should be said that apolar molecules are transparent in the spectral domain considered by infrared and the wave number of the transition is given by the subtraction of two energy in  $\text{cm}^{-1}$  units of the states if they take place

$$\varepsilon_{v+1 \rightarrow v} = G(v+1 \rightarrow v) = \frac{E_v}{hc} = \left(v+1 + \frac{1}{2}\right) \bar{\omega}_{osc} - \left(v + \frac{1}{2}\right) \bar{\omega}_{osc} = \bar{\omega}_{osc}$$

This is again evident if we consider the absorption or emission mechanism in classical absorption terms, e.g. the vibrating molecule only absorbs energy from the radiation with which it can interact coherently, which must be a radiation of its own oscillation frequency.

Those transitions called thermal transition and the first overtones transition occur when  $v = 0 \rightarrow v = 2$  and the energy

$E = 2E_{\text{fundamental}}$  the second overtones transition occur when  $v = 0 \rightarrow v = 3$  and the energy  $E = 3E_{\text{fundamental}}$  **for harmonic oscillation**

## Boltzmann distribution

The Boltzmann equation together with the vibrational energy level expression gives the ratio of the population  $N_v$  of the  $v$ th vibrational level to  $N_0$ , that of the zero-point level, as

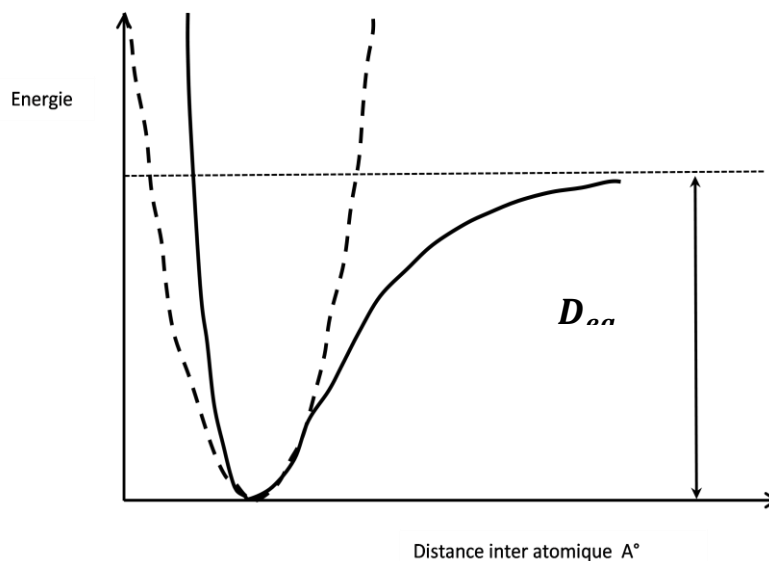
$$\frac{N_v}{N_0} = \exp\left(-\frac{hcv\bar{\omega}}{kT}\right)$$

Where  $\bar{\omega}$  is the vibration wavenumber and  $v$  the vibrational quantum number. Since this ratio is, for example, only 0.10 for  $v=1$  and  $\bar{\omega} = 470 \text{ cm}^{-1}$  we can see that rotational transitions in excited vibrational states are generally very weak unless either the molecule is particularly

heavy, leading to a relatively small value of  $\bar{\omega}$ , or the temperature is high; however, the negative exponential nature of means that increasing the temperature has only quite a small effect on populations. The population of first state and second arise this lead to appear hot transitions. (Marowsky and Smirnov 2012)

## Anharmonic Oscillator

The molecules do not respond perfectly to the laws of a harmonic oscillator model, the bonds are elastic but are not managed by Hooke's law, they are stretched to a breaking point, (dissociation, breakage) of the molecule into atoms, the restoring force cancels out and at short distance the electronic clouds interpenetrate and the repulsion force enormously increases the interaction potential energy tends towards a constant. For an amplitude of 10% of the length of the connection the behaviour of the connection becomes complicated. The graphic comparison suggests that the two models coincide at the beginning only. (Turbiner and Rosales 2023)



Curve in points harmonic oscillator, inharmonic oscillator

Morse gives an empirical relation which is called Morse function which describes the potential

$$E = D_{eq} \left[ (1 - \exp a(r_{eq} - r)) \right]^2$$

Schrodinger's equation

$$\left( \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \xi^2} + D_e (1 - \exp(-\xi a))^2 \right) \Psi_{vib} = E_{vib} \Psi_{vib}$$

$a$  ; is an observation,  $D_{eq}$  dissociation energy.

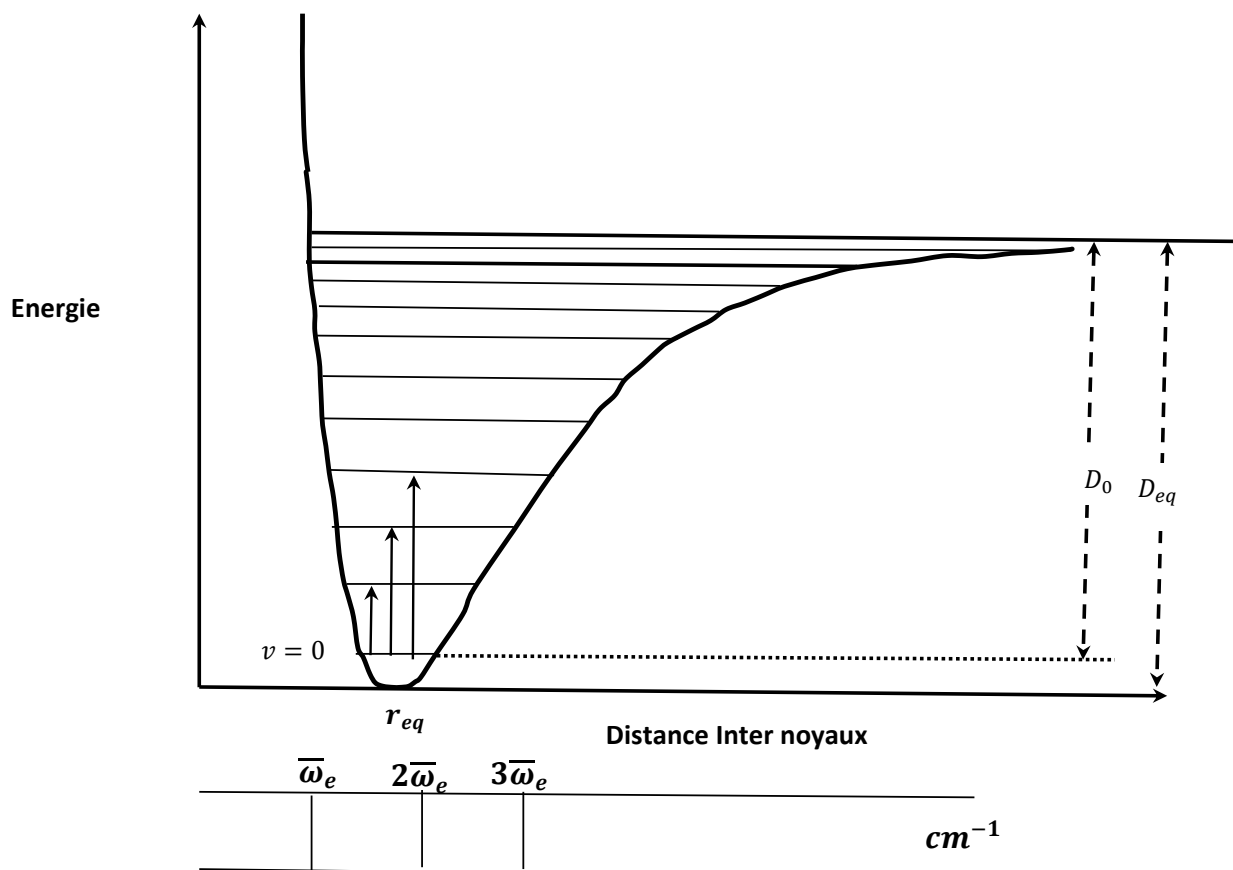
Energy levels of vibrational transitions

We find two types , thermal absorption  $\Delta v = 1$  and overtones  $\Delta v = 2, 3, 4$  the levels energie ar given by the expression

$$G(v) = \varepsilon_v = \left( v + \frac{1}{2} \right) \bar{\omega}_e - \left( v + \frac{1}{2} \right)^2 \bar{\omega}_e x_e \quad (cm^{-1})(v = 0, 1, 2 \dots \dots)$$

$\bar{\omega}_e$  The wave number

$x_e$  Anharmonicity constant. For an elongation vibration is always small and positive ( $\approx +0.01$ ).



The overtones occur when  $E_0^2; E_0^3; E_0^4$

$v = 0 \rightarrow v = 1, \Delta v = 1$  with considerable intensity

$$\begin{aligned}\Delta G = \Delta \varepsilon &= \varepsilon_{v=0} - \varepsilon_{v=1} \\ &= \left(1 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(1 + \frac{1}{2}\right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e \right\} \\ &= \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}\end{aligned}$$

$v = 0 \rightarrow v = 2, \Delta v = 2$  with small intensity first overtone

$$\begin{aligned}\Delta \varepsilon = \varepsilon_{v=2} - \varepsilon_{v=0} &= \left(2 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(2 + \frac{1}{2}\right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e \right\} \\ &= 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}\end{aligned}$$

$v = 0 \rightarrow v = 3, \Delta v = 3$  with normally negligible intensity

$$\begin{aligned}\Delta \varepsilon = \varepsilon_{v=3} - \varepsilon_{v=0} &= \left(3 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(3 + \frac{1}{2}\right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e \right\} \\ &= 3\bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}\end{aligned}$$

$v = 0 \rightarrow v = 4, \Delta v = 4$  with normally negligible intensity

$$\begin{aligned}\Delta \varepsilon = \varepsilon_{v=4} - \varepsilon_{v=0} &= \left(4 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(4 + \frac{1}{2}\right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e \right\} \\ &= 4\bar{\omega}_e (1 - 5x_e) \text{ cm}^{-1}\end{aligned}$$

$v = 0 \rightarrow v = 5, \Delta v = 5$  with normally negligible intensity

$$\begin{aligned}\Delta \varepsilon = \varepsilon_{v=5} - \varepsilon_{v=0} &= \left(5 + \frac{1}{2}\right) \bar{\omega}_e - x_e \left(5 + \frac{1}{2}\right)^2 \bar{\omega}_e - \left\{ \frac{1}{2} \bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e \right\} \\ &= 5\bar{\omega}_e (1 - 6x_e) \text{ cm}^{-1}\end{aligned}$$

Example

Determine the dissociation energy?

To determine the dissociation energy, we set  $dE/dv$  equal to zero to determine the maximum value of the vibrational quantum number  $v$ .

$$\bar{\omega}_e - 2 \left(v + \frac{1}{2}\right) \bar{\omega}_e x_e \Rightarrow \left(v + \frac{1}{2}\right)_{max} = \frac{\bar{\omega}_e}{2\bar{\omega}_e x_e}$$

Substituting into the energy expression above gives

$$\begin{aligned}
 D_e = E(v_{max}) &= \frac{\bar{\omega}_e}{2\bar{\omega}_e x_e} \bar{\omega}_e - \left( \frac{\bar{\omega}_e}{2\bar{\omega}_e x_e} \right)^2 \bar{\omega}_e x_e \\
 &= \frac{\bar{\omega}_e}{2\bar{\omega}_e x_e} \left( \bar{\omega}_e - \frac{\bar{\omega}_e}{2\bar{\omega}_e x_e} \bar{\omega}_e x_e \right) = \frac{\bar{\omega}_e}{2\bar{\omega}_e x_e} \left( \bar{\omega}_e - \frac{\bar{\omega}_e}{2} \right) = \frac{\bar{\omega}_e^2}{4\bar{\omega}_e x_e} \\
 &= \frac{\bar{\omega}_e}{4x_e}
 \end{aligned}$$

And

$$D_0 = D_e - E(0) = \frac{\bar{\omega}_e}{4x_e} - \left( 0 + \frac{1}{2} \right) \bar{\omega}_e - \left( 0 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e$$

**Exemple2** (Puri, Sharma and Pathania 2008)

For the molecule BH,  $\bar{\omega}_e = 2368 \text{ cm}^{-1}$  and the anharmonicity constant  $\bar{\omega}_e x_e = 49 \text{ cm}^{-1}$  calculate the vibrational terms of the first four vibrational levels and determine the spacing between them and calculated the first overtone and second overtone

$$G(0) = \varepsilon_v = \left( 0 + \frac{1}{2} \right) 2368 - \left( 0 + \frac{1}{2} \right)^2 49 = 1184 - 12 =$$

**1172 cm<sup>-1</sup> zero point energy**

$$G(1) = \varepsilon_v = \left( 1 + \frac{1}{2} \right) 2368 - \left( 1 + \frac{1}{2} \right)^2 49 = 3552 - 110 = 3442 \text{ cm}^{-1}$$

$$G(2) = \varepsilon_v = \left( 2 + \frac{1}{2} \right) 2368 - \left( 2 + \frac{1}{2} \right)^2 49 = 5920 - 306 = 5614 \text{ cm}^{-1}$$

$$G(3) = \varepsilon_v = \left( 3 + \frac{1}{2} \right) 2368 - \left( 3 + \frac{1}{2} \right)^2 49 = 8288 - 600 = 7688 \text{ cm}^{-1}$$

The spacing between the energy levels are

$$G(1) - G(0) = 3442 - 1172 = 2270 \text{ cm}^{-1} \text{ fundamental}$$

$$G(2) - G(1) = 5614 - 3442 = 2172 \text{ cm}^{-1}$$

$$G(3) - G(2) = 7688 - 5616 = 2074 \text{ cm}^{-1}$$

Note the energy levels are not equally spaced and the spacing goes with increase in the vibrational quantum number

Calculated overtones

$$G(1) - G(0) = 3442 - 1172 = 2270 \text{ cm}^{-1} \text{ fundamental}$$

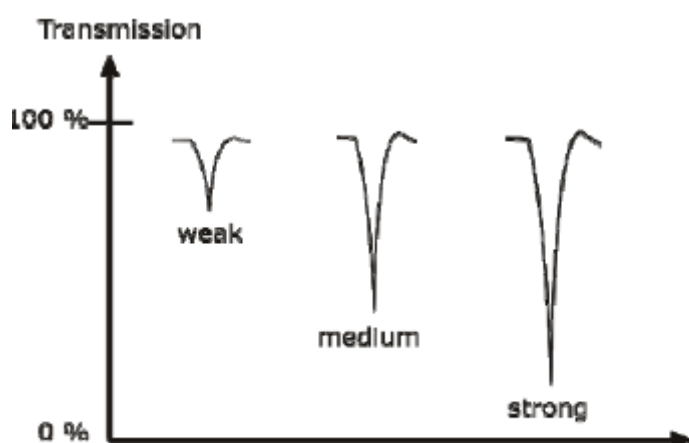
$$G(2) - G(0) = 5614 - 1172 = 4442 \text{ cm}^{-1} \text{ first overtone}$$

$$G(3) - G(0) = 7688 - 1172 = 6516 \text{ cm}^{-1} \text{ second overtone}$$

## Allowed transitions

For a vibration of a molecule to give rise to an absorption spectrum, the electric dipole moment of the molecule must vary during the vibration. The basis of this rule is that the molecule can only oscillate the electromagnetic field if it has an electric dipole moment which oscillates when the molecule vibrates at the same frequency. The molecule does not need to have a permanent dipole: the rule only requires a variation of the dipole moment, possibly starting from zero. Some vibrations do not affect the dipole moment of the molecule (for example, the elongation movement of a homonuclear diatomic molecule), and there is therefore neither absorption nor emission of radiation. Homonuclear diatomic molecules are therefore inactive in the infrared, because their dipole moment remains zero regardless of the length of the bond, while heteronuclear diatomic molecules (which have a dipole moment that changes when the bond elongates and contracts ) are active in the infrared.

IR bands can be classified as strong (s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis for the shape it can be narrow or broad. The below bands are narrow. (Colthup, Daly and Wiberley 1975)



Observed vibrational frequencies and calculated force constants for some diatomic molecules

Molecules	$G = \bar{\nu}(cm^{-1})$	Reduced mass $\mu(Kg)$	$k(Nm^{-1})$
$N_2$	2331	$1.1625 * 10^{-26}$	2240
$CO$	2141	$1.1384 * 10^{-26}$	1860
$NO$	1776	$1.2397 * 10^{-26}$	1550
$O_2$	1556	$1.3279 * 10^{-26}$	1140
$HF$	3958	$0.15658 * 10^{-26}$	870
$H_2$	4159	$0.08367 * 10^{-26}$	510
$HCl$	2886	$0.16272 * 10^{-26}$	480
$F_2$	892	$1.5773 * 10^{-26}$	450
$I_2$	213	$10.536 * 10^{-26}$	170
$NaCl$	378	$2.3162 * 10^{-26}$	120

Example

The fundamental vibration frequency of HCl is  $2.890 \text{ cm}^{-1}$   
 calculate the force constant of this molecule the atomic masses are  
 $H = 1.673 * 10^{-27} \text{ kg}$   $^{35}\text{Cl} = 58.03 * 10^{-27} \text{ kg}$

The reduce mass  $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.673 \times 10^{-27} \text{ kg}) (58 \times 10^{-27} \text{ kg})}{(1.673 \times 10^{-27} \text{ kg}) + (58 \times 10^{-27} \text{ kg})} = 1.626 \times 10^{-27} \text{ kg}$

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

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \left(3 \times 10^{10} \frac{\text{cm}}{\text{s}}\right)^2 (2890 \text{ cm}^{-1})^2 (1.626 \times 10^{-27} \text{ kg}) = 483 \text{ kg s}^{-2}$$

$$483 \text{ kg s}^{-2} * \frac{m}{m} = 483 \text{ N/m}$$

Example2

The Fundamentals and first overtone transition of  $^{14}\text{N}^{16}\text{O}$  are concentrated at  $1876.06$  and  $3724.20 \text{ cm}^{-1}$  respectively evaluate the aquilibrium vibration frequency the anharmonicity the exact zero point energy and the force constant of the molecule.

$$\bar{\omega}_e(1 - 2x_e) = 1876.06 \text{ cm}^{-1} \dots\dots\dots 1$$

$$2\bar{\omega}_e(1 - 3x_e) = 3724.20 \text{ cm}^{-1} \dots\dots\dots 2$$

$$G(v) = (v + 1/2)\omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e \quad ; v=0,1,2,3,\dots\dots$$

$$\frac{1}{2} \Rightarrow \frac{\bar{\omega}'_e(1 - 2x_e)}{2\bar{\omega}'_e(1 - 3x_e)} = \frac{1876.06}{3724.20}$$

$$\frac{(1 - 2x_e)}{(1 - 3x_e)} = 2 * \frac{1876.06}{3724.20}$$

$$(1 - 2x_e) = (1 - 3x_e) 2 * \frac{1876.06}{3724.20}$$

$$(1 - 2x_e) = (2 * \frac{1876.06}{3724.20} - 3 * 2 * \frac{1876.06}{3724.20} x_e)$$

$$(1 - 1 * 2 * \frac{1876.06}{3724.20}) = (2x_e - 3 * 2 * \frac{1876.06}{3724.20} x_e)$$

$$x_e = \frac{\left(2 - \left(3 * 2 * \frac{1876.06}{3724.20}\right)\right)}{\left(1 - \left(1 * 2 * \frac{1876.06}{3724.20}\right)\right)}$$

$$x_e = 7.332 * 10^{-3}$$

$$\overline{\omega}'_e = 1903.96 cm^{-1}$$

*zero point energy*

$$\varepsilon_e = \frac{1}{2} \overline{\omega}'_e \left(1 - \frac{x_e}{4}\right) = 948.2 cm^{-1}$$

*force constante*

$$k = 4\pi^2 \overline{\omega}'_e{}^2 c^2 \mu$$

$$\mu = \frac{23.25 * 10^{-27} * 26.56 * 10^{-27}}{23.25 * 10^{-27} + 26.56 * 10^{-27}}$$

$$k = 4\pi^2 (19.3.96 * 100)^2 (3 * 10^8)^2 12.39 * 10^{-27} = 1594 N/m$$

## Exercises

### Exercies1

Determine the units of expressions

$$\frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}; \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

calculate the elongation frequencies for the bonds

bond	C=C	C-H	C-D
K in dyn/cm	$10 * 10^5$	$5 * 10^5$	$5 * 10^5$

$$\bar{\nu} = 4.12 \sqrt{\frac{k}{\mu}}$$

### Ex2

We give the fundamental vibration frequency HBr is  $2890\text{cm}^{-1}$   
calculate the force constant k?

### Ex3

The Morse code potential is given by the formula

$$V = E = D_{eq} [ (1 - \exp a(r_{eq} - r))^2 ]$$

Give the expression for the frequency if  $(r_{eq} - r) \rightarrow 0$  ?

$$e^{ax} \cong 1 + ax$$

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!}$$

### Ex4

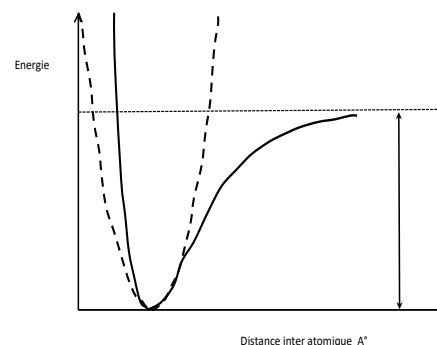
The first absorption lines are obtained at  $2345, 15,4661.40,$   
 $6983.73\text{cm}^{-1}$

Calculate

$\bar{\omega}_e, x_e$  et K ?

### Ex6

Determine on the graph the part of the repulsion  
and the part of the attraction



## ChapterV

## ROTATIONAL SPECTROSCOPY (micro waves )

When the energy of a molecule changes, spectral lines can be observed. This variation in energy is often manifested by the emission of a photon. Therefore, the appearance of spectral lines in a molecule has the same origin as in atoms. However, molecular spectroscopy is much more complex than atomic spectroscopy. Indeed, in a molecule, the spectral lines may result from electronic transitions, from rotational and/or vibrational motions, or from a combination of both, known as vibro-rotational transitions.

**Rotation of the diatomic molecule** The molecule rotating around its center of gravity From the point of view of classical mechanics, a diatomic molecule can be considered like a rigid rotator (distance fixed during rotation) formed of two particles  $m_1$  and  $m_2$  of respective masses  $m_1$  and  $m_2$ . (Banwell 1972)

$$\sum_i^{n>1} m_i r_i = \sum_i^2 m_i r_i = m_1 r_1 + m_2 r_2 = 0$$

Therefore

$$m_1 r_1 = m_2 r_2$$

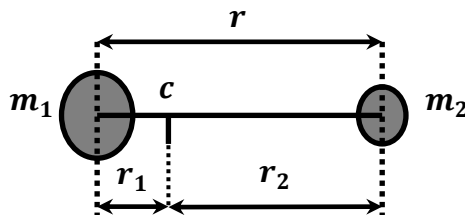


Fig :diatomique

The interatomic distance represents the length of the bond.

$$r_1 + r_2 = r$$

$$r_1 = r - r_2$$

$$r_2 = r - r_1$$

$$m_1 r_1 - m_2 (r - r_1) = m_1 r_1 - (r m_2 - m_2 r_1)$$

$$r_1 = \frac{m_2 r}{m_1 + m_2}; r_2 = \frac{m_1 r}{m_1 + m_2}$$

$$I = m_1 r_1^2 + m_2 r_2^2 = r_1 r_1 m_1 + r_2 r_2 m_2; m_1 r_1 = m_2 r_2$$

$$(m_2 r_2 r_1 + m_1 r_1 r_2)$$

$$I = (m_1 + m_2) \frac{m_2}{(m_1 + m_2)} * \frac{m_1}{m_1 + m_2} r^2$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

$\mu$  ; the reduced mass of the system

When the molecule rotates around its center of gravity  $c$ , the atoms of mass  $m_1$  and  $m_2$  have the same rotation speed

$$V_1 = r_1 \omega \text{ and } V_2 = r_2 \omega$$

The energy of the system is given by the expression

$$E_c = \frac{1}{2} I \omega^2$$

The total angular momentum is given by the relation

$$\vec{L} = \sum_i^n \vec{r}_i \wedge \vec{p}_i = \vec{r}_1 \wedge m \vec{V}_1 + \vec{r}_2 \wedge m \vec{V}_2$$

$$L = r_1 m_1 V_1 + r_2 m_2 V_2$$

$$L = r_1 m_1 r_1 \omega + r_2 m_2 r_2 \omega$$

$$L = m_1 \omega r_1^2 + m_2 \omega r_2^2$$

$$L = \omega (m_1 r_1^2 + m_2 r_2^2) = I \omega$$

hence

$$E_{\text{rotationel}} = \frac{I * (I \omega^2)}{2 * I} = \frac{(I \omega)^2}{2I} = \frac{L^2}{2I} = \frac{\left(\frac{h}{2\pi}\right)^2}{2I}$$

The spectrum obtained gives discrete values of the energy it's convenient to add quantum number

$$E_{\text{rotationel}} = \frac{I * (I \omega^2)}{2 * I} = \frac{(I \omega)^2}{2I} = \frac{L^2}{2I}$$

Represents state number 1 or the first energy level, to have the transition energies according to the energy of the ground state;

$$E_{\text{rotationel}} = \frac{h^2}{8\pi^2} * \frac{1}{I} * J * (J + 1) \text{ with } j = 0, 1, 2, \dots$$

$J$  ; rotational quantum number

$$\text{for } J = 0 \text{ fundamental state } E_{J=0} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 0 * (0 + 1) = 0$$

$$\text{for } J = 1 \text{ we have } E_{J=1} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 1 * (1 + 1) = 2\left(\frac{1}{I} * \frac{h^2}{8\pi^2}\right)$$

$$J = 2 \quad E_{J=2} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 1 * (2 + 1) = 3\left(\frac{1}{I} * \frac{h^2}{8\pi^2}\right)$$

$$J = 3 \quad E_{J=3} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 1 * (3 + 1) = 4\left(\frac{1}{I} * \frac{h^2}{8\pi^2}\right)$$

The transition energy represents the difference in energy between two consecutive levels.

;

$$\begin{aligned} \Delta E_J^{J+1} &= E_{J+1} - E_J \\ &= \frac{1}{I} * \frac{h^2}{8\pi^2} * (J + 1) * ((J + 1) + 1) - \frac{1}{I} * \frac{h^2}{8\pi^2} * J * (J + 1) \end{aligned}$$

$$\Delta E_J^{J+1} = \frac{1}{I} * \frac{h^2}{8\pi^2} (J + 1)$$

$$\begin{aligned} \text{for the transition } J0 \rightarrow 1 \text{ the energy is given by } \Delta E_0^1 \\ = 1 \left( \frac{1}{I} * \frac{h^2}{8\pi^2} \right) = B \end{aligned}$$

$B$  is rotational constant

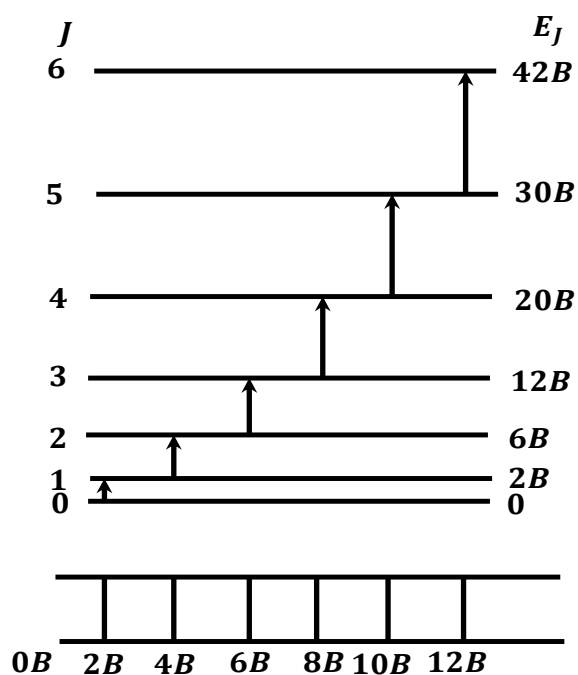
$$J1 \rightarrow 2 \quad \Delta E_1^2 = 2\left(\frac{1}{I} * \frac{h^2}{8\pi^2}\right)$$

$$J2 \rightarrow 3 \quad \Delta E_2^3 = 3\left(\frac{1}{I} * \frac{h^2}{8\pi^2}\right)$$

$$J3 \rightarrow 4 \quad \Delta E_3^4 = 4\left(\frac{1}{I} * \frac{h^2}{8\pi^2}\right)$$

We can also write the wave number (energy in wave number)

$$F_J = F(J) = \varepsilon_J = E_J/hc = \frac{h}{8\pi^2} * \frac{1}{Ic} * J * (J + 1) = BJ(J + 1)$$

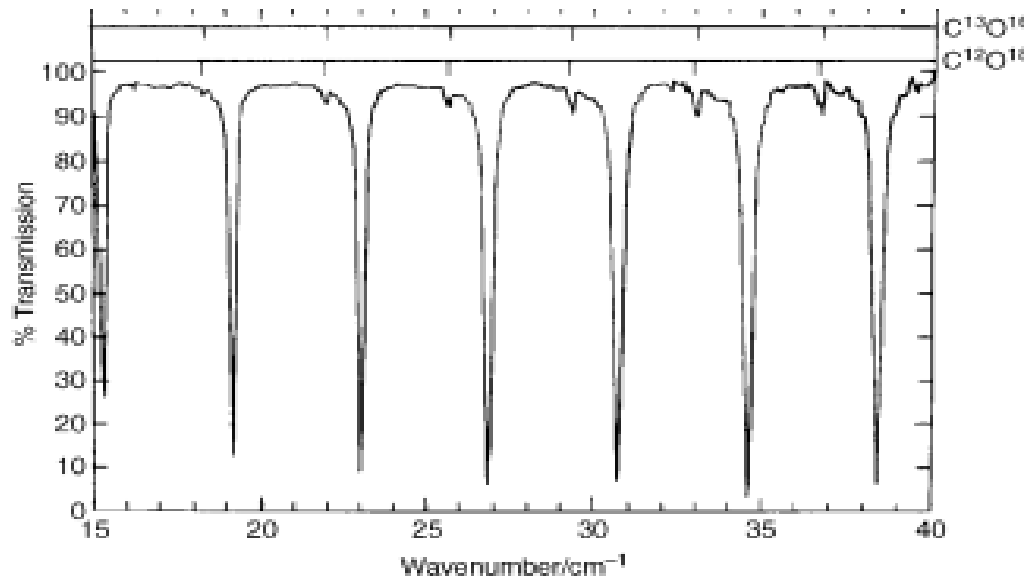


**Figure Allowed rotational energies**

Spectrum

The transition occur between to levels and the energy of absorption is the difference in energy of the considered stats of the two levels hence

$$\begin{aligned}
 \epsilon_{J=1} - \epsilon_{J=0} &= \frac{E_J}{hc} = 2B - 0B \\
 \epsilon_{J=1} - \epsilon_{J=0} &= \frac{E_J}{hc} = 2B - 0B \\
 \bar{\nu}_{J=0 \rightarrow J=1} &= \epsilon_{J=1} - \epsilon_{J=0} = 2B \text{ cm}^{-1} \\
 \bar{\nu}_{J=1 \rightarrow J=2} &= \epsilon_{J=2} - \epsilon_{J=1} = 4B \text{ cm}^{-1} \\
 \bar{\nu}_{J=2 \rightarrow J=3} &= \epsilon_{J=3} - \epsilon_{J=2} = 6B \text{ cm}^{-1} \\
 \bar{\nu}_{J \rightarrow J+1} &= \epsilon_{J=2} - \epsilon_{J=1} = B(J+1)(J+2) - BJ(J+1) \\
 &= B(J^2 + 3J + 2) - B(J^2 + J) = 2B(J+1) \text{ cm}^{-1}
 \end{aligned}$$



To have a transition it is necessary that  $\Delta J = \pm 1$ , in addition the molecule must have a dipole moment like HCl, HI. While O<sub>2</sub> does not have a dipole moment we proceed to the RAMAN Rotation, with the selection rule  $\Delta J = \pm 2$ . The excitation by a mono-wave  $\bar{\nu}_0$  radiation, that is to say a constant energy in the microwave domain gives a spectrum with three regions an absorption region with the same energy called Rayleigh with two other regions called stocks **LINES with an energy raiser of  $4B$  and antistocks LINES lowered by  $4B$  regards to  $\bar{\nu}_0$  respectively that reveal spectrum and the method of excitation in this case the energy is increased or decreased**

$$E_{\text{rotational}} = \frac{h^2}{8\pi^2} * \frac{1}{I} * J * (J + 1) \text{ avec } j = 0, 2, 4, \dots$$

**J ; is a quantum number due to rotation**

$$\text{for } J = 0 \text{ the fundamental state } E_{J=0} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 0 * (0 + 1) = 0$$

$$\text{for } J = 2 ; E_{J=2} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 2 * (2 + 1) = 6 \left( \frac{1}{I} * \frac{h^2}{8\pi^2} \right)$$

$$J = 4 ; E_{J=0} = \frac{1}{I} * \frac{h^2}{8\pi^2} * 4 * (4 + 1) = 20 \left( \frac{1}{I} * \frac{h^2}{8\pi^2} \right)$$

$$\text{for the transition } \Delta E_J^{J+2} = E_{J+2} - E_J$$

$$= \frac{1}{I} * \frac{h^2}{8\pi^2} * (J + 2) * ((J + 2) + 1) - \frac{1}{I} * \frac{h^2}{8\pi^2} * J * (J + 1)$$

$$\Delta E_j^{j+2} = \frac{1}{I} * \frac{h^2}{8\pi^2} (4J + 6) \quad J = 0, 1, 2 \dots$$

*if  $J = 0 \rightarrow 2$  energy transition  $\Delta E_0^2 = 6(\frac{1}{I} * \frac{h^2}{8\pi^2})$*

$$J=1 \rightarrow 3 ; \Delta E_1^3 = 10(\frac{1}{I} * \frac{h^2}{8\pi^2})$$

$$J=2 \rightarrow 4 ; \Delta E_2^4 = 14(\frac{1}{I} * \frac{h^2}{8\pi^2})$$

$$J=3 \rightarrow 5 ; \Delta E_3^5 = 18(\frac{1}{I} * \frac{h^2}{8\pi^2})$$

The figure gives the transition in case of it will show the separation lines (Lewis and Edwards 2001)

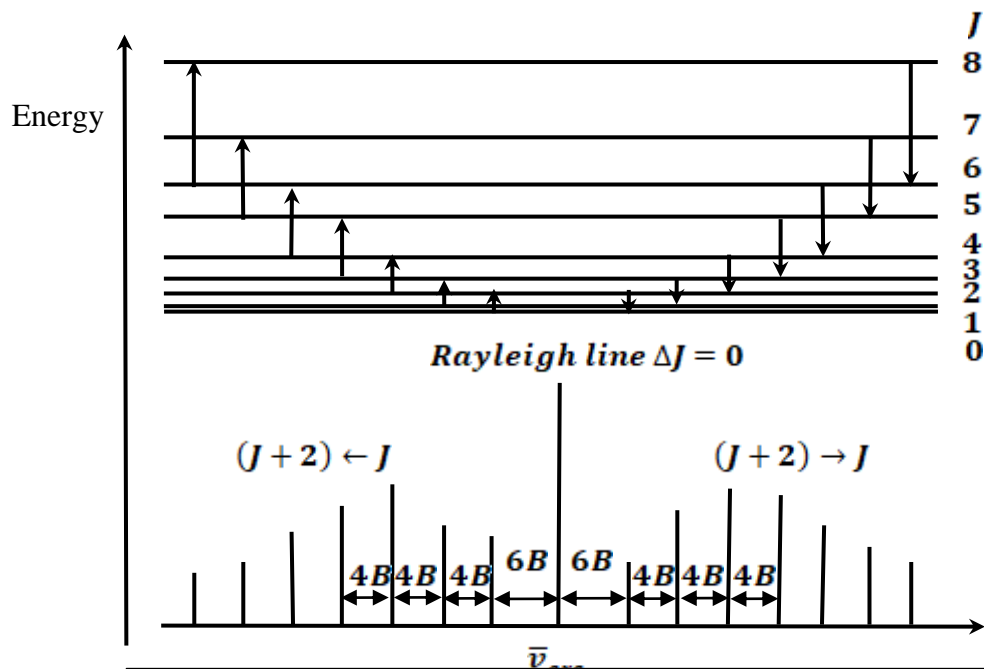


Fig : Rotational raman spectrum of rigid diatomic molecule

Thus the space between two successive lines is  $\frac{4B}{h}$ .

Example

Estimate the minimum kinetic energy at which a neutron, in a collision with a molecule of gaseous oxygen, can lose energy by exciting molecular rotation. The bond length of oxygen molecule is  $1.2 \text{ \AA}$

$$E_J = \frac{h^2}{8I\pi^2} J(J+1)$$

$$\mu = \frac{\left(16 \frac{\text{kg}}{\text{kmol}}\right) \left(16 \frac{\text{kg}}{\text{kmol}}\right)}{\left(32 \frac{\text{kg}}{\text{kmol}}\right) (6.02 \cdot 10^{23})} = 1.329 \cdot 10^{-26} \text{ kg}$$

$$\begin{aligned} E_{\min} = E_0^1 &= \frac{h^2}{8I\pi^2} = \frac{(6.624 \cdot 10^{-34} \text{ Js})^2}{8 \cdot 3.14^2 (1.329 \cdot 10^{-26} \text{ kg})(1.2 \cdot 10^{-10} \text{ m})^2} \\ &= 0.2908 \cdot 10^{-22} \text{ Joule} \\ &= \frac{0.2908 \cdot 10^{-22} \text{ J}}{1.6 \cdot 10^{-19} \frac{\text{J}}{\text{eV}}} = 0.18 \cdot 10^{-3} \text{ eV} \end{aligned}$$

Spectrum line intensity and widths

It gives the probability of transitions between the different transition states. It should be noted that the states  $\Delta J=2$  are non-permitted and prohibited states (for molecules with a dipole moment), in other words the energy is equal to zero. the Boltzmann distribution gives at a temperature T

$$\frac{N_J}{N_0} = g_i \exp\left(-\frac{E_J}{kT}\right) = (2J+1) \exp\left(-\frac{E_J}{kT}\right)$$

$N_0$  population in initial state at ambient temperature

$g_i$  is the degeneracy

The most populated state for the derivative is zero  $\frac{\partial \left(\frac{N_J}{N_0}\right)}{\partial J} = 0$  with respect to J hence

$$\begin{aligned}
 \frac{d \left(\frac{N_J}{N_0}\right)}{dJ} = 0 &= (2J + 1) \exp \left( -\frac{\frac{h^2}{8\pi^2} * \frac{1}{I} * J * (J + 1)}{kT} \right) \\
 &= \left( 2 - \frac{B}{kT} * (2J + 1)((J + 1) + J) \right) \\
 &* \exp \left( -\frac{\frac{h^2}{8\pi^2} * \frac{1}{I} * J * (J + 1)}{kT} \right) = 0 = 2 - \frac{B}{kT} (2J + 1)^2 = 0 \\
 \Rightarrow \frac{B}{kT} (2J + 1)^2 &= 2 \\
 2 \frac{kT}{B} &= (2J + 1)^2 \Rightarrow 2J = \sqrt{\frac{2kT}{B}} - 1 \\
 \sqrt{\frac{2kT}{B}} - 1 &= 2J \\
 \frac{1}{2} \sqrt{\frac{2kT}{B}} - \frac{1}{2} &= J \\
 \sqrt{\frac{2kT}{4B}} - \frac{1}{2} &= J \\
 hc\bar{B} &= B
 \end{aligned}$$

The maximum population is for  $J_{max}$  (Bhuyan 2023)

$$J_{max} = \sqrt{\frac{kT}{2hc\bar{B}}} - \frac{1}{2}$$

Example

Calculate  $J_{max}$  for rigid diatomic molecule for which at 300K the rotational constant is  $1.566 \text{ cm}^{-1}$

$$J_{max} = \left\{ \frac{kT}{2hcB} \right\}^2 - \frac{1}{2}$$

$$= \left\{ \frac{(1.38 \cdot 10^{-26} \text{ JK})(300 \text{ K})}{2(6.627 \cdot 10^{-34} \text{ Js}) \left( 3 \cdot 10^{10} \frac{\text{cm}}{\text{s}} \right) (1.566 \text{ cm}^{-1})} \right\}^{\frac{1}{2}} - \frac{1}{2}$$

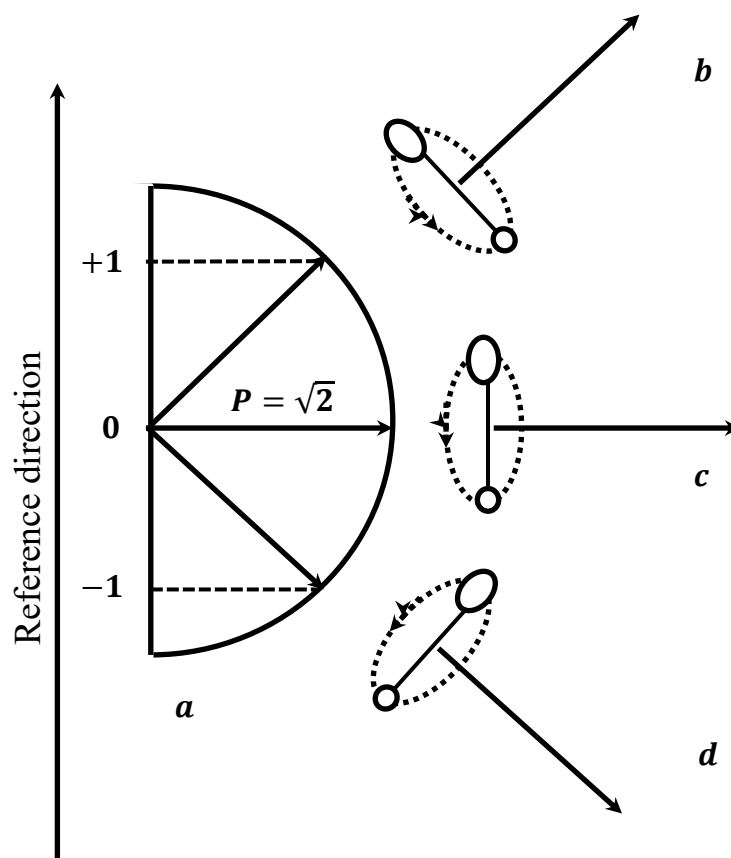
$$= 7.56 = 8$$

The angular momentum

The angular momentum is given by the expression

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} = \sqrt{J(J+1)} \text{ unité}$$

for  $J=1$  Which gives a vector of  $\sqrt{2}$  which induces the possibilities;



**We can easily write (easily)  $2J+1$  degenerate states**

**Spectroscopic lines are not infinitely narrow.**

**An important cause of broadening in gaseous samples and the Doppler effect in which the frequency of the radiation is shifted as the source approaches or moves away from the observer. When an emitting source an average of frequency  $\nu$  moves away at speed the observer detects an average of frequency**

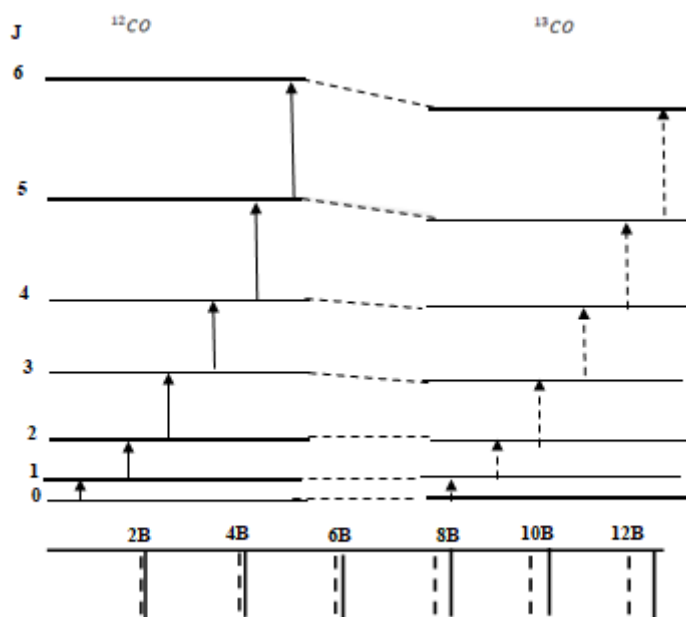
$$\nu' = \left( \frac{1 - \frac{s}{c}}{1 + \frac{s}{c}} \right)^{1/2} c \text{ radiation speed}$$

$$\delta\lambda = \frac{2\lambda}{c} \sqrt{\frac{2RT \ln 2}{M}}, M \text{ molecular weight}$$

**Another cause linked to line broadening is the lifetime of the excited states involved..**

## Effect of isotopes

The substitution of the carbon 12 atom by a carbon 13 atom in the carbon oxide molecule produces a slight increase in the reduced mass, therefore a concomitant decrease in the rotation constant. The interval between the rotation levels of the  $^{13}\text{C}=\text{O}$  molecule is therefore a little smaller and the rotation lines are moved towards lower values. (ARULDHAS 2007)



## Example

What is the change in rotational constant  $B$  when hydrogen is replaced by deuterium  $D$  in the hydrogen molecule? assuming the two molecules has the same bond length

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

$$\mu = \frac{m_H}{2} \quad \mu' = \frac{m_D}{2}$$

$$\frac{B}{B'} = \frac{2m_H}{m_H} = 2 \quad B' = \frac{B}{2}$$

Change in rotational constant

$$B' - B = \frac{B}{2}$$

## EXAMPLE2

What is the average period rotation of HCl molecule if it is in J=1 state

The intermolecular distance is 0.1274nm.givenn the mass of chlorine and hydrogen

Are  $1.673 \cdot 10^{-27}$  kg and  $58.06 \cdot 10^{-27}$ kg

$$\omega^2 = \frac{h^2 J(J+1)}{4\pi^2 I^2}$$

$$I = \mu r^2 = \frac{(1.673 \cdot 10^{-27} \text{ kg})(58.06 \cdot 10^{-27} \text{ kg})(0.1274 \cdot 10^{-9} \text{ m})^2}{59.7333 \cdot 10^{-27} \text{ kg}} \\ = 0.0264 \cdot 10^{-45} \text{ kgm}^2$$

$$\omega = \frac{h\sqrt{J(J+1)}}{2\pi I} = \frac{(6.624 \cdot 10^{-34} \text{ Js})\sqrt{2}}{2\pi(0.02 \cdot 10^{-45} \text{ s}^{-1})} = 56.5116 \cdot 10^{11} \text{ radian s}^{-1}$$

**Period of rotation**

$$T = \frac{2\pi}{\omega} = \frac{2\pi}{56.5116 \cdot 10^{11} \text{ s}^{-1}} = 1.112 \cdot 10^{-12} \text{ s}$$

### Example3

the first rotational line of  $^{12}\text{C}^{16}\text{O}$  is observed at  $2B = 3.842335\text{cm}^{-1}$  and that of  $^m\text{C}^{16}\text{O}$  at  $2B' = 3.67337\text{cm}^{-1}$  calculate the atomic weight of  $^m\text{C}$  assuming the of  $^{16}\text{O}$  to be 15.9949.

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

$$\frac{\mu'}{\mu} = \frac{27.9949}{12 * 15.9949} \frac{m * 15.9949}{(m + 15.9949)}$$

$$\frac{B}{B'} = \frac{3.84235\text{cm}^{-1}}{3.67337\text{cm}^{-1}}$$

*the atomic weight is  $m = 13.001$*

### Example4

**E** For diatomic molecule  $^1\text{H}^{19}\text{F}$  the energy for rotation at transition  $J=0$  to  $J=1$  is 500.72 GHz

Assuming the molecule to be rigid rotor give the energy of transition at  $J=3$  to  $J=4$  in  $\text{cm}^{-1}$

Calculate the energy transition at  $J=3$  to  $J=4$  if we have  $^2\text{D}^{19}\text{F}$  assuming that the two molecules have the same bond length?

Calculate the bond length?

Mass molar for hydrogen is 1 uma , 19 uma for fluorine and 2 for Deuterium

$$2B=500.72\text{GHz}$$

$$J = 0 \text{ to } j = 1 \quad 2B$$

$$J = 1 \text{ to } j = 2 \quad 2B$$

$$J = 2 \text{ to } j = 3 \quad 2B$$

$$J = 3 \text{ to } j = 4 \quad 2B$$

The transition energy for J=3 to J=4

$$4 * 2B = \frac{4 * 500.72 \cdot 10^9}{3 \cdot 10^{10}} = 66.8 \text{ cm}^{-1}$$

$$\mu = \frac{1 * 19}{1 + 19} * 1,7 \times 10^{-27} \text{ kg} = 1.615 \cdot 10^{-27} \text{ kg}$$

$$\mu' = \frac{2 * 19}{2 + 19} * 1,7 \times 10^{-27} = 3,076 \cdot 10^{-27} \text{ kg}$$

$$\frac{2B}{2B'} = \frac{\mu'}{\mu}; 2B' = \mu \frac{2B}{\mu'} = \frac{16.15 * 10^{-27} \text{ kg}}{3,076 \cdot 10^{-27} \text{ kg}} \cdot 66.8 \text{ cm}^{-1} = 35.07 \text{ cm}^{-1}$$

The bond length

$$2B = \frac{h}{4cI\pi^2}, I = \frac{h}{8cB\pi^2} = \frac{6.626 \cdot 10^{-34} \text{ Js}}{4 * 3 * 10^8 * 68.8 * 10^2 * 3.14 * 3.14} \\ = 8.14009 * 10^{-47} \text{ kgm}^2$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{8.14009 * 10^{-47}}{1.615 \cdot 10^{-27}}} = 2.24 \cdot 10^{-10} \text{ m} = 2.24 \text{ \AA}$$

## Non-rigid rotator

### Biatomic molecules

The centrifugal force  $m r \omega^2$  is balanced by an inrush force which accompanies the stretching of the connection  $r_0$ . The stretching of the bond which occurs for the angular velocity is therefore given by the expression)(Gupta 2007)

$$k(r - r_0) = m v^2 / r = m r \omega^2 \text{ (harmonic field )}$$

**The rearrangement, gives the distorted bond length as**

$$r = \frac{k r_0}{k - m \omega^2}$$

Since the energy of the rotating system is the sum of kinetic and potential energy, the total energy can be written as

$$E = \frac{1}{2} I \omega^2 + \frac{1}{2} k (r - r_0)^2$$

**So,**

$$\begin{aligned} E &= \frac{1}{2} I \omega^2 + \frac{1}{2} \frac{k m^2 r^2 \omega^4}{k^2} \\ &= \frac{1}{2} I \omega^2 + \frac{1}{2} \frac{(I \omega^2)^2}{k r^2} \end{aligned}$$

**The angular momentum ; quantum restriction quantified by**

$$\sqrt{J(J+1)} * \left( \frac{h}{2\pi} \right)$$

**We can deduce**

$$E_J = \frac{h^2}{8\pi^2 m I} J(J+1) + \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2$$

**Replacing r with**

$$r = \frac{k r_0}{k - m \omega^2}$$

**We will have**

$$E_J = \frac{h^2}{8\pi^2 m r_0^2} J(J+1) - \frac{h^4}{16\pi^2 m^2 r_0^6} J^2(J+1)^2 + \frac{h^4}{32\pi^4 m^2 r_0^6} J^2(J+1)^2$$

$$= \frac{h^2}{8\pi^2 m r_0^2} J(J+1) - \frac{h^4}{32\pi^2 m^2 r_0^6} J^2(J+1)^2$$

Multiplying by  $\frac{1}{hc}$  o get the wave number

$$\begin{aligned} &= \frac{h}{8\pi^2 m I c} J(J+1) - \frac{h^3 m}{32\pi^4 I^3 k c} J^2(J+1)^2 \\ &= \bar{B} J(J+1) - \frac{4\bar{B}^3}{\bar{\omega}^2} J^2(J+1)^2 \end{aligned}$$

$$\bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \quad \text{Vibration energy calculated in wave number}$$

For rotational energy levels it is customary to write this expression as

$$\text{wave numbre of the levels} = \bar{B} J(J+1) - \bar{D} J^2(J+1)^2$$

$\bar{D}$  Centrifugal distortion constant

The value of  $\bar{D}$  is always smaller than that of  $\bar{B}$ .

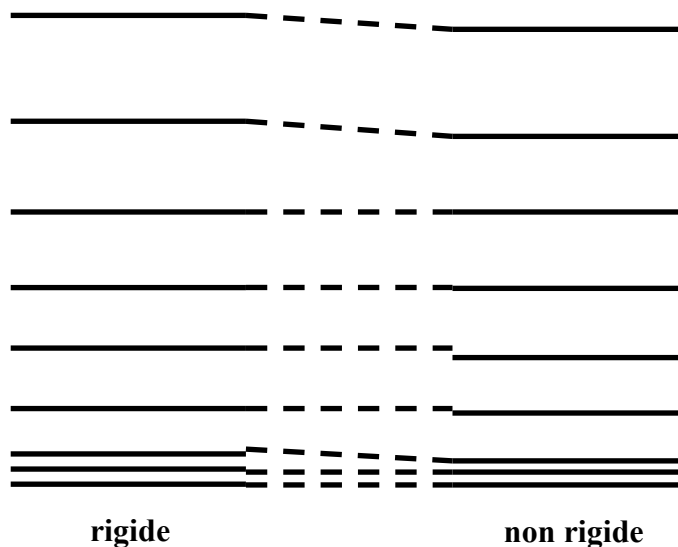


Fig centrifugal effect on the energy

### Example

Rotational and centrifugal distortion constant of HCl molecule are  $10.593 \text{ cm}^{-1}$  and  $5.3 \cdot 10^{-4} \text{ cm}^{-1}$  respectively .calculate the vibrational frequency and force constant of the

centrifugat distorsion constante molecule  $\frac{4B^3}{\bar{\nu}^2}$

$$\bar{\nu} = \sqrt{\left[ 4 \frac{(10.593 \text{ cm}^{-1})^3}{5.3 \cdot 10^{-4} \text{ cm}^{-1}} \right]} = 2995.2 \text{ cm}^{-1} = 2995.2 \cdot 10^2 \text{ m}^{-1}$$

Force constante  $k = 4\pi^2 c^2 \mu \bar{\nu}^2$

$$\mu = \frac{(1.673 \cdot 10^{-27} \text{ kg})(58.06 \cdot 10^{-27} \text{ kg})}{59.733 \cdot 10^{-27} \text{ kg}} = 1.6261 \cdot 10^{-27} \text{ kg}$$

$$k = 4\pi^2 \left( 3 \cdot 10^8 \frac{\text{m}}{\text{s}} \right)^2 (1.6261 \cdot 10^{-27} \text{ kg})(2995.2 \cdot 10^2 \text{ m}^{-1})^2 \\ = 517.8 \text{ Nm}^{-1}$$

The transition energy for the non-rigid is given by the expression

$$\bar{\nu}_{(J \rightarrow J+1)} = \bar{B}(J+1)(J+2) - \bar{D}(J+1)^2(J+2)^2 - \bar{B}J(J+1) + \bar{D}J^2(J+1)^2 \\ = 2\bar{B}_v(J+1) - 4\bar{D}_v(J+1)^3 \quad \text{cm}^{-1}$$

As the term  $4\bar{D}(J+1)^3$  is always positive, the separation between energy levels decreases as J increases. It can say, in the excited states the amplitude of vibration of the atoms is expected to be larger which increases the moment of inertia.

The data in the table shows the approximations to converge to the results

experimental for HCl.

Transitio n J→J+1	$\bar{\nu}_{\text{observé}} \text{ cm}^{-1}$	$\bar{\nu}_{\text{cal}} = 2\bar{B}(J+1)$ avec $\bar{B} = 10.34$ $\text{cm}^{-1}$	$\bar{\nu}_{J \rightarrow J+1} = 2\bar{B}(J+1) - \bar{D}(J+1)^3$ $\bar{B} = 10.395 \text{ cm}^{-1}, \bar{D} =$ $0.0004 \text{ cm}^{-1}$
3→4	83.08	82.72	83.06

4→5	104.1	103.40	103.75
5→6	124.30	124.08	124.39
6→7	145.03	144.76	144.98
7→8	165.51	165.44	165.50
8→9	185.86	186.12	185.94
9→10	206.38	206.80	206.30
10→11	226.50	227.48	226.55

If the force field is inharmonic the expression of energy levels becomes

$$\epsilon_j = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 + \dots \text{ cm}^{-1}$$

H,K,etc., Small constants depend on the geometry of the molecule. It should be noted that modern spectroscopic data are given by the harmonic force field formula.

J	$\bar{\nu}_{obs}$	$\bar{\nu}_{cal}$	$\overline{\Delta\nu}_{obs}$	$B(1/2^* \overline{\Delta\nu}_{obs})$	r(nm)
0	41.08	41.11	41.11	20.56	0.0929
1	82.19	82.18	40.96	20.48	0.0931
2	123.15	123.15	40.85	20.43	0.0932
3	164.00	163.94	40.62	20.31	0.0935
4	204.62	204.55	40.31	20.16	0.0938
5	244.93	244.89	40.08	20.04	0.0941
6	285.01	284.93	39.64	19.82	0.0941

7	324.65	324.61			
			39.28	19.64	0.0951
8	363.93	402.70			
			38.89	19.45	0.0955
9	402.82	403.72			
			38.31	19.16	0.0965
10	441.13	441.00			
			37.83	18.91	0.0963
11	478.94	478.74			

Tableau observed data of HF spectrum  $\bar{\nu} = 2B(J+1)$

Example

As shown in table The observed rotation spectrum of HF shows the transition  $J = 0 \rightarrow J = 1$  the absorption at  $41.11\text{cm}^{-1}$ , the the spacing between adjacent absorption is  $40.08\text{cm}^{-1}$  around  $J = 5 \rightarrow J = 6$  transition and  $37.81\text{ cm}^{-1}$  around  $J = 10 \rightarrow J = 11$  transition .Calculate B values

$$J = 0 \rightarrow J = 1 \quad 2B = 41.11\text{cm}^{-1} \quad B = 2056\text{ m}^{-1}$$

$$J = 5 \rightarrow J = 6 \quad 2B = 40.08\text{cm}^{-1}$$

$$J = 10 \rightarrow J = 11 \quad 2B = 37.81\text{ cm}^{-1}$$

$$B = \frac{h}{8\pi^2 Ic}$$

$$B = 2056\text{ m}^{-1} \text{ gives } I = \frac{6.62 \times 10^{-34}\text{Js}}{8\pi^2 \times 2056\text{ m}^{-1} \times 3 \times 10^8\text{m/s}} \\ = 1.362 \times 10^{-47}\text{kgm}^2$$

$$\mu = \frac{19 \times 1}{19 + 1} (6.023 \times 10^{23})^{-1} = 0.15658 \times 10^{-5}\text{kg}$$

$$B = 2004 \text{ cm}^{-1} \quad I = 1.3971 \cdot 10^{-47} \text{ kgm}^2$$

$$B = 1891 \text{ cm}^{-1} \quad I = 1.481 \cdot 10^{-47} \text{ kgm}^2$$

The transition including centrifugal distortion ,the expression of the frequency of transition is

$$F_j = \Delta \bar{\nu} = 2B(J + 1) - 4D(J + 1)^3$$

As the term  $4D(J + 1)^3$  is always positive, the separation between energy levels decreases as J increases. In other words, in the excited states the amplitude of vibration of the atoms is expected to be larger which increases the moment of inertia.

J	$\bar{\nu}_{obs}$	$\bar{\nu}_{cal}$	$\overline{\Delta\nu}_{obs}$	$B(1/2^* \overline{\Delta\nu}_{obs})$	r(nm)	Transitions $2B(J+1) - 4D(J+1)^3$
0	41.08	41.11				
			41.11	20.56	0.0929	$2B - 4D$
1	82.19	82.18				
			40.96	20.48	0.0931	$2B2 - 4 * 2^3 D$
2	123.15	123.15				
			40.85	20.43	0.0932	$2B3 - 4 * 3^3 D$
3	164.00	163.94				
			40.62	20.31	0.0935	$2B4 - 4 * 4^3 D$
4	204.62	204.55				
			40.31	20.16	0.0938	$2B5 - 4 * 5^3 D$
5	244.93	244.89				
			40.08	20.04	0.0941	$2B6 - 4 * 6^3 D$
6	285.01	284.93				
			39.64	19.82	0.0941	$2B7 - 4 * 7^3 D$
7	324.65	324.61				
			39.28	19.64	0.0951	$2B8 - 4 * 8^3 D$
8	363.93	402.70				
			38.89	19.45	0.0955	$2B9 - 4 * 9^3 D$
9	402.82	403.72				
			38.31	19.16	0.0965	$20B - 4 * 10^3 D$
10	441.13	441.00				
			37.83	18.91	0.0963	$22B - 4 * 11^3 D$
11	478.94	478.74				

Example

Three consecutive lines in rotational spectrum of diatomic molecule are observed at 84.544, 101.355 and 118.355 cm<sup>-1</sup> assign these lines to their appropriate  $J \rightarrow J'$  transition and deduce values of B and D

.Hence evaluate the approximation vibrational frequency of the molecule consider  $D \ll B$

The transition  $J \rightarrow J + 1$  gives the frequency

$$F_j = \Delta \bar{\nu} = 2B(J + 1) - 4D(J + 1)^3$$

$$84.544 \text{ cm}^{-1} = 2B(J + 1) - 4D(J + 1)^3$$

$$101.355 \text{ cm}^{-1} = 2B(J + 2) - 4D(J + 2)^3$$

$$118.355 \text{ cm}^{-1} = 2B(J + 3) - 4D(J + 3)^3$$

$$101.355 - 84.544 = 16.811 \text{ cm}^{-1} = 2B - 4D\{(J + 2)^3 - (J + 1)^3\}$$

Since  $D \ll B$  the value of B can be obtained by neglecting the term of D hence

$$16.811 \text{ cm}^{-1} = 2B$$

$$84.544 \text{ cm}^{-1} = 2 \times 16.811(J + 1)$$

$$J = 4 \text{ (the result must be an integer)}$$

Therefore the line  $84.544 \text{ cm}^{-1}$  corresponds to  $J = 4 \rightarrow J =$

5 transition, the one at  $101.355 \text{ cm}^{-1}$  is due to  $J = 5 \rightarrow J = 6$  and the one at  $118.112 \text{ cm}^{-1}$  is due to  $J = 6 \rightarrow J = 7$ .

$$84.544 \text{ cm}^{-1} = 2B5 - 4D125$$

$$101.355 \text{ cm}^{-1} = 2B6 - 4D216$$

Solving  $B = 8.473 \text{ cm}^{-1}$ ,  $D = 3.7 \times 10^{-4} \text{ cm}^{-1}$

$$D = \frac{4B^3}{\bar{\nu}^2}$$

$$\bar{\nu}^2 = \frac{4(8.473 \text{ cm}^{-1})^3}{3.7 \times 10^{-4} \text{ cm}^{-1}}, \bar{\nu} = 2564.4 \text{ cm}^{-1}$$

## Linear rotator top three atoms (Townes and Schawlow 2013)

The OCS carbon oxysulfide molecule is a linear molecule where the atoms are aligned on the same line. These molecules show a simple spectrum in the microwave region.

The energy levels are given by the formula (in harmonic field)

$$= BJ(J + 1) - DJ^2(J + 1)^2 + \dots \text{ cm}^{-1}$$

The spectrum shows a separation of  $2B$  modified by the distortion constant. The moment of inertia of these molecules is greater than that

of diatomic molecules The value of B must be small and the lines are more and more separated the value of  $B=10B = 10cm^{-1}$

**For diatomic molecule  $B = 1cm^{-1}$**

Triatomic

**for triatomic molecules and larger molecules B become more smaller.**

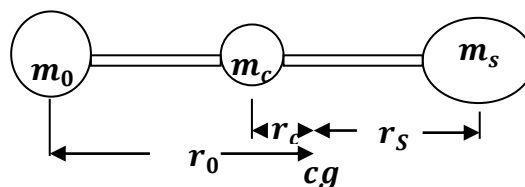
Molecules exhibiting a dipole moment like OCS have a microwave spectrum but molecules lacking a dipole moment are not active in the microwave domain like. OCO (CO<sub>2</sub>). Isotopes have no effect on the dipole moment so the molecule <sup>16</sup>O<sup>18</sup>O remains inactive. the linear (non-cyclic) polyatomic molecule of N atoms has N-1 bonds

**Table the microwave spectrum of OCS.**

Transition	$\bar{\nu}_{obs}(cm^{-1})$	$\Delta\bar{\nu}$	$B(cm^{-1})$
J→J+1			
0→1	.....	2*0.4055	0.2027
1→2	0.8109	0.4054	0.2027
2→3	1.2163	0.4054	0.2027
3→4	1.6217	0.4054	0.2027
4→5	2.0271		

**For the first four transitions the distortion effect is weak for  $B = 0.2027cm^{-1}$**

$$\bar{B} = \frac{h}{8cI\pi^2} = 137,95 * 10^{-47} cm^{-1}.$$



$$I = m_0(r_{co} + r_c)^2 + m_c r_c^2 + m_s(r_{cs} - r_c)^2$$

$$I = M r_c^2 + 2r_c(m_0 r_{co} + m_s r_{cs}) + m_0 r_{co}^2 + m_s r_{cs}^2$$

$$I = m_0 r_{co}^2 + m_s r_{cs}^2 - \frac{(m_0 r_{co} - m_s r_{cs})^2}{M}$$

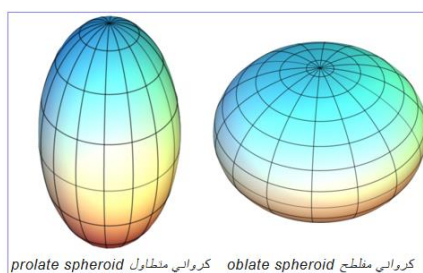
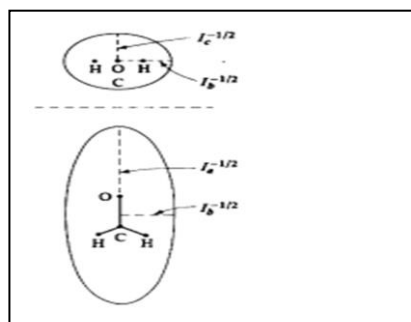
For the molecule  $^{18}\text{OCS}$  the expression of  $I$  is

$$I' = m'_0 r_{co}^2 + m_s r_{cs}^2 - \frac{(m'_0 r_{co} - m_s r_{cs})^2}{M'}$$

The observed spectra show the effect of isotopes, which shows the consistency of the hypotheses with the results found.

**Symmetrical rotator** (Kuhn, Försterling and Waldeck 2009)

These molecules have equal moments of inertia, in this case the molecule does not have a dipole moment, it is transparent in the spectral domain considered but during the deformation a weak dipole moment can appear (generated) so the spectrum obtained is very weak.



*spherical top*  $I_a = I_b = I_c$   
*prolate symmetric top*  $I_a \neq I_b = I_c$   
*oblate symmetric top*  $I_a = I_b \neq I_c$   
*asymmetric top*  $I_a \neq I_b \neq I_c$

$I_a$  takes the small value  $I_c$  the large value

As in a linear molecule, the rotation in a symmetric rotator is accompanied by centrifugal forces which tend to modify the effective moments of inertia. For a rotation around any axis of the molecule, this dynamic effect forces the atoms to move away from the axis of rotation and increases the moment of inertia around this axis.

Energy of a symmetric rotator

As the linear molecule the permitted energy levels can be obtained by classical equation

$$E = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 = \frac{P_A^2}{2I_A} + \frac{P_B^2}{2I_B} + \frac{P_C^2}{2I_C}$$

$P_A, P_B, P_C$  are the angular momentum along the three principal axes. for a symmetrical rotator top  $I_B = I_C$   
the quantum restriction Gives

$$\sqrt{J(J+1)} \frac{h}{2\pi} \quad J = 0, 1, 2 \dots$$

We have three axes, the angular momentum along the principal axis is quantified as

$K \frac{h}{2\pi}$  Avec  $K = 0, \pm 1, \pm 2, \dots, \pm J$  since J is the total angular momentum.

The values plus and minus  $\pm J$  correspond to the possibility of rotation with the hands of the watch or in the opposite direction of the hands of the watch in relation to the main (single) axis, these quantum restrictions lead to

$$P_A^2 = K^2 \left( \frac{h}{2\pi} \right)^2$$

and

$$\begin{aligned} P_A^2 + P_B^2 &= J(J+1) \left( \frac{h}{2\pi} \right)^2 - K^2 \left( \frac{h}{2\pi} \right)^2 \\ E_{K,J} &= K^2 \frac{h^2}{8\pi^2 I_A} + J(J+1) \frac{h^2}{8\pi^2 I_B} - K^2 \frac{h^2}{8\pi^2 I_B} \text{ en erg} \\ &= J(J+1) \frac{h}{8\pi^2 c I_B} + K^2 \left( \frac{h}{8\pi^2 c I_A} - \frac{h}{8\pi^2 c I_B} \right) \text{ en cm}^{-1} \end{aligned}$$

It is still practical to introduce a rotation constant  $\bar{B}$  and  $\bar{A}$  are defined by

$$\bar{B} = \frac{h^2}{8\pi^2 c I_B} \text{ en cm}^{-1}, \bar{A} = \frac{h^2}{8\pi^2 c I_A} = \text{en cm}^{-1} I_A = I_{\parallel}, I_B = I_{\perp}$$

hence

$$\text{wave numbre} = \bar{B}J(J+1) + (\bar{A} - \bar{B})K^2$$

$$J = 0, 1, 2 \dots; K = 0 \pm 1, \pm 2 \dots$$

This expression gives the same energy as the solution of the Schrödinger equation for a symmetrical top. The quantum number  $J$  represents the total angular momentum of the system, however  $K$  determines its component on the principal axis:

This equation corresponds to a rigid top, and a term must be introduced to show the distortion of the connection. The energy shift due to this effect is very small.

The figure shows the energy diagram which illustrates the prediction of the Ket  $J$  values which gives two possibilities. The molecule which has  $I_A$  smaller than  $I_B = I_C$  is called prolate ( $I_{\perp} < I_{\parallel}$  the rotator is called spheroid flattened (oblate) like benzene,  $\text{CH}_3\text{CN}$ ) for such a molecule  $K^2$  is positive. Increasing the value of  $K$  for a given value of  $J$  will increase the energy. The molecule with  $I_A$  larger than  $I_B = I_C$  is called oblate (if  $I_{\perp} > I_{\parallel}$  the rotator is said to be an elongated spheroid (prolate) like a rugby ball example  $\text{CH}_3\text{Cl}$ ) the value of  $K^2$  is negative. a given value of  $J$  the increase in  $K$  decreases the energy. It should be emphasized that the appearance of  $K$  in the equation as a square term leads to the same energy for a state with positive or negative values of  $K$  the energy for that state, so that all levels with  $K \neq 0$  are doubly degenerate.

$$\bar{\nu}_{(J+1, K \rightarrow J, K)} = BJ + 1J + 2 + (A - B)K^2 - [BJ(J+1) + (A - B)K^2]$$

$$= 2B(J+1) \text{ cm}^{-1}$$

The spectrum is independent of  $K$ , the rotation along the axes of symmetry does not induce a change in the dipole moment; the sum of the dipole moments is equal to zero.  $J(J+1)$  and  $K$ . For an prolate rotator

$$F_v(J, K) = B_v J(J+1) - D_J J^2(J+1)^2 + D_J(A_v - B_v)K^2 - D_K K^4 - D_{KJ}(J+1)JK^2 - \dots \quad (***)$$

Three distortion constants namely  $D_J, D_K, D_{KJ}$

$$(the\ transition\ (wave\ number) = 2B \{J + 1\} - 2D_{JK} (J + 1) K^2 - 4D_J (J + 1)^3)$$

The dependence of rotational constants on the vibrational state is assumed implicitly. The correction terms for centrifugal distortion depend only on angular momentum forces. This must be the case, because the distortion effects do not depend on the direction of rotation of the axis orientation. For a rigid symmetric top (the equation) indicates that the authorized transition does not depend on K. This degeneracy K can be partially lifted by a non-zero  $D_{JK}$  term which allows  $K^2$  to enter the rotation frequency expression. From (\*\*), the frequencies of a symmetric molecule exhibiting detectable centrifugal distortion effects are

;

$$v = 2B \{J + 1\} - 2D_{JK} (J + 1) K^2 - 4D_J (J + 1)^3$$

The molecule presents the deformation of elongation and deformation thus the molecule has a dipole moment generating a microwave spectrum

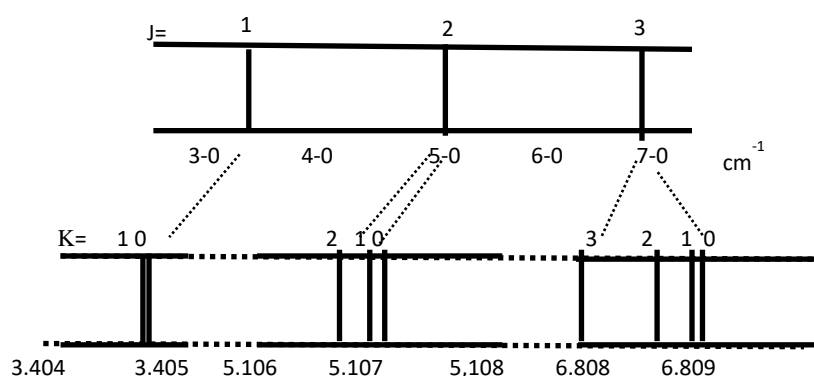


Fig: A diagrammatic representation of rotational spectrum of the symmetric top molecule methane fluoride  $CH_3F$

$$J = 0, K = 0 \quad \bar{\nu}_{JK} = 2B - 4D_J \text{cm}^{-1}$$

$$J = 1, K = 0 \quad \bar{\nu}_{JK} = 4B - 32D_J \text{cm}^{-1}$$

$$K = \pm 1 \bar{\nu}_{JK} = 4B - 32D_J - 4D_{JK} \text{cm}^{-1}$$

$$J = 2, K = 0 \quad \bar{\nu}_{JK} = 6B - 108D_J \text{cm}^{-1}$$

$$K = \pm 1 \bar{\nu}_{JK} = 6B - 108D_J - 6D_{JK} \text{cm}^{-1}$$

$$K = \pm 2 \bar{\nu}_{JK} = 6B - 108D_J - 24D_{JK} \text{cm}^{-1}$$

According to the CH<sub>3</sub>F spectrum we will have the following values

$$B = 0,851204$$

$$D_J = 2,00 * 10^{-6} \text{cm}^{-1}$$

$$D_{JK} = 1,47 * 10^{-5} \text{cm}^{-1}$$

J	K	$\bar{\nu}_{obs} \text{ cm}^{-1}$	$\bar{\nu}_{cal} \text{ cm}^{-1}$
	1		
1	0	3.40475	3.404752
	1	3.40470	3.404693
2	0	5.10701	5.107008
	1	5.10692	5.106920
	2	5.10665	5.106655
3	0	6.80912	6.809120
	1	6.80900	6.809002
	2	6.80865	6.808649
	3	6.80806	6.808062

Table microwave spectrum of methyl fluoride

For a rotator oblate top

$$F(J, K) = B_v J(J + 1) + (C_v - B_v) K^2 - DK^4 - DJ^2[J + 1]^2 - D_{JK} J(J + 1) K^2$$

The transition frequencies are given for both oblate and prolate rotator tops by

$$v(J + 1, k \rightarrow J, K) = F(J + 1, K) - F(J, K)$$

We have

$v(J + 1, k \rightarrow J, K) = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_{J,K}(J + 1)K^2$   
 if  $I_A = I_{\parallel} = I_B = I_{\perp}$  the rotator is said to be spherical (same linear molecule expression)

$$\text{wave number} = \bar{B}J(J + 1)$$

Selection rule

To have an emission or absorption of electromagnetic radiation .  
 For the absorption experiment, the part of the selection rule corresponding to an increase in the appropriate system energy is

$$\Delta J = 0, \pm 1, \dots; \Delta K = 0 \text{ pour } K \neq 0$$

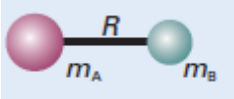
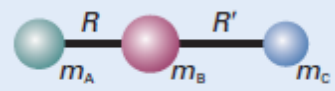
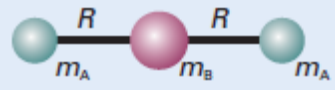
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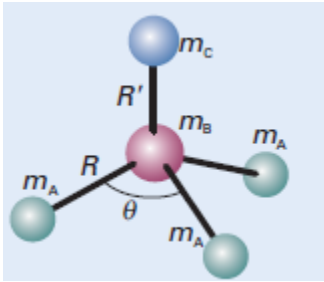
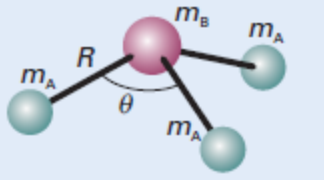
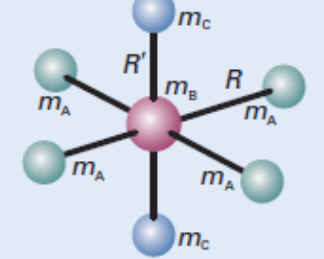
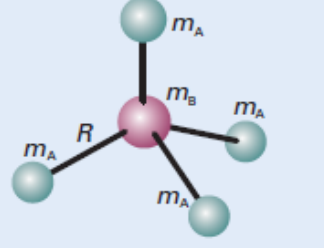
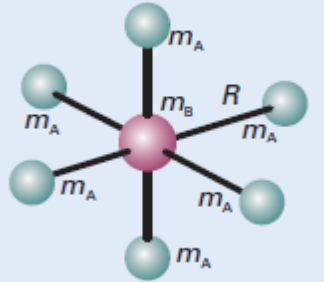
$$\Delta J = \pm 1, \dots; \Delta K = 0 \text{ pour } K = 0$$

For absorption the energy of the system increases the appropriate values

$$\Delta J = +1 \quad \Delta K = 0$$

$$B_v J(J + 1) - D_v J^2(J + 1)^2 + D'_v f(J, k). (\text{Atkins and de Paula 2010})$$

<b>Diatomic rotator</b> 	$I = \mu R^2 \quad \mu = \frac{m_A m_B}{m}$
<b>Tri atomic linear</b> 	$I = m_A R^2 + m_C R'^2 - \frac{(m_A R + m_C R')^2}{m}$
	$I = m_A R^2$

<p><b>rotator symetric</b></p> 	$I_{\parallel} = 2m_A(1 - \cos\theta)R^2$ $I_{\perp} = m_A(1 - \cos\theta)R^2 + \frac{m_A}{m}(m_B + m_C)(1 + 2\cos\theta)R^2 + \frac{m_C}{m} \left\{ (3m_A + m_B)R' + 6m_A R \left[ \frac{1}{3}(1 + 2\cos\theta) \right]^{\frac{1}{2}} \right\} R'$
	$I_{\parallel} = 2m_A(1 - \cos\theta)R^2$ $I_{\perp} = m_A(1 - \cos\theta)R^2 + \frac{m_A m_B}{m}(1 + 2\cos\theta)R^2$
	$I_{\parallel} = 4m_A R^2$ $I_{\perp} = 2m_A R^2 + 2m_A R'^2$
<p><b>Spheric rotator</b></p> 	$I = \frac{8}{3}m_A R^2$
	$I = 4m_A R^2$

The rotating atoms are subjected to centrifugal forces deforming the geometry of the molecule, and thus modifying the moment of inertia which suggests that the length of the bond has undergone stretching (elongation). The energy levels are slightly brought together which does not predict the model of a rigid rotator. This effect is taken into account by subtracting a term from the energy which results in the expression;

$$E_J = E_{rotational} = \frac{1}{I} * \frac{h^2}{8\pi^2} * J * (J + 1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2 (J + 1)^2 (**)$$

$$\epsilon_j = \frac{E_j}{hc} = * \frac{h}{8\pi^2} * \frac{1}{Ic} * J * (J + 1) = BJ(J + 1) - DJ^2(J + 1)^2 cm^{-1}$$

$$\frac{h^4}{32\pi^4 I^2 r^2 k} = D$$

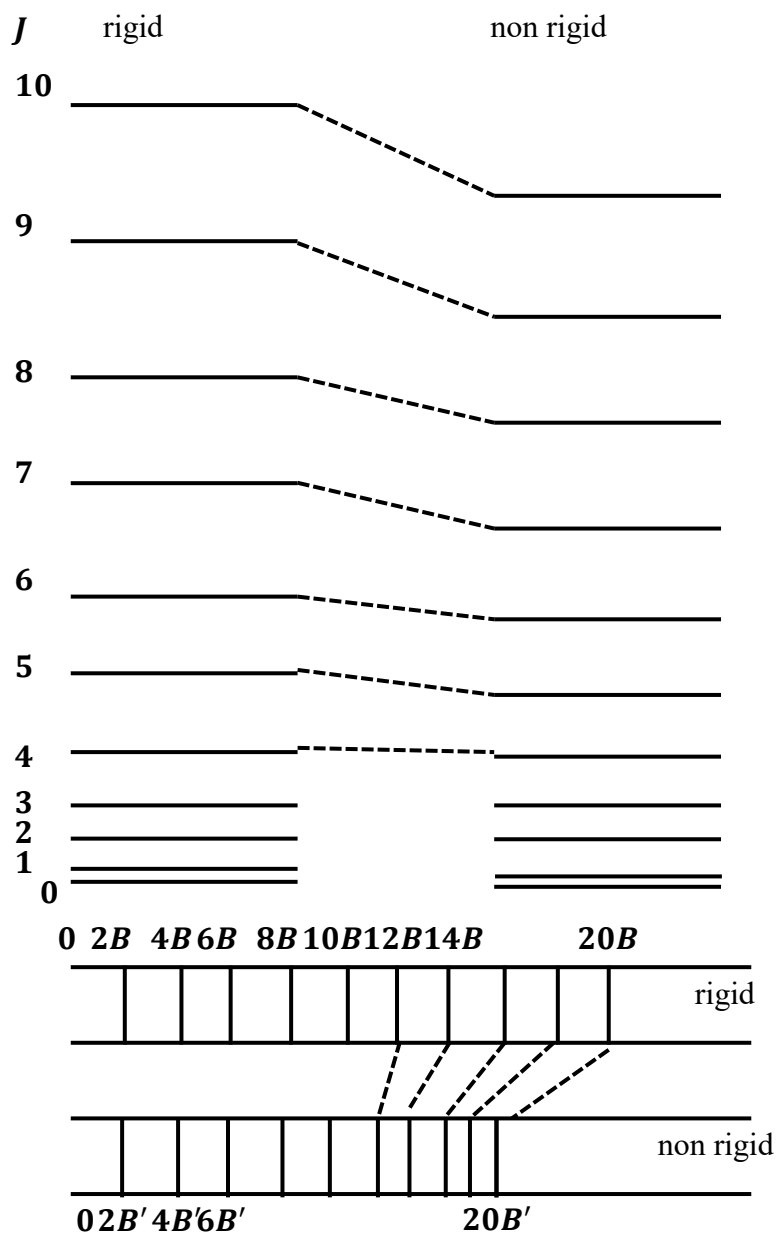
(\*\*)This expression shows that the field of the force is harmonic if the field of the force is inharmonic the expression energy levels becomes

$$\epsilon_j = BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + KJ^4(J + 1)^4 + \dots cm^{-1}$$

H,K,etc., Small constants depend on the geometry of the molecule. It should be noted that modern spectroscopic data are given by the harmonic force field formula (\*\*).

D in terms of B

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2} ; \bar{\omega} \text{ is the vibration frequency of the bond}$$



**Fig : The changing in rotational levels and rotational spectrum when passing from rigid to non-rigid diatomic molecule**

A certain number of nonlinear molecules can be symbolized by a symmetric rotator having two moments of inertia, which is a rigid rotator in which the moments of inertia about two axes are the same  $I_{\perp}$  but are different from the third  $I_{\parallel}$  (all three being different from zero, if  $I_{\perp} > I_{\parallel}$  the rotator is said to be a spheroid elongated like a rugby ball example  $\text{CH}_3\text{Cl}$  if  $I_{\perp} < I_{\parallel}$  the rotator is said to be a spheroid flattened like benzene). Ammonia,  $\text{NH}_3$ , and phosphorus pentachloride,  $\text{PCl}_5$  are examples. The energy levels of a symmetric rotor are determined by two quantum numbers, J and K,

$$E_{J,K} = hcBJ(J + 1) + hc(A - B)K^2$$

The rotation constants A and B correspond to the moments of inertia parallel and perpendicular to the axis of the molecule

$$A = \frac{h}{8\pi cI_{\parallel}}; B = \frac{h}{8\pi cI_{\perp}}$$

The molecule has the total angular momentum (J) which is the sum of all the angular moments (two directions of rotation) The quantum number K (angular momentum along the principal axis) indicates the amplitude of the rotation of the molecule around its axis: when  $K = 0$ , the molecule flips completely; when  $K = \pm J$ , it rotates mainly around its axis of symmetry. Intermediate values of K correspond to a mixture of the two rotation modes. The spherical rotor is a special case of symmetrical rotor, it is a rigid body having three equal moments of inertia (like a sphere). Methane,  $\text{CH}_4$ , and the octahedral molecule  $\text{SF}_6$  are examples..

when  $I_{\parallel} = I_{\perp}$ ,  $A = B$  and the energy levels are simplified by giving the same expression as in the equation

$$E_J = hcBJ(J + 1)$$

### Rotational Transitions(Nugent 1959)

A general selection rule specifies the general characteristics that a molecule must possess to have a spectrum of a given type (in other words, what conditions must the molecule satisfy so that it

can absorb or emit in the microwave region). For a rotation of a molecule to give rise to an absorption or emission spectrum, the molecule must be polar (with a dipole moment). The classic basis of this rule is that a stationary observer who watches the rotation of the polar molecule sees its partial charges move forward or backward, and their movement induces an oscillation of the field. tetrahedral ( $\text{CH}_4$ , for example), octahedral ( $\text{SF}_6$ ), linear symmetric ( $\text{CO}_2$ ), and diatomic mononuclear ( $\text{H}_2$ ) molecules therefore do not have rotation spectra. The heteronuclear diatomic molecule ( $\text{HCl}$ ) and the less symmetrical polar polyatomic molecules ( $\text{NH}_3$ ) have rotation spectra. A specific selection rule indicates the quantum states between which transitions can occur, as long as these are permitted by the general selection rule. For rotation transitions, the specific selection rules are which transitions can occur, as long as these are allowed by the general selection rule. For rotation transitions, the specific selection rules are

$$\Delta J = \mp 1, \Delta K = 0$$

Example

A  $^{14}\text{NH}_3$  molecule is symmetric rotor bond length 101.2 pm and HNH bond angle  $106.7^\circ$ . calculate its rotational terms.

$$m_A = 1.0078u, m_B = 14.0031u, R = 101.2 \text{ pm and } \theta = 106.7^\circ$$

$$\begin{aligned} I_{\parallel} &= 2m_A(1 - \cos\theta)R^2 \\ &= 2 * 1.0078 * 1.66054 \times 10^{-27} * (1 - \cos 106.7) \\ &\quad * (101.2 * 10^{-12})^2 = 4.4128 * 10^{-47} \text{ kg m}^2 \end{aligned}$$

$$I_{\perp} = m_A(1 - \cos\theta)R^2 + \frac{m_A m_B}{m} (1 + 2\cos\theta)R^2 = 2.8059 * 10^{-47} \text{ kg m}^2$$

$$\text{Hence } A = \frac{h}{4\pi c I_{\parallel}} = 6.344 \text{ cm}^{-1} \text{ and } B = \frac{h}{4\pi c I_{\perp}} = 9.777 \text{ cm}^{-1}$$

$$F(J, K) = BJ(J + 1) + (A - B)K^2 \quad J = 0, 1, 2, \dots \quad K = 0, \pm 1, \pm 2, \dots, \pm J$$

$$F(J, K) = 9.977J(J + 1) - 3.633K^2 \text{ cm}^{-1}$$

For  $J = 1$ , the energy needed for the molecule to rotate mainly about its figure axis ( $K = \pm J$ ) is equivalent to  $16.321 \text{ cm}^{-1}$  (489.3 GHz), but

End over End rotation(  $K = 0$ ) corresponds to 19.95 cm<sup>-1</sup> (598.1GHz).

Example 1

$$E_{J,K} = hcBJ(J + 1) + hc(A - B)K^2$$

Write the transitions

$$E(J + 1, K) - E(J, K) = 2BJ(J + 1)$$

The transitions is independent of  $K$

<b>J=0</b>	<b>K=0</b>	$E_{0,0} = 0$	$\Delta J = 1 - 0 \quad \Delta K$ $= 0 - 0 \quad E_{1,0}$ $- E_{0,0}$	$E_{1,0}$ $- E_{0,0}$ $= 2hcB$
<b>J=1</b>	<b>K=0</b>	$E_{1,0} = 2hcB$		
	<b>K=1</b>	$E_{J,K} = 2hcB + hc(A - B)$	$\Delta J = 2 - 1 \quad \Delta K$ $= 0 - 0 \quad E_{2,0}$ $- E_{1,0}$	<b><math>4hcB</math></b>
	<b>K=-1</b>	$E_{J,K} = 2hcB + hc(A - B)$	$\Delta J = 2 - 1 \quad \Delta K$ $= 1 - 1 \quad E_{2,1}$ $- E_{1,1}$	
<b>J=2</b>	<b>K=0</b>	$E_{J,K} = 6hcB$	$\Delta J = 2 - 1 \quad \Delta K$ $= -1$ $- (-1) \quad E_{2,-1}$ $- E_{1,-1}$	
	<b>1</b>	$E_{J,K} = 6hcB + hc(A - B)$		

	2	$E_{J,K} = 6hcB + 4hc(A - B)$		
	-1	$E_{J,K} = 6hcB + hc(A - B)$		
	-2	$E_{J,K} = 6hcB + 4hc(A - B)$		

### **Stark effect (Sathyanarayana 2015)**

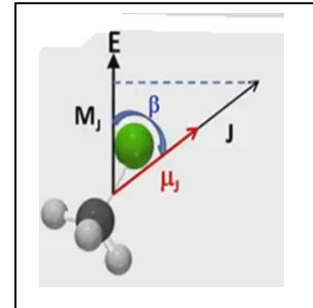
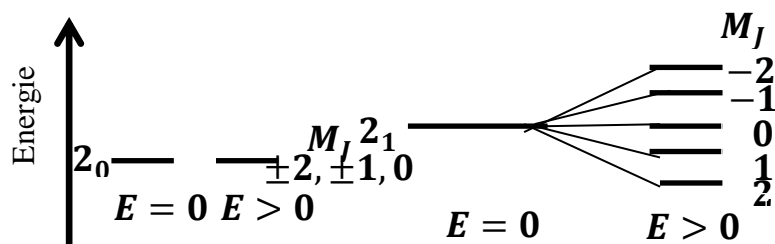
Recalling that the Zeeman effect is the effect of magnetic induction energy on the hydrogen emission spectrum which induces the bursting of Bohr lines which leads to the observation of the effect of magnetic moment which bursts the lines which makes the magnetic moment appear, the latter is linked to the quantum box and the sublayers. Likewise for the Stark effect which is an effect of the external electric field which also induces the bursting of lines (separation of states) the calculation of energies shows the appearance of a new quantum number  $M_J=0, \pm 1, \dots, \pm J$ ; the states of degeneration are  $2i+1$

When the electric field is applied, it interacts with the dipole moment of the molecule. According to classical physics, the interaction energy is given by  $\vec{E} \cdot \vec{\mu}$  since both are vector quantities. If the angle between the two vectors is  $\Theta$ , the interaction energy can be written as  $-\mu E \cos\theta$ , where  $\mu$  and  $E$  are the lengths of the vectors which represent the dipole moment and the electric field, respectively. Another way of thinking about it is that the interaction depends on the projection of along the direction of the electric field. For molecules

linear, the angular momentum vector is always perpendicular to the internuclear axis and therefore to the dipole moment. So the average rotation brings the dipole completely to zero, and there is therefore no first order Stark effect. There is, however, a second-order Stark effect in the presence of strong electric fields,

where the division of energy levels goes as the square of the Electric Field Strength.

$$\left[ \begin{aligned} E_{stark}^2 &= -\frac{\mu^2 E^2 (J(J+1) - 3M_J^2) M_J}{2hc\bar{B}J(J+1)(2J+1)(3J+2)} \quad J \neq 0 \\ E_{stark}^2 &= -\frac{\mu^2 E^2}{6hc\bar{B}} \quad J = 0 \end{aligned} \right.$$



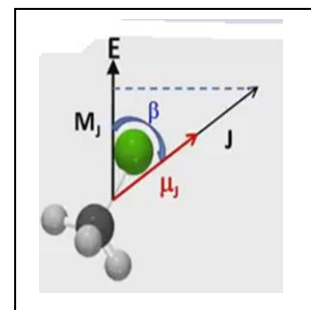
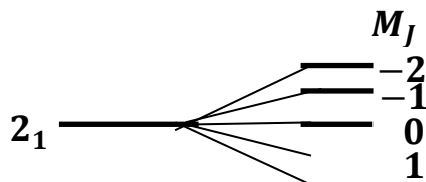
Example

CH3Cl at a dipole moment of  $3.123331107 \text{ cm}^{-1}\text{mV}^{-1}$  evaluate the energy of the Stark effect (first order,  $K=1$ ) from state  $2_1$  knowing that the molecule is exposed to an electric field of  $2 \text{ kV/m}$ .

$$E_{stark}^1 = -\frac{\mu E K M_J}{J(J+1)}, \mu E = 0,062466 \text{ cm}^{-1}$$

$$J = 2, K = 1, M_J = \mp 2, \mp 1, 0$$

$$\begin{aligned} E_{stark}^1 &= \frac{\mu E}{3} = 0.020822, E_{stark}^1 = \frac{\mu E}{6} 0.010411, 0 \text{ cm}^{-1}, -\frac{\mu E}{3} \\ &= -0.020822 \text{ cm}^{-1}, -\frac{\mu E}{6} = 0.020822 \text{ cm}^{-1} \end{aligned}$$



$$E = 0 \quad \overline{\overline{E > 0}}^2$$

Example1

The first several Raman frequency of  $^{14}\text{N}_2$  are 19908; 27857 ; 35812 ; 43762 ; 51721 and 59662  $\text{cm}^{-1}$  these lines are due to pure rotational transitions with  $j = 1, 2, 3, 4$  5 and 6 the reduce mass is  $162651 * 10^{-26} \text{ Kg}$  What is the internuclear distance  $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{Hz}^{-1}$ .

$$27857 - 19908 = 7949$$

$$35812 - 27857 = 7955$$

$$35812 - 43762 = 7950$$

$$51721 - 43762 = 7959$$

$$59662 - 5172 = 7941$$

$$\frac{7949 + 7955 + 7950 + 7959 + 7941}{5} = 4B = 7.951$$

$$B = 19878 \text{m}^{-1} \quad ; \quad r_{eq} = \left( \frac{h}{8\pi^2 c \mu B} \right)^{\frac{1}{2}} =$$

$$\left[ \frac{6.62310^{-34} \text{Js}}{8\pi^2 * 3 * 10^8 \text{ms}^{-1} 12651 * 10^{-26}} \right]^{\frac{1}{2}} = 110 \text{ pm}$$

$$\Delta E_J^{J+2} = E_{J+2} - E_J$$

$$= \frac{1}{I} * \frac{h^2}{8\pi^2} * (J+2) * ((J+2)+1) - \frac{1}{I} * \frac{h^2}{8\pi^2} * J * (J+1)$$

$$\frac{-D(J+2) * (j+3)^2 + D(J) * (j+1)^2}{B * ((J+2) * ((J+2)+1) - J * (J+1))}$$

$$-D[(J+2)^2 * (j+3)^2 - (J)^2 * (j+1)^2]$$

J=1

$$19908 = B * ((1+2) * ((1+2)+1) - 1 * (1+1))$$

$$-D[(1+2)^2 * (1+3)^2 - (1)^2 * (1+1)^2]$$

$$19908 = (10B) - (104D) \dots \dots \dots 1$$

$$27857 = B * ((2 + 2) * ((2 + 2) + 1) - 2 * (2 + 1))$$

$$-D[(2 + 2)^2 * (2 + 3)^2 - (2)^2 * (2 + 1)^2]$$

$$27857 = B * (16) - 364D \dots \dots \dots 2$$

$$\underline{2*10^{-1}*16}$$

$$\left( \frac{27857 * 10 - 19908 * 16}{1664} \right) = 356,64 \text{ cm}^{-1}$$

Example2

Calculate the ratio of molecules in typical excitation state rotational ,vibrational and electric energy level to that lowest ,energy level, assuming that the levels are 30 cm<sup>-1</sup>,1000cm<sup>-1</sup> and 40000cm<sup>-1</sup>,respectively above the lowest energy level ,the rotational level for J=4

Calculate the ratio of molecules in typical excitation state rotational ,vibrational and electric energy level to that lowest ,energy level, assuming that the levels are 30 cm<sup>-1</sup>,1000cm<sup>-1</sup> and 40000cm<sup>-1</sup>,respectively above the lowest energy level ,the rotational level for J=4

$$\frac{N_J}{N_0} = \frac{2J + 1}{1} e^{\left( -\frac{6.626 \cdot 10^{-34} \text{ Js} \cdot 2.998 \cdot 10^{10} \text{ cm s}^{-1} \cdot 30 \text{ cm}^{-1}}{1.381 \cdot 10^{-23} \text{ JK}^{-1} \cdot 298 \text{ K}} \right)} = 7.786(25^\circ \text{C})$$

8.70at 1000°C

	25°C		1000°C	
J	30	15	15	30
0	0,865187869	0,93015476	0,966669484	0,983193513
1	2,595563608	2,79046427	2,900008453	2,94958054
2	4,325939346	4,65077378	4,833347422	4,915967566

3	6,056315085	6,51108329	6,766686391	6,882354593
4	7,786690823	8,3713928	8,70002536	8,848741619
5	9,517066562	10,2317023	10,63336433	10,81512865
6	11,2474423	12,0920118	12,5667033	12,78151567
7	12,97781804	13,9523213	14,50004227	14,7479027
8	14,70819378	15,8126308	16,43338124	16,71428973
9	16,43856952	17,6729404	18,36672021	18,68067675
10	18,16894525	19,5332499	20,30005917	20,64706378
11	19,89932099	21,3935594	22,23339814	22,6134508
12	21,62969673	23,2538689	24,16673711	24,57983783
13	23,36007247	25,1141784	26,10007608	26,54622486
14	25,09044821	26,9744879	28,03341505	28,51261188
15	26,82082395	28,8347974	29,96675402	30,47899891
16	28,55119968	30,6951069	31,90009299	32,44538594
17	30,28157542	32,5554164	33,83343196	34,41177296

For vibrational energy level for  $1000\text{ cm}^{-1}$

$$\frac{N_v}{N_0} = e^{\left( -\frac{6.626 \cdot 10^{-34} \text{Js} \cdot 2.998 \cdot 10^{10} \text{ cm s}^{-1} \cdot 1000 \text{ cm}^{-1}}{1.381 \cdot 10^{-23} \text{ JK}^{-1} \cdot 298 \text{ K}} \right)} = 8.01 \cdot 10^{-3} (25^\circ \text{C})$$

$$= 0.323 (1000^\circ \text{C})$$

For electronic energy level

$$\frac{N_e}{N_0} = e^{\left( -\frac{6.626 \cdot 10^{-34} \text{Js} \cdot 2.998 \cdot 10^{10} \text{ cm s}^{-1} \cdot 40000 \text{ cm}^{-1}}{1.381 \cdot 10^{-23} \text{ JK}^{-1} \cdot 298 \text{ K}} \right)} = 1.40 \cdot 10^{-84} (25^\circ \text{C})$$

$$= 2.35 \cdot 10^{-20} (1000^\circ \text{C})$$

The rotational energy levels are extremely populated than are vibrational energy levels which in turn are much heavily populated than electronic energy levels.

The calculation also show who the population increase with increasing temperature

This can explain the hot bond and overtones absorption in infrared domain

## Exercises

**Ex**

give the units of the expressions

$$\frac{h^2}{8\pi^2 I}, \frac{h}{8\pi^2 I c}$$

**Ex1**

Calculate the rotational energy levels in joule for  $J=0, 1, 2$  for  $^{12}\text{C}^{16}\text{O}$  then transform the units into  $\text{cm}^{-1}$  the length of the bond  $1,11283 \text{ \AA}$  ( $0,11283 \cdot 10^{-10} \text{ cm}$ )

Calculate frequencies?

**Ex2**

The wave number to excite the molecule  $^1\text{H}^{35}\text{Cl}$  (rigid) is  $63.56 \text{ cm}^{-1}$  for the transition  $J=0 \leftarrow 1$

Calculate the moment of inertia?

Calculate bond length?

**Ex3**

The wave number of an incident wave in RAMAN spectrophotometer =  $20623 \text{ cm}^{-1}$

What is the stock radiation diffusion wavenumber for  $J_4 \leftarrow 2$  transition of  $^{16}\text{O}_2$ ?

**Ex4**

The RAMAN rotation spectrum of de  $^{19}\text{F}$  ( $m(^{19}\text{F})=18,9984 \text{ u}$ ) presents a series of lines spaced  $0,9752 \text{ cm}^{-1}$  and an equivalent series of antistock lines

Calculate the bond length of the molecule?

**Ex5**

Which molecules exhibit a RAMAN rotation spectrum?

**CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CH<sub>3</sub>, SF<sub>6</sub>, N<sub>2</sub>O?**

**Ex6**

**Calculate the most populated rotational level of Br<sub>2</sub> ( $\bar{\nu}$  321cm<sup>-1</sup>) between the first and second excited vibrational states at 298K and 800K?**

**Ex7**

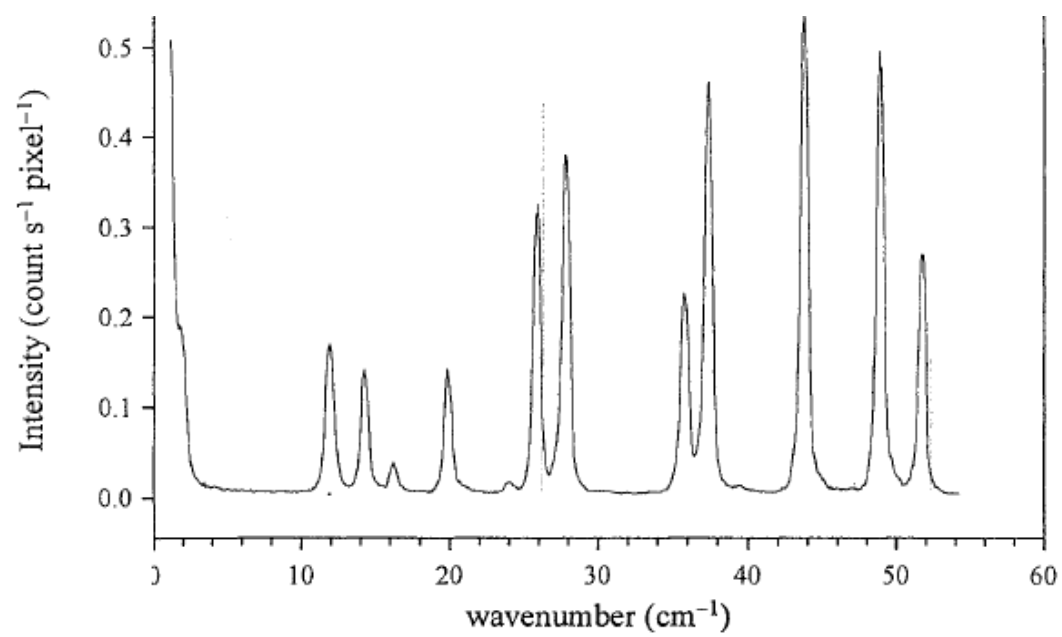
**Calculate the energy for the radiation of wave number  $\bar{\nu} = 1.00\text{cm}^{-1}$  what type of molecular process does this radiation correspond to?**

région	Micro-wave	far infrared	Infrared	Visible UV
<b>Frequency/Hz</b>	<b><math>10^9 - 10^{11}</math></b>	<b><math>10^{11} - 10^{13}</math></b>	<b><math>10^{13} - 10^{14}</math></b>	<b><math>10^{14} - 10^{16}</math></b>
<b>Wave lenght /m</b>	<b><math>3 * 10^{-1} - 3 * 10^{-3}</math></b>	<b><math>3 * 10^{-3} - 3 * 10^{-5}</math></b>	<b><math>3 * 10^{-5} - 6,9 * 10^{-7}</math></b>	<b><math>6,9 * 10^{-7} - 2 * 10^{-7}</math></b>
<b>Wave number /cm<sup>-1</sup></b>	<b>0,033 – 3,3</b>	<b>3,3 – 3 30</b>	<b>330 – 14500</b>	<b>14500 – 50000</b>
<b>Energy /Jmolécule<sup>-1</sup></b>	<b><math>6,6 * 10^{-25} - 6,6 * 10^{-23}</math></b>	<b><math>6,6 * 10^{-23} - 6,6 * 10^{-21}</math></b>	<b><math>6,6 * 10^{-21} - 2,9 * 10^{-19}</math></b>	<b><math>2,9 * 10^{-19} - 1,0 * 10^{-18}</math></b>
<b>molecular Proces</b>	<b>polyatomic Rotation</b>	<b>Rotation small molecules</b>	<b>Vibration and flexible bands</b>	<b>Electronic transitions</b>

**Ex**

**The pure rotational raman spectra N<sub>2</sub> and O<sub>2</sub> mixture with laser power 1W and 514.5nm is given below rebuilt the spectre theoretically ? Indicate absorption line for each molecule ?**

$$r_{N=N} = 145\text{pm} \quad r_{O=O} = 121\text{pm}$$

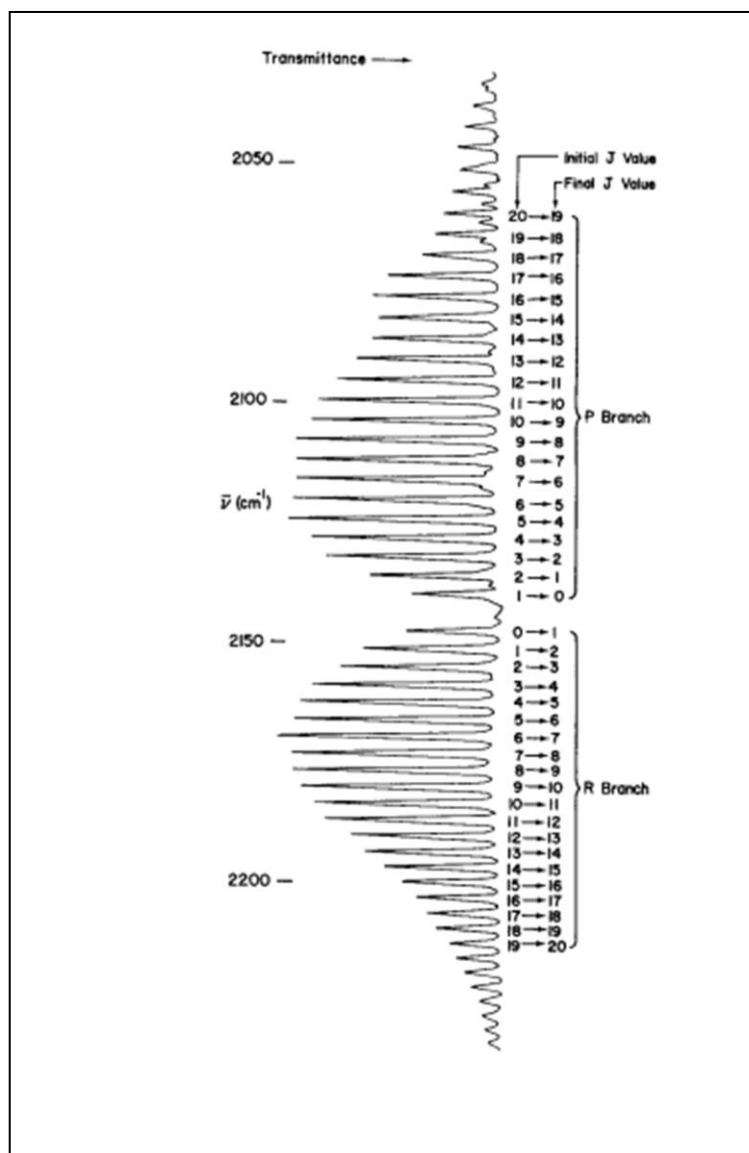


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**lakhdar69**

Chapter VI

## Oscillation-rotational (Willock 2009)



## Fig carbon monoxide Vib-Rot spectrum

### Spectrum analysis

The spectrum shows a combination of two movements of the molecule, vibration combined with a rotational movement. the energy belongs to the IR domain. the discussion of the spectrum suggests that there are two branches separated by a gap, it remains to observe the space between two spokes, equidistant or not, this leads us to think about the moment of inertia and arrive at the interatomic length, chemical bond.

### Energy calculation(Dahoo and Lakhlifi 2018)

**We can write the energy of the system as a sum of the vibration and rotation energy**

$$E = E_{vib} + E_{rot}$$
$$S(v, J) = G(v) + F(J)$$

**The rotational energy for a rigid top is given by the expression**

$$E_{rot} = \frac{h^2}{8\pi^2} * \frac{1}{I} * J * (J + 1)$$

**However, the rotational energy is given by the expression**

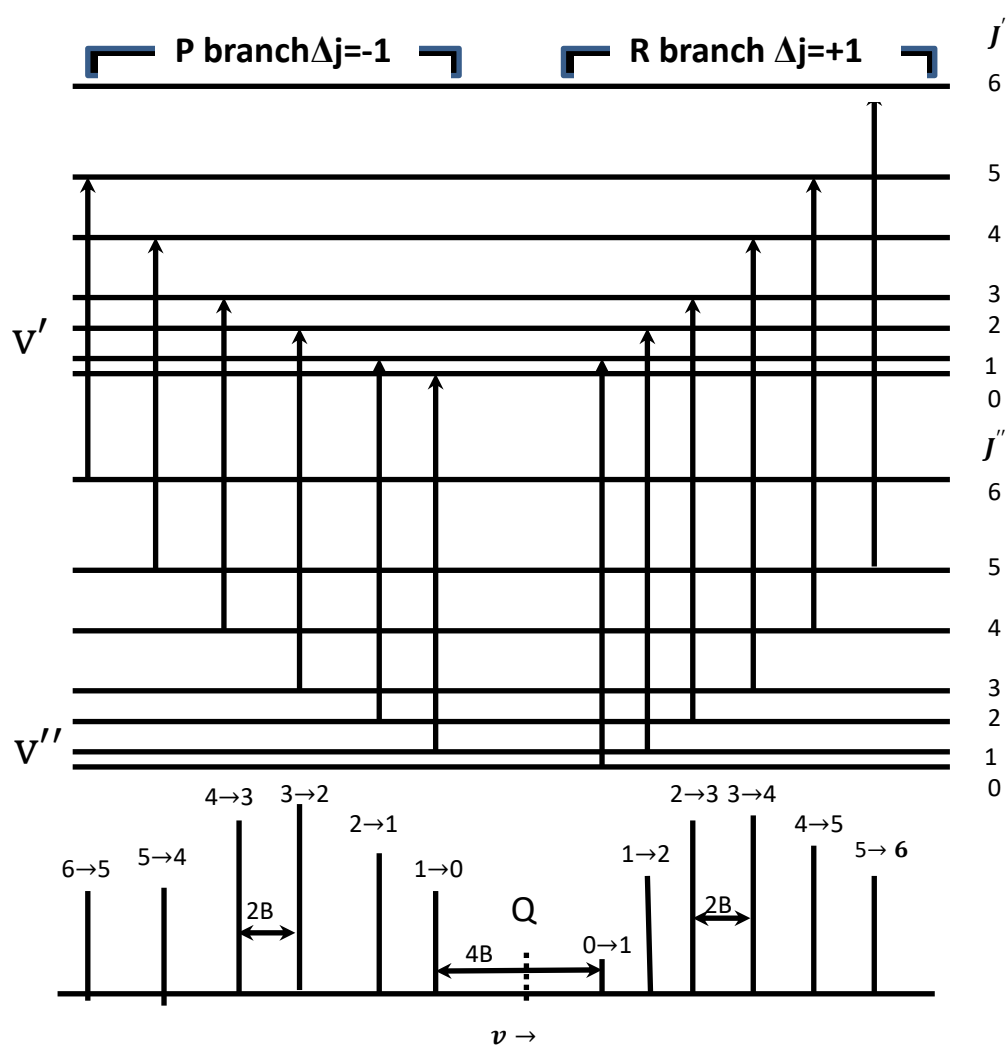
$$E_{vib} = \left(v + \frac{1}{2}\right) h\omega_{osc}$$

**And It Producer**

$$E = \frac{h^2}{8I\pi^2} * J * (J + 1) + \left(v + \frac{1}{2}\right) h\omega_{osc}$$

**This expression connects two quantum numbers  $v$  and  $J$ . This expression is an approximation because it does not take distortions into account. If we take the spectrum of HCl the distortion is clear because the space between the lines of the P branch is different from that of the lines of the R branch since now we think of**

calculating the moment of inertia which is appropriate to say that the interatomic distances vary (Steinfeld 2012)



For the transitions we can first think of an oscillation transition of

$$T(v, (j')) \rightarrow T((v + 1), (j''))$$

Is each state confines a series of transitions, then the rotation transitions  $j' \rightarrow j''$  for the two branches. the figure above

The energy in wave number for the branch R(j) without the distortion effect (the lines are equidistant)

$$T = \overline{\omega}_0 + B(J + 1)(J + 2) - 2Bj(J + 1) = \overline{\omega}_0 + 2Bj + 2B$$

The energy in wave number for the branch P(j) without the distortion effect

$$T = \overline{\omega}_0 + B(J - 1)(J) - Bj(J + 1) = \overline{\omega}_0 - 2Bj$$

If we take into account the distortion effect and the vibro-rotational coupling effect (di Lauro 2013)

$$G(v) = \varepsilon_v = \left(v + \frac{1}{2}\right) \overline{\omega}_e - \left(v + \frac{1}{2}\right)^2 \overline{\omega}_e x_e \quad (cm^{-1})(v = 0, 1, 2 \dots \dots)$$

$$wave\ number = \overline{B}J(J + 1) - \overline{D}J^2(J + 1)^2 - \alpha_e J(J + 1) \left(v + \frac{1}{2}\right)$$

$$E_{v,J} = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e + B_e J(J + 1) - D J^2(J + 1)^2 - \alpha_e J(J + 1) \left(v + \frac{1}{2}\right) \quad (joule)$$

$$\frac{E_{vJ}}{hc} = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e + \bar{B}_e J(J+1) - \bar{D}_e J^2(J+1)^2 - \bar{\alpha}_e J(J+1) \left(v + \frac{1}{2}\right) \text{ cm}^{-1}$$

$$\frac{E_{vJ}}{hc} = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e + \left(\bar{B}_e - \bar{\alpha}_e \left(v + \frac{1}{2}\right)\right) (J(J+1)) \text{ cm}^{-1}$$

$$\bar{B}_v = \bar{B}_e - \bar{\alpha}_e \left(v + \frac{1}{2}\right)$$

Where  $\bar{B}_e$  the equilibrium state of the molecule at the bottom of the potential energy curve

Where  $v$  is the vibrational quantum number

$\bar{\omega}_e$  is the vibrational frequency the subscript e indicate equilibrium which essentially at the bottom of the potential well

$x_e$  is the anharmonicity constant fitting the decrease in vibration level spacing

$\bar{B}_e$  the rotational constant

$\bar{D}_e$  is the centrifugal distortion constant

$\bar{\alpha}_e$  is the vibrational-rotation coupling constant  
the Q branch is transparent

Transition occur where  $\Delta v = \mp 1$   $\Delta J = 0, \mp 1$   
Q branch

$\Delta v = 0 \rightarrow 1$   $\Delta J = 0$  for Q branch

$$\begin{aligned}
\frac{E_{v+1J}}{hc} - \frac{E_{vJ}}{hc} &= \frac{\Delta E_Q}{hc} \\
&= \left( \left( v + 1 + \frac{1}{2} \right) \bar{\omega}_e - \left( v + 1 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e + \bar{B}_e J(J+1) \right. \\
&\quad \left. - \bar{D}_e J^2(J+1)^2 - \bar{\alpha}_e J(J+1) \left( v + 1 + \frac{1}{2} \right) \right) \\
&\quad - \left( \left( 0 + \frac{1}{2} \right) \bar{\omega}_e - \left( 0 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e + \bar{B}_e J(J+1) - \bar{D}_e J^2(J+1)^2 \right. \\
&\quad \left. - \bar{\alpha}_e J(J+1) \left( 0 + \frac{1}{2} \right) \right)
\end{aligned}$$

$$\frac{\Delta E_Q}{hc} = \bar{\omega}_e - 2\bar{\omega}_e x_e - \bar{\alpha}_e J(J+1) \quad \text{with} \quad \bar{\omega}_0 = \bar{\omega}_e - 2\bar{\omega}_e x_e$$

R branche

$\Delta \nu = 0 \rightarrow 1$   $\Delta J = +1$  for R branche

$$\begin{aligned}
\frac{E_{v+1J+1}}{hc} - \frac{E_{vJ}}{hc} &= \frac{\Delta E_R}{hc} \\
&= \left( \left( v + 1 + \frac{1}{2} \right) \bar{\omega}_e - \left( v + 1 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e \right. \\
&\quad + \bar{B}_e(J+1)(J+1+1) - \bar{D}_e(J+1)^2(J+1+1)^2 \\
&\quad \left. - \bar{\alpha}_e(J+1)(J+1+1) \left( v + 1 + \frac{1}{2} \right) \right) \\
&\quad - \left( \left( 0 + \frac{1}{2} \right) \bar{\omega}_e - \left( 0 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e + \bar{B}_e J(J+1) - \bar{D}_e J^2(J+1)^2 \right. \\
&\quad \left. - \bar{\alpha}_e J(J+1) \left( 0 + \frac{1}{2} \right) \right) \\
&= \bar{\omega}_0 + \bar{B}_e(2J+2) - \bar{\alpha}_e(J^2 + 4J + 3) \\
&\quad - \bar{D}_e(4J^3 + 12J^2 + 12J + 4) \\
&= \bar{\omega}_0 + \bar{B}_e(2J+2) - \bar{\alpha}_e(J^2 + 4J + 3) - 4\bar{D}_e(J+1)^3 = \\
(1+x)^3 &= (1+x)(x^2 + 2x + 1) = (x^3 + 2x^2 + x + x^2 + 2x + 1) \\
&= (x^3 + 3x^2 + 3x + 1)
\end{aligned}$$

**P branche**

**The transitions  $\Delta v = 0 \rightarrow 1$   $\Delta J = -1$  for P branche**

$$\begin{aligned}
\frac{E_{v+1J-1}}{hc} - \frac{E_{vJ}}{hc} &= \frac{\Delta E_p}{hc} \\
&= \left( \left( v + 1 + \frac{1}{2} \right) \bar{\omega}_e - \left( v + 1 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e + \bar{B}_e (J - 1)(J) \right. \\
&\quad \left. - \bar{D}_e (J - 1)^2 (J)^2 - \bar{\alpha}_e (J + 1)(J) \left( \frac{1}{2} \right) \right) \\
&\quad - \left( \left( 0 + \frac{1}{2} \right) \bar{\omega}_e - \left( 0 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e + \bar{B}_e J(J + 1) - \bar{D}_e J^2 (J + 1)^2 \right. \\
&\quad \left. - \bar{\alpha}_e J(J + 1) \left( 0 + \frac{1}{2} \right) \right) \\
&= \bar{\omega}_0 - \bar{B}_e (2J) - \bar{\alpha}_e (J^2 - 2J) + \bar{D}_e (4J^3)
\end{aligned}$$

$$P(1) = \bar{\omega}_0 - \bar{B}_e(2) - \bar{\alpha}_e(-1) + \bar{D}_e(4) \text{ for } J = 1$$

$$P(2) = \bar{\omega}_0 - \bar{B}_e(2 * 2) - \bar{\alpha}_e(0) + \bar{D}_e(32) \text{ for } J = 2$$

$$P(3) = \bar{\omega}_0 - \bar{B}_e(2 * 3) - \bar{\alpha}_e(3) + \bar{D}_e(108) \text{ for } J = 3$$

$$P(4) = \bar{\omega}_0 - \bar{B}_e(2 * 4) - \bar{\alpha}_e(8) + \bar{D}_e(256) \text{ for } J = 4$$

$$R(J) = \omega_0 + \bar{B}_e(2J + 2) - \bar{\alpha}_e(J^2 + 4J + 3) - 4\bar{D}_e(J + 1)^3$$

$$R(0) = \omega_0 + \bar{B}_e(0 + 2) - \bar{\alpha}_e(0 + 0 + 3) - 4\bar{D}_e(0 + 1)^3$$

$$R(0) = \omega_0 + (2)\bar{B}_e - (3)\bar{\alpha}_e - 4\bar{D}_e$$

$$R(1) = \omega_0 + \bar{B}_e(2 * 1 + 2) - \bar{\alpha}_e(1^2 + 4 * 1 + 3) - 4\bar{D}_e(1 + 1)^3$$

$$R(1) = \omega_0 + (4)\bar{B}_e - \bar{\alpha}_e(8) - 32\bar{D}_e$$

$$R(2) = \omega_0 + 6\bar{B}_e - 15\bar{\alpha}_e - 108\bar{D}_e$$

$$R(3) = \omega_0 + \bar{B}_e(2 * 3 + 2) - \bar{\alpha}_e(3^2 + 4 * 3 + 3) - 4\bar{D}_e(1 + 3)^3$$

$$R(3) = \omega_0 + 8\bar{B}_e - 24\bar{\alpha}_e - 256\bar{D}_e$$

$$R(4) = \omega_0 + \bar{B}_e 10 - \bar{\alpha}_e 35 - 500\bar{D}_e$$

$$P(1) + R(0) = 2\bar{\omega}_0 - 4\bar{\alpha}_e$$

$$P(1) - R(0) = \bar{\omega}_0 - \bar{B}_e(2) - \bar{\alpha}_e(-1) + \bar{D}_e(4)$$

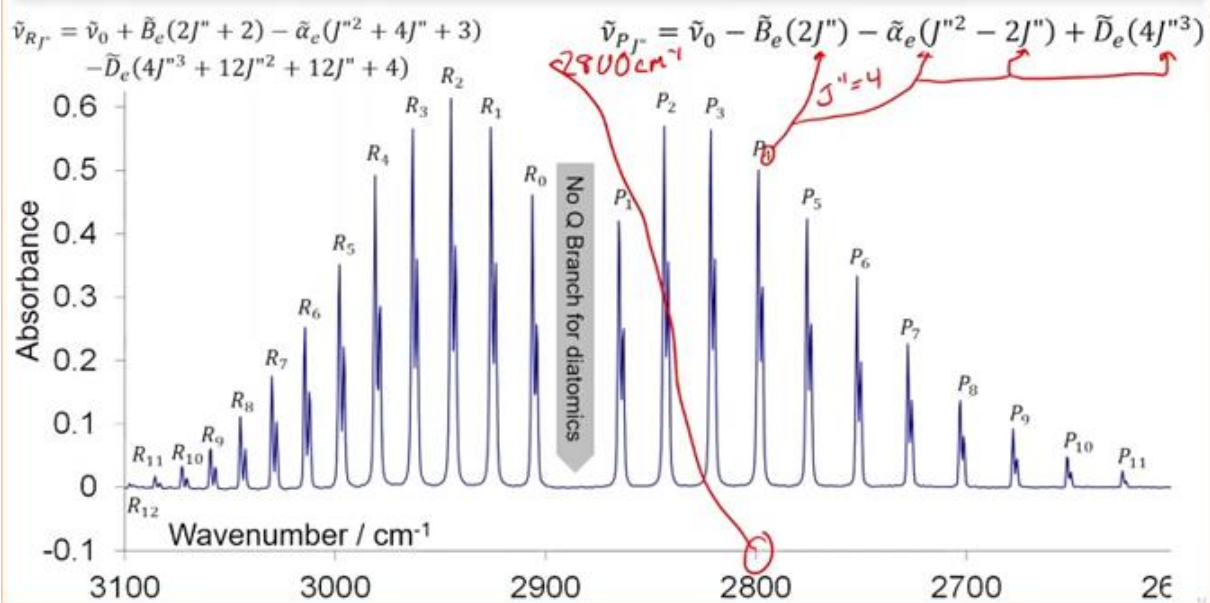
$$-\omega_0 - (2)\bar{B}_e + (3)\bar{\alpha}_e + 4\bar{D}_e = 2\bar{\alpha}_e + 8\bar{D}_e$$

$$P(1) - R(0) = -4\bar{B}_e + 2\bar{\alpha}_e + 8\bar{D}_e$$

We can give form the spectrum vib-rot of HCl the following absorption values

$P(1) = \bar{\omega}_0 - \bar{B}_e(2) - \bar{\alpha}_e(-1) + \bar{D}_e(4)$	$R(0) = \bar{\omega}_0 + 2\bar{B}_e - 3\bar{\alpha}_e - 4\bar{D}_e$ $= 2900\text{cm}^{-1}$
$P(2) = \bar{\omega}_0 - 4\bar{B}_e - 0\bar{\alpha}_e + 32\bar{D}_e$	$R(1) = \bar{\omega}_0 + 6\bar{B}_e - 8\bar{\alpha}_e$ $- 32\bar{D}_e$
$P(3) = \bar{\omega}_0 - \bar{B}_e(2 * 3) - \bar{\alpha}_e(3)$ $+ \bar{D}_e(108)$	$R(2) = \bar{\omega}_0 + 6\bar{B}_e - 15\bar{\alpha}_e$ $- 108\bar{D}_e$
$P(4) = \bar{\omega}_0 - \bar{B}_e(2 * 4) - \bar{\alpha}_e(8)$ $+ \bar{D}_e(256) = 2800\text{ cm}^{-1}$	$R(3) = \bar{\omega}_0 + 8\bar{B}_e - 24\bar{\alpha}_e$ $- 256\bar{D}_e$
$P(8) = \bar{\omega}_0 - 48\bar{\alpha}_e + 2048\bar{D}_e = 2700\text{cm}^{-1}$	$R(4) = \bar{\omega}_0 + 10\bar{B}_e - 35\bar{\alpha}_e$ $- 500\bar{D}_e$
	$= \bar{\omega}_0 + 12\bar{B}_e - 84\bar{\alpha}_e - 864\bar{D}_e$ $= 3000\text{cm}^{-1}$

## Rovibrational IR Spectrum of HCl(g)



## exercises

**Ex**

**Given the levels Ro-Vib energy in  $\text{cm}^{-1}$**

$$\varepsilon_{vJ} = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e + B_e J(J+1) - D J^2(J+1)^2 \text{ cm}^{-1}$$

**Where  $v=0,1,2,\dots$  and  $j=0,1,2,\dots$**

**The selection rules for the combined motions are the same as those for separate motions that is  $\Delta v = \mp 1, \pm 2$  and  $J = \mp 1$**

**Write the expression in terms of frequency of P branche , R branche and Q branche  $\bar{\nu}_Q, \bar{\nu}_P, \bar{\nu}_R$**

**Ex**

**Estimate the position of the band centre and B value for HCl**

**Molecule from the few lines of the P and R branches listed below**

line	$\bar{\nu} \text{ cm}^{-1}$	line	$\bar{\nu} \text{ cm}^{-1}$
$P_1$	2,865.10	$R_1$	2,906.24
$P_2$	2,843.62	$R_2$	2,925.90
$P_3$	2,821.56	$R_3$	2,944.90
$P_4$	2,798.94	$R_4$	2,963.29

$$\bar{\nu}_{P,R} = \bar{\nu}_0 + 2Bm \quad m = \mp 1, \mp 2, \mp 3, \dots$$

**$\bar{\nu}_0$  = sum of all 8 readings divided by 8**

$$\bar{\nu}_0 = \frac{2,306.55}{8} = 2,883.69 \text{ cm}^{-1}$$

$$\bar{\nu}_{R_0} - \bar{\nu}_{P_1} = 4B = 41.14 \text{ cm}^{-1}$$

$$\bar{\nu}_{R_1} - \bar{\nu}_{P_2} = 8B = 82.28 \text{ cm}^{-1}$$

$$\bar{\nu}_{R_2} - \bar{\nu}_{P_3} = 12B = 123.34 \text{ cm}^{-1}$$

$$\bar{\nu}_{R_3} - \bar{\nu}_{P_4} = 16B = 134.35 \text{ cm}^{-1}$$

$$B = 10.28 \text{ cm}^{-1}$$

For more accurate value the term D must be taken in consideration

**Ex**

Calculate the energy in  $\text{cm}^{-1}$  of the photon absorption when NO molecule goes from the state  $v = 0, J'' = 0$  to  $v = 0, J' = 1$ . Assume that  $v = 0$  and  $v = 1$  states have the same B value given  $\bar{\nu}_e = 1,904 \text{ cm}^{-1}$ ,  $x_e = 0.00733$ ,  $r_{\text{NO}} = 0.1151 \text{ nm}$

**Ex1**

The rotational vibration spectrum of carbon monoxide includes in the near infrared an intense band in the region of  $2100\text{-}2200 \text{ cm}^{-1}$ . With a low resolution device we obtain the following series of lines  $2124, 2128, 2132, 2132, 2136, 2140, 2148, 2152, 2156, 2160 \text{ cm}^{-1}$ . Determine the moment of inertia, the interatomic distance and the vibration frequency of the molecule?

Determine the value of the centrifugal distortion constant of the molecule?

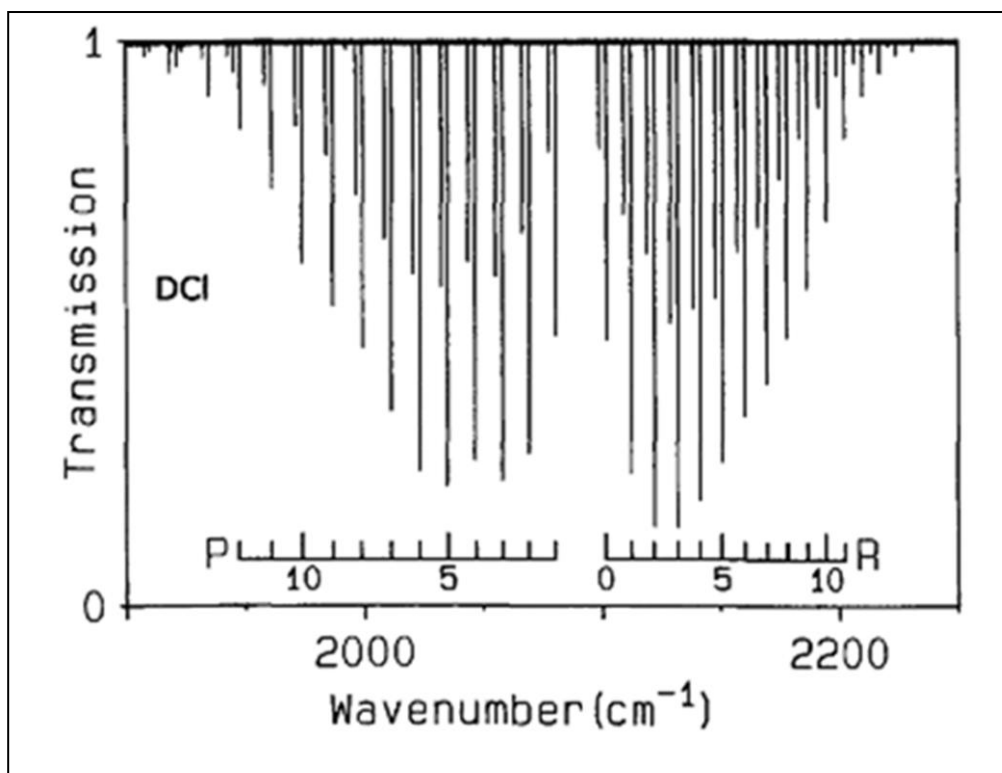
**Ex2**

Establishing the formulas giving the wave number  $\bar{\nu}_P$  and  $\bar{\nu}_R$  and in the P and R branches of the rotation vibration spectrum of HCl between the states  $v'' = 0$  et  $v' = 4$  (higher) makes it possible to reveal the numbers of waves of the following lines

$$R(0) = 8418.163 \text{ cm}^{-1} \quad R(1) = 8421.728 \text{ cm}^{-1}$$

$$P(1) = 8410.613 \text{ cm}^{-1} \quad P(2) = 8406.628 \text{ cm}^{-1}$$

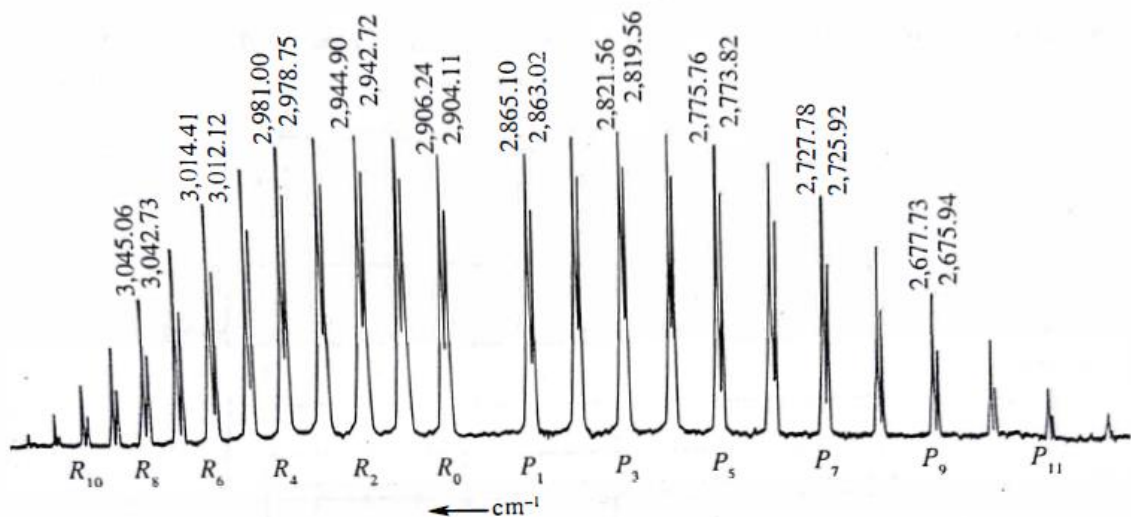
Neglecting centrifugal distortion when treating HCl in the harmonic oscillator approximation Calculate the distortion constants  $B_{v''}$  and  $B_{v'}$  deduce calculations for DCl and compare with spectrum?



**Fig :the fundamental vibration –rotation band of  $D^{35}\text{Cl}$  and  $D^{37}\text{Cl}$**

**EX**

**The fundamental band for HC lines centred at  $2.886\text{ cm}^{-1}$  .Assuming that internuclear distance is  $1.276\text{\AA}$ , calculate the wave number of the first two lines of each of the P and R branches of HCl. Compare with HCl spectrum?**



$$\mu_{HCl} = \frac{(1.008)(35.45)}{(36.46)(6.023 \times 10^{23})} = 1.6275 \times 10^{-27} \text{ kg}$$

$$B = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 1.6275 \times 10^{-27} (1.276 \times 10^{-10})^2 \times 3 \times 10^8} = 10.6129 \text{ cm}^{-1}$$

The lines without distortion effect

$$\bar{\nu}_{P,R} = \bar{\nu}_0 + 2Bm \quad ; m = \mp 1, \mp 2, \mp 3, \dots$$

$$\begin{aligned} \bar{\nu}_{P1} &= 2,886 - 2 \times 10.6129 \\ &= 2,864.77 \text{ cm}^{-1} \text{ (from spectrum } 2865.10 \text{ cm}^{-1}) \\ \bar{\nu}_{P2} &= 2,886 - 4 \times 10.6129 = 2,843.55 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \bar{\nu}_{R0} &= 2,886 + 2 \times 10.6129 \\ &= 2,907.23 \text{ cm}^{-1} \text{ (from spectrum } 2906.24 \text{ cm}^{-1}) \\ \bar{\nu}_{R1} &= 2,886 + 4 \times 10.6129 = 2,928.45 \text{ cm}^{-1} \end{aligned}$$

Ex1

The rotational vibration spectrum of carbon monoxide includes in the near infrared an intense band in the region of 2100-2200 cm<sup>-1</sup>.

With a low resolution device we obtain the following series of lines  
2124, 2128, 2132, 2132, 2136, 2140, 2148, 2152, 2156, 2160cm<sup>-1</sup>

Determine the moment of inertia, the interatomic distance and the  
vibration frequency of the molecule?

Determine the value of the centrifugal distortion constant of the  
molecule?

We observe

$$2128-2124=4$$

$$2124-2128=4$$

$$2128-2128=4$$

$$2134-2132=4$$

$$2140-2148=8 \quad \omega_0 = 2140 + \frac{2140-2148}{2}$$

$$2152-2148=4$$

$$2156-2152=4$$

$$2160-2156=4$$

*B = constante the distortion effect not observed*

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