### 25.2 Surface composition

- $\Box$  ultrahigh vacuum (UHV), pressures lower than about  $10^{-7}$  Pa.
- escape depth, the maximum depth from which ejected electrons come.
- photoemission spectroscopy, photoelectron spectroscopy applied to surfaces.

secondary-ion mass spectrometry (SIMS), a technique in which a surface is ionized by bombardment with other ions and the secondary ions that emerge from the surface are detected by a mass spectrometer.

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### 25.2 Surface composition (cont..)

reflection-absorption infrared spectroscopy (RAIRS), a technique for obtaining the infrared absorption spectrum of the adsorbate.

surface-enhanced Raman scattering (SERS), strong enhancement of the Raman spectrum of the adsorbate.

electron energy loss spectroscopy (EELS or HREELS), a technique in which the energy loss suffered by a beam of electrons is monitored when they are reflected from a surface.

Auger electron spectroscopy (AES), spectroscopy based on the Auger effect.

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### 25.2 Surface composition (cont..)

- reconstruction, modification of the substrate surface layers in response to adsorbates.
- Iow-energy electron diffraction (LEED), electron diffraction by surfaces.
- molecular beam scattering (MBS), the scattering of a beam of adsorbate molecules by a surface.

# **Light-molecule interaction**

## The quantum mechanics interpretation

$$\hat{\mathcal{H}}(q,t) = \hat{H}(q) - \hat{\mu} \cdot \hat{\mathbf{E}} = \hat{H}(q) + \hat{H}'(q,t)$$

### where

 $\hat{H}'(q,t)$  is the small time-dependent perturbation in the Hamitonian due to the light-molecule interaction

$$\hat{\mu} = \sum q_i \hat{\mathbf{r}}_i$$
 is the dipole moment of the molecule

**E** is the electric field of the light



# **Molecular rotation**



Figure 1.5 The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

# **Molecular vibrations**











Figure 1.6 The symmetric stretching vibration of the carbon dioxide molecule with amplitude much exaggerated.

# **Degrees of freedom**



Stretching



In-plane bending



Total degrees of freedom in motion: translation, rotation, and *vibration* 

Degrees of freedom in vibrations: Linear molecules with N atoms: 3N-5 vibrational modes Non-linear molecules with N atoms: 3N-6 vibrational modes

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# Motions of a free water molecule





# Motions of water molecules in liquid water





# An example: 6 different vibrations of a CH<sub>2</sub> group



## **A typical RAIRS spectrometer**





IR spectra of C<sub>2</sub>H<sub>4</sub> on Pt(111)

Table 8.1	Symmetric	stretching	frequencies	for	C-C and
C-H bo	nds in ethy	ne, ethene,	and ethane		

	CC symmetric stretch (cm <sup>-1</sup> )	CH symmetric stretch (cm <sup>-1</sup> )
Ethyne, HC=CH	1974	3374
Ethene, H <sub>2</sub> C=CH <sub>2</sub>	1620	3020
Ethane, H <sub>3</sub> C-CH <sub>3</sub>	990	2870

Figure 8.7 Infra-red spectra of ethene adsorbed on Pt surfaces: (a) RAIRS of ethylidyne on Pt(111), (b) transmission infra-red spectrum of ethene adsorbed on platinum supported on silica, and (c) the modes observed for ethylidyne. ((a) and (b) reproduced with permission from M. A. Chesters, C. De la Cruz, P. Gardner, E. M. McCash, P. Pudney, G. Shahid and N. Sheppard, J. Chem. Soc. Faraday Trans., 86(15), 2757-2763, 1990.)

### **Linear polarization spectroscopy**



FIG. 1.6. Forces generated on a dipole by an oscillating electric field. These forces tend to alternately increase and decrease the dipole spacing.



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### **Orientation of SiH bonds on diamond surfaces**









### H on Si(111): An ideal H-terminated surface





**Figure 23** Internal reflection spectra of HF-treated Si(111) surfaces. (a) Surface treated with pH-modified buffered HF (pH 9–10)(solid curve) and with dilute HF (100:1  $H_2O$ :HF)(dashed curve,) (b) s-polarization for surface treatment with pH-modified buffered HF (pH 9–10). Inset: High resolution spectrum of Si(111) surface treated with pH-modified buffered HF (pH 9–10). (From Ref. 60.)

Higashi et al. Appl. Phys. Lett. **56**, 656 (1990)

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## **Helium atom scattering (HAS)**



Advantages of using helium atoms as scattering agents:

•The lightweight helium atoms at thermal energies do not penetrate into the bulk of the material being studied and so is surface-sensitive.

•The de Broglie wavelength of helium atoms is on the order of the interatomic spacing of materials.

•Helium atoms are neutral and thus insensitive to surface charges.

•Helium atoms are chemically inert and non-destructive to the sample.

## A typical HAS spectrometer

•The helium atom beam is created through free adiabatic expansion of helium at a pressure of ~200 bar into a low-vacuum chamber through a small (~5-10  $\mu$ m) nozzle

•Typical helium atom energies produced are 5 – 200 meV, with a very narrow energy spread of less than 1 meV.



## The Maxwell-Boltzmann distribution of molecular speeds

$$f(u) = 4\pi u^2 \left(\frac{m}{2\pi k_{\rm B}T}\right)^{3/2} e^{-mu^2/2k_{\rm B}T}$$

The distribution of speeds for nitrogen gas molecules at 3 different temperatures



The distribution of speeds of 3 different gases at the same temperature



### Apparatus for studying molecular speed distribution



### Hindered motions of adsorbate



Figure 8.9 (a) Inelastic helium scattering for CO adsorbed on a Pt(111) surface at 300 K. The feature observed at  $129 \text{ cm}^{-1}$  is due to the hindered rotation which is illustrated in (b), while those at 48 and 96 cm<sup>-1</sup> are due to the hindered translation mode shown in (c) and its first overtone. ((a) is reproduced with permission from A. Lahee, P. Toennies and Ch. Wöll, Surface Science, 177, 371, 1986.)

## **Degrees of freedom**



**Total degrees of freedom in motion**: translation, rotation, and <u>vibration</u>

Degrees of freedom in vibrations: Linear molecules with N atoms: 3N-5 vibrational modes Non-linear molecules with N atoms: 3N-6 vibrational modes

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## **Electron energy loss spectroscopy (EELS)**

High-resolution electron energy loss spectroscopy (HREELS)



Figure 8.2 The principle of the EELS experiment where  $\theta_i$  is the angle of incidence,  $\theta_i$  is the angle of reflection,  $E_p$  is the energy of the incident beam (the primary energy), and  $E_p \pm h\nu$  the energy of the loss electrons.

Banwell & McCash, Fundamentals of Molecular Spectroscopy, 4th Ed., Tata McGraw-Hill, 1994



## A typical EEL spectrometer



Figure 8.1 The electron energy loss spectrometer.



## EEL spectra of C<sub>2</sub>H<sub>2</sub> on Cu(111)





### **IR versus EEL spectra**



**Figure 7.13**. RAIRS spectrum of a monlayer of CO adsorbed on a Cu (111) surface at 95 K in comparison with analogous data obtained using electron energy loss spectroscopy, after Chesters *et al.* [10]



Figure 8.1 Processes occurring in (a) ultraviolet photoelectron spectroscopy (UPS), (b) X-ray photoelectron spectroscopy (XPS), (c) Auger electron spectroscopy (AES)

### **Photoelectron spectroscopy (PES)**

Photoelectron spectroscopy involves the ejection of electrons from atoms or molecules following bombardment by monochromatic photons. The ejected electrons are called photoelectrons and were mentioned, in the context of the photoelectric effect, in Section 1.2. The effect was observed originally on surfaces of easily ionizable metals, such as the alkali metals. Bombardment of the surface with photons of tunable frequency does not produce any photoelectrons until the threshold frequency is reached (see Figure 1.2). At this frequency,  $v_{t}$ , the photon energy is just sufficient to overcome the work function  $\Phi$  of the metal, so that

$$hv_i = \Phi$$
 (8.1)

At higher frequencies the excess energy of the photons is converted into kinetic energy of the photoelectrons

$$hv = \Phi + \frac{1}{2}m_e v^2 \tag{8.2}$$

where  $m_e$  and v are their mass and velocity.

Work functions of alkali metal surfaces are only a few electronvolts<sup>†</sup> so that the energy of near ultraviolet radiation is sufficient to produce ionization.

Photoelectron spectroscopy is a simple extension of the photoelectric effect involving the use of higher energy incident photons and applied to the study not only of solid surfaces but also of samples in the gas phase. Equations (8.1) and (8.2) still apply but, for gas phase measurements in particular, the work function is usually replaced by the ionization energy  $I^{\ddagger}_{\downarrow}$ , so that equation (8.2) becomes

$$hv = l + \frac{1}{2}m_e v^2 \tag{8.3}$$

 $hv = E_{\text{KE}} + BE$  (binding energy)

### **A typical PES spectrometer**



Figure 8.2 The principal components of a photoelectron spectrometer

### **UV photoelectron spectrum of CO**



Figure 6.21 The photoelectron spectrum of carbon monoxide.

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### X-ray photoelectron spectra





Figure 8.13 The MgK $\alpha$  oxygen 1s and carbon 1s XPS spectra of a 2:1 mixture of CO and CO<sub>2</sub> gases. (Reproduced, with permission, from Allan, C. J., and Siegbahn, K. (November 1971), *Publication No. UUIP-754*, p. 48, Uppsala University Institute of Physics)

Figure 8.14 The monochromatized AlK $\alpha$  carbon 1s XPS spectrum of ethyltrifluoroacetate showing the chemical shifts relative to an ionization energy of 291.2 eV. (Reproduced, with permission, from Gelius, U., Basilier, E., Svensson, S., Bergmark, T., and Siegbahn, K., J. Electron Spectrosc., 2, 405, 1974)

### Analysis of Electron Spectra of Carbon Allotropes (Diamond, Graphite, Fullerene) by Density Functional Theory Calculations Using the Model Molecules

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# **Auger electron spectroscopy (AES)** $E_{\text{Auger}} + E_{z} = E_{x} - E_{y}$ or $E_{\text{Auger}} = E_{x} - E_{y} - E_{z}$ EAuger Ionization limit $E_z = 0 = 0$ $E_y = 0 = 0$ Energy (a) Ground state (b) Initial (c) Auger (d) Final state excited state process







**Figure 8.25** (a) The  $KL_{II,III}L_{II,III}$  ( ${}^{1}D_{2}$  and  ${}^{1}S_{0}$ ) Auger spectrum of sulphur in a gaseous mixture of SF<sub>6</sub>, SO<sub>2</sub>, and OCS, compared with (b) the S 2*p* X-ray photoelectron spectrum of a mixture of the same gases. (Reproduced, with permission, from Aslund, L., Kelfve, P., Siegbahn, H., Goscinski, O., Fellner-Feldegg, H., Hamrin, K., Blomster, B., and Siegbahn, K., *Chem. Phys. Letters*, **40**, 353, 1976)

## **Diamond growth by chemical vapor deposition (CVD)**









Figure 1. Auger spectra of natural diamonds (A to C), CVD diamonds (D to G), HOPG (H) and glassy carbon (I). A<sub>0</sub> is the main peak and A<sub>1</sub> is the satellite peak which shows the significant difference between sp<sup>3</sup>- and sp<sup>2</sup>-bound carbons.

HOPG: highly oriented pyrolytic graphite



### H on Si(111): An ideal H-terminated surface





**Figure 23** Internal reflection spectra of HF-treated Si(111) surfaces. (a) Surface treated with pH-modified buffered HF (pH 9–10)(solid curve) and with dilute HF (100:1 H<sub>2</sub>O:HF)(dashed curve,) (b) s-polarization for surface treatment with pH-modified buffered HF (pH 9–10). Inset: High resolution spectrum of Si(111) surface treated with pH-modified buffered HF (pH 9–10). (From Ref. 60.)

Higashi et al. Appl. Phys. Lett. **56**, 656 (1990)

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### Attenuated total reflection (ATR) spectroscopy



"Evanescent" means "tending to vanish", which is appropriate because the intensity of evanescent waves decays exponentially (rather than sinusoidally) with distance from the interface at which they are formed.

Evanescent waves are formed when sinusoidal waves are (internally) reflected off an interface at an angle greater than the critical angle so that total internal reflection occurs.



### **Total internal reflection**



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http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/totint.html

### **Penetration depth of evanescent wave**

The penetration depth  $(d_p)$  into the sample is typically between 0.5 and 2 um, with the exact value being determined by the wavelength of light  $(\lambda)$ , the angle of incidence  $(\theta)$  and the indices of refraction for the ATR crystal  $(n_1)$  and the medium  $(n_2)$  being probed.

$$d_{\rm p} = \frac{\lambda}{2\pi n_1 (\sin^2\theta - n_{21}^2)^{1/2}}$$

where

$$n_{21} = n_2/n_1$$





### **Evidence and applications of ATR**





Fingerprints on a glass of water made visible by frustrated total internal reflection

Fig. 2. Schematic diagram of inkless fingerprint recording instrument. The finger is pressed against the hypotenuse of the prism (P) illuminated by the light source (S) and imaged onto the screen or photofilm (F) by the lens (L) and mirror (M). Total reflection is destroyed only where contact is made between the skin and the prism, i.e., at the ridges but not at the valleys, and thus a high contrast image of surface reliefs is obtained.





*Figure 5.* Using a pipette to add a liquid sample to a ZnSe HATR trough plate.



Figure 1. A Mid-Infrared spectrum of Hexene.



## The Beer's law

$$T = \frac{I}{I_0} = 10^{-\alpha \ell} = 10^{-\varepsilon \ell c}$$
$$A = -\log_{10}\left(\frac{I}{I_0}\right)$$

 $A = \varepsilon \ell c = \alpha \ell$ 



librations

The vibrational spectra of liquid water

### Main vibrations of liquid ordinary and heavy water

	liquid H <sub>2</sub> O (25°C)		liquid D <sub>2</sub> O (25°C)	
Vibration(s) [942]	<i>v</i> , cm <sup>-1</sup>	E <sub>0</sub> , M <sup>-1</sup> cm <sup>-1</sup>	<i>v</i> , cm <sup>-1</sup>	E <sub>0'</sub> M <sup>-1</sup> cm <sup>-1</sup>
v <sub>2</sub>	1643.5	21.65	1209.4	17.10
combination of $v_2$ + libration	2127.5	3.46	1555.0	1.88
$v_1^{}$ , $v_3^{}$ , and overtone of $v_2^{}$	3404.0 <sup>e</sup>	100.61	2504.0	69.68

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## **Biological applications of ATR**

### Total internal reflection fluorescence (TIRF) microscope

The development of the microscope aims to imaging molecular events occurring on cellular surfaces such as cell adhesion, binding of cells by hormones, secretion of neurotransmitters, and membrane dynamics.



## **TIRF microscopy**



#### **TIRFM Specimen Illumination Configurations**



- 1. Objective
- 2. Emission beam (signal)
- 3. Immersion oil
- 4. Cover slip
- 5. Specimen
- 6. Evanescent wave range (<200 nm)
- 7. Excitation beam
- 8. Quartz prism

### **Advantages of TIRF microscopy**

In cell and molecular biology, a large number of molecular events occur on cellular surfaces such as cell adhesion, binding of cells by hormones, secretion of neurotransmitters, and membrane dynamics. However, when these molecules are excited and detected with a conventional fluorescence microscope, the resulting fluorescence from those fluorophores bound to the surface is often overwhelmed by the background fluorescence due to the much larger population of non-bound molecules.





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### Impact: 125.1 Biosensor analysis

- biosensor analysis, the detection of changes in the optical properties of a surface in contact with a biopolymer.
- plasma, a dense gas of charged particles.
- plasmons, oscillations in electron density.
- evanescent wave, an oscillation in electron density that propagates away from a surface.
- surface plasmon resonance, the absorption of energy from an incident beam of electromagnetic radiation by surface plasmons.

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**Fig. 25.26** The experimental arrangement for the observation of surface plasmon resonance, as explained in the text.

Chapter 25. Processes at solid surfaces

## **Principle of surface plasma resonance (SPR)**

The incident wave vector is given by the following expression:

$$K_i = \left(\frac{2\pi}{\lambda}\right) n \sin \theta_i$$

where  $K_i$  is a component of the incident light wave vector parallel to the prism Interface,  $\theta_i$  is the incident light angle,  $\lambda$  is the wavelength of the incident light and n is the refractive index of the prism.

The wave vector of the plasmon mode is described by the following expression

$$K_{P} = \left(\frac{2\pi}{\lambda}\right) \sqrt{\frac{\varepsilon_{1}\varepsilon_{2}}{\varepsilon_{1} + \varepsilon_{2}}}$$

where  $K_p$  is the surface plasmon wave vector and  $\varepsilon_1$  and  $\varepsilon_2$  are the complex dielectric constants of the metal film and the dielectric exit medium, respectively.

Smith et al. Appl. Spectrosc. 57, 320A (2003)



### SPR occurs when

$$K_i = K_p$$

The intensity of the reflected light will decrease where SPR exists, thereby giving rise to a well defined minimum in the reflectance intensity.

• If the incident angle is fixed and polychromatic and light is reflected from the surface, then light will be adsorbed by the resonance at particular wavelengths giving rise to a typical SPR minimum in the reflectance spectrum.

• If monochromatic light is reflected from the surface over a range of incident angles, then a similar reflectance minimum will occur with respect to the incident angle.





**Fig. 25.27** The time dependence of a surface plasmon resonance signal, R, showing the effect of binding of a ligand to a biopolymer adsorbed on to a surface. Binding leads to an increase in R until an equilibrium value,  $R_{eq}$ , is obtained. Passing a solution containing no ligand over the surface leads to dissociation and decrease in R.



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Chapter 25. Processes at solid surfaces



Analyte Mass Transport

 $A_0 \stackrel{k_m}{\Leftrightarrow} A$ 

The concentration of analyte at the surface (A) is related to the concentration of injected analyte ( $A_0$ ) by  $k_m$ , the mass transport coefficient.

Complex (AB) Formation  $A + B \stackrel{\mathsf{k}_{a}}{\Leftrightarrow} AB$   $\stackrel{\mathsf{k}_{a}}{\overset{\mathsf{k}_{d}}{\leftarrow}} AB$ 

Where the forward (on) and reverse (off) rates are  $k_a$  and  $k_d$ , respectively.

http://www.labtech.co.uk/downloads/nomadics\_principles.pdf

### PROCESSES AT ELECTRODES

### 25.8 The electrode-surface interface

- electrical double layer, a sheet of one charge at the surface of the electrode and a sheet of opposite charge next to it in the solution.
- □ Galvani potential difference, the potential difference between the bulk of the metal electrode and the bulk of the solution.
- Helmholtz layer model, a model of the double layer in which the solvated ions arrange themselves along the surface of the electrode but are held away from it by their hydration spheres.

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### 25.8 The electrode-surface interface (cont..)

- outer Helmholtz plane (OHP), the outer sheet of charge.
- □ inner Helmholtz plane (IHP), the inner sheet of charge.
- Gouy-Chapman model, a model of he double layer in which the outer layer is diffuse.
- diffuse double layer, an inner layer of charge and an outer ionic diffuse atmosphere.
- Stern model, a model of the double layer in which the ions closest to the electrode are constrained into a rigid plane while outside that plane the ions are dispersed as in the Gouy-Chapman model.

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### The electrode-surface interface

Fig. 25.30 A simple model of the electrode-solution interface treats it as two rigid planes of charge. One plane, the outer Helmholtz plane (OHP), is due to the ions with their solvating molecules and the other plane is that of the electrode itself. The plot shows the dependence of the electric potential with distance from the electrode surface according to this model. Between the electrode surface and the OHP, the potential varies linearly from  $\varphi_{M}$ , the value in the metal, to  $\varphi_{\rm S}$ , the value in the bulk of the solution.



### The electrode-surface interface



**Fig. 25.31** The Gouy–Chapman model of the electrical double layer treats the outer region as an atmosphere of counter-charge, similar to the Debye–Hückel theory of ion atmospheres. The plot of electrical potential against distance from the electrode surface shows the meaning of the diffuse double layer (see text for details).



### The electrode-surface interface

Fig. 25.32 A representation of the Stern model of the electrode–solution interface. The model incorporates the idea of an outer Helmholtz plane near the electrode surface and of a diffuse double layer further away from the surface.

### Zeta potentials of colloids



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•The zeta potential is the electric potential at the radius of shear relative to its value in the distant, bulk medium.

•The radius of shear is the radius of the sphere that captures the rigid layer of charge attached to a colloid particle.

http://www.malvern.com/LabEng/technology/zeta\_potential/zeta\_potential\_LDE.htm

### What is zeta potential?

•Most particles dispersed in an aqueous system will acquire a surface charge, principally either by ionization of surface groups, or adsorption of charged species.

•These surface charges modify the distribution of the surrounding ions, resulting in a layer around the particle that is different to the bulk solution.

•If the particle moves, under Brownian motion for example, this layer moves as part of the particle.

•The zeta potential is the potential at the point in this layer where it moves past the bulk solution. This is usually called the slipping plane.

•In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.



•Zeta potential is one of the main forces that mediate interparticle interactions. The significance of zeta potential is that its value can be related to the stability of colloidal dispersions.

•Particles with a high zeta potential of the same charge sign, either positive or negative, will repel each other. Colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate.

Zeta potential [mV]	Stability behavior of the colloid		
from 0 to $\pm 5$ ,	Rapid coagulation or flocculation		
from $\pm 10$ to $\pm 30$	Incipient instability		
from $\pm 30$ to $\pm 40$	Moderate stability		
from $\pm 40$ to $\pm 60$	Good stability		
more than ±61	Excellent stability		

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The zeta potential is sensitive to the concentration and type of ions (such as pH) in solution.



## **Laser Doppler Velocimetry**

•Laser beams are aligned at the stationary layer in the cell.

•At the crossing point of the beams, Young's interference fringes of known spacing are formed.

•Particles moving through the fringes under the influence of the applied electric field scatter light whose intensity fluctuates with a frequency that is related to the particles velocity.

•A frequency spectrum is produced from which the mobility and hence zeta potential are calculated

