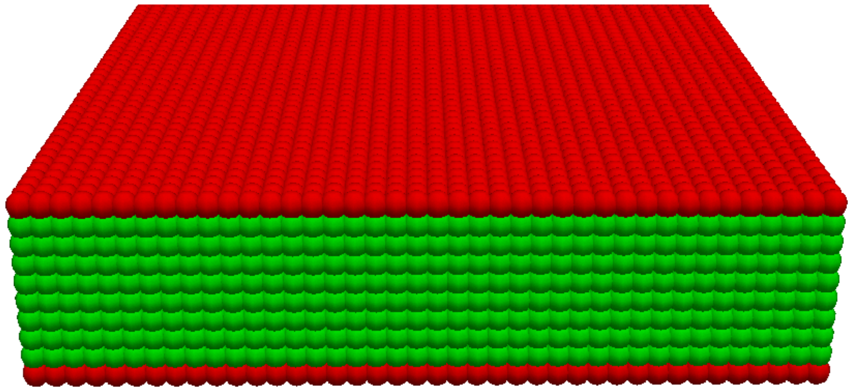
SPECTROSCOPIC TECHNIQUES FOR PROBING SOLID SURFACES

- The surface of a solid can be probed by several spectroscopic techniques.
- Spectroscopic methods can provide information regarding ***surface topography, chemical species on the surface, horizontal and vertical distribution of species etc.***



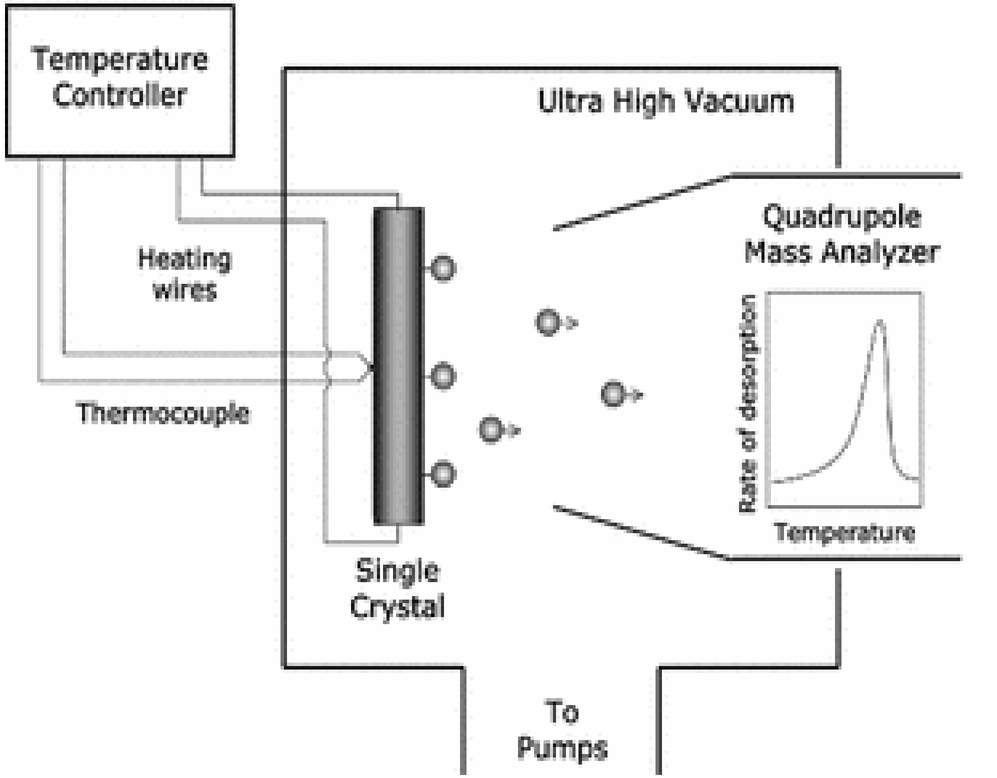
The spectroscopic techniques function by a 'beam-in'-'beam-out' mechanism.

TEMPERATURE PROGRAMMED DESORPTION (TPD)

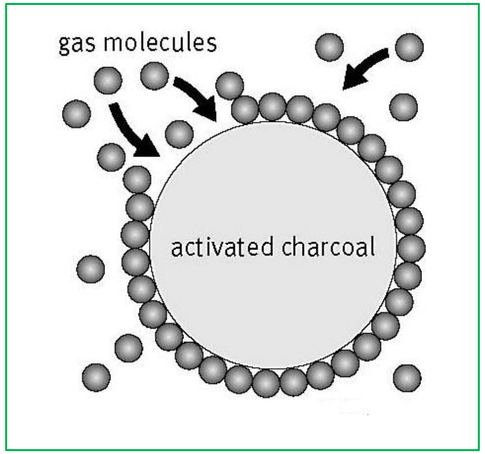
- **Temperature programmed desorption** (**TPD**) is the method of observing desorbed molecules from a surface when the surface temperature is increased.
- The desorption pattern of a crystal upon temperature variation can be studied by Temperature Programmed Desorption (TPD) technique.
- It is extensively used for the study of single crystal characteristics. TPD is often known as temperature programmed reaction spectroscopy (TPRS) since this is also used to study the surface reactions.

Basic experimental requirements for TPD

- Adsorption of one or more molecular species onto the sample surface at low temperature.
- Heating of sample in a controlled manner and monitoring the evolved species from the solid surface by mass spectrometry. A quadrupole mass spetctrometer (QMS) is generally used as the detector.



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

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

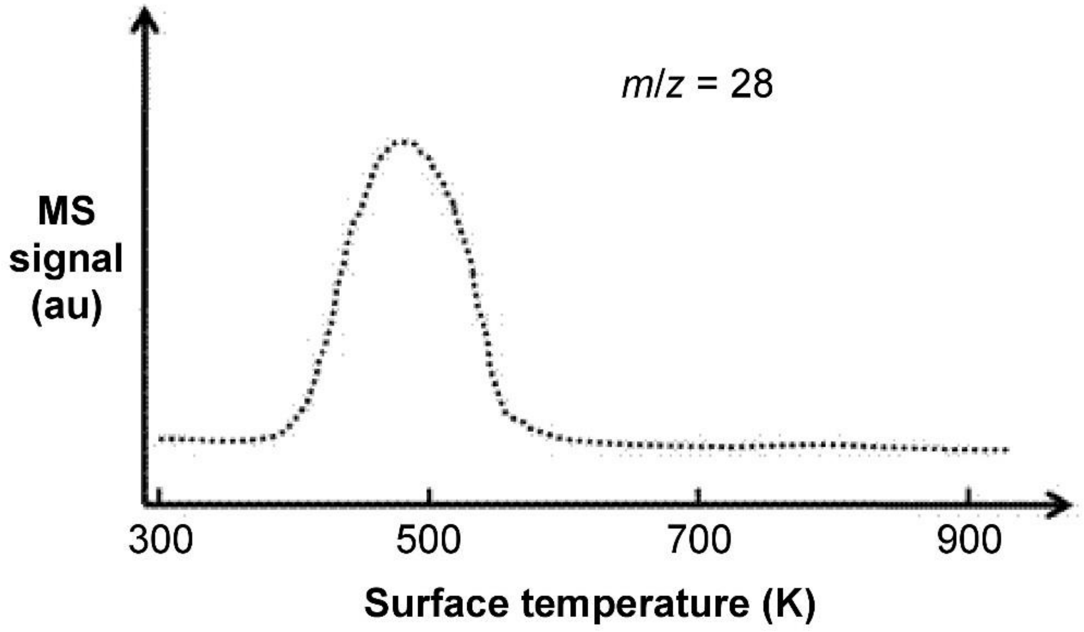
- The desorption from the surface takes place at a particular temperature when the activation energy barrier is crossed.
- The rate of desorption is given by:

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

Where, ‘N’ is a term representing the coverage

TPD SPECTRUM

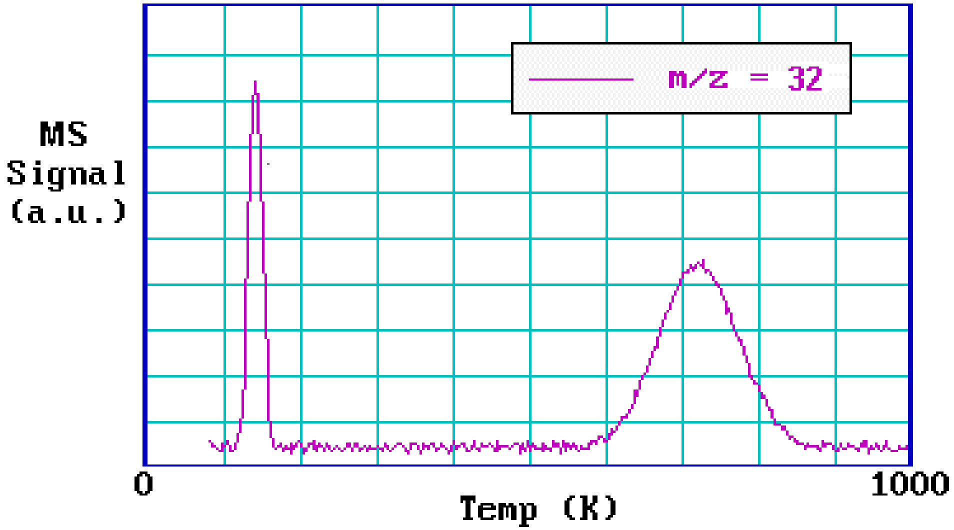
- The intensity of the desorption signal is proportional to the rate at which the surface concentration of adsorbed species is decreasing.
- The data obtained from TPD experiments is recorded as the intensity variation of recorded mass fragment *vs* time/temperature..



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

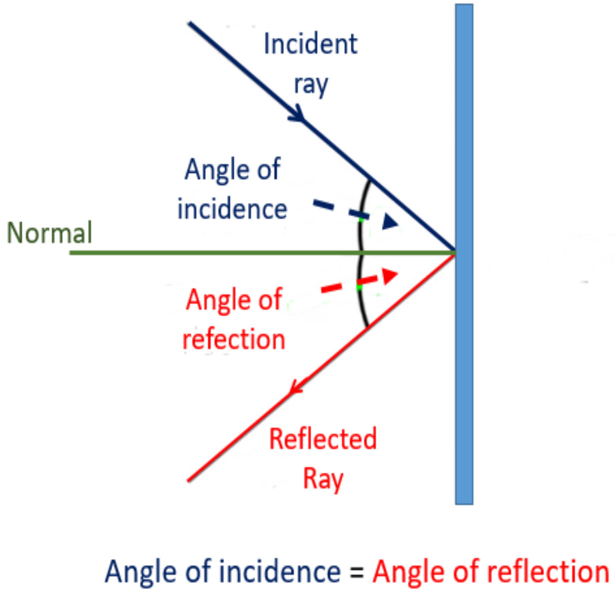
Information can be obtained from the TPD spectrum:

- 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.

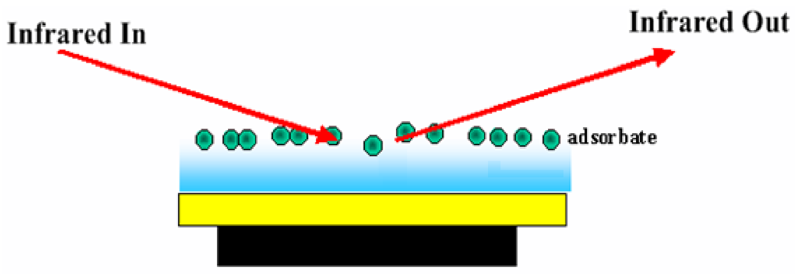


REFLECTION-ABSORPTION IR SPECTROSCOPY

- 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.



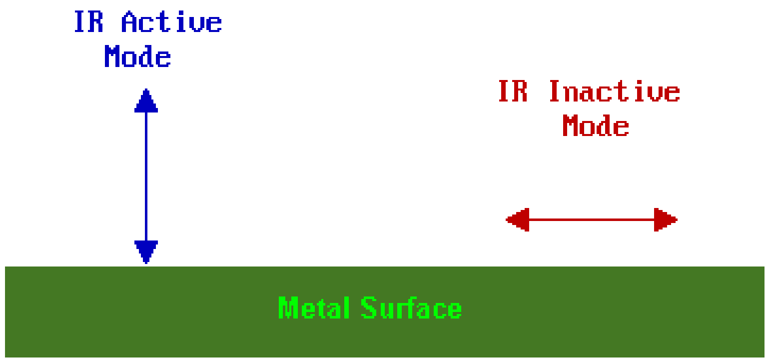
Instrumental Set-Up



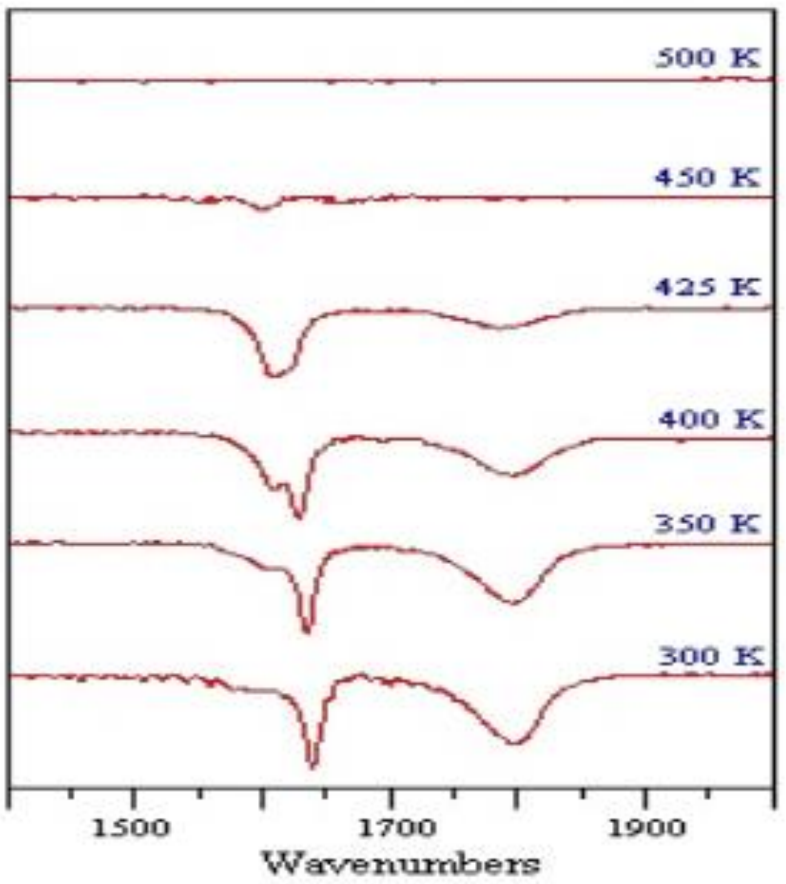
- The peaks corresponding to the vibrational modes of adsorbates are observed in RAIRS.
- The vibrational modes corresponding to metal-adsorbate bond, which usually appears below 600 cm-1 are not observed in RAIRS.

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.

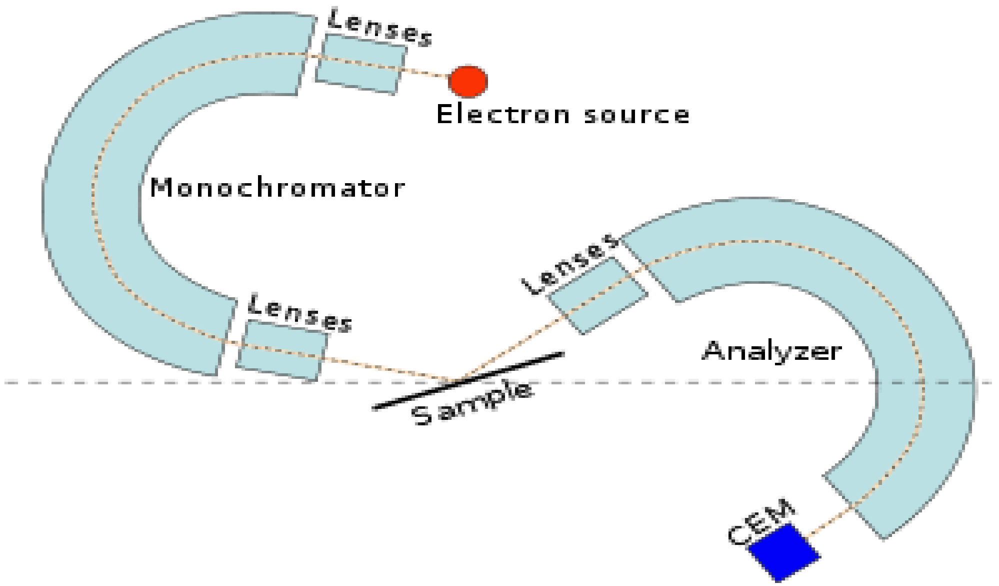


HIGH RESOLUTION ELECTRON-ENERGY LOSS SPECTROSCOPY (HREELS)

- Electron energy loss spectroscopy utilizes the scattering of electrons with low energy inorder 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.