# 2.2: How do Molecules Bond to Surfaces?

There are two principal modes of adsorption of molecules on surfaces: Physical Adsorption (physisorption ) and Chemical Adsorption (chemisorption). The basis of distinction is the nature of the bonding between the molecule and the surface with:

- **Physical Adsorption**: the only bonding is by weak Van der Waals - type forces. There is no significant redistribution of electron density in either the molecule or at the substrate surface.
- **Chemisorption**: a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character.

Typical Characteristics of Adsorption Processes

| | **Chemisorption** | **Physisorption** |
|---|---|---|
| Material Specificity (variation between substrates of different chemical composition) | Substantial variation between materials | Slight dependence upon substrate composition |
| Crystallographic Specificity (variation between different surface planes of the same crystal) | Marked variation between crystal planes | Virtually independent of surface atomic geometry |
| Temperature Range (over which adsorption occurs) | Virtually unlimited (but a given molecule may effectively adsorb only over a small range) | Near or below the condensation point of the gas (e.g. Xe < 100 K, $CO_2$ < 200 K) |
| Adsorption Enthalpy | Wide range (related to the chemical bond strength) - typically 40 - 800 kJ $mol^{-1}$ | Related to factors like molecular mass and polarity - typically 5-40 kJ $mol^{-1}$ (similar to heat of liquefaction) |
| Nature of Adsorption | Often dissociative<br>May be irreversible | Non-dissociative<br>Reversible |
| Saturation Uptake | Limited to one monolayer | Multilayer uptake possible |
| Kinetics of Adsorption | Very variable - often an activated process | Fast - since it is a non-activated process |

The most definitive method for establishing the formation of a chemical bond between the adsorbing molecule and the substrate (i.e. chemisorption) is to use an appropriate spectroscopic technique, for example

- IR (Section 5.4 ) to observe the vibrational frequency of the substrate/adsorbate bond
- UPS (Section 5.3 ) to monitor intensity & energy shifts in the valence orbitals of the adsorbate and substrate