

ADSORPTION FROM SOLUTIONS

Adsorption from solution is the process of preferential adsorption of solutes or solvent molecules from a solution by the adsorbent.

Eg: Decolorization of raw sugar by animal charcoal & Adsorption of oxalic acid from a solution by charcoal.

The adsorption process from solutions may be attributed to two factors:

- The decrease in interfacial tension by adsorption and
- Charged surface of the adsorbent attaches oppositely charged ions from solution.

Characteristic features of adsorption from solution:

- The extent of adsorption increases with the concentration of the solution.
- The adsorption is reversible in nature.
- The extent of adsorption increase if the solute is taken in a solvent with low solubility.
- More strongly adsorbable substance displaces a less strongly adsorbable substance from the surface.
- Freundlich adsorption isotherm is found to be applicable in adsorption from solutions.



Positive and Negative Adsorption:



- Positive adsorption involves the **adsorption of solutes** from the solution. This leads to a decrease in the concentration of solution.

Example: adsorption of oxalic acid by charcoal. This type of adsorption follows Freundlich adsorption equation.

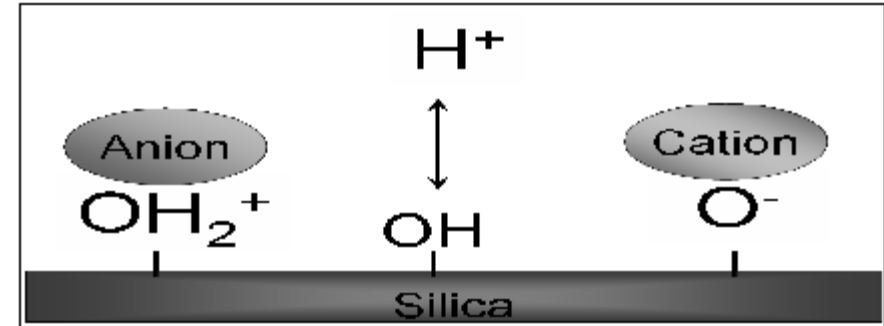
- Negative adsorption involves the **adsorption of solvent molecules** from the solution. This leads to an increase in the concentration of solution.

Example adsorption of solvent molecules by black charcoal from KCl solution.

Electrostatic Adsorption:

- The adsorption of particles by electrostatic interaction is termed electrostatic adsorption.
- The solid adsorbents acquire an electrostatic charge when it is in contact with the solution. The acquired charges on the surface will have a tendency to attract oppositely charged ions of solutes from the solutions. This is termed electrostatic adsorption.
- The electrostatic adsorption may take place over and above the mechanical adsorption.

For example: *Silica powder acquires negative charge on contact with water. When it is shaken with positively charged ferric hydroxide sol, the filtrate will be colourless due to electrostatic adsorption.*



GIBBS ADSORPTION ISOTHERM

Gibbs adsorption isotherm is the relationship between the adsorption and change in the surface tension of the solvent due to the addition of the solute.

Consider a solution of solute '2' in solvent '1'. The concentration of the solute at the surface will be different from that in the bulk of the solution. The accumulation of the solutes at the surface takes place by lowering the surface tension of liquid. This is explained by Gibbs adsorption equation.

The free energy of the system of solution depends on the number of moles of solvent (n_1), number of moles of solute (n_2) and the exposed surface area of the solution (A).

$$G = f(n_1, n_2, A)$$

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$$\therefore dG = \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2, A} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1, A} dn_2 + \left(\frac{\partial G}{\partial A} \right)_{T, P, n_1, n_2} dA$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma dA \text{----- (1)}$$

Where, γ is the surface tension or surface free energy. The above equation (1) can be integrated to get:

$$G = \mu_1 n_1 + \mu_2 n_2 + \gamma A \text{----- (2)}$$

Complete differential of (2) gives:

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \gamma dA + A d\gamma \text{----- (3)}$$

Comparing equations (1) and (3), we get

$$n_1 d\mu_1 + n_2 d\mu_2 + A d\gamma = 0 \text{----- (4)}$$

Equation (4) is applicable to the surface phase of the solution only. The remaining solution unaffected by the surface force is known as the bulk phase. Let n_1^0 and n_2^0 are the number of moles of solutes and solvent in the bulk phase. The bulk phase is not affected by surface forces. Hence the equation for the bulk phase is given by:

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad \text{-----(5)}$$

Multiplying equation (5) with $\frac{n_1}{n_1^0}$ and subsequently subtracting it from equation (4), we get

$$\left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right) d\mu_2 + A d\gamma = 0$$

Or,
$$\frac{d\gamma}{d\mu_2} = - \frac{\left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right)}{A} \quad \text{-----(6)}$$

The term in the parenthesis on the numerator of RHS of the above equation represents the excess concentration of the solute present at the surface of the liquid. The excess surface concentration per unit area of the surface is called the surface excess of the solute. It is represented by the symbol (Γ). The surface excess is given by;

$$\Gamma = \left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right) / A$$

Applying the above in equation (6), we get

$$\frac{d\gamma}{d\mu_2} = -\Gamma \text{-----(7)}$$

Relationship between Surface excess and concentration of the solute:

The chemical potential of a solute in a solution is given by

$$\mu_2 = \mu_2^0 + RT \ln a_2$$

Where a_2 is the activity of the solute.

Differentiating wrt a_2 we get;

$$\frac{d\mu_2}{da_2} = RT \times \frac{1}{a_2}$$

Or, $d\mu_2 = RT d \ln a_2$

Putting this in equation (7), we get

$$\frac{d\gamma}{RT d \ln a_2} = -\Gamma$$

$$\Gamma = -\frac{a_2}{RT} \frac{d\gamma}{da_2}$$

For dilute solutions, activity can be replaced by concentration 'c'.

Then,

$$\Gamma = -\frac{c}{RT} \frac{d\gamma}{dc}$$

The above equation is known as the Gibbs adsorption isotherm.

PROPERTIES OF GIBBS ADSORPTION ISOTHERM:

The term surface excess represents the extent of adsorption from solutions.

When Γ is positive, the adsorption is positive adsorption. When Γ is negative, the adsorption is negative adsorption.

Γ is positive:

This is possible only when $\frac{d\gamma}{dc}$ is negative

It means that for positive adsorption to occur, the addition of the solute lowers the surface tension of the solution

Γ is Negative

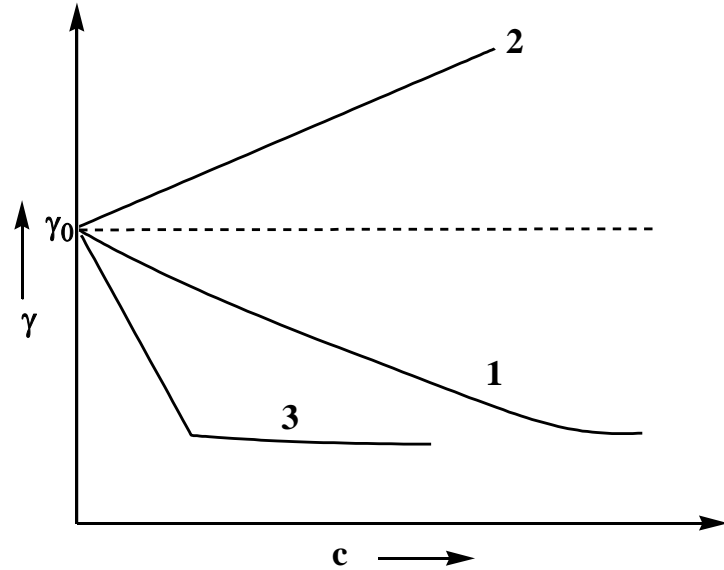
This occurs when $\frac{d\gamma}{dc}$ is positive

It means that when negative adsorption occur, the addition of the solute increases the surface tension of the solution.

$$\Gamma = -\frac{c}{RT} \frac{d\gamma}{dc}$$

SURFACE TENSION VS CONCENTRATION DIAGRAMS:

Surface tensions for the interface of an aqueous solutions for different types of solutes can be represented as follows.



Curve 1 represents positive adsorption. This is shown by un-ionised organic compounds in dilute solutions.

Curve 2 represents negative adsorption. This is shown by inorganic electrolytes and highly hydrated organic compounds.

Curve 3 represents high positive adsorption shown by soluble amphipathic species.

1. Domain and Barker Method:

- Domain and Barker studied adsorption of nonylic acid from aqueous solution at the liquid-air interface.
- An aqueous solution of nonylic acid is taken in a long pipe.
- Air is blown into the pipe to form bubbles. Bubbles containing nonylic acid is collected and analysed.
- The surface excess is calculated by the expression

$$\Gamma = \frac{w_1 (c_s - c_b)}{S}$$

Where, S is the total surface area of the bubbles.

c_s is the surface layer concentration, c_b is the bulk concentration.

w_1 is the weight of the solvent in w gram of the solution.

- Γ values calculated from this method is found to be different from the theoretical values.
- Bensen method is similar to Domain & Barker method. In this method the bubbles of air are passed through the solution of amyl alcohol.

2. The Microtome Method:

- McBain and co-workers employed a microtome which consisted of a sharp blade mounted on a carriage that rested on rails.
- The carriage could be propelled at high speeds. The surface layer of the liquid is cut-off by means of a rapidly moving microtome. A thin layer is retained in a silver reservoir in the blade.
- The surface excess is then given by:

$$\Gamma = \frac{\Delta c}{A} \left[\frac{w}{1 + c + \Delta c} \right]$$

Where, c is the concentration of the solution

Δc is the difference in concentration between the solution and the microtome sample.

A is the area of the surface sample and

w is the weight of the sample.

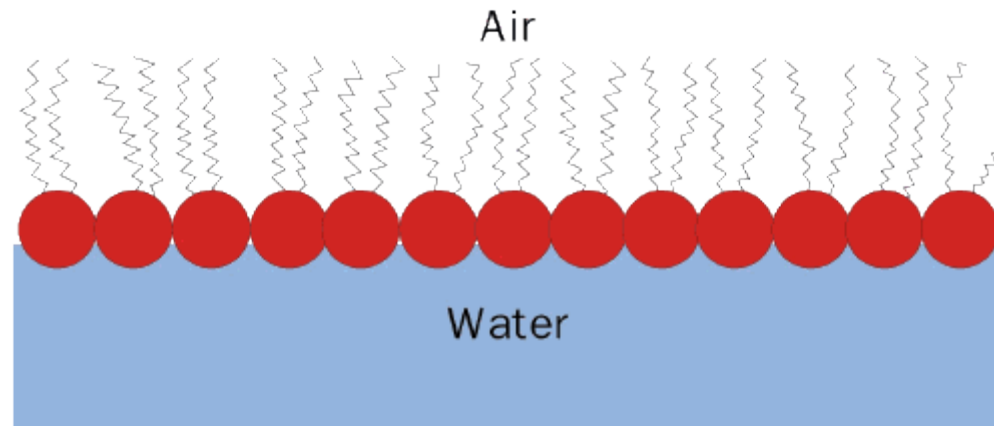


3. Tracer Method:

- The solute is labelled with a radioisotope like ^{14}C or ^{35}S .
- A detector is placed close to the surface.
- The measured radioactivity corresponds to the concentration of labelled solutes at the surface.

STRUCTURE OF SURFACE FILMS

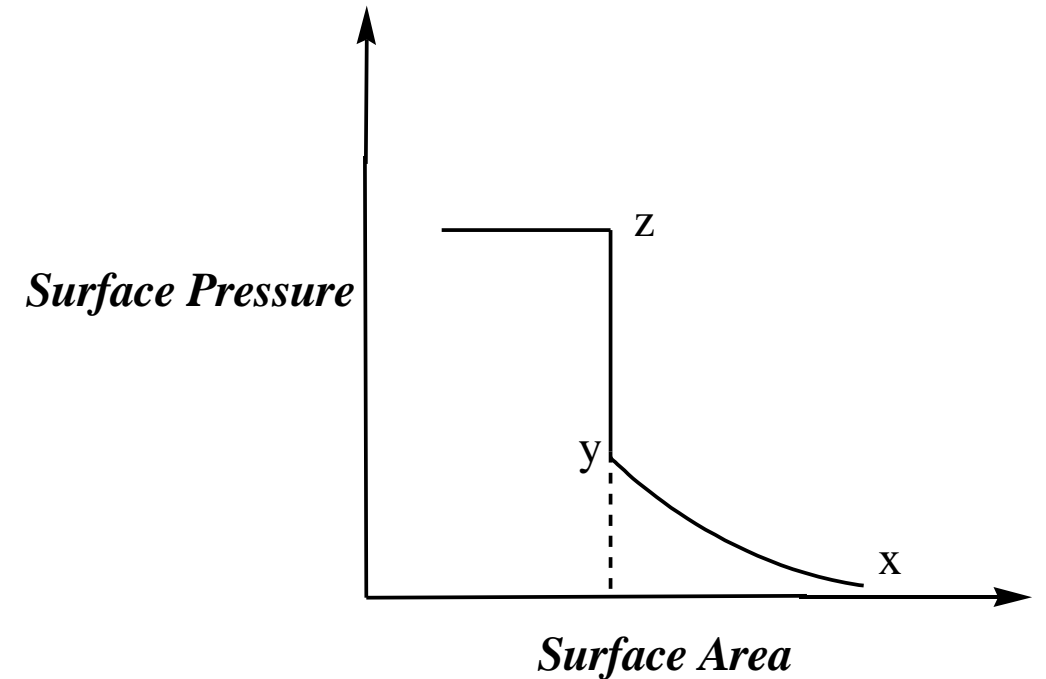
- Surface films are formed when the constituent molecules adsorb onto the surface of a liquid.
- The constituent molecules consist of a hydrophilic end group (polar group) and a hydrophobic chain.



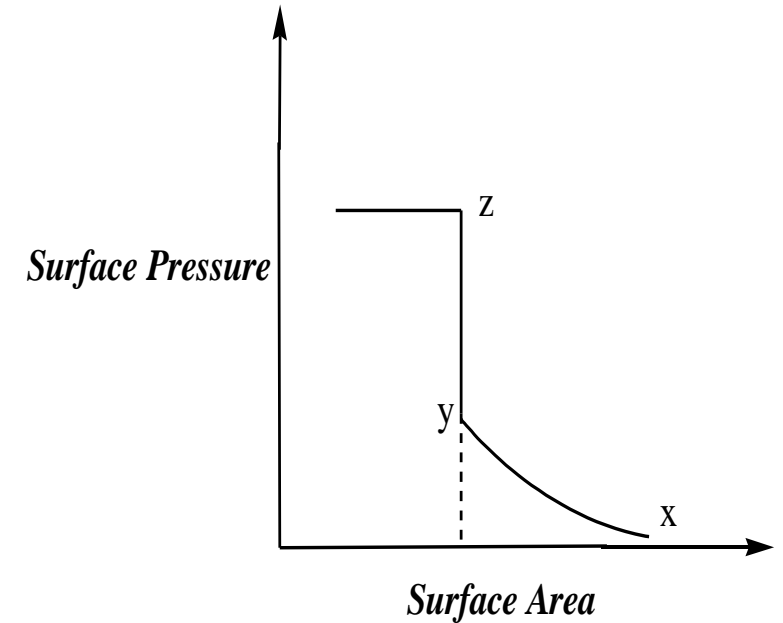
- The solubility of molecules in water decreases if the length of the hydrophobic chain increases.
- Information regarding the structure and orientation of molecules in surface film can be obtained from the surface pressure – area diagrams of surface films.

SURFACE PRESSURE (π) – AREA (A) ISOTHERMS:

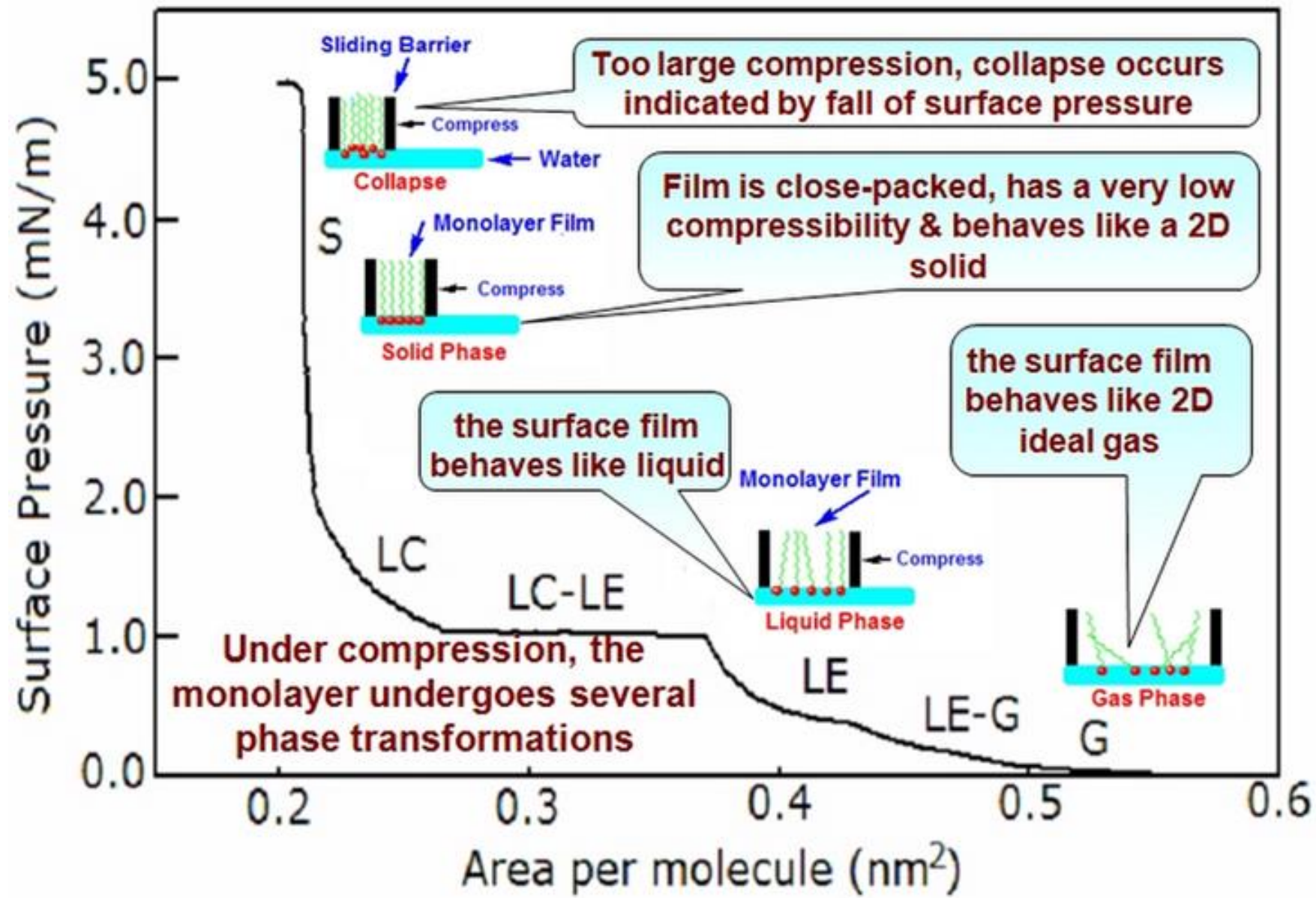
- π – A isotherms are obtained when surface pressure is plotted against area molecules covered by the adsorbate at a constant temperature.
- The shapes of the isotherms depend on the nature of the surface films.
- An isotherm is recorded by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure.
- Depending on the material being studied, repeated compressions and expansions could be necessary to achieve a reproducible trace.

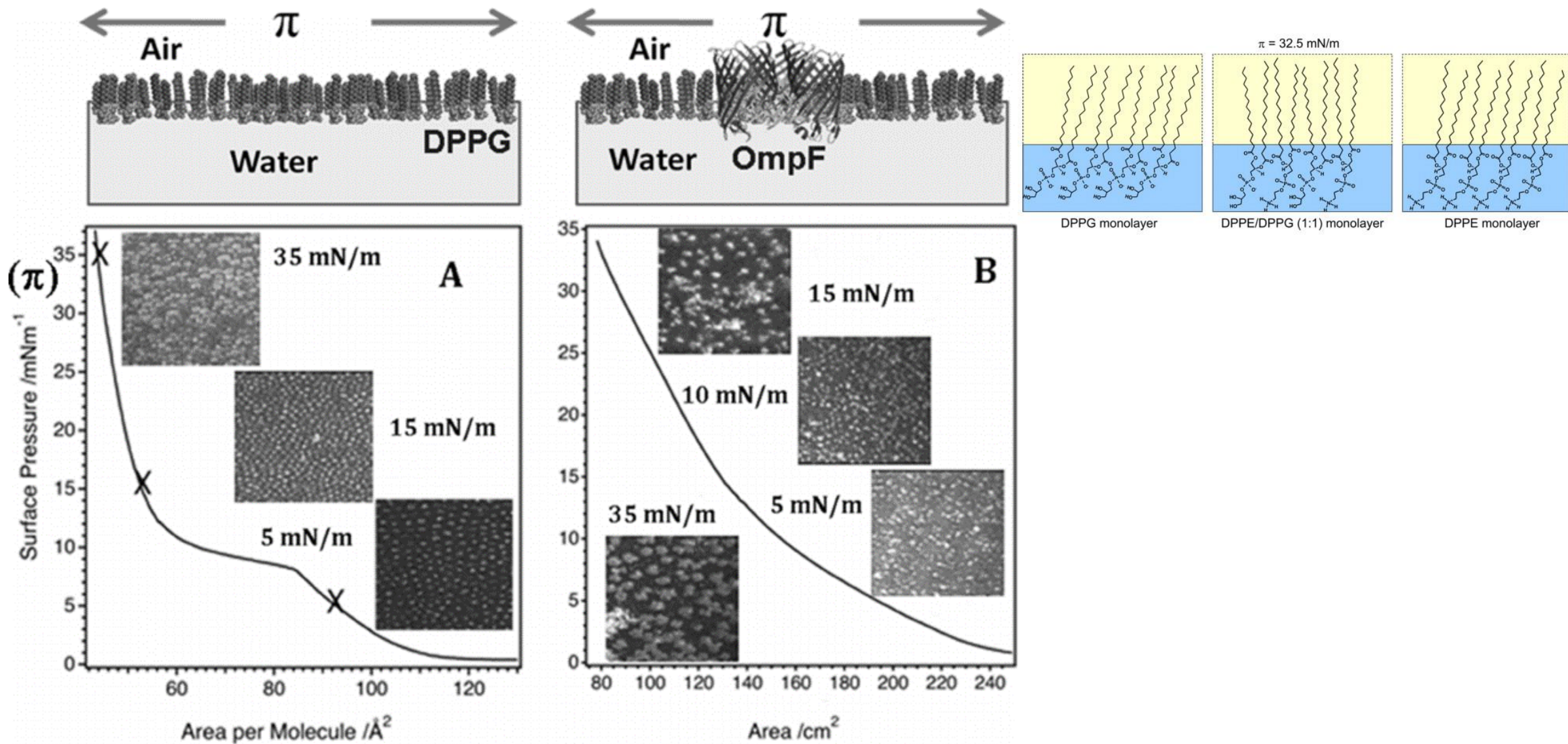


- The 'xy' portion indicates that when the surface pressure is increased gradually, the area decreases upto point 'y'.
- The film becomes rigid at point 'y' and further increase of pressure does not result in any contraction of the area.
- The area corresponding to point 'y' is the area of monolayer when the molecules are closely packed.
- At point 'z' there is a sudden reduction in the area by which the film collapses and buckles and folds. The surface pressure corresponds to the collapsing point is known as the Collapse Pressure of the surface film. Collapse pressure is the highest surface pressure a film can withstand.



- *The compressibility of a surface film can be obtained from the steepness of the 'xy' region of the isotherm. If the 'xy' region is more steep then the surface film is less compressible, while a flat or less steep 'xy' region on the isotherm indicates high compressibility of surface films.*



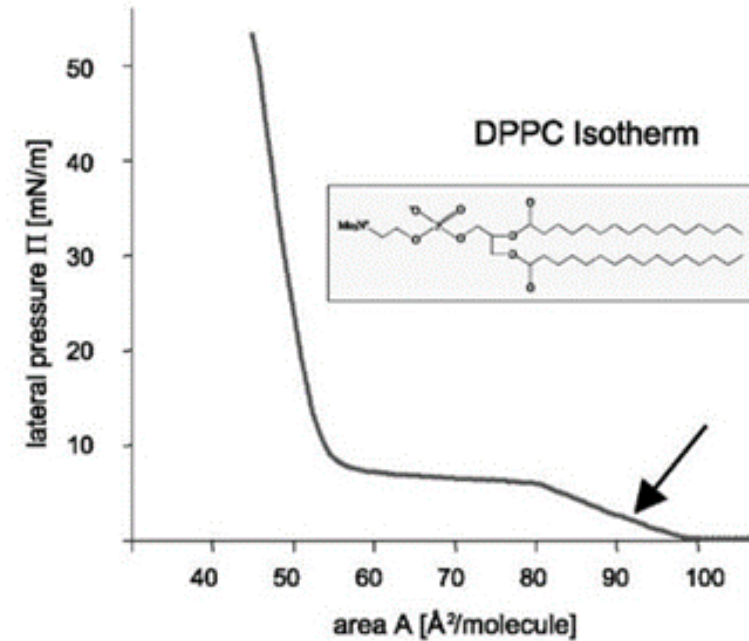
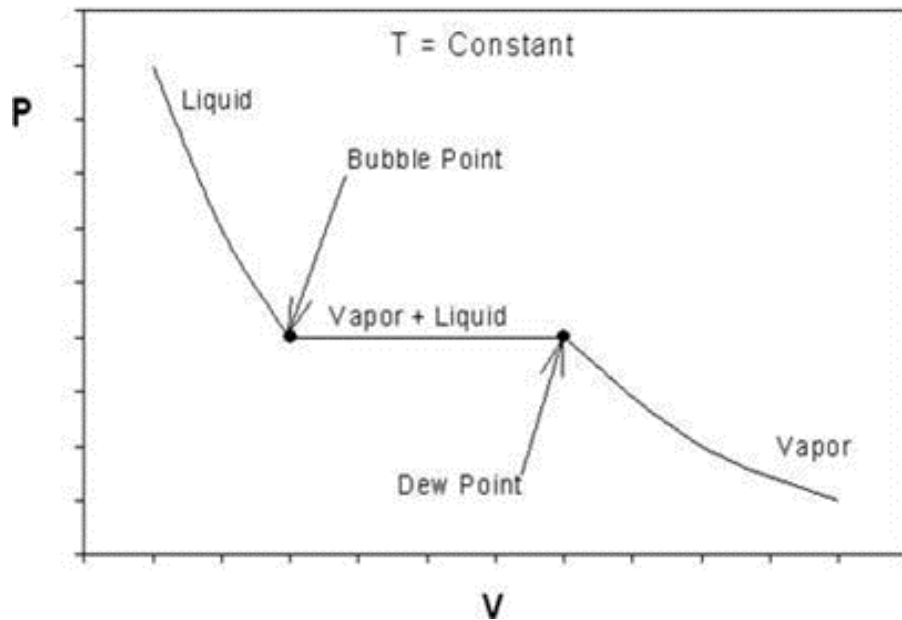


DPPG (dipalmitoyl-phosphatidylglycerol, sodium salt)

outer membrane protein OmpF

ANALOGY BETWEEN SURFACE FILM SURFACE FILMS AND GASES

i) *P-V isotherm of gases and π -A isotherm of surface films:*



ii) For ideal gas the equation of state may be given as

$$PV = nRT$$

while for a surface film similar equation may be obtained as;

$$\pi A = n^\sigma RT$$

Where n^σ is the number of moles of gas present in the monolayer.

THEORY OF TPD

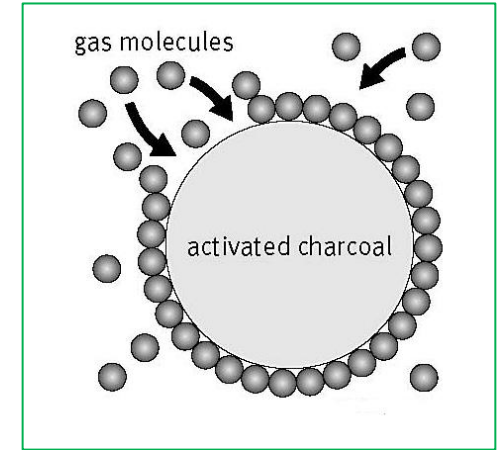
- In the TPD process, temperature is increased linearly with time from an initial temperature (T_0).
- The temperature at time 't' is given by

$$T(t) = T_0 + \left(\frac{dT}{dt} \right) t$$

- The desorption from the surface takes place at a particular temperature when the activation energy barrier is crossed.
- The rate of desorption is given by:

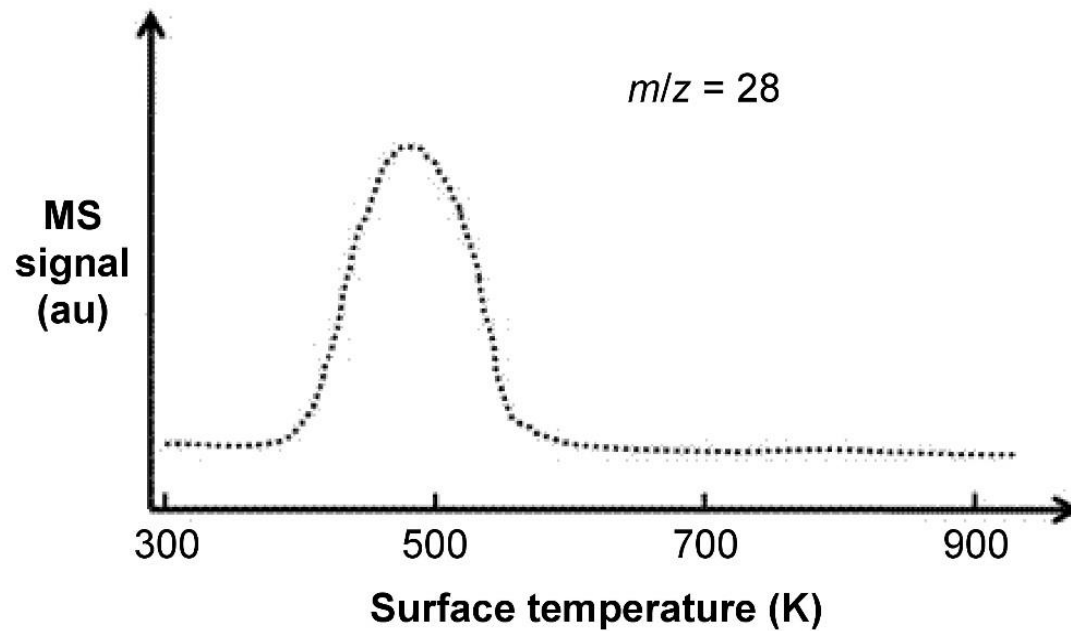
$$R_{des} = N \cdot \exp\left(-\frac{E_a^{des}}{RT} \right)$$

Where, 'N' is a term representing the coverage



TPD SPECTRUM

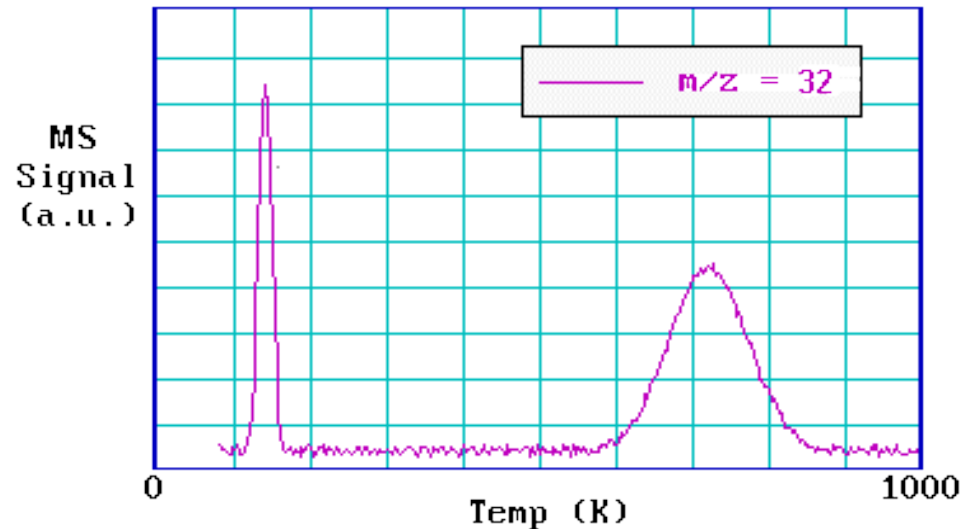
- The intensity of the desorption signal is proportional to the rate at which the surface concentration of adsorbed species is decreasing.
- The data obtained from TPD experiments is recorded as the intensity variation of recorded mass fragment vs time/temperature..



TPD spectrum following adsorption of CO onto a Pd(111) crystal at 300 K.

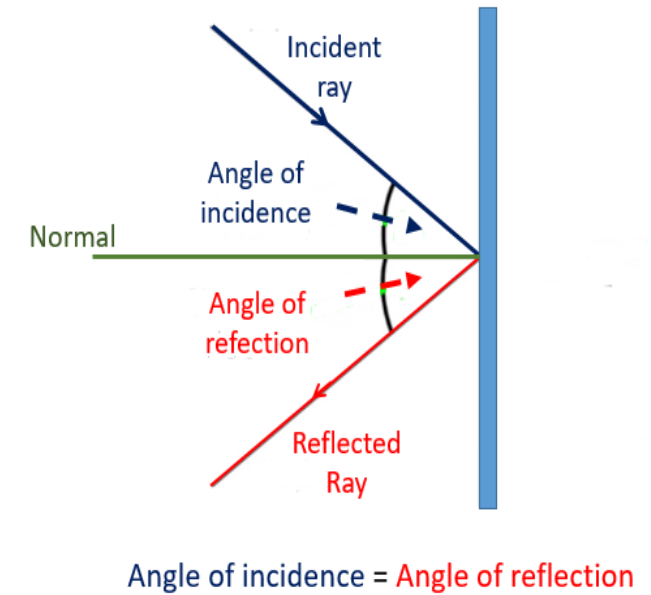
Information can be obtained from the TPD spectrum:

- The **area** under the peak is directly proportional to the **amount of adsorbed species** or to the surface coverage.
- The **kinetics** of the peak profile give information on the **state of aggregation** of the adsorbed species.
- The **position of the peak** is related to the enthalpy of adsorption or **strength of binding** to the surface.
- The presence of **multiple peaks** in the TPD spectrum indicates that there are **more than one type of binding** state for a molecule on a surface. The homogeneity of a surface can be confirmed by absence of multiple peaks.

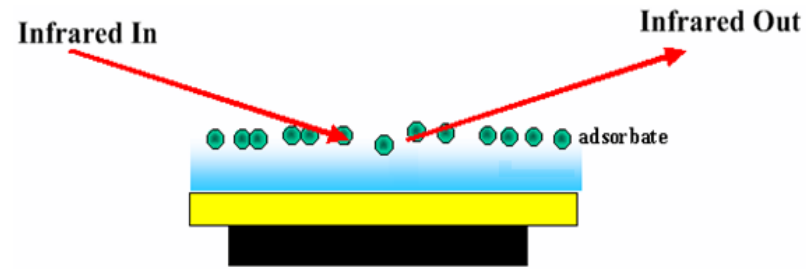


REFLECTION-ABSORPTION IR SPECTROSCOPY

- Vibrational spectroscopy provides information about the molecular species on surfaces and any other species generated by surface reactions.
- Infrared reflection–absorption spectroscopy (IRRAS or RAIRS) is an optical technique used to study thin (often submonolayer) films adsorbed on reflective substrates such as metals.
- Experimentally, it involves measuring the change in the reflectance spectrum of the substrate that accompanies adsorption.
- In reflection-absorption IR spectroscopy the IR beam is specularly reflected from the front face of a highly- reflective sample like a single crystal surface.
- Specular reflection is a type of surface reflectance often described as a mirror-like reflection of light from the surface. In specular reflection, the incident light is reflected into a single outgoing direction. The specular reflection is represented below.



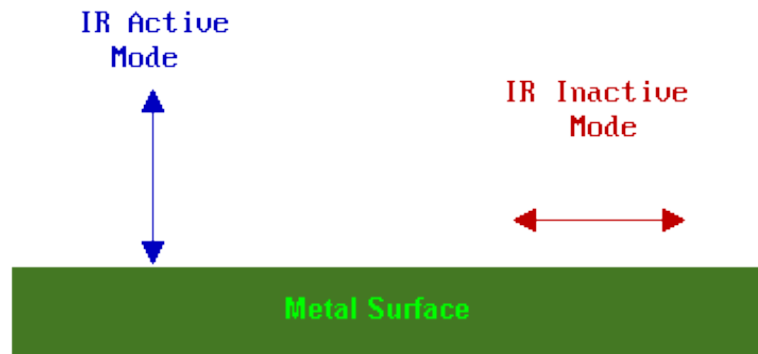
Instrumental Set-Up



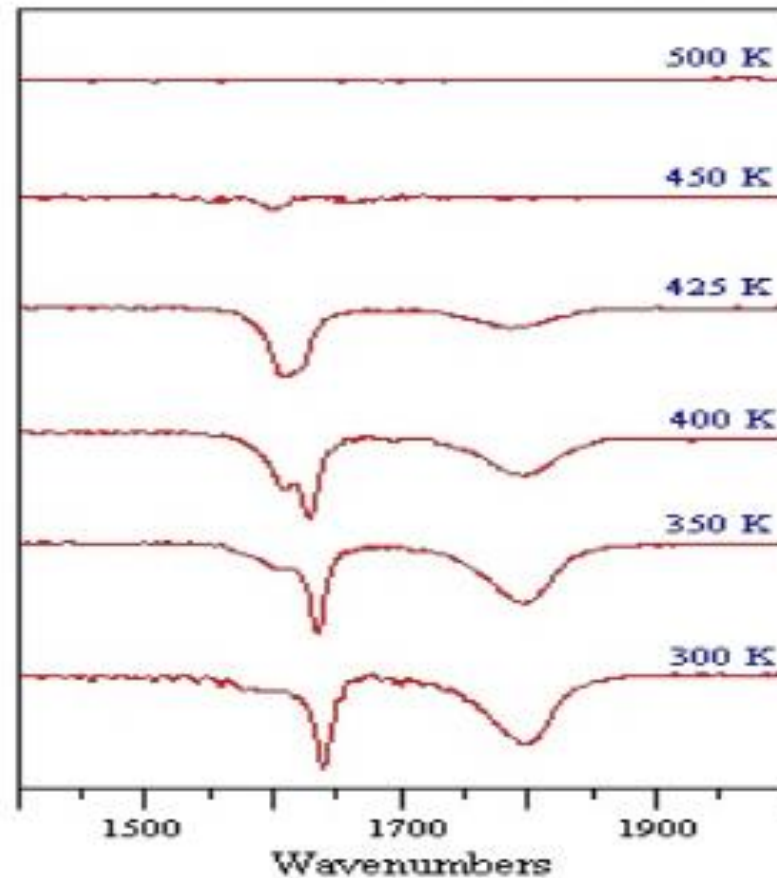
- The peaks corresponding to the vibrational modes of adsorbates are observed in RAIRS.
- The vibrational modes corresponding to metal-adsorbate bond, which usually appears below 600 cm^{-1} are not observed in RAIRS.

Surface Dipole Selection Rule

Only those vibrational modes which give rise to an oscillating dipole perpendicular to the surface are IR active and give rise to peaks.



RAIRS is specially used to study the adsorption of CO on solid surfaces. Also for NO & HCN adsorption on Pt surface. An example for N-O spectra of NO adsorption on Pt is given below.

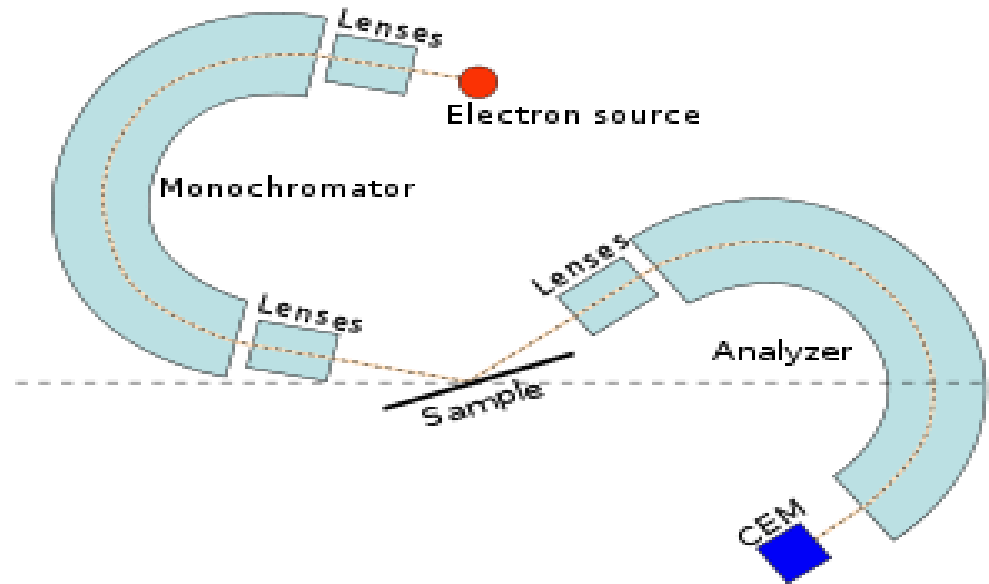


HIGH RESOLUTION ELECTRON-ENERGY LOSS SPECTROSCOPY (HREELS)

- Electron energy loss spectroscopy utilizes the scattering of electrons with low energy in order to measure the vibrational spectra of surface species.
- EELS is the most suitable vibrational technique to study the crystal surfaces.

The experimental procedure involves the following steps:

- Well defined beam of electrons from the electron monochromator with a fixed incident energy is made to fall on the surface.
- The scattered electrons are analysed using an appropriate electron energy analyser.



E_0 is the energy of the incident beam and E is the energy of the scattered beam. When $E = E_0$, elastic scattering takes place and we get an elastic peak in the spectrum.

The output data is obtained as a plot of **number of electrons with a particular energy** *vs* the **energy loss**. The magnitude of energy loss ($\Delta E = E_0 - E$) is equal to the vibrational quantum.

EELS possess a variable selection rule. Vibrational methods are observed in both specular and off-specular modes. In specular mode, the scattering generally occurs by a long-range dipole mechanism while in the off-specular mode, the scattering takes place by a short-range impact.

The surface-carbon stretching in a carbonyl adsorption can be easily observed in EELS.

