SURFACES: AN INTRODUCTION

1.1 HISTORICAL PERSPECTIVE

Surface science in general and surface chemistry in particular have a long and distinguished history. The spontaneous spreading of oil on water was described in ancient times and was studied by Benjamin Franklin. A timeline of the historical development of surface chemistry since then is shown in Figure 1.1. The application of catalysis started in the early 1800s, with the discovery of the platinum (Pt)-surface-catalyzed reaction of \( \text{H}_2 \) and \( \text{O}_2 \) in 1823 by Dobereiner. He used this reaction in his “lighter” (i.e., a portable flame) source, of which he sold a large number. By 1835 [1], the discovery of heterogeneous catalysis was complete thanks to the studies of Kirchhoff, Davy, Henry, Philips, Faraday, and Berzelius. It was at about this time that the Daguerre process was introduced for photography. The study of tribology, or friction, also started around this time, coinciding with the industrial revolution.

Introduction to Surface Chemistry and Catalysis, Second Edition. By Gabor A. Somorjai and Yimin Li
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although some level of understanding of friction appears in the work of Leonardo da Vinci. Surface-catalyzed chemistry-based technologies first appeared in the period of 1860–1912, starting with the Deacon process ($2\text{HCl} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2$), SO$_2$ oxidation to SO$_3$ (Messel, 1875), the reaction of methane (CH$_4$) with steam to produce CO and H$_2$ (Mond, 1888), ammonia (NH$_3$) oxidation (Ostwald, 1901), ethylene (C$_2$H$_4$) hydrogenation (Sabatier, 1902), and NH$_3$ synthesis (Haber, Mittasch, 1905–1912). Surface tension measurements and recognition of equilibrium constraints on surface-chemical processes led to the development of the thermodynamics of surface phases by Gibbs (1877). The existence of polyatomic or polymolecular aggregates that lack crystallinity and diffuse slowly (e.g., gelatine and albumin) was described in 1861 by Graham, who called these systems “colloids”. Polymolecular aggregates that exhibit internal structure were called “micelles” by Nageli, and stable metal colloids were prepared by Faraday. However, the colloid subfield of surface chemistry gained prominence at the beginning of the 20th century with the rise of the paint industry and the preparation of artificial rubbers. Studies of light bulb filament lifetimes, high-surface-area gas absorbers in the gas mask, and gas-separation technologies in other forms, led to investigations of atomic and molecular adsorption (Langmuir, 1915). The properties of chemisorbed and physisorbed monolayers, adsorption isotherms, dissociative adsorption, energy exchange, and sticking upon gas–surface collisions were studied. Studies of electrode surfaces in electrochemistry led to the detection of the surface space charge [2] (for a review of electrochemistry in the 19th century, see Ref. [3]). The surface diffraction of electrons was discovered by Davisson and Germer (1927). Major academic and industrial laboratories focusing on surface studies have been formed in Germany (Haber, Polanyi, Farkas, Bonhoefer), the United Kingdom (Rideal, Roberts, Bowden), the
United States (Langmuir, Emmett, Harkins, Taylor, Ipatief, Adams), and many other countries. They have helped to bring surface chemistry into the center of development of chemistry—both because of the intellectual challenge to understand the rich diversity of surface phenomena and because of its importance in chemical and energy conversion technologies.

In the early 1950s, focus in chemistry research shifted to studies of gas-phase molecular processes, as many new techniques were developed to study gas-phase species on the molecular level. This was not the case in surface and interface chemistry, although the newly developed field-ion and electron microscopies did provide atomic level information on surface structure. The development of surface-chemistry-based technologies continued at a very high rate, however, especially in areas of petroleum refining and the production of commodity chemicals. Then, in the late 1950s, the rise of the solid-state-device-based electronics industry and the availability of economical ultrahigh vacuum systems (UHV) (developed by research in space sciences) provided surface chemistry with new challenges and opportunities, resulting in an explosive growth of the discipline. Clean surfaces of single crystals could be studied for the first time, and the preparation of surfaces and interfaces with known atomic structure and controlled composition was driving the development of microelectronics and computer technologies. New surface instrumentation and techniques have been developed that permit the study of surface properties on the atomic scale. Many of the most frequently used surface characterization techniques are listed in Table 1.1. Most of these have been developed since the 1960s.

As a result of the sudden availability of surface characterization techniques, macroscopic surface phenomena (adsorption, bonding, catalysis, oxidation and other surface reactions, diffusion, desorption, melting and other phase transformation, growth, nucleation, charge transport, atom, ion, and electron scattering, friction, hardness, lubrication) are being re-examined on the molecular scale. This finding has led to a remarkable growth of surface chemistry that has continued uninterrupted to date. The discipline has again become one of the frontier areas of chemistry. The newly gained knowledge of the molecular ingredients of surface phenomena has given birth to a steady stream of high-technology products, including new hard coatings that passivate surfaces; chemically treated glass, semiconductor, metal, and polymer surfaces, where the treatment imparts unique surface properties; newly designed catalysts, chemical sensors, and carbon fiber composites; surface-space-charge-based copying; and new methods of electric, magnetic, and optical signal processing and storage. Molecular surface chemistry is being utilized increasingly in biological science.

1.2 SURFACES AND INTERFACES: CLASSIFICATION OF PROPERTIES

Condensed phases (solids and liquids) must have surfaces or interfaces. The suit of an astronaut maneuvering in outer space represents a solid—vacuum interface (Fig. 1.2a); a basketball player jumping to score is a moving solid—gas interface (Fig. 1.2b); a sailboat moving over the waves is a solid—liquid interface (Fig. 1.2c); a tire sliding at the solid—solid interface (Fig. 1.2d). The surface of a lake is a liquid—gas interface. Olive oil poured on top of an open bottle of wine to prevent air oxidation forms a liquid—liquid interface. These interfaces exhibit some remarkable physical and chemical properties. The chemical behavior of surfaces is responsible for heterogeneous catalysis (e.g., NH₃ synthesis) and gas separations (as in the extraction of oxygen and nitrogen from air) by selective adsorption. Mechanical surface
<table>
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<tr>
<th>Acronym</th>
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<th>Description</th>
<th>Primary Surface Information</th>
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<tbody>
<tr>
<td></td>
<td>Adsorption or selective chemisorptions [4]</td>
<td>Atoms or molecules are physisorbed into a porous structure (e.g., a zeolite or a sample of coal) or onto a surface, and the amount of gas adsorbed is a measure of the surface area available for adsorption. Chemisorption of atoms or molecules on surfaces yields surface concentration of selected elements or adsorption sites.</td>
<td>Surface area, adsorption site concentration</td>
</tr>
<tr>
<td>AD</td>
<td>Atom or helium diffraction [5–16]</td>
<td>Monoenergetic beams of atoms are scattered from ordered surfaces and detected as a function of scattering angle. This gives structural information on the outermost layer of the surface. Atom diffraction is extremely sensitive to surface ordering and defects.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>AEAPS</td>
<td>Auger electron appearance potential spectroscopy [5–7, 17–20]</td>
<td>A monoenergetic beam of electrons is used to excite atoms in the near surface region. As the beam energy is swept, variations in the sample emission current occur as the beam energy sweeps over the energy of an Auger transition in the sample. Also known as APAES.</td>
<td>Chemical composition</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy [5–7, 17, 19, 21–32]</td>
<td>Core-hole excitations are created, usually by 1–10-keV incident electrons; Auger electrons of characteristic energies are emitted through a two-electron process as excited atoms decay to their ground state. AES gives information on the near-surface chemical composition.</td>
<td>Chemical composition</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy [33–40]</td>
<td>Very similar to scanning tunneling microscopy (STM). In this technique, however, the attractive van der Waals forces between the surface and the probe cause a bending of the probe. This deflection is measurable by a variety of means. Because this technique does not require a current between the probe and the surface, nonconducting surfaces may be imaged.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>APAES</td>
<td>Appearance potential auger electron spectroscopy</td>
<td>See AEAPS.</td>
<td></td>
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<tr>
<td>Technique</td>
<td>Description</td>
<td>Domain</td>
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<tr>
<td>APXPS</td>
<td>Appearance potential X-ray photoemission spectroscopy [5–7, 19] The EAPFS excitation cross section is monitored by fluorescence from core hole decay (also known as SXAPS).</td>
<td>Chemical composition</td>
<td></td>
</tr>
<tr>
<td>ARAES</td>
<td>Angle-resolved auger electron spectroscopy [41] Auger electrons are detected as a function of angle to provide information on the spatial distribution or environment of the excited atoms (see AES).</td>
<td>Surface structure</td>
<td></td>
</tr>
<tr>
<td>ARPEFS</td>
<td>Angle-resolved photoemission extended fine structure [41–43] Electrons are detected at given angles after being photoemitted by polarized synchrotron radiation. The interference in the detected photoemission intensity as a function of electron energy ~100–500 eV above the excitation threshold gives structural information.</td>
<td>Surface structure</td>
<td></td>
</tr>
<tr>
<td>ARPES</td>
<td>Angle-resolved photoemission spectroscopy [6, 27, 44–47] A general term for structure-sensitive photoemission techniques, including ARPEFS, ARXPS, ARUPS, and ARXPD.</td>
<td>Electronic structure, surface structure</td>
<td></td>
</tr>
<tr>
<td>ARUPS</td>
<td>Angle-resolved ultraviolet photoemission spectroscopy [6, 45, 48–51] Electrons photoemitted from the valence and conduction bands of a surface are detected as a function of angle. This gives information on the dispersion of these bands (which is related to surface structure) and also gives structural information from the diffraction of the emitted electrons.</td>
<td>Valence band structure, bonding</td>
<td></td>
</tr>
<tr>
<td>ARXPD</td>
<td>Angle-resolved X-ray photoelectron diffraction [6, 41, 42, 52–54] Similar to ARXPS and ARPEFS. The angular variation in the photoemission intensity is measured at a fixed energy above the excitation threshold to provide structural information.</td>
<td>Surface structure</td>
<td></td>
</tr>
<tr>
<td>ARXPS</td>
<td>Angle-resolved X-ray photoemission spectroscopy [6, 41, 42, 52, 53] The diffraction of electrons photoemitted from core levels gives structural information on the surface.</td>
<td>Surface structure</td>
<td></td>
</tr>
<tr>
<td>CEM</td>
<td>Conversion electron Mössbauer spectroscopy [7, 55–58] A surface-sensitive version of Mössbauer spectroscopy. Like Mössbauer spectroscopy, this technique is limited to some isotopes of certain metals. After a nucleus is excited by γ-ray absorption, it can undergo inverse β-decay, creating a core hole. The decay of core holes by Auger processes within an electron mean free path of the surface produces a signal. Detecting emitted electrons as a function of energy gives some depth profile information because the changing electron mean free path.</td>
<td>Chemical environment, oxidation state</td>
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<tr>
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<tbody>
<tr>
<td>DAPS</td>
<td>Disappearance potential spectroscopy [5–7, 19]</td>
<td>The EAPFS cross section is monitored by variations in the intensity of electrons back-scattered from the surface.</td>
<td>Chemical composition</td>
</tr>
<tr>
<td>EAPFS</td>
<td>Electron appearance potential fine structure [6, 59]</td>
<td>A fine-structure technique (see EXAFS). Core holes are excited by monoenergetic electrons. The modulation in the excitation cross section as the beam energy is varied may be monitored through absorption, fluorescence, or Auger emission.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>ELNES</td>
<td>Electron energy loss near edge structure</td>
<td>Similar to NEXAFS, except monoenergetic high-energy electrons ~60–300 keV excite core holes.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>ELS or EELS</td>
<td>Electron energy loss spectromscopy [6, 7, 23, 26, 44, 60–63]</td>
<td>Monoenergetic electrons are scattered off a surface, and the energy losses are determined. This gives information on the electronic excitations of the surface and the adsorbed molecules.</td>
<td>Electronic structure, surface structure</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron spectroscopy for chemical analysis [5–7, 19, 25, 64–66]</td>
<td>Now generally called XPS.</td>
<td>Composition, oxidation state</td>
</tr>
<tr>
<td>ESDIAD or PSD</td>
<td>Electron (photon)-stimulated ion angular distribution [5–7, 11, 67–72]</td>
<td>Electrons or photons break chemical bonds in absorbed atoms or molecules, causing ionized atoms or radicals to be ejected from the surface along the axis of the broken bond by Coulomb repulsion. The angular distribution of these ions gives information on the bonding geometry of adsorbed molecules.</td>
<td>Bonding geometry, molecular orientation</td>
</tr>
<tr>
<td></td>
<td>Ellipsometry [73]</td>
<td>Used to determine thickness of an adsorbed film. A circular polarized beam of light is reflected from a surface, and the change in the polarization characteristics of the light gives information about the surface film.</td>
<td>Layer thickness</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure [6, 11, 74–80]</td>
<td>Monoenergetic photons excite a core hole. The modulation of the absorption cross section with energy at 100–500 eV above the excitation threshold yields information on the radial distances to the neighboring atoms. The cross section can be measured by fluorescence as the core holes decay or by attenuation of the transmitted photon beam. EXAFS is one of the many “fine-structure” techniques.</td>
<td>Local surface structure and coordination numbers</td>
</tr>
<tr>
<td>Technique</td>
<td>Description</td>
<td>Applications</td>
<td></td>
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<tr>
<td>EXELFS</td>
<td>Extended X-ray energy loss fine structure [6]</td>
<td>Local surface structure and coordination numbers</td>
<td></td>
</tr>
<tr>
<td>FEM</td>
<td>Field emission microscopy [5–7, 14, 23, 25, 81, 82]</td>
<td>Surface structure</td>
<td></td>
</tr>
<tr>
<td>FIM</td>
<td>Field ionization microscopy [5–7, 14, 23, 25, 82, 83]</td>
<td>Surface structure and surface diffusion</td>
<td></td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy [84–86]</td>
<td>Bonding geometry and strength</td>
<td></td>
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<tr>
<td>HEIS</td>
<td>High-energy ion scattering spectroscopy [6, 14, 87, 88]</td>
<td>Surface structure</td>
<td></td>
</tr>
<tr>
<td>HPXPS</td>
<td>High-pressure X-ray photoelectron spectroscopy [89, 90]</td>
<td>Composition, oxidation state</td>
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<tr>
<td>HREELS</td>
<td>High-resolution electron energy loss spectroscopy [5, 6, 91–93]</td>
<td>A monoenergetic electron beam, $\sim 2$–$10$ eV, is scattered off a surface; and the energy losses between $\sim 0.5$ eV to bulk and surface phonons and vibrational excitations of adsorbates are measured as a function of angle and energy (also called EELS).</td>
<td>Bonding geometry, surface atom vibrations</td>
</tr>
<tr>
<td>INS</td>
<td>Ion-neutralization spectroscopy [5, 6, 94]</td>
<td>Slow ionized atoms, usually He$^+$, strike a surface, where they are neutralized in a two-electron process that can eject a surface electron (a process similar to Auger emission from the valence band). The ejected electrons are detected as a function of energy, and the surface density of states can be determined from the energy distribution. The interpretation is more complicated than for SPI or UPS.</td>
<td>Valence bands</td>
</tr>
<tr>
<td>IP</td>
<td>Inverse photo-emission [95–100]</td>
<td>The absorption of electrons by a surface is measured as a function of energy and angle. This technique gives information about conduction bands and unoccupied levels.</td>
<td>Electronic structure</td>
</tr>
<tr>
<td>IRAS</td>
<td>Infrared reflection adsorption spectroscopy [6, 62, 63, 86, 101, 102]</td>
<td>The vibrational modes of adsorbed molecules on a surface are studied by monitoring the absorption or emission of IR radiation from thermally excited modes as a function of energy.</td>
<td>Molecular structure</td>
</tr>
<tr>
<td>ISS</td>
<td>Ion scattering spectroscopy [5–7, 11, 103, 104]</td>
<td>Ions are scattered from a surface, and the chemical composition of the surface may be determined by the momentum transfer to surface atoms. The energy range is $\sim 1$ keV to $10$ MeV, and the lower energies are more surface sensitive. At higher energies, this technique is also known as Rutherford back-scattering (RBS). A compilation of surface structures determined with ion scattering summarizing the pre-1988 literature appears in Ref. [105].</td>
<td>Surface structure, composition</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Source(s)</td>
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<tr>
<td>LEED</td>
<td>Monoenergetic electrons below ~500 eV are elastically back-scattered from a surface and detected as a function of energy and angle. This gives information on the structure of the near-surface region. A compilation of surface structures summarizing the pre-1986 literature appears in Ref. [110].</td>
<td>[5–7, 11, 13–15, 23, 25, 26, 106–109]</td>
<td></td>
</tr>
<tr>
<td>LEIS</td>
<td>Low-energy ions below ~5 eV are scattered from a surface, and the ion “shadowing” gives information on the surface structure. At these low energies the surface-atom ion-scattering cross section is very large, resulting in large surface sensitivity. Accuracy is limited because the low-energy ion-scattering cross sections are not well known.</td>
<td>[6, 7, 14, 111, 112]</td>
<td></td>
</tr>
<tr>
<td>LEPD</td>
<td>Similar to LEED with positrons as the incident particle. The interaction potential is somewhat different than for electrons, so the form of the structural information is modified.</td>
<td>[113, 114]</td>
<td></td>
</tr>
<tr>
<td>MEED</td>
<td>Similar to LEED, except the energy range is higher, ~300–1000 eV.</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>MEIS</td>
<td>Similar to HEIS, except that incident ion energies are ~50–500 keV.</td>
<td>[7, 14]</td>
<td></td>
</tr>
<tr>
<td>Neutron diffraction [115–117]</td>
<td>Neutron diffraction is not an explicitly surface sensitive technique, but neutron diffraction experiments on large-surface-area samples have provided important structural information on adsorbed molecules and also on surface phase transitions.</td>
<td>[74, 75, 118–120]</td>
<td></td>
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</tbody>
</table>

**NEXAFS**

A core hole is excited as in fine-structure techniques (see EXAFS, SEXAFS, AR-PEFS, NPD, APD, EXELFS, SEELFS) except that the fine structure within ~30 eV of the excitation threshold is measured. Multiple scattering is much stronger at low electron energies, so this technique is sensitive to the local 3D geometry, not just the radial separation between the source atom and its neighbors. The excitation cross section may be monitored by detecting the photoemitted electrons or the Auger electrons emitted during the core-hole decay.

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TABLE 1.1  Continued

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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance [121, 122]</td>
<td>NMR is not an explicitly surface-sensitive technique, but NMR data on large surface area samples (≥1 m²) have provided useful data on molecular adsorption geometries. The nucleus magnetic moment interacts with an externally applied magnetic field and provides spectra highly dependent on the nuclear environment of the sample. The signal intensity is directly proportional to the concentration of the active species. This method is limited to the analysis of magnetically active nuclei.</td>
<td>Chemical state</td>
</tr>
<tr>
<td>NPD</td>
<td>Normal photoelectron diffraction [41, 42]</td>
<td>Similar to ARPEFS, but with a somewhat lower energy range.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>PM-RAIRS</td>
<td>Polarization-modulated reflection-</td>
<td>An reflection–absorption IR spectroscopy that utilizes the IR selection rule on metal surfaces to achieve the surface sensitivity.</td>
<td>Molecular structure, surface reaction</td>
</tr>
<tr>
<td></td>
<td>absorption infrared spectroscopy [123–125]</td>
<td></td>
<td>intermediates</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford back-scattering [5, 6, 126,</td>
<td>Similar to ISS, except that the main focus is on depth-profiling and composition. The momentum transfer in back-scattering collisions between nuclei is used to identify the nuclear masses in the sample, and the smaller, gradual momentum loss of the incident nucleus through electron–nucleus interactions provides depth-profile information.</td>
<td>Composition</td>
</tr>
<tr>
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<td>127]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection high-energy electron</td>
<td>Monoenergetic electrons below ~1–20 keV are elastically scattered from a surface at glancing incidence, and detected as a function of energy and angle for small forward-scattering angles. Back-scattering is less important at high energies, and glancing incidence is used to enhance surface sensitivity.</td>
<td>Surface structure, structure of thin films</td>
</tr>
<tr>
<td></td>
<td>diffraction [6, 7, 13, 14, 25, 128]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEELFS</td>
<td>Surface electron energy loss fine</td>
<td>A fine-structure technique similar to EXELFS, except the incident electron is more surface sensitive because of the lower excitation energy. A compilation of surface structures determined using SEELFS and SEXAFS summarizing the pre-1990 literature appears in Ref. [131].</td>
<td>Surface structure</td>
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<tr>
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<td>structure [80, 129, 130]</td>
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<tr>
<td>Technique</td>
<td>Description</td>
<td>Application</td>
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<tr>
<td>SERS</td>
<td>Surface enhanced Raman spectroscopy [62, 132, 133]</td>
<td>Some surface geometries (rough surfaces) concentrate the electric fields of Raman scattering cross section so that it is surface sensitive. This gives information on surface vibrational modes, and some information on geometry via selection rules.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>SEXAFS</td>
<td>Surface extended X-ray absorption fine structure [6, 11, 75, 129, 134–136]</td>
<td>A more surface-sensitive version of EXAFS, where the excitation cross-section fine structure is monitored by detecting the photoemitted electrons (PE–SEX–AFS), Auger electrons emitted during core-hole decay (Auger–SEXAFS), or ions excited by photoelectrons and desorbed from the surface (PSD–SEX–AFS).</td>
<td>Surface structure</td>
</tr>
<tr>
<td>SFA</td>
<td>Surface force apparatus [137–140]</td>
<td>Two bent mica sheets with atomically smooth surfaces are brought together with distance of separation in the nanometer range. The forces acting on molecular layers between the mica plates perpendicular and parallel to the plate surfaces can be measured.</td>
<td>Forces acting on molecules squeezed between mica plates are measured.</td>
</tr>
<tr>
<td>SFG</td>
<td>Sum frequency generation [141–143]</td>
<td>Similar m SHG. One of the lasers has a tunable frequency that permits variation of the second harmonic signal. In this way, the vibrational excitation of the adsorbed molecules is achieved.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>SHG</td>
<td>Second harmonic generation [141, 144, 145]</td>
<td>A surface is illuminated with a high-intensity laser, and photons are generated at the second harmonic frequency through nonlinear optical processes. For many materials, only the surface region has the appropriate symmetry to produce the SHG signal. The nonlinear polarizability tensor depends on the nature and geometry of adsorbed atoms and molecules.</td>
<td>Electronic structure, molecular orientation</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry [5–7, 104, 146–152]</td>
<td>Ions and ionized clusters ejected from a surface during ion bombardment are detected with a mass spectrometer. Surface chemical composition and some information on bonding can be extracted from SIMS ion fragment distributions.</td>
<td>Surface composition</td>
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<tr>
<td>SPI</td>
<td>Surface penning ionization [5, 26]</td>
<td>Neutral atoms, usually He, in electronically excited states collide with a surface at thermal energies. A surface electron may tunnel into an unoccupied electronic level of the incoming gas atom, causing the incident atom to ionize and eject an electron, which is then detected. This technique measures the density of states near the Fermi level of the substrate and is highly surface sensitive.</td>
<td>Electronic structure</td>
</tr>
<tr>
<td>SLEED</td>
<td>Spin-polarized low-energy electron diffraction [27, 153]</td>
<td>Similar to LEED, except the incident electron beam is spin polarized. This fact is particularly useful for the study of surface magnetism and magnetic ordering.</td>
<td>Magnetic structure</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy [5, 38, 154–160]</td>
<td>The topography of a surface is measured by mechanically scanning of a probe over a surface. The distance from the probe to the surface is measured by the probe-surface tunneling current. Angstrom resolution of surface features is routinely obtained.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>SXAPS</td>
<td>Soft X-ray appearance potential spectroscopy</td>
<td>Another name for APXPS.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy [14, 15, 161, 162]</td>
<td>TEM can provide surface information for carefully prepared and oriented bulk samples. Real images have been formed of the edges of crystals where surface planes and surface diffusions have been observed. Diffraction patterns of reconstructed surfaces, superimposed on the bulk diffraction pattern, have also provided surface structural information.</td>
<td>Surface structure</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal desorption spectroscopy [6, 163–167]</td>
<td>An adsorbate-covered surface is heated, usually at a linear rate, and the desorbing atoms or molecules are detected with a mass spectrometer. This gives information on the nature of adsorbate species and some information on adsorption energies and the surface structure.</td>
<td>Composition, heat of adsorption, surface structure</td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Relevant Measurements</td>
<td></td>
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<tr>
<td>------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>TDP</td>
<td>Temperature programmed desorption [6, 165–167]</td>
<td>Composition, heat of adsorption, surface structure</td>
<td></td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoemission spectroscopy [5–7, 23, 25, 26, 45, 94, 168, 169]</td>
<td>Valence band structure</td>
<td></td>
</tr>
<tr>
<td>Work function measurements</td>
<td>Changes in a substrate's work function during the adsorption of atoms and molecules provide information about charge transfer between the adsorbate and the substrate and also about chemical bonding.</td>
<td>Electronic structure</td>
<td></td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near-edge structure</td>
<td>Another name for NEXAFS.</td>
<td></td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoemission spectroscopy [5, 7, 12, 64–66, 172, 173]</td>
<td>Composition, oxidation state</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction [174–176]</td>
<td>Surface structure</td>
<td></td>
</tr>
</tbody>
</table>

TDP: Temperature programmed desorption

Similar to TDS, except the surface may be heated at a nonuniform rate to obtain more selective information on adsorption energies.

UPS: Ultraviolet photoemission spectroscopy

Electrons photoemitted from the valence and conduction bands are detected as a function of energy to measure the electronic density of states near the surface. This gives information on the bonding of adsorbates to the surface (see ARUPS).

Work function measurements

Changes in a substrate's work function during the adsorption of atoms and molecules provide information about charge transfer between the adsorbate and the substrate and also about chemical bonding.

XANES: X-ray absorption near-edge structure

Another name for NEXAFS.

XPS: X-ray photoemission spectroscopy

Electrons photoemitted from atomic core levels are detected as a function of energy. The shifts of core-level energies give information on the chemical environment of the atoms (see ARXPS, ARXPD).

XRD: X-ray diffraction

X-ray diffraction has been carried out at extreme glancing angles of incidence where total reflection ensures surface sensitivity. This provides structural information that can be interpreted by well-known methods. An extremely high X-ray flux is required to obtain useful data from single-crystal surfaces. Bulk X-ray diffraction is used to determine the structure of organometallic clusters, which provide comparisons to molecules adsorbed on surfaces.
properties give rise to adhesion, friction, or sliding. Magnetic surfaces are used for information storage (e.g., magnetic tape or computer disk drive). Optical surface phenomena are responsible for color and texture perception, total internal reflection needed for transmission through glass fibers, and the generation of second and higher harmonic frequencies in nonlinear laser optics. The electrical behavior of surfaces often gives rise to surface charge buildup, which is used for image transfer in xerography and for electron transport in integrated circuitry (Fig. 1.3).

Surfaces and interfaces are favorite media of evolution. Both photosynthetic and biological systems, the brain (Fig. 1.4) and the leaf (Fig. 1.5), evolve and improve by ever increasing their interface area or their interface/volume ratio. The large number of folds in the human brain (Fig. 1.4) helps to maximize the number of surface sites, which also facilitate charge transport and the transport of molecules. A leaf is a high-surface-area system designed to maximize the absorption of sunlight in order to carry out chlorophyll-catalyzed photosynthesis at optimum rates (Fig. 1.5). The spine of the sea urchin has remarkable strength that is achieved by the layered structure of an inorganic–organic composite, namely, single-crystalline calcium carbonate (CaCO₃) that grows on ordered layers of acidic macromolecules deposited on layers of protein (Fig. 1.6). These are but some of the examples that show how external surfaces are frequently used in nature.

Figure 1.2. Interfaces are ever-present in our lives. (a) An astronaut representing the solid–vacuum interface; (b) a jumping basketball player representing the solid–gas interface; (c) a sailboat representing the solid–liquid interface; and (d) a tire representing the solid–solid interface. (See color insert.)
Figure 1.3. Integrated microelectronic circuits are the heart of computers and other electronic devices. Miniaturization increases their speed and permits the performance of more functions per unit area. A close-up view of a transistor circuit element with the size of (a) 0.35 μm and (b) 70 nm. As the integrated circuits are made increasingly more compact, their surface/volume ratio increases and essentially makes them surface devices. (c) The Intel Pentium 4 microprocessor. (Courtesy of Paul Davies, Intel Corporation.)

Figure 1.4. The intricate folds of the human brain expose the large interface area of this remarkable organ. The brain may be viewed as a device with enormous solid–liquid interface area. (See color insert.)
1.3 EXTERNAL SURFACES

1.3.1 Surface Concentration

The concentration of atoms or molecules at the surface of a solid or liquid can be estimated from the bulk density. For a bulk density of 1 g cm\(^{-3}\) (e.g., water), the molecular density \(\rho\), in units of molecules per cubic centimeter (cm\(^3\)), is \(\sim 5 \times 10^{22}\). The surface concentration of

Figure 1.5. The coleus leaf. Photosynthesis involves the absorption of sunlight and the reactions of H\(_2\)O and CO\(_2\) to produce organic molecules and oxygen. High-surface-area systems (e.g., the plant leaf) are most efficient to carry out photosynthesis. (Courtesy of Stefan Eberhard, Complex Carbohydrate Research Center, The University of Georgia, Athens, GA.) (See color insert.)

Figure 1.6. Spine of a sea urchin. Schematic diagram of the composite layer structure that makes up the spine of the sea urchin. Crystalline CaCO\(_3\) grows on an acidic macromolecular layer that is bound to protein layers. The spine is a single crystal of CaCO\(_3\) with its 001 axis parallel to the growth axis. (Courtesy of S. Weiner, L. Addadi, and A. Berman, Weizmann Institute of Science, Rehovot, Israel.)
molecules $\sigma$ (molecules cm$^{-2}$) is proportional to $\rho^{2/3}$, assuming a cube-like packing, and is thus on the order of $10^{15}$ molecules cm$^{-2}$. Because the densities of most solids or liquids are all within a factor of 10 or so of each other, $10^{15}$ molecules cm$^{-2}$ is a good order-of-magnitude estimate of the surface concentration of atoms or molecules for most solids or liquids. Of course, surface atom concentration of crystalline solids may vary by a factor of 2 or 3, depending on the type of packing of atoms at a particular crystal face.

### 1.3.1.1 Clusters and Small Particles

If a cluster is small enough, all of the atoms in the cluster are by necessity “surface atoms”. As a cluster grows in size, some atoms may become completely surrounded by neighboring atoms and are thus no longer on the “surface” (Fig. 1.7). We frequently describe the concentration of surface atoms in a cluster with a given size by its dispersion $D$, where $D$ is the ratio of the number of surface atoms to the total number of atoms:

$$D = \frac{\text{number of surface atoms}}{\text{total number of atoms}}$$

For very small particles, $D$ is unity. As the particle grows and some atoms become surrounded by their neighbors, the dispersion decreases. The volume of a cluster is roughly proportional to $d^3$, the cubic of the cluster size, as is the total number of atoms in the cluster. The surface area of a cluster is roughly proportional to $d^2$. Therefore, the dispersion of a cluster is roughly to scale unit $1/d$, the inverse of the cluster size (see right panel in Fig. 1.7).

Of course, the dispersion, $D$, also depends somewhat on the shape of the particle and how the atoms are packed [177]. For two clusters with the same volume, but different shapes (e.g., a cube and a sphere), the spherical cluster has a smaller surface area than the cubic cluster. Therefore, it is expected that, for the clusters to consist of the same number of atoms, the dispersion decreases.

**Figure 1.7.** Cubic clusters with the face-centered cubic (fcc) packing of 14, 50, 110, 194, and 302 atoms (the left panel). In the smallest cluster, all of the atoms are on the surface. However, the dispersion defined as the number of surface atoms divided by the total number of atoms in the cluster, declines rapidly with increasing cluster size, which is shown in the right panel of the figure. The size $d$ is the length of the edge of the cubic clusters. The lattice constant of the fcc clusters is assumed to be 3.9 Å, which is close to that of the Pt crystal.
rounder their shape, the lower the dispersion. Figure 1.8 compares the number of surface atoms on a cubic and a truncated cubic cluster. For a given total number of atoms, the truncated cubic cluster has fewer surface atoms than the cubic cluster.

Heterogeneous catalysts increase the rates of formation of product molecules and modify the relative distribution of the products. Most catalysts, including those used to produce fuels and chemicals ranging from high-octane gasoline to polyethylene (PE), are in the form of small particles with a size range of 1–10 nm. This is because chemical reactions are facilitated by surface atoms instead of bulk atoms. The increase in the dispersion of catalysts lowers the material cost of producing the catalysts without changing their catalytic activity.

1.3.1.2 Thin Films. When metals or semiconductors are exposed to the atmosphere, a thin layer of oxide is spontaneously formed on their surfaces. The oxide layer may not be visible to your eyes since it is only a few nanometers thick, but it could serve as a protective layer against corrosion, or a insulation layer in the electronic devices, or an active phase in catalytic reactions.

Thin films are of great importance to many real-world problems. Their material costs are very small compared to bulk materials, and they perform the same function when it comes to surface processes. A monolayer of Rh (Fig. 1.9a), a very expensive metal, which contains only $\sim 10^{15}$ metal atoms/cm$^2$, can catalyze the reduction of nitrous oxide (NO) to dinitrogen (N$_2$) by its reaction with CO in the catalytic converter of an automobile. Diamond is the hardest material in nature, but it is too expensive to be used directly for cutting and drilling tools in the daily life. Deposition of diamond as a thin film on shaped tools again
can solve this problem (Fig. 1.9b). By using modern chemical vapor deposition or other vapor deposition techniques, a diamond layer as thick as a few micrometers (μm) can be routinely grown on various substrates in order to improve the mechanical properties (e.g., hardness and wear resistance) of cutting and drilling tools.

Modern computer information technology is all built on the devices with complex thin-film structures. The transistors shown in Figure 1.3a and b are made by alternatively depositing and etching the thin films of Si and insulator materials. The hard drive disk for information storage is made of multiple thin layers on the top of a glass substrate (Fig. 1.9c). The first organic lubricant layer and the second hard C layer are used to protect the surface against impact and scratching by the reading head. Under the operating conditions, the disk may spin as fast as 15,000 revolutions per minutes (rpm) and the reading head is just ~3 nm away from the surface, so the protective layers are the key to improving the lifetime of the hard drive. Under the protective layers, another multilayer forms the magnetic medium for information storage.

1.3.2 Internal Surfaces: Microporous Solids

Microporous solids are materials that are full of pores of molecular dimensions or larger. These materials have large internal surface areas. Many clays have layer structures that
can accommodate molecules between the layers by a process called intercalation. Graphite will swell with water vapor to several times its original thickness (Fig. 1.10) as water molecules become incorporated between the graphitic carbon layers.

Crystalline alumina silicates, often called zeolites, have ordered cages of molecular dimensions [178, 179] where molecules can adsorb or undergo chemical reactions (Fig. 1.11). These materials are also called molecular sieves, because they may preferentially

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**Figure 1.10.** Intercalation compounds of graphite: C\textsubscript{24}K (top) and C\textsubscript{8}K (bottom). The color changes from black (graphite) are due to the transfer of electrons from the metal-to-carbon layers. (Courtesy of Tom Weller, Mark Ellerby and Neal Skipper, Department of Physics & Astronomy, London’s Global University.) (See color insert.)

**Figure 1.11.** Microporous molecular sieve. There are many alumina silicates in nature that have pores with molecular dimensions. These are called zeolites. Synthetic zeolites are also produced in large numbers, mostly from silicates, phosphates, and borates. They are used as selective absorbers of gases or liquids, and are the catalysts utilized in the largest volume in chemical and petroleum technologies. (See color insert.)
adsorb certain molecules according to their size or polarizability. This property is of great commercial importance and may be used to separate mixtures of gases (air) or liquids or to carry out selective chemical reactions. Bones of mammals are made out of calcium apatite, which has a highly porous structure, with pores on the order of 10 nm (100 Å) in diameter. Coal [180, 181] and char have porous structures, with pore diameters on the order of $10^2 - 10^3$ nm ($10^3 - 10^4$ Å). These materials have a very large internal surface areas, in the range of $100 - 400$ m$^2$ g$^{-1}$ of solid. As this short survey has shown, nature has provided us with many useful microporous materials; and many synthetic microporous substances are used in technology, both to separate gas and liquid mixtures by selective adsorption and to carry out surface reactions selectively in their pores, which are often of molecular dimensions. Because surface reaction rate (product molecules formed per second) is proportional to surface area, materials with high internal surface areas carry out surface reactions at very high rates.

1.4 CLEAN SURFACES

In order to study atomically clean surfaces, we must work under so-called ultrahigh vacuum (UHV) conditions [182–185], as the following rough calculation shows. We know that the concentration of atoms on the surface of a solid is on the order of $10^{15}$ cm$^{-2}$. To keep the surface clean for 1 s or 1 h, then, the flux of molecules incident on the initially clean surface must therefore be less than $\sim 10^{15}$ molecules$^{-1}$ cm$^{-2}$ s$^{-1}$ or $\sim 10^{12}$ molecules$^{-1}$ cm$^{-2}$ s$^{-1}$, respectively. From the kinetic theory of gases [186], the flux, $F$, of molecules striking the surface of unit area at a given ambient pressure, $P$, is

$$F = \frac{N_A P}{\sqrt{2 \pi MRT}}$$  \hspace{1cm} (1.2)

or

$$F \text{ (atoms}^{-1} \text{ cm}^{-2} \text{s}^{-1}) = 2.63 \times 10^{20} \frac{P \text{ (Pa)}}{\sqrt{M \text{ (g mol}^{-1})} T \text{(K)}}$$ \hspace{1cm} (1.3)

or

$$F \text{ (atoms cm}^{-2} \text{s}^{-1}) = 3.51 \times 10^{22} \frac{P \text{ (Torr)}}{\sqrt{M \text{ (g mol}^{-1})} T \text{(K)}}$$ \hspace{1cm} (1.4)

where $M$ is the average molar weight of the gaseous species, $T$ is the temperature, and $N_A$ is Avogadro’s number. Substituting $P = 4 \times 10^{-4}$ Pa ($3 \times 10^{-6}$ Torr) and using the values $M = 28$ g mol$^{-1}$ and $T = 300$ K, we obtain $F = 10^{15}$ molecules$^{-1}$ cm$^{-2}$ s$^{-1}$. Thus, at this pressure the surface is covered with a monolayer of gas within seconds, assuming that each incident gas molecule “sticks”. For this reason, the unit of gas exposure is $1.33 \times 10^{-4}$ Pa·s ($10^{-6}$ Torr·s), which is called the Langmuir (L). Thus, a 1-L exposure will cover a surface with a monolayer amount of gas molecules, assuming a sticking coefficient of unity. At pressures on the order of $1.33 \times 10^{-7}$ Pa ($10^{-9}$ Torr), it may take $10^3$ s before a surface is covered completely.
In practice, one usually wants to study a surface without worrying about contamination from ambient gases. Current surface-science techniques can easily detect contamination on the order of 1% of a monolayer. Then, this will be our operational definition of “clean”. Thus, UHV conditions (<1.33 \times 10^{-7} \text{ Pa} = 10^{-9} \text{ Torr}) are required to maintain a clean surface for \( \sim 1 \text{ h} \), the time usually needed to perform experiments on clean surfaces.

### 1.5 INTERFACES

In most circumstances, however, and certainly in our Earth’s environment, surfaces are continually exposed to gases or liquids or placed in contact with other solids. As a result, we end up investigating the properties of interfaces (i.e., between a solid and gas, a solid and a liquid, a solid and a solid, and even between two immiscible liquids). Thus, unless specifically prepared otherwise, surfaces are always covered with a layer of atoms or molecules from the neighboring phase (Fig. 1.12).

![Figure 1.12. Schematic diagram of interfaces (e.g., solid–liquid, liquid–liquid, liquid–gas, solid–solid, and solid–gas interfaces).](image)
1.5.1 Adsorption

On approaching the surface, each atom or molecule encounters an attractive potential that ultimately will bind it to the surface under proper circumstances. The process that involves trapping of atoms or molecules that are incident on the surface is called adsorption. It is always an exothermic process. For historical reasons, the heat of adsorption, $\Delta H_{\text{ads}}$, is always denoted as having a positive sign—unlike the enthalpy, $\Delta H$, which for an exothermic process would be negative according to usual thermodynamic convention.

The residence time, $\tau$, of an adsorbed atom is given

$$\tau = \tau_0 \exp \left( \frac{\Delta H_{\text{ads}}}{RT} \right)$$

(1.5)

where $\tau_0$ is correlated with the surface atom vibration times (it is frequently on the order of $10^{-12}$ s), $T$ is the temperature, and $R$ is the gas constant. The value of $\tau$ can be 1 s or longer at 300 K for $\Delta H_{\text{ads}} > 63$ kJ mol$^{-1}$ (15 kcal mol$^{-1}$). The surface concentration $\sigma$ (in molecules cm$^{-2}$) of adsorbed molecules on an initially clean surface is given by the product of the incident flux, $F$, and the residence time

$$\sigma = F \tau$$

(1.6)

The surface of the material on which adsorption occurs is often called the substrate. Substrate–adsorbate bonds are usually stronger than the bonds between adsorbed molecules. As a result, the monolayer of adsorbate bonded to the substrate is held most tenaciously and is difficult to remove. Therefore, the properties of real surfaces are usually determined in the presence of an adsorbed monolayer. For this reason, in the chapters that follow we will discuss the various properties of surfaces when clean and also when covered with a monolayer of adsorbate.

1.5.2 Thickness of Surface Layers

A surface or interface may be defined as comprising of either one atomic layer or several layers in the near-surface region. Usually, the phenomena or the systems studied define the number of atomic layers that must be considered as part of the surface. For example, the chemical bond between an adsorbed molecule and atoms in the topmost atomic layer of a metal can be described rather well by considering the properties of one monolayer of adsorbate and one monolayer of substrate atoms. However, the build up of charge at the surface of an electrical insulator may induce an electric field that extends $>100$ layers into the solid. When such a surface is in contact with a liquid, the electric field due to the surface charge accumulation also extends into the liquid several molecular layers deep. In this circumstance, the interface must be defined as many atomic layers thick on both sides of the surface in order to properly describe the electrical properties of the interface.

1.6 THE TECHNIQUES OF SURFACE SCIENCE

Over the last four decades, a large number of techniques have been developed to study various surface properties, including structure, composition, oxidation states, and changes of
chemical, electronic, and mechanical properties. The emphasis has been on surface probes that monitor properties on the molecular level and are sensitive enough to detect ever smaller numbers of surface atoms. The frontiers of surface instrumentation are constantly being pushed toward detection of finer detail: atomic spatial resolution, ever smaller energy resolution, and shorter time scales. Because no one technique provides all the necessary information about surface atoms, the tendency is to use a combination of techniques. The most commonly used techniques involve the scattering, absorption, or emission of photons, electrons, atoms, and ions, although some important surface-analysis techniques cannot be classified this way.

Electrons, atoms, and ions are used primarily to investigate external surfaces and require low ambient pressures during their application. Photons can be used to study both internal and external surfaces because of their much lower scattering cross sections. They can also be employed at high-gas pressures and for studies of solid–liquid and solid–solid interfaces.

Because many surface probes require high vacuum during their application, most surface science instruments are also equipped with high-pressure or environmental cells. The sample to be analyzed is first subjected to the usual high-pressure and/or high-temperature conditions encountered during reactions in the environmental cell. Then it is transferred into the evacuated chamber where the surface probe is located for surface analysis. One such apparatus is shown in Figure 1.13.

Sample preparation is always an important part of surface studies. Single crystals are oriented by X-ray back-diffraction, cut, and polished. They are then ion bombarded or chemically treated to remove undesirable impurities from their surfaces.

Thin films are deposited from vapor by sublimation, sputtering, or the use of plasma-assisted chemical vapor deposition. Materials of high internal surface area are prepared from a sol–gel or by calcination at high temperatures. The genesis and environmental history of the surface is primarily responsible for its structure and composition and must always be carefully monitored.

Figure 1.13. Photograph of a stainless steel chamber used for surface studies. It is equipped with surface characterization instruments that are used in UHV and with a high-pressure cell that is shown in both open (a) and closed (b) positions. The cell is used to expose the samples to high pressures and temperatures. The chamber can be evacuated to $10^{-10}$ Torr and equipped with windows on steel flanges with glass–metal seals for easy viewing. The flanges are mounted using Cu gaskets to avoid the use of lubricated seals so that the chamber can be “baked” at high temperatures (~200°C) to clean its internal surfaces. A manipulator that is used to mount the sample provides motion in three dimensions (3D) and permits cooling and heating. Gas analysis is provided by a mass spectrometer mounted on the chamber. The pressure is measured by ionization and thermocouple gauges.
Table 1.1 lists many of the surface science techniques that have been used most frequently in recent years to learn about the interface on the atomic scale [15–187]. The names of the techniques, their acronyms, and brief descriptions are provided, along with references, if a more detailed study of the capabilities and limitations of a particular technique is desired. We also indicate the primary surface information that can be obtained by the application of each technique. Detailed discussions of these techniques are outside the scope of this book. The reader is referred to review papers that describe the principles of operation for each, the instrumentation, and some of the findings of the experiments that used this technique. Many surface-science techniques are used in combination to obtain a more complete characterization of the structure (atomic, molecular, electronic) and the composition (including oxidation states) of atoms and molecules at the interface with increasing spatial and time resolution.

1.7 SUMMARY AND CONCEPTS

- The surface concentration of atoms or molecules is on the order of $10^{15}$ for most solids and liquids.
- Small particles used in surface studies are frequently described in terms of their dispersion.
- Thin films and microporous solids are systems with high surface-volume ratios.
- Many surface-science studies focus on interfaces (solid–gas, solid–liquid, and solid–solid), since surfaces are covered with adsorbates under the practical conditions in which they are utilized.
- The definition of how many atomic layers constitute the “surface region” depends on the surface phenomena under investigation. For example, one atomic or molecular layer can be responsible for most surface chemical properties, whereas almost $10^3$ layers are required to investigate surface effects in electron or photon transport.
- Most techniques provide information on only one side of the surface–adsorbate bond. Future instrumentation developments aim for molecular level studies at buried interfaces, of both sides of the surface chemical bonds, and on an ever shorter time scale (time-resolved studies).
- Photon, electron, atom, and ion scattering are utilized most frequently to study surface atomic and electronic structures and composition. Vacuum or reduced pressures at the interface is needed during experiments using electrons, atoms, and ions. As a result, we know more about the properties of the solid–vacuum and solid–gas interfaces than about solid–liquid, solid–solid, and liquid–liquid interfaces.
- Clean, adsorbate-free surfaces must be prepared in UHV.
- Selective adsorption of atoms and molecules are also important tools for studies of surface composition and bonding.

1.8 PROBLEMS

1.1 Calculate the concentration of surface atoms (atoms cm$^{-2}$) for a droplet of mercury (Hg), a piece of copper (Cu) and a drop benzene (C$_6$H$_6$).

1.2 (a) What is the gas flux striking a surface in air at 1 atm and 300 K?
(b) Calculate the pressure necessary to keep a 1-cm$^2$ Cu surface clean for 1 h at 300 K, assuming a sticking coefficient of 1 and no dissociation of the gas upon adsorption.

**1.3** In most cases, of course, the sticking coefficients are $\ll 1$. Using the following sticking coefficient for O$_2$, calculate the pressure necessary to keep a 1-cm$^2$ Cu surface “clean” for 1 s, 1 h, and 8 h at 300 K (the latter times correspond to times for “fast” or “relaxed” experiments, respectively). According to Ref. [188], $\sigma = 0.01$, 0.2, and 0.001 for the (100), (110), and (111) faces of Cu, respectively.

**1.4** At 1-atm air pressure, compute the volume of N$_2$ gas that is adsorbed on 10 g of zeolite with a surface area of 400 m$^2$ g$^{-1}$. Assume a surface area of 16.2 Å$^2$ per nitrogen molecule.

**1.5** What is the residence time of molecular nitrogen in a zeolite at 77 and 300 K? Assume a heat of adsorption of 15 kJ mol$^{-1}$ and $\tau_0 = 10^{-12}$ s.

**REFERENCES**

REFERENCES


32 S U R F A C E S : A N I N T R O D U C T I O N


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