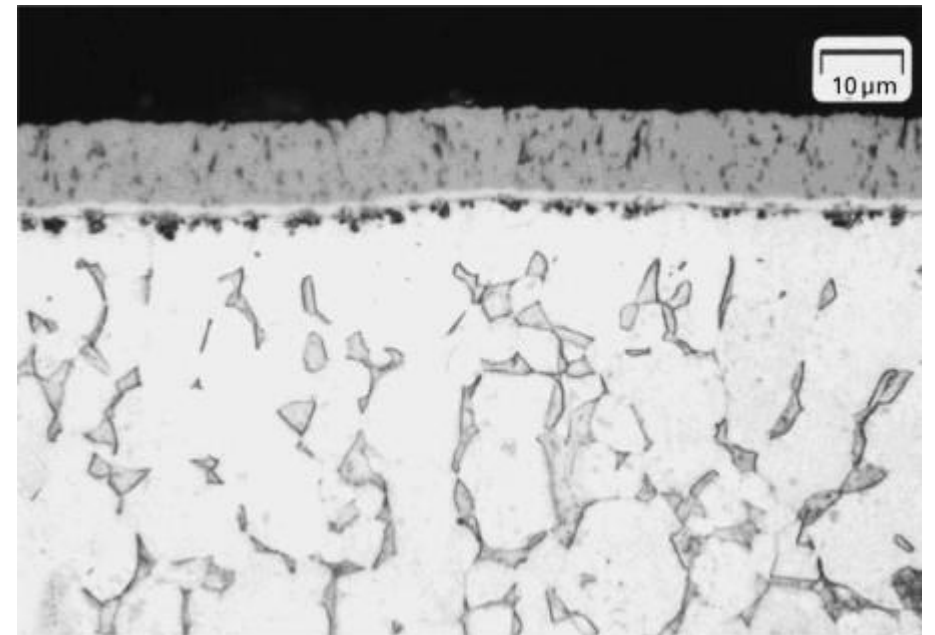
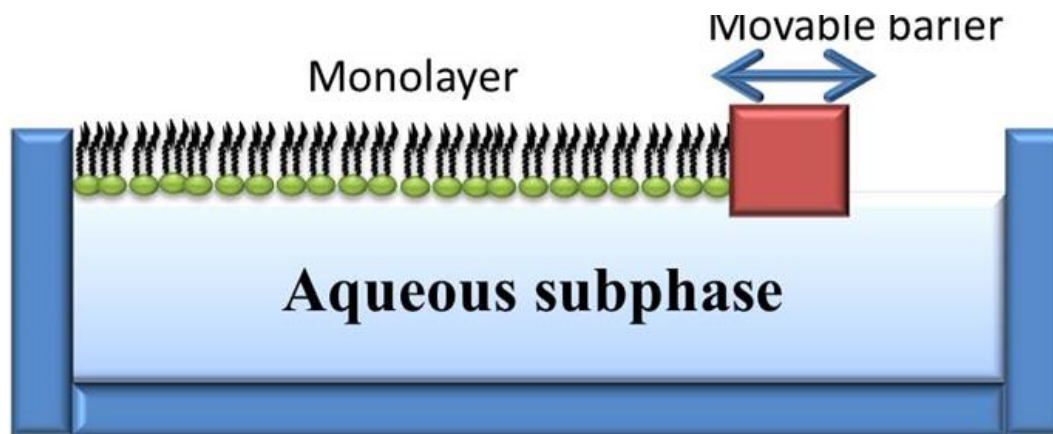


SURFACE FILMS

- **Surface Film** – Film of a layer of substance spread over a surface, whose thickness is so small that the gravitational effects are negligible.
- **Surface Film – Monolayer films - one molecule thick**
- **Duplex Film** – Surface film possess two separate interface.



Stearic acid and lauryl alcohol spread spontaneously on the water surface and produces a surface film.

SURFACE FILM PRESSURE

- **Surface film pressure or surface pressure – Difference between the surface tension of the pure solvent (γ^0) and that of the solution (γ).**

$$\pi = \gamma^0 - \gamma$$

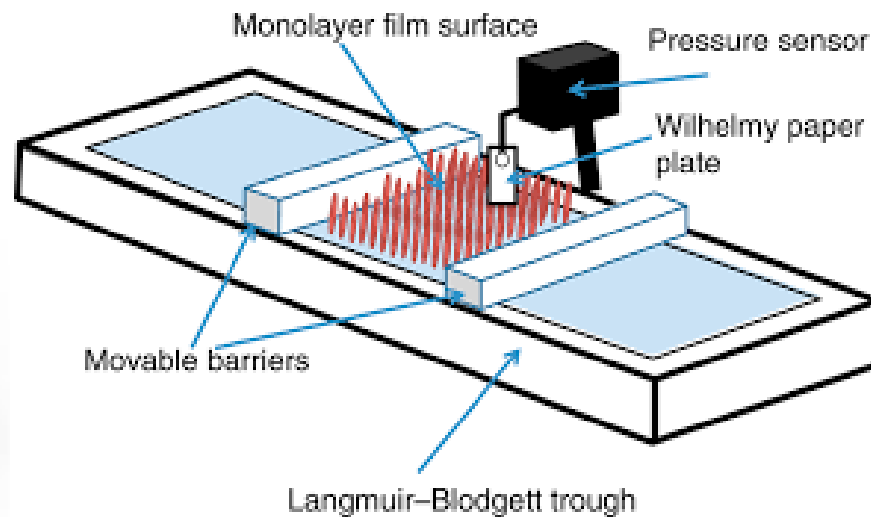
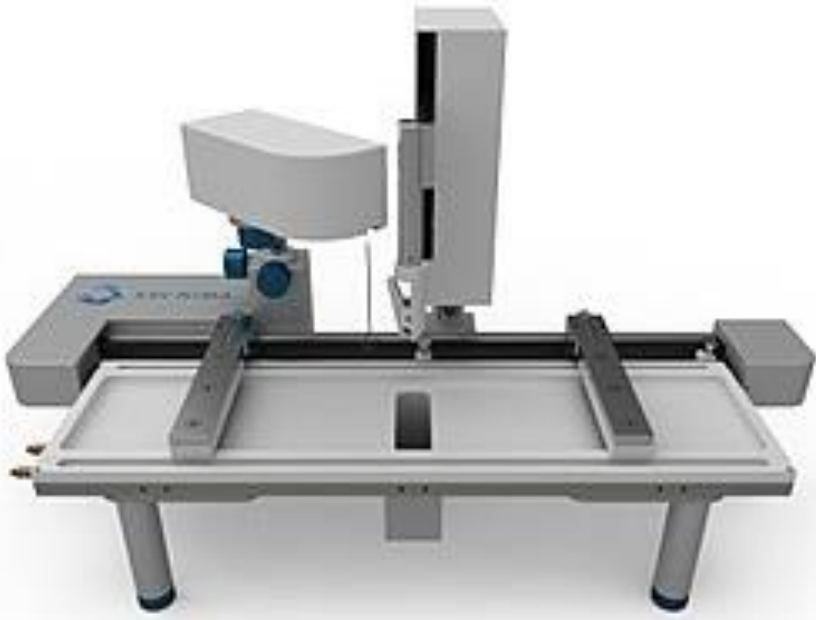
- **Surface tension of the pure solvent get lowered by the addition of a solute.**
- **The extent of lowering of surface tension is expressed in terms of the surface pressure.**
- **Unit of Film pressure is N/m or dynes/m**

MEASUREMENT OF SURFACE PRESSURE

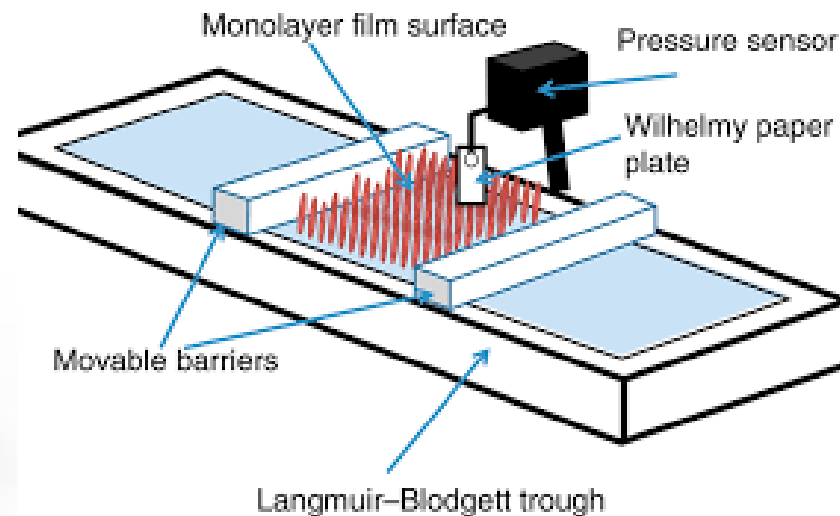
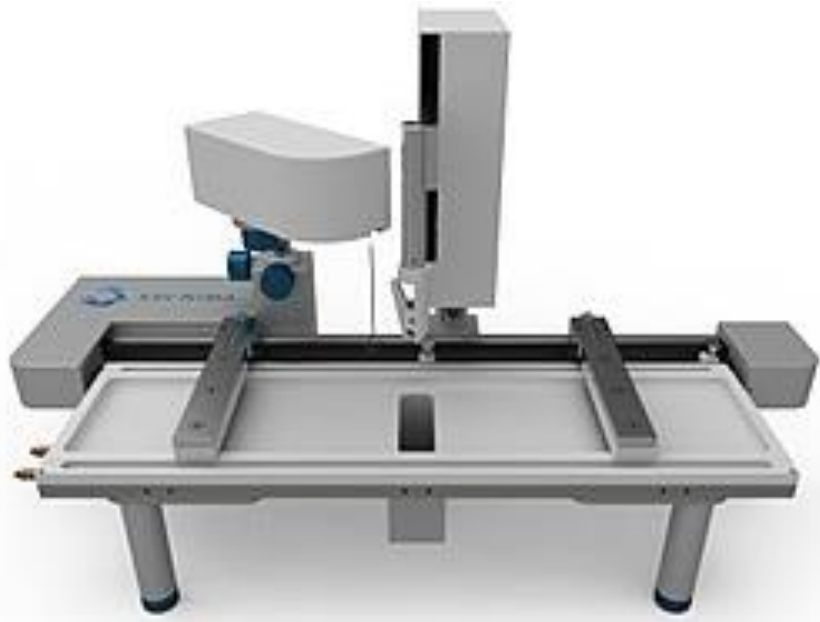
- Langmuir Film Balance

- **Main Components**

- Fixed Barrier – Strip of mica float on the surface, connected to torsion wire
- Sweeping Barrier – Fixed at the ends to sweep the surface
- Compression Barrier – Floating barrier upon the surface and prevents the leakage of surface films past the float
- Trough - Tray to keep the liquid

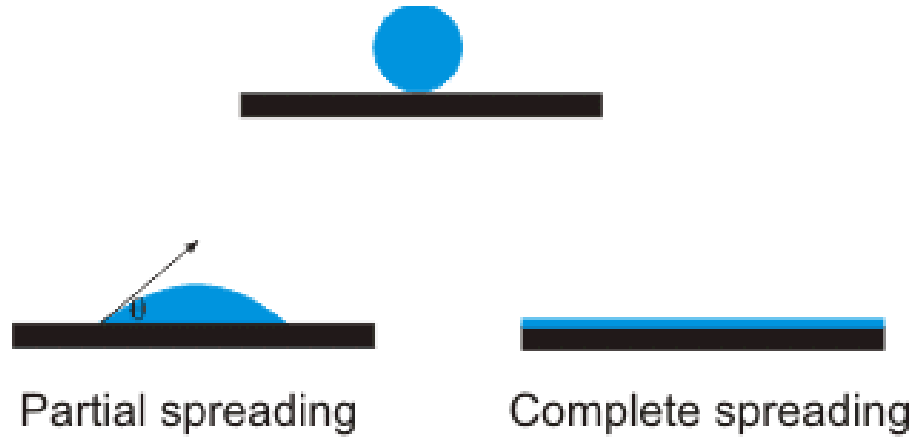


- Small amount of the surfactant surface is dissolved in a volatile solvent and poured onto the surface of water.
- Sweeping barrier is advanced towards the compression barrier.
- Compression barrier is then moved across the water surface.
- Surface pressure exerted on the fixed barrier is then measured using the torsion wire.



Criteria for Spreading of One Liquid over Another

Consider the spreading of liquid B on liquid A.



Spreading Coefficient, $S_{B/A}$ – Determines the possibility of spreading of B on A

The surface free energy of the system is given by:

$$G = f(A_A, A_B, A_{AB})$$

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$$dG = \left(\frac{\partial G}{\partial A_A} \right) dA_A + \left(\frac{\partial G}{\partial A_B} \right) dA_B + \left(\frac{\partial G}{\partial A_{AB}} \right) dA_{AB}$$

The relationship between the changes in area is given by;

$$dA_A = -dA_B = -dA_{AB}$$

Surface Tension - The ratio of free energy to surface area

$$dG = \gamma_A dA_A + \gamma_B dA_B + \gamma_{AB} dA_{AB}$$

$$dG = -\gamma_A dA_B + \gamma_B dA_B + \gamma_{AB} dA_B$$

$$dG = -\gamma_A dA_B + \gamma_B dA_B + \gamma_{AB} dA_B$$

$$\left(\frac{\partial G}{\partial A_B} \right)_{area} = -\gamma_A + \gamma_B + \gamma_{AB}$$

Spreading coefficient, $S_{B/A}$ is defined as the free energy change for spreading of the film of a liquid B on A

$$S_{B/A} = - \left(\frac{\partial G}{\partial A_B} \right)_{area} \quad S_{B/A} = \gamma_A - \gamma_B - \gamma_{AB}$$

- Spreading coefficient, $S_{B/A}$ will be positive when the derivative is negative.
- a decrease in free energy due to the spreading of B on A
- the spreading will be spontaneous, if the spreading co-efficient is positive.

Spreading Co-efficient and Works of Cohesion and Adhesion:

The spreading coefficient can also be expressed in terms of the **work of adhesion of A to B** (W_{AB}) and the **work of cohesion of B** (W_{BB})

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}$$

W_{AB} is also referred to as the work necessary for separating one cm² of interface AB into two liquid vapour interfaces A and B.

$$W_{BB} = 2\gamma_B$$

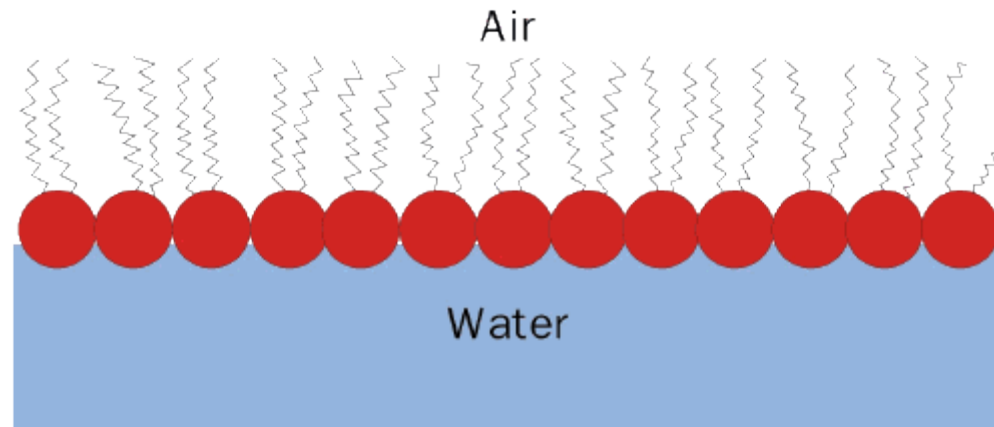
$$S_{B/A} = W_{AB} - W_{BB}$$

- The spreading coefficient value gives the indication about the spreading of a layer on other.
- The spreading happens when a liquid of low surface tension is kept on another liquid with high surface tension.
- Benzene and long chain alcohols with a low surface tension will spread on water.
- Almost all liquids will spread to yield a film on mercury surface.

Benzene and long chain alcohols with a low surface tension will spread on water. While almost all liquids will spread to yield a film on mercury surface.

STRUCTURE OF SURFACE FILMS

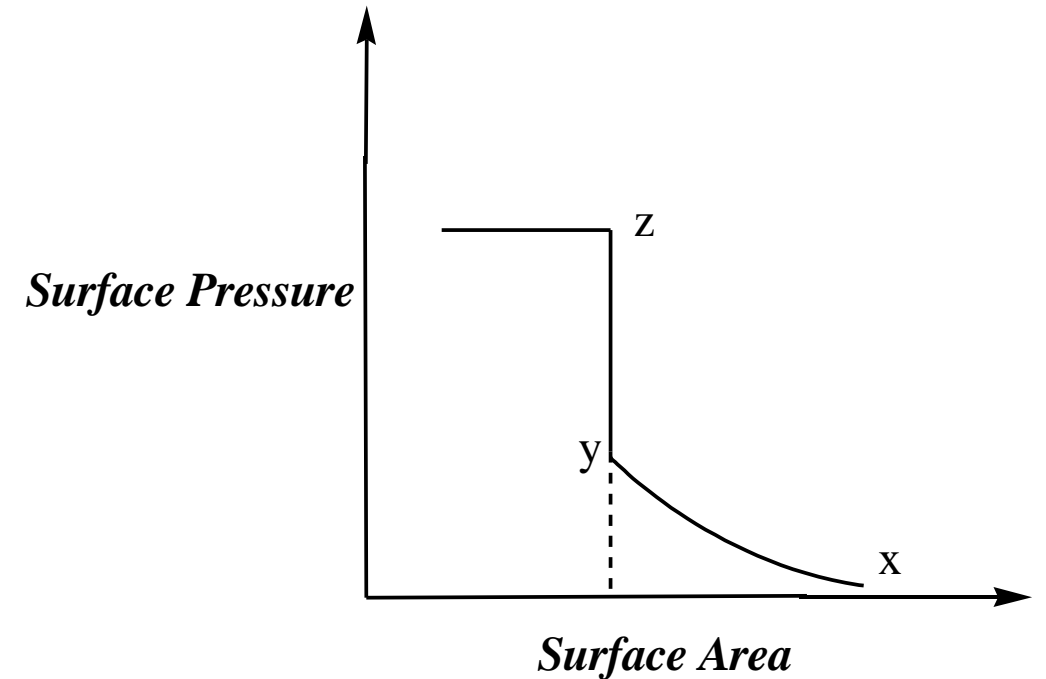
- Surface films are formed when the constituent molecules adsorb onto the surface of a liquid.
- The constituent molecules consist of a hydrophilic end group (polar group) and a hydrophobic chain.



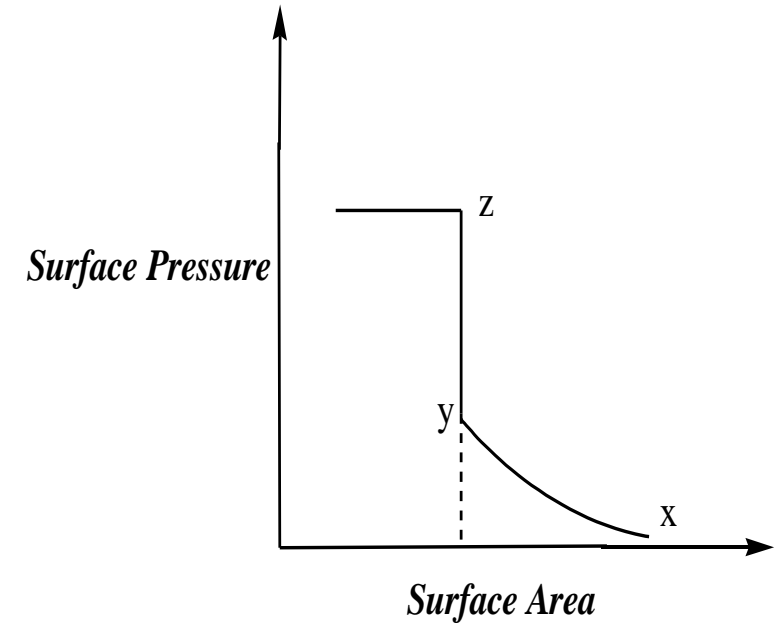
- The solubility of molecules in water decreases if the length of the hydrophobic chain increases.
- Information regarding the structure and orientation of molecules in surface film can be obtained from the surface pressure – area diagrams of surface films.

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

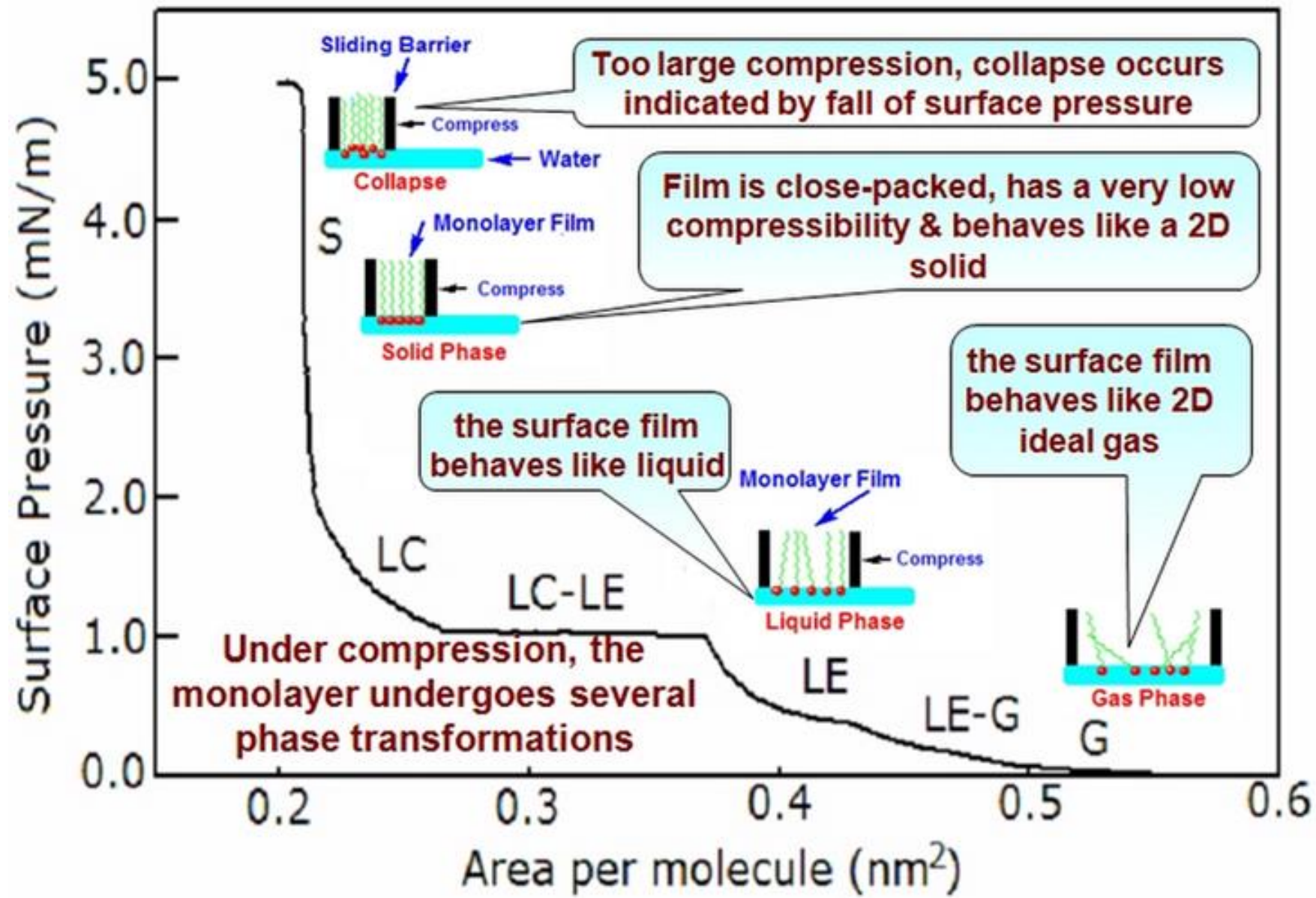
- π – A isotherms are obtained when surface pressure is plotted against area molecules covered by the adsorbate at a constant temperature.
- The shapes of the isotherms depend on the nature of the surface films.
- An isotherm is recorded by compressing the film (reducing the area with the barriers) at 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.

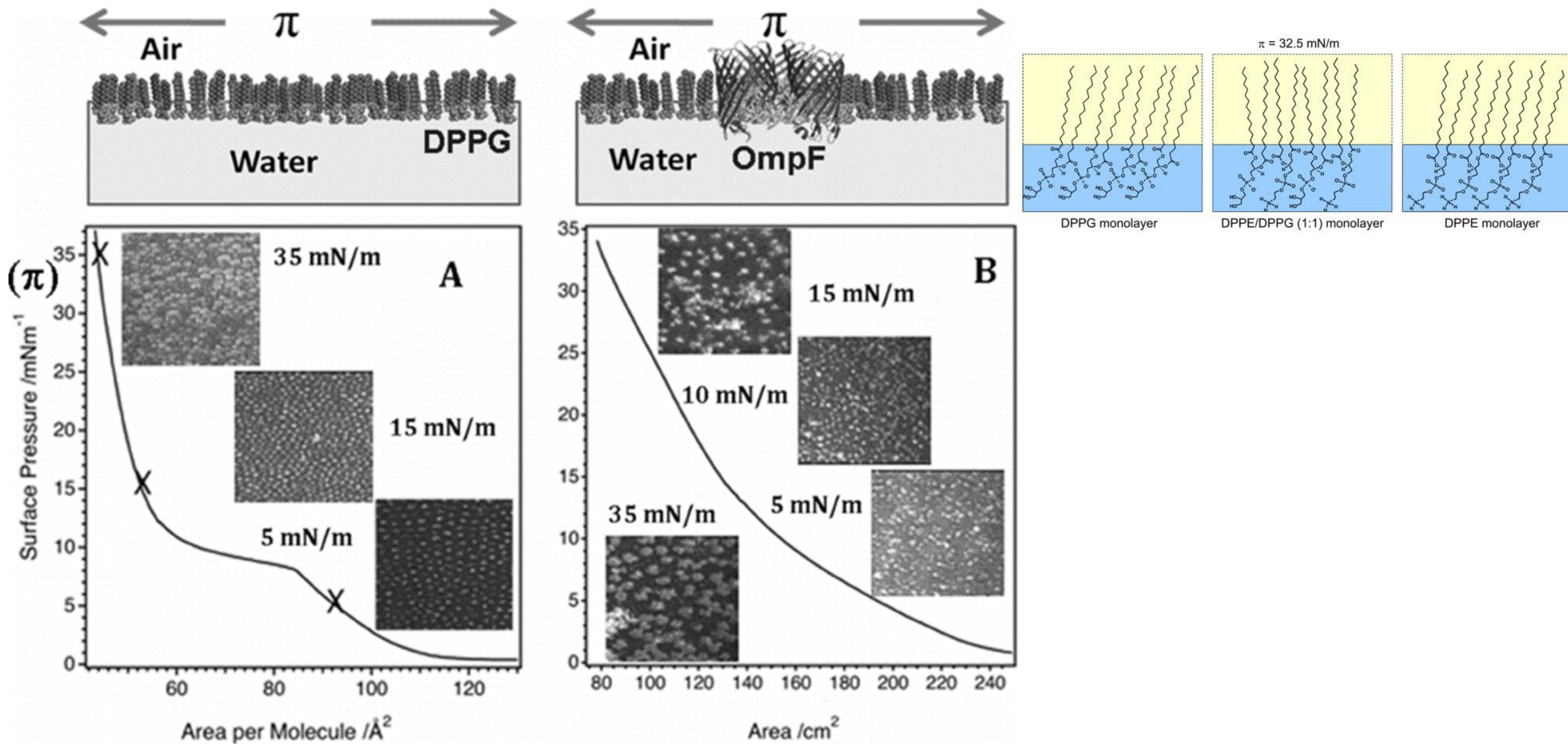


- The 'xy' portion indicates that when the surface pressure is increased gradually, the area decreases upto point 'y'.
- The film becomes rigid at point 'y' and further increase of pressure does not result in any contraction of the area.
- The area corresponding to point 'y' is the area of monolayer 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.*



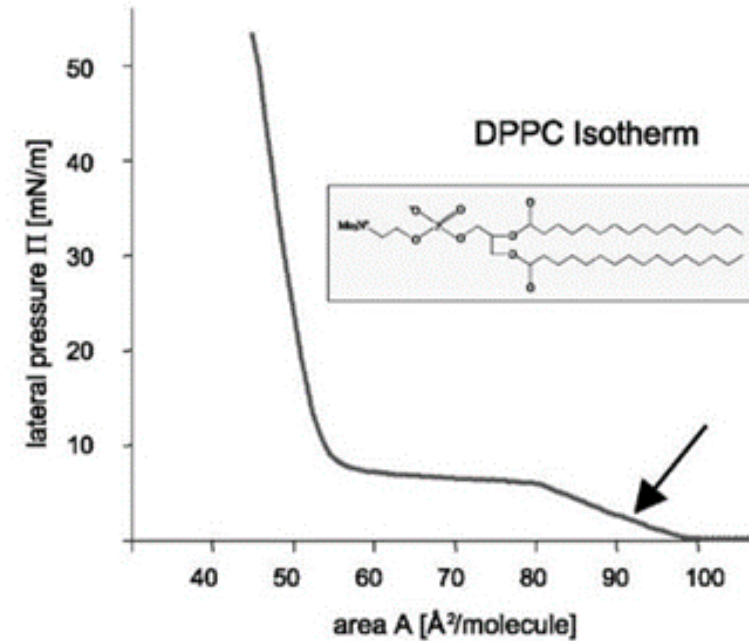
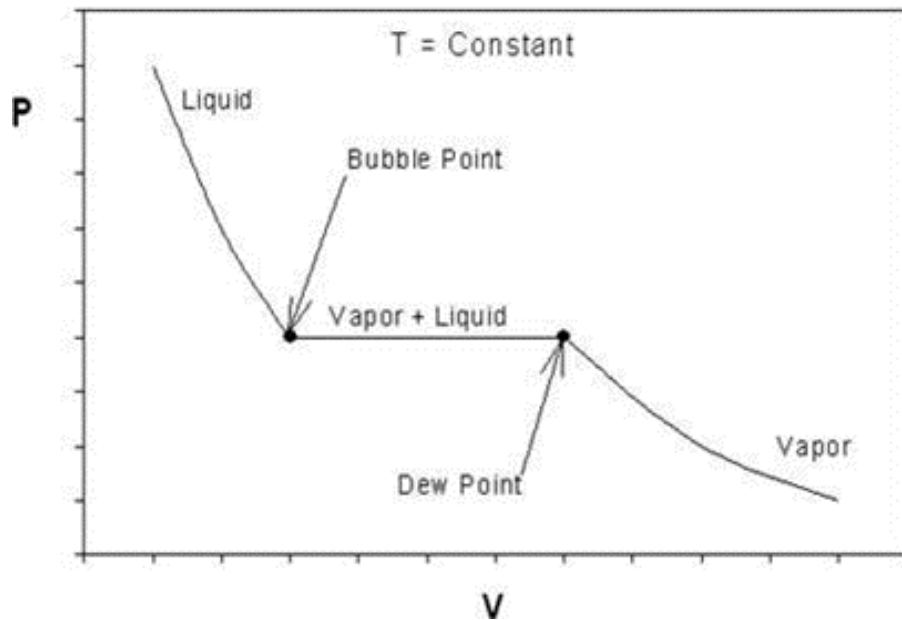


DPPG (dipalmitoyl-phosphatidylglycerol, sodium salt)

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

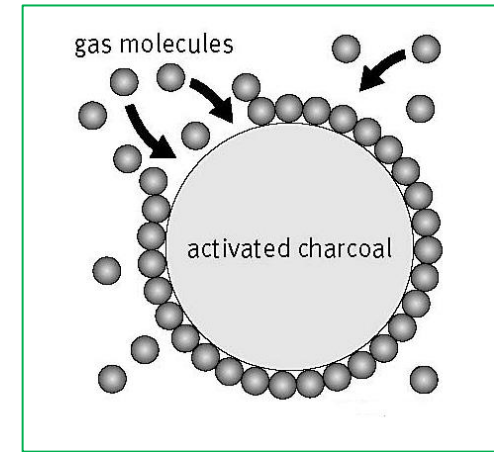
- In the TPD process, temperature is increased linearly with time from an initial temperature (T_0).
- The temperature at time 't' is given by

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

- 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:

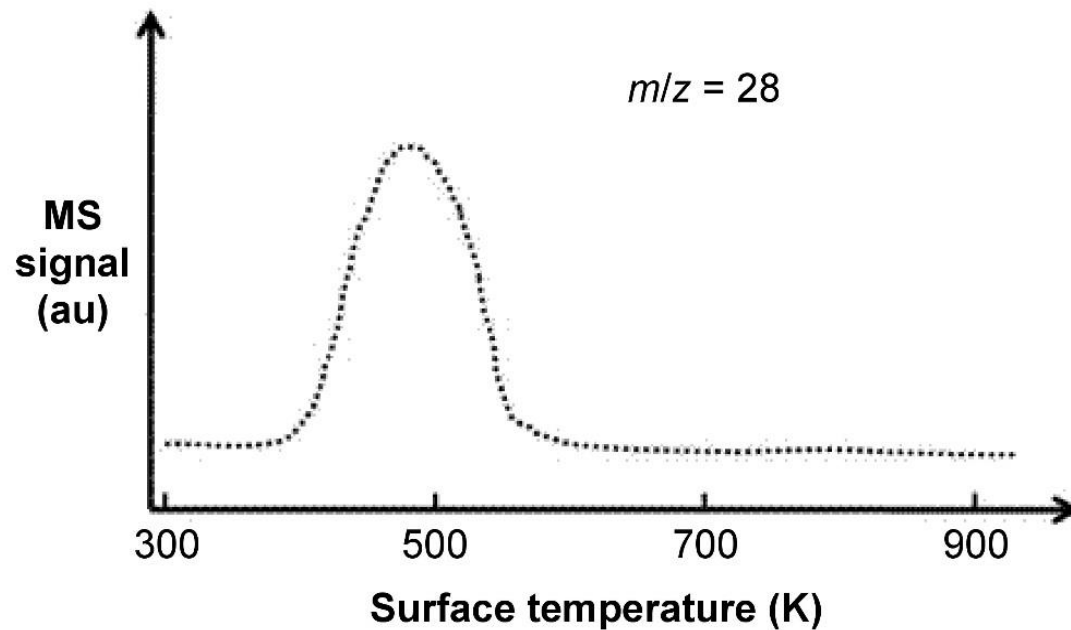
$$R_{des} = N \cdot \exp\left(-\frac{E_a^{des}}{RT} \right)$$

Where, 'N' is a term representing the coverage



TPD SPECTRUM

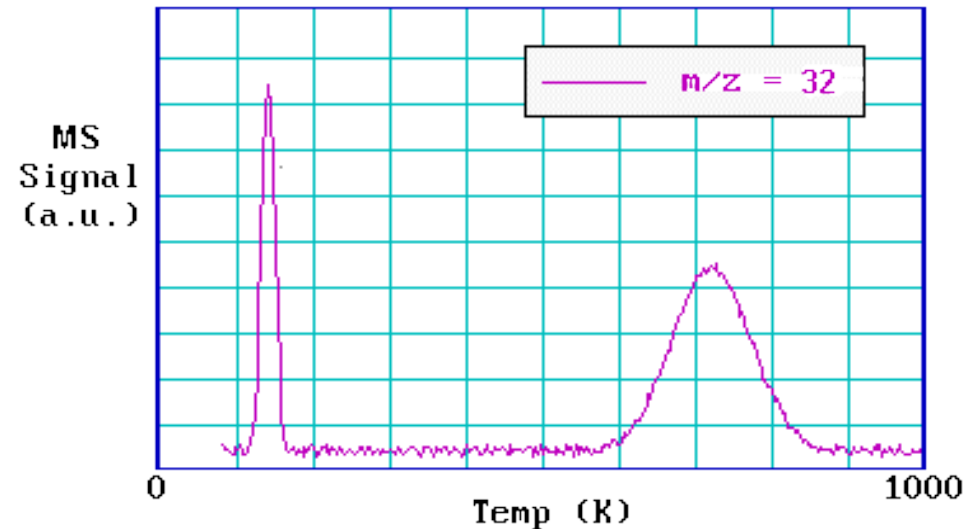
- The intensity of the desorption signal is proportional to the rate at which the surface concentration of adsorbed species is decreasing.
- The data obtained from TPD experiments is recorded as the intensity variation of recorded mass fragment vs time/temperature..



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

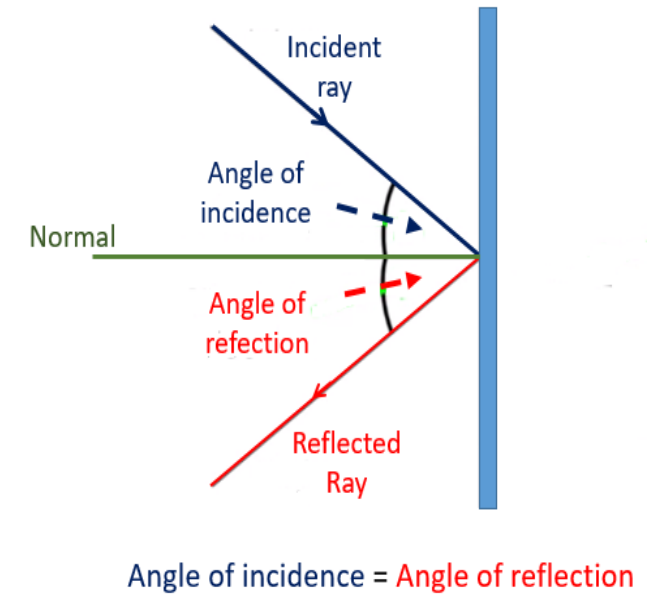
Information can be obtained from the TPD spectrum:

- 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.

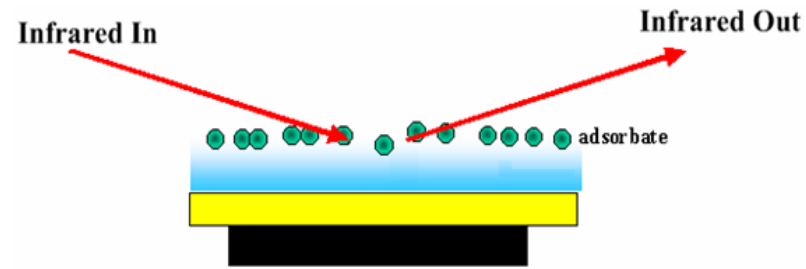


REFLECTION-ABSORPTION IR SPECTROSCOPY

- 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.



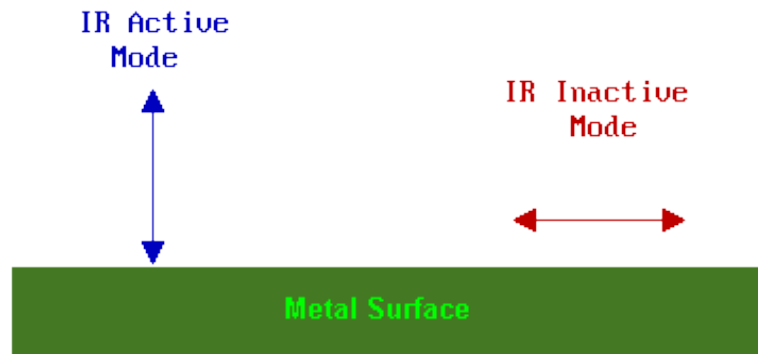
Instrumental Set-Up



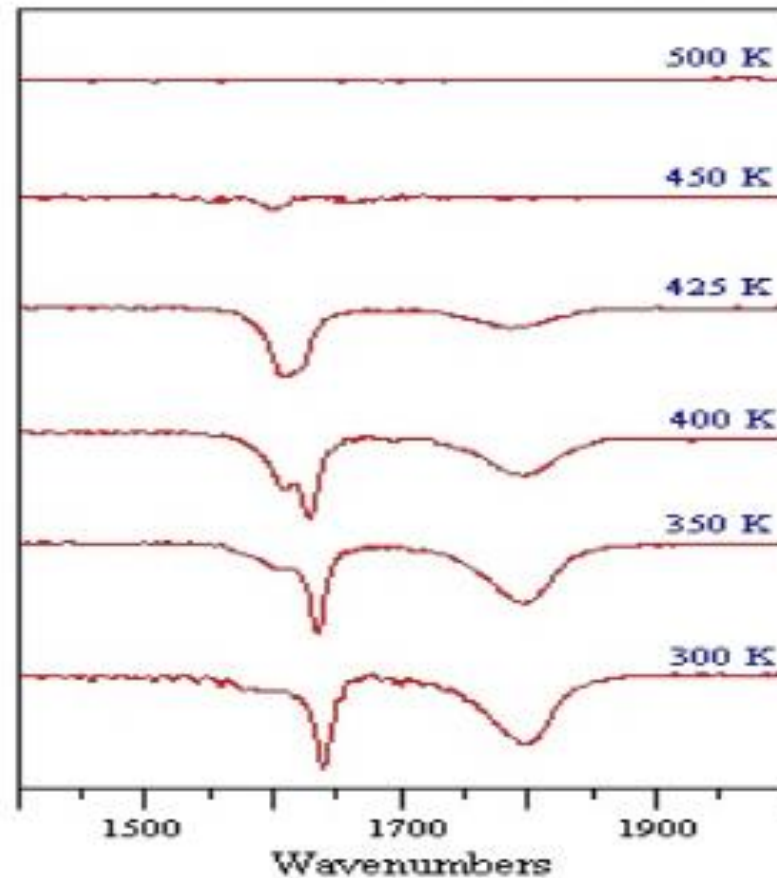
- The peaks corresponding to the vibrational modes of adsorbates are observed in RAIRS.
- The vibrational modes corresponding to metal-adsorbate bond, which usually appears below 600 cm^{-1} are not observed in RAIRS.

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.

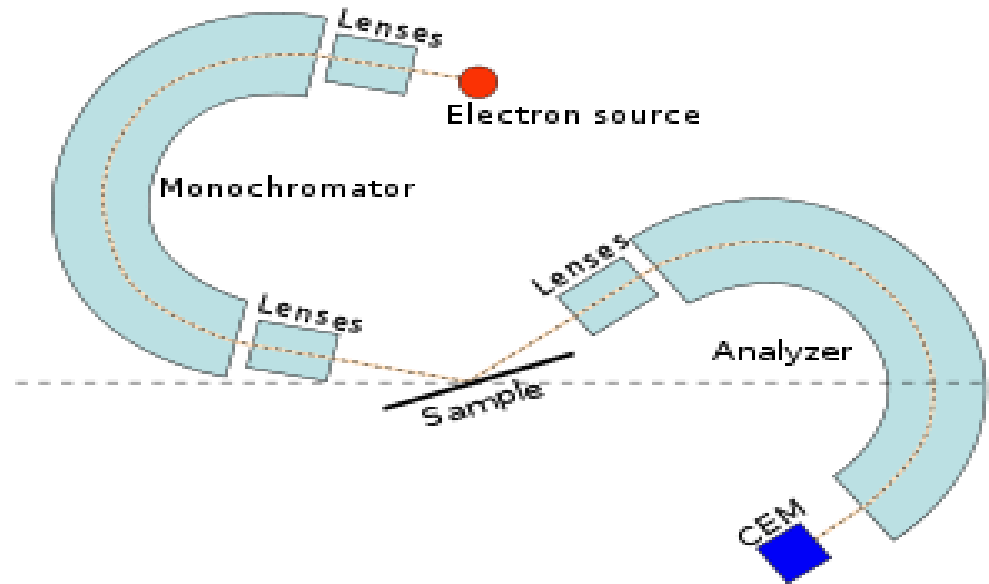


HIGH RESOLUTION ELECTRON-ENERGY LOSS SPECTROSCOPY (HREELS)

- 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.

