

Spectroscopy

**Analysis of the electromagnetic radiation emitted,
absorbed or scattered by atoms and molecules**

Harmonic oscillator

A particle vibrates backwards and forwards restrained by a spring that obeys Hook's law ---- states that the restoring force is proportional to the displacement x

$$\text{Restoring force} = -k_f x$$

$$k_f = \text{force constant}$$

A stiff spring has a high force constant (the restoring force is strong even for a small displacement)

negative sign in the equation is included because the displacement to the right (to positive x) corresponds to a force directed to the left

Force is the negative slope of the potential energy

$$F = -dV/dx$$

$$dV = -Fdx$$

Integrate both sides from $x = 0$, where the potential energy is $V(0)$, to x , where the potential energy is $V(x)$

$$V(x) - V(0) = -\int F(x)dx$$

$$\text{Substitute } F(x) = -k_f x$$

$$V(x) - V(0) = \frac{1}{2} k_f x^2$$

Because the potential energy of the oscillator has its lowest value at $x = 0$, it is common to choose $V(0) = 0$

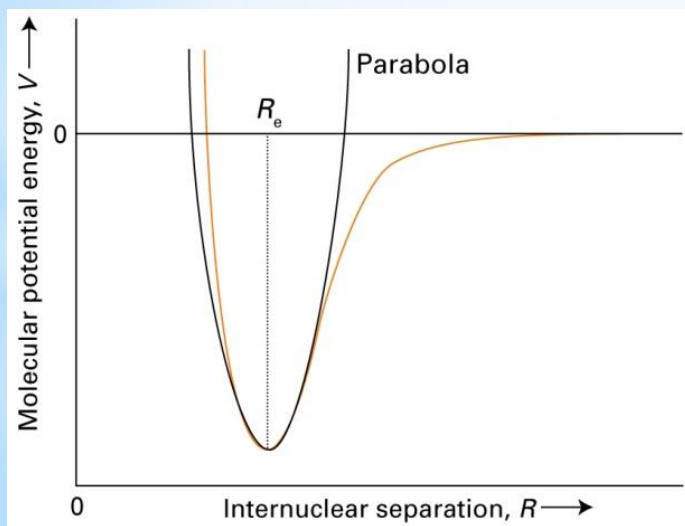
$$V(x) = (\frac{1}{2})k_f x^2$$

VIBRATIONAL SPECTROSCOPY

All molecule are capable of vibrating - different modes

Benzene – vibrate in 30 different modes

Many of these vibrations can be excited by the absorption of electromagnetic radiation --- frequencies at which absorption occurs gives information about the identity of the molecule



In regions close to the equilibrium bond length R_e , the potential energy can be approximated by a parabola (a curve of the form $y \propto x^2$)

$$V(x) = (\frac{1}{2})k_f x^2$$

$x = R - R_e$ displacement from equilibrium
 k_f = force constant of the bond (N m^{-1})

steeper the walls of the potential (the stiffer the bond) ---- the greater is the k_f

PE in the equation has the same form as that for the harmonic oscillator

PE curve of a diatomic molecule as its bond is lengthened by pulling one atom away from the other or shortened by pressing it into the other

For two atoms of masses m_A and m_B joined by a bond of force constant k_f , the energy levels are

$$E_v = (v + \frac{1}{2})h\nu \quad v = 0, 1, 2, \dots$$

$$\nu = (1/2\pi)(k_f/\mu)^{1/2}$$

$$\mu = m_A m_B / (m_A + m_B)$$

μ ----- effective mass of the molecule ----- a measure of the quantity of matter moved during the vibration

For HI , $\mu = m_H$

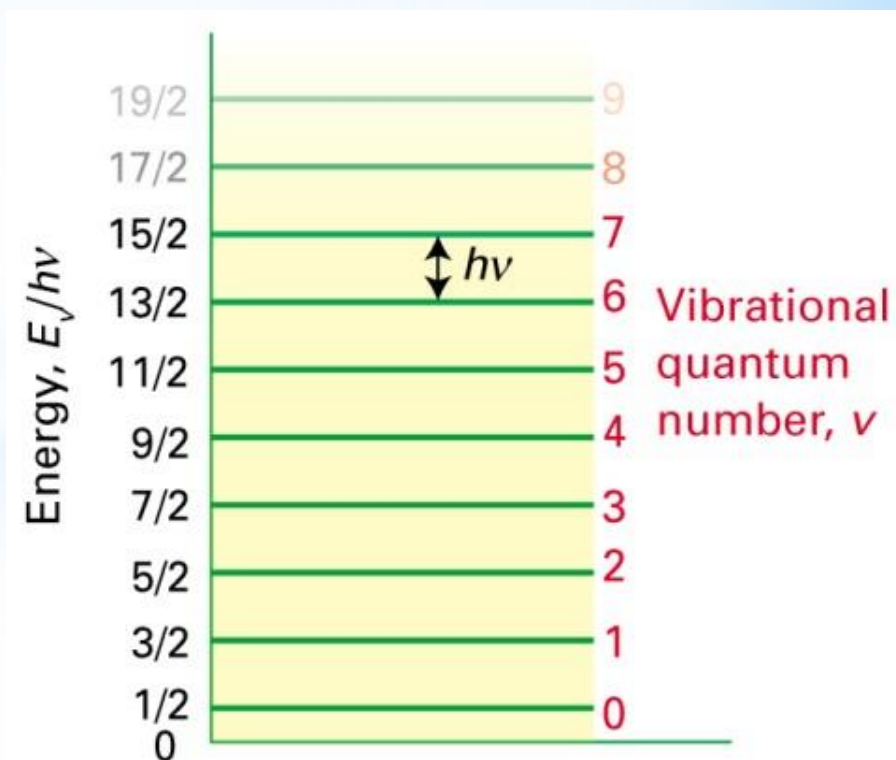
homonuclear diatomic molecule

$$m_A = m_B = m$$

$$\mu = \frac{1}{2} (m)$$

Vibrational transitions are expressed as wavenumber

$$E_v = (v + \frac{1}{2})hc\bar{\nu}$$



VIBRATIONAL TRANSITIONS

Typical vibrational frequencies are of the order of $10^{13} - 10^{14}$ Hz

Transition can be induced with radiation of this frequency --- IR radiation

Vibrational transitions are observed by infrared spectroscopy

Wave numbers typically in the range $300 - 4000\text{ cm}^{-1}$

Bond dipole moment, the measure of polarity of a chemical bond

dipole moment ----- measure of net polarity in a molecule

If a molecule contains polar bonds that are unevenly distributed about the center, there will be an uneven charge distribution across the entire molecule, making it a polar molecule.

Polar molecules exhibit a large difference in electrical charge (a positive end and a negative end), otherwise known as a dipole moment.

ammonia (NH_3) --- polar molecule

ammonia consists of one nitrogen atom covalently bonded to three hydrogen atoms

nitrogen has a partial negative charge (denoted by a minus sign on N) and hydrogen a partial positive charge (which is denoted by a plus sign on each H)

The presence of both a positive and negative charge on the molecule means that ammonia is polar and, therefore, exhibits a net dipole moment

SI unit for electric dipole moment is the **coulomb-meter**

Bond dipole moments are commonly measured in debyes (D)

Gross selection rule ----- specifies the general features of a molecule must have if it is to have a spectrum of a given kind

Gross selection rule for vibrational spectra

For a vibrational transition to occur as a result of absorption or emission of a photon, the electric dipole moment of the molecule must change during vibration

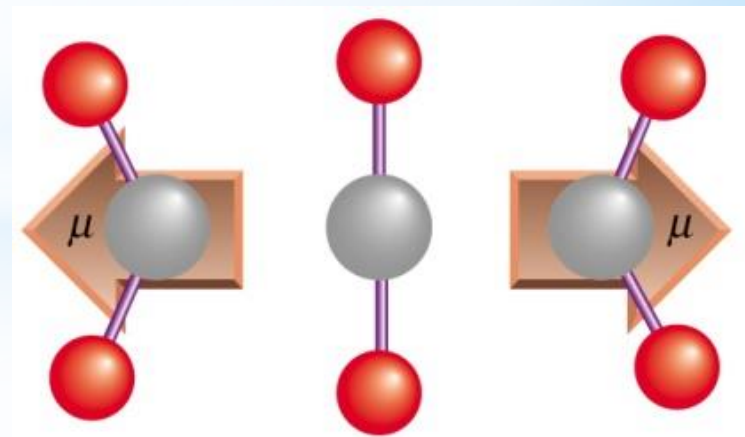
----- molecule need not have a permanent dipole ----- requires only a change in dipole moment, **possibly from zero**

Stretching motion of a homonuclear diatomic molecule does not change its electric dipole moment from zero ---- vibrations of such molecules neither absorb nor generate radiation ----- IR inactive

Heteronuclear diatomic molecules, with dipole moments that changes as the bond vibrates are IR active

Oscillation of a molecule, even if it is nonpolar, may results in an oscillating dipole that can interact with the electromagnetic field

O-C-O stretching and contracting symmetrically ---- infrared inactive



Bending mode of carbon dioxide

Specific selection rule ----- specifies what change in quantum number may occur

A transition that is permitted by the specific selection rule -----allowed transition

Transition that is disallowed by a specific selection rule ----- forbidden transition

Specific selection rule for vibrational transitions

$$\Delta v = \pm 1$$

Change in the energy for the transition from a state with quantum number v to one with quantum number $v + 1$

$$\Delta E = E_{v+1} - E_v = (v + 3/2)hc\bar{\nu} - (v + 1/2)hc\bar{\nu} = hc\bar{\nu}$$

Absorption occurs when the incident radiation provides photons with this energy

Molecules with stiff bonds have high vibrational wavenumbers

Bending modes are usually less stiff than stretching modes ----- bends typically occur at lower wavenumbers than stretches in a spectrum

At room temperature, molecules are in their vibrational ground states $v = 0$ ----- most intense spectral transition is from $v = 0$ to $v = 1$

ANHARMONICITY

$$\Delta E = E_{v+1} - E_v = (v + 3/2)hc\bar{\nu} - (v + 1/2)hc\bar{\nu} = hc\bar{\nu}$$

vibrational transition energies in the above equation are only approximate
----- based on the **parabolic approximation** to the actual potential energy curve

A parabola cannot be correct at all extensions because it does not allow a molecule to dissociate

----- **motion becomes anharmonic** ----- restoring force is no longer proportional to the displacement

Actual curve is less confining than a parabola ----- the energy levels become less widely spaced at high excitation

Convergence of levels at high vibrational quantum numbers

$$E_v = (v + \frac{1}{2})hc\bar{\nu} - (v + \frac{1}{2})^2hc\bar{\nu}x_e + \text{-----}$$

x_e = anharmonicity constant

Anharmonicity accounts for the additional weak absorption lines called overtones, corresponding to transitions **$\Delta v = \pm 2, \pm 3, \dots$**

Number of Vibrational Modes

molecules exhibit **three types of motions**: translations (external), rotations (internal) and vibrations (internal).

Degree of freedom is the number of variables required to describe the motion of a particle completely.

An atom moving in 3-D space: 3 coordinates are adequate (to mention the location) so its degree of freedom is 3 --- Its motion is purely translational --- translation of the centre-of-mass (a point representing the mean position of the matter in a body)

For a molecule made of N atoms (or ions): the degree of freedom becomes $3N$, because each atom has 3 degrees of freedom.

since these atoms are bonded together, all motions are not translational; some become rotational, some others vibrational.

For non-linear molecules, all rotational motions can be described in terms of rotations around 3 axes, the rotational degree of freedom is 3 and the remaining $3N-6$ degrees of freedom constitute vibrational motion.

For a linear molecule, rotation around its own axis is no rotation because it **leave the molecule unchanged**. So there are only 2 rotational degrees of freedom for any linear molecule leaving $3N-5$ degrees of freedom for vibration.

degrees of vibrational modes for linear molecules: $3N-5$

degrees of freedom for nonlinear molecules: $3N-6$

VIBRATION OF POLYATOMIC MOLECULES

Each atom can be displaced along any of three perpendicular axes

Total number of such displacements in a molecule consisting of N atoms = $3N$

Three of these displacement correspond to **movement of the centre of mass** of the molecule -
---- **translational motion** of the molecule as a whole

Remaining $3N-3$ displacements are '**internal modes**' of the molecule that leave its **centre of mass unchanged**

Three angles are needed to specify the orientation of a nonlinear molecule in space ----- three of the $3N-3$ internal displacements leave all bond angles and bond lengths unchanged but change the orientation of the molecule as a whole ---- **rotations**

$3N-6$ displacements that **change neither the centre of mass of the molecule nor the orientation of the molecule in space** ----- $3N-6$ displacements are vibration modes

In case of linear molecule, only two angles are needed to specify its orientation in space -----
 $3N-5$ vibrational modes

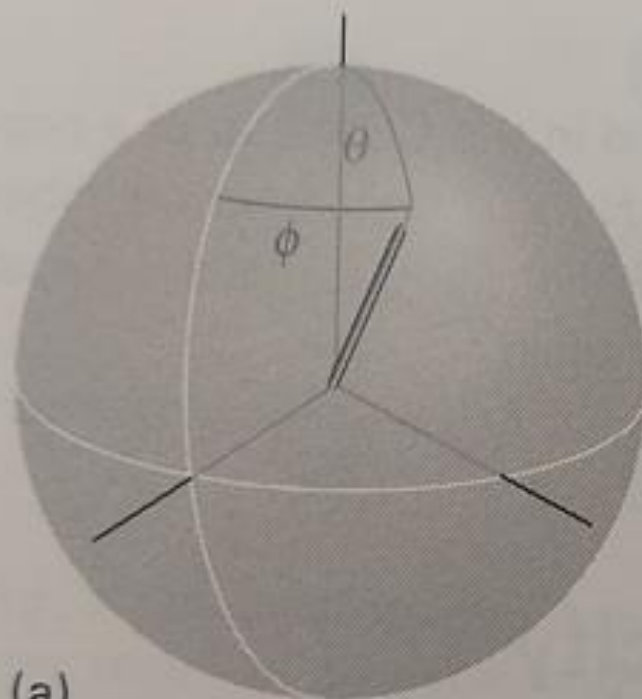
Number of modes of vibrations in polyatomic molecule

Nonlinear molecule: $3N-6$

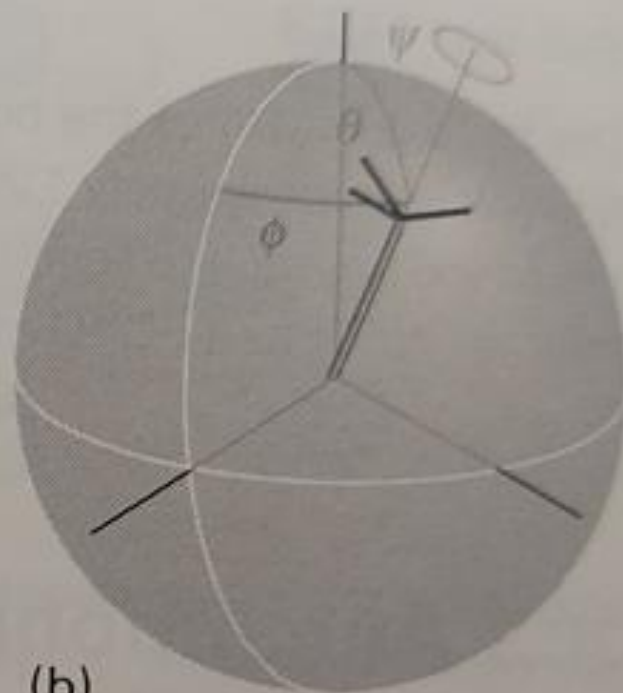
Linear molecule: $3N-5$

H_2O ---- triatomic and non linear ---- three modes of vibrations

CO_2 ---- triatomic and linear ----- four modes of vibrations



(a)

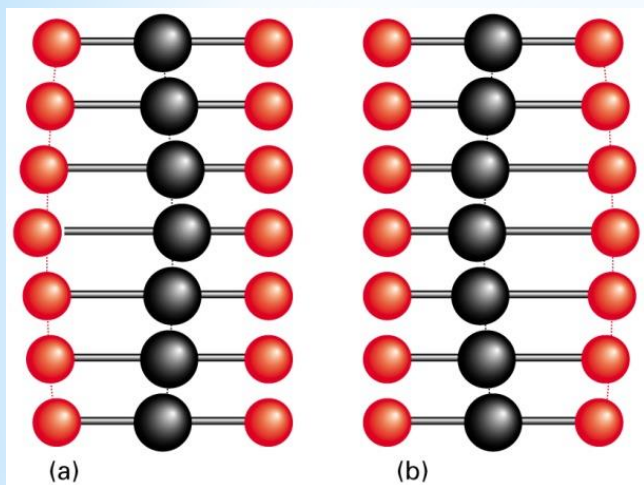


(b)

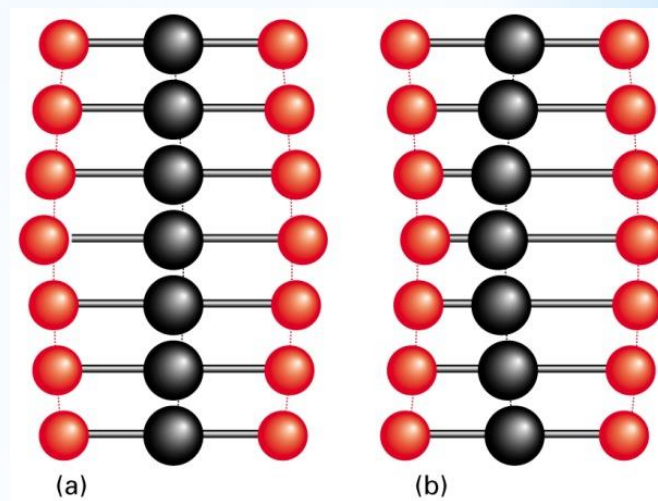
Fig. 4 (a) The orientation of a linear molecule requires the specification of two angles (the colatitude, θ , and longitude, ϕ , of its axis). (b) The orientation of a nonlinear molecule requires the specification of three angles (the latitude and longitude of its axis and the angle of twist (the azimuthal angle, ψ) around that axis).

Description of the vibrational motion of a polyatomic molecule is much simpler if various combinations of the stretching and bending motion of individual bonds are considered

Individual carbon – oxygen bond stretches ν_L and ν_R



As the stationary atom is linked to the C atom, it does not remain stationary for long. If one vibration begins, it rapidly stimulates the other to occur



ν_1
Symmetric stretch

ν_3
Antisymmetric stretch
Two O atoms move in same direction and opposite to the C atom

ν_2 degenerate bending (Two)

A normal mode is an independent, synchronous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal modes



Antisymmetric stretching ----- Infrared radiation at 2349 cm^{-1}

two equal-energy bending vibrations in CO_2 are identical except that one bending mode is in the plane of the paper, and one is out of the plane----- Infrared radiation at 667 cm^{-1}

Symmetric stretch of CO_2 leaves the dipole moment unchanged, so this mode is IR inactive

The fact that CO_2 absorbs IR, enables CO_2 to act as a green house gas by absorbing the IR radiation emitted from the surface of the earth

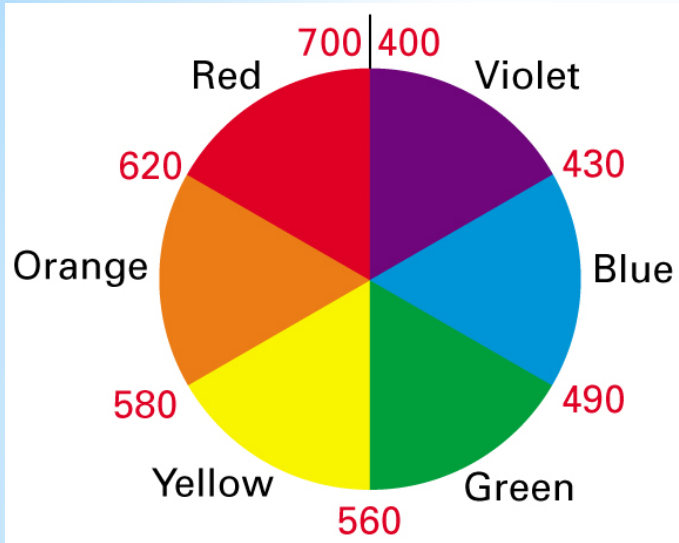
ELECTRONIC SPECTROSCOPY

White light is a mixture of all different colors

Removal by absorption of any one of these colours from white light results in the complementary colour being observed

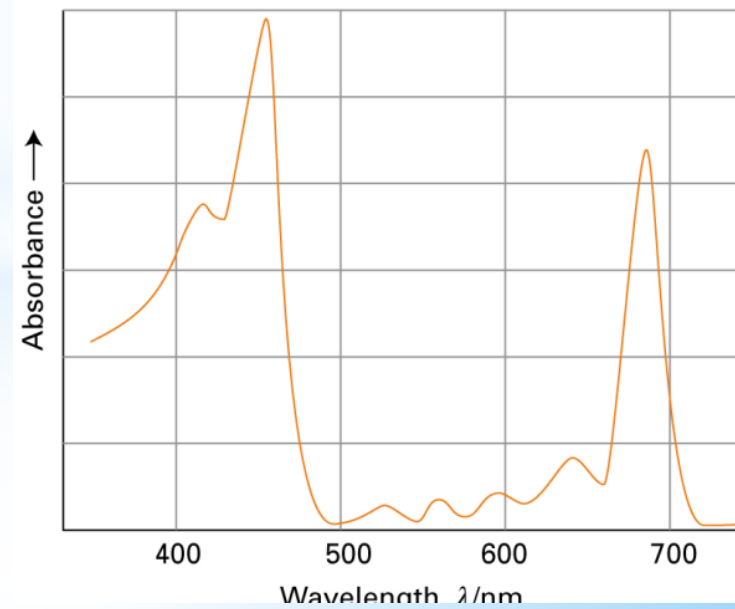
Absorption of 420 - 430 nm light renders a substance yellow colour

Absorption of 500 - 520 nm light makes a substance red in colour



An object may appear green because it absorb red light ----- it may also appear green because it absorb all colours from the incident light except green

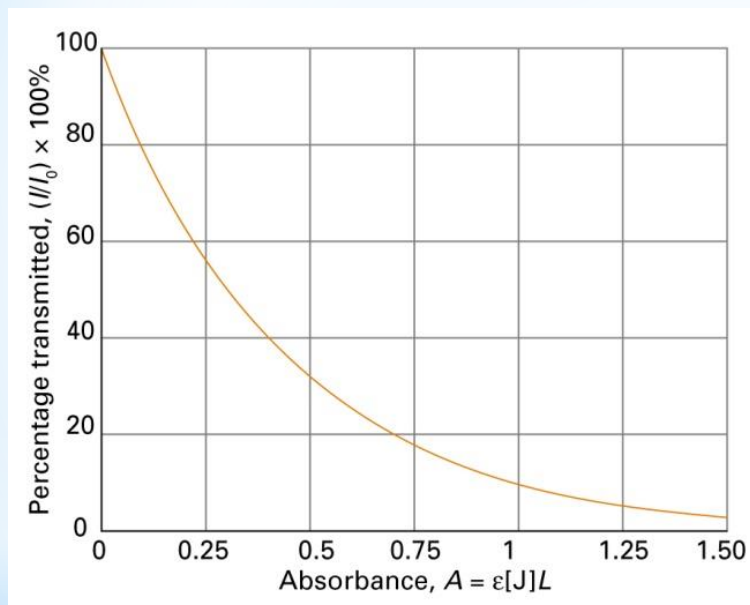
Chlorophyll absorbs red and blue light and that green light is not absorbed ----- reason for green colour of vegetation



Intensity of absorption of radiation at a particular frequency is related to the molar concentration and the path length through the sample

Beer-Lambert law

$$A = \epsilon[J]L$$



A = absorbance

ε = molar absorption coefficient

L = path length

I₀ = intensity of incident radiation

I = intensity of transmitted radiation

T = transmittance

$$I = I_0 10^{-\epsilon[J]L}$$

$$T = I/I_0 = 10^{-\epsilon[J]L}$$

$$\log T = \log (I/I_0) = -\epsilon[J]L$$

$$\log (I_0/I) = A = \epsilon[J]L$$

$$\% \text{ Transmittance, } \%T = 100 T$$

$$I/I_0 = \%T/100$$

$$100/\%T = I_0/I$$

$$\log 100 - \log \%T = \log (I_0/I)$$

$$\text{Absorbance} = \log_{10}(I_0/I)$$

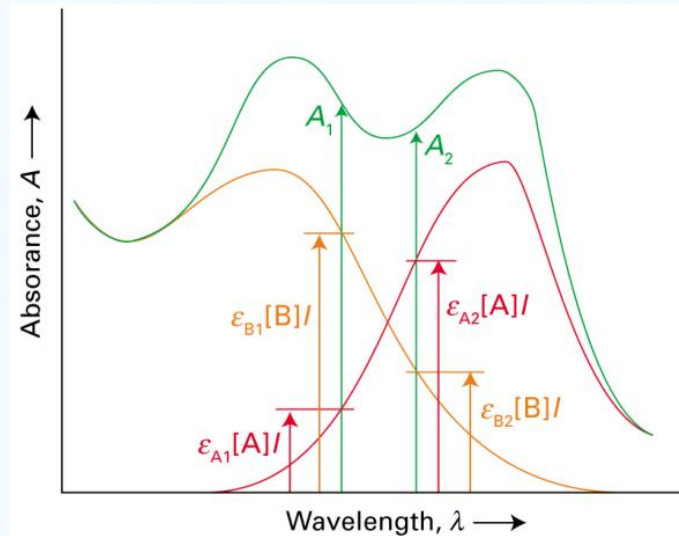
$$2 - \log \%T = \text{Absorbance}$$

$$2 - \log\%T = \text{Absorbance}$$

%T	log %T	A = 2-log%T
100	2	0
90	1.9542	0.04575
75	1.8750	0.12497
50	1.6989	0.30102
10	1	1
9	0.9542	1.04575
8	0.9030	1.09691
7	0.84509	1.15490
6	0.77815	1.22184
5	0.69897	1.30102
4	0.60206	1.39794
3	0.47712	1.52287
2	0.30103	1.69897
1	0	2
0.1	-1	3
0.01	-2	4

Analysis of mixtures by electronic spectroscopy

If the sample is a mixture of two components A and B, then the measurements at two wavelengths are used to find out individual concentrations



$$A = A_A + A_B = \epsilon_A[A]l + \epsilon_B[B]l = (\epsilon_A[A] + \epsilon_B[B])l$$

$$(\epsilon_{A1}[A] + \epsilon_{B1}[B])l = A_1$$

$$(\epsilon_{A2}[A] + \epsilon_{B2}[B])l = A_2$$

A_1 = absorbance at wavelength λ_1

A_2 = absorbance at wavelength λ_2

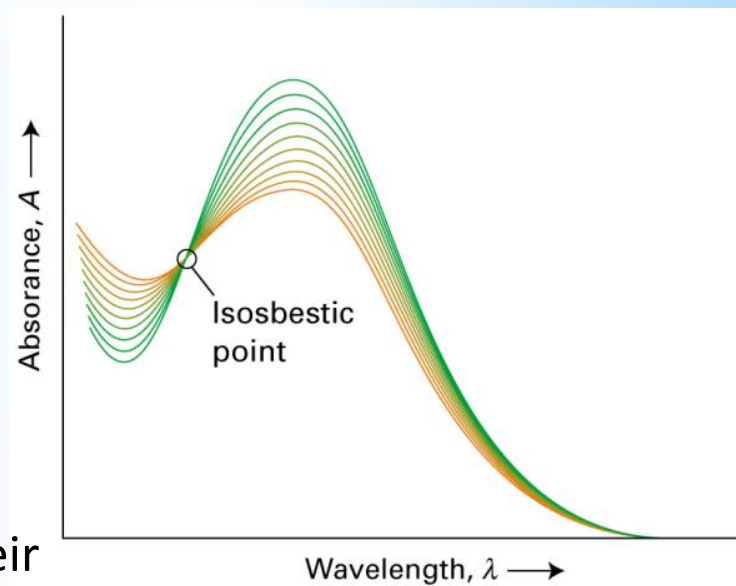
$$[A] = \frac{\epsilon_{B2}A_1 - \epsilon_{B1}A_2}{(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})l}$$

$$[B] = \frac{\epsilon_{A1}A_2 - \epsilon_{A2}A_1}{(\epsilon_{A1}\epsilon_{B2} - \epsilon_{A2}\epsilon_{B1})l}$$

There may be a wavelength at which the molar absorption coefficient of the two species are equal

$$A_{\text{iso}} = (\epsilon_{\text{iso}}[A] + \epsilon_{\text{iso}}[B])l = \epsilon_{\text{iso}}([A] + [B])l$$

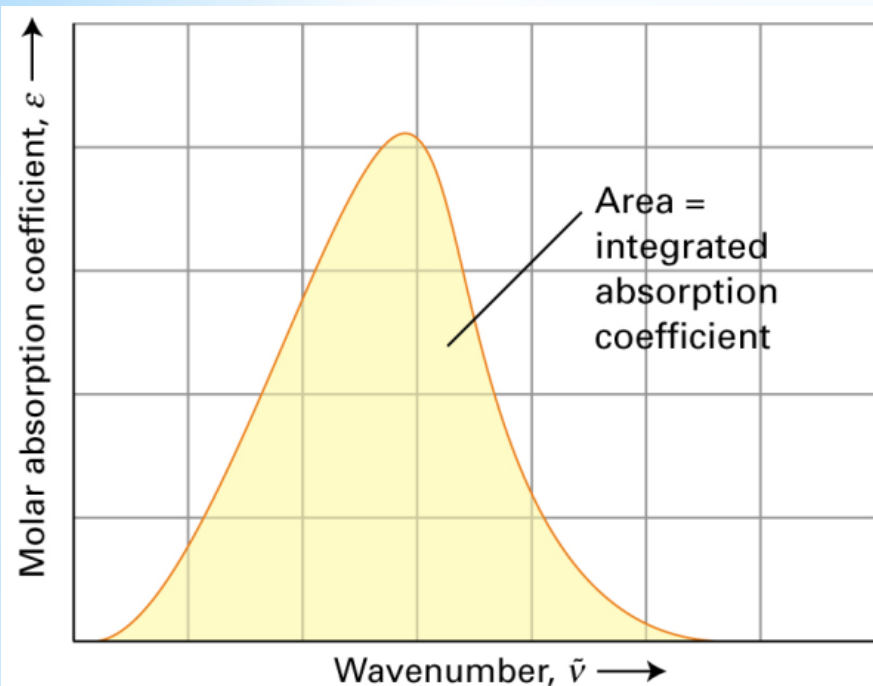
Even if A and B are interconverted in a reaction of the form $A \rightarrow B$ or its reverse, then because of their **total concentration remains constant**, so does A_{iso}



It is very unlikely that three or more species would have the same molar absorption coefficients at a single wavelength

Observation of isosbestic point is compelling evidence that a solution consists of only two solutes in equilibrium with each other with no intermediates

INTEGRATED ABSORPTION COEFFICIENT



Molar absorption coefficient depends on the frequency of the incident radiation and is greatest when the absorption is most intense

Absorption bands generally spread over a range of wavenumbers

Absorption at a single wavenumber might not give a true indication of the intensity

----- reported as **integrated absorption coefficient**

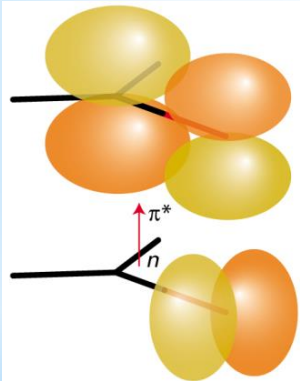
----- area under the plot of the molar absorption coefficient against wavenumber

SPECIFIC TYPES OF TRANSITIONS

Absorption of a photon can often be traced to the excitation of an electron that is localised on a small group of atoms

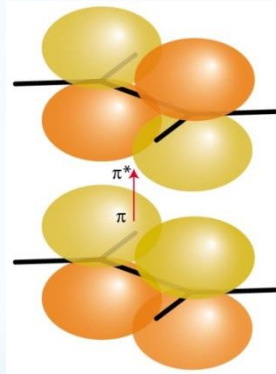
----- Absorption at about 290 nm ----- normally observed when a carbonyl group is present

Chromophores ---- groups with characteristic optical absorptions -----their presence often accounts for the colors of many substances



$n \rightarrow \pi^*$ transition

Absorption energy 4 eV
C = O group



$\pi \rightarrow \pi^*$ transition

Absorption energy 7 eV
(unconjugated double bond)
180 nm

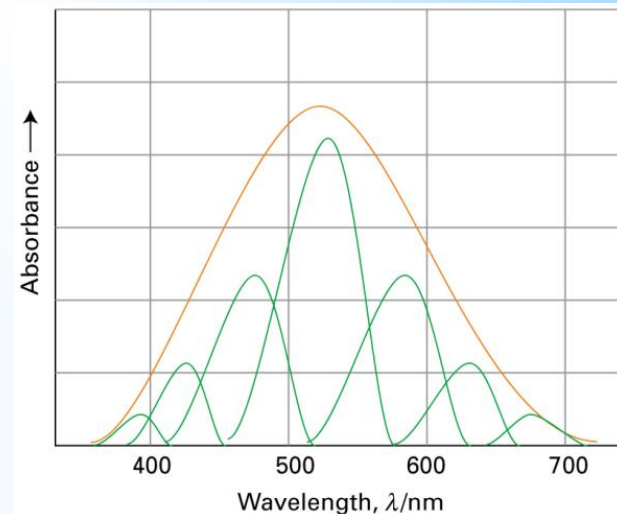
When the double bond is a part of a conjugated chain, the energies of the molecular orbitals lie closer together and the transition shifts into the visible region of the spectrum

Absorption band is broad

Electronic absorption band

- consists of many superimposed bands
- merge together to give a single broad

band



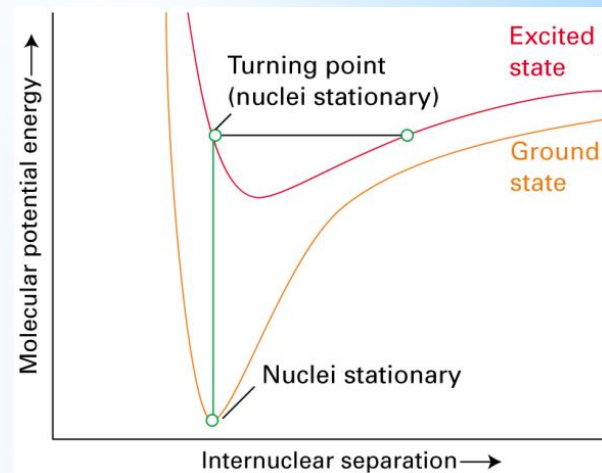
After an electronic transition,

- electron density has migrated to a different part of the molecule
- nuclei are subjected to different forces

some of the energy used to redistribute an electron is used to stimulate the vibrations of the absorbing molecules

Vibrational structure of a band explained by the **Franck-Condon principle**

----- initial, stationary, equilibrium separation of the nuclei in the initial electronic state becomes the new, stationary, turning point ----- one of the end points of a nuclear swing, in the final electronic state



Most likely final vibrational state

----- a **vertical line** is drawn from the minimum of the lower curve (the starting point for the transition) up to the point at which the line intersects the curve representing the upper electronic state

According to Franck-Condon principle,

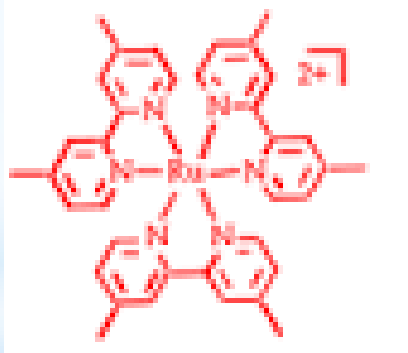
----- most intense electronic transition is from the ground vibration state to the **vibrational state that lies vertically above** it in the upper electronic state

electronically excited molecule may be formed in one of several excited vibrational states all with turning points nearly vertically above the minimum of the lower curve ----- **absorption occurs at several different frequencies**

- d-d transitions
- Charge transfer transitions

LMCT $\text{KMnO}_4, \text{K}_2\text{Cr}_2\text{O}_7$

MLCT



Most intense electronic transitions responsible for the colour of many d-metal complexes are charge transfer transitions