Force Measurement: Surface Force Apparatus

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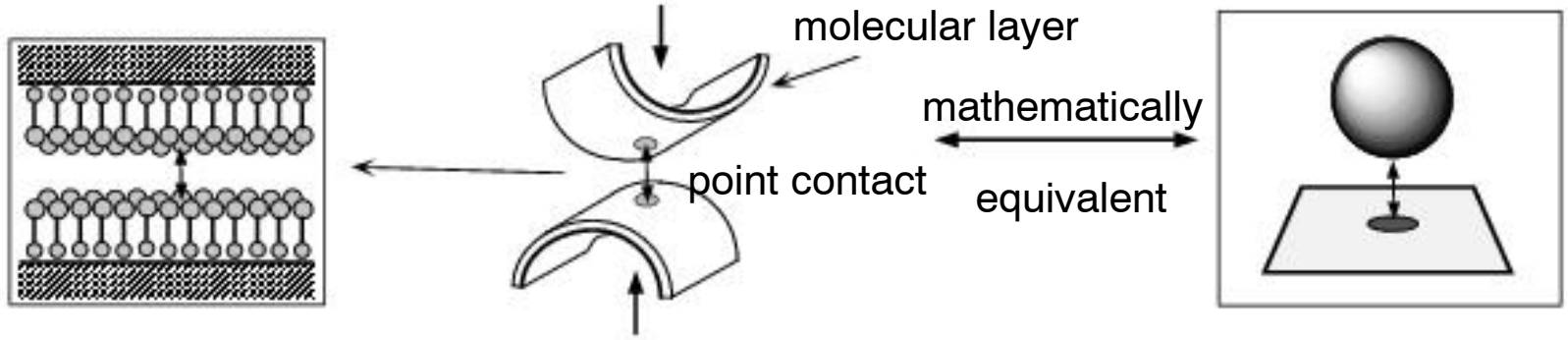


surface force apparatus measures the **force** acting between two **surfaces** coming into contact

crossed cylinder geometry of mica sheets used in SFA is mathematically equivalent to sphere on flat surface contact

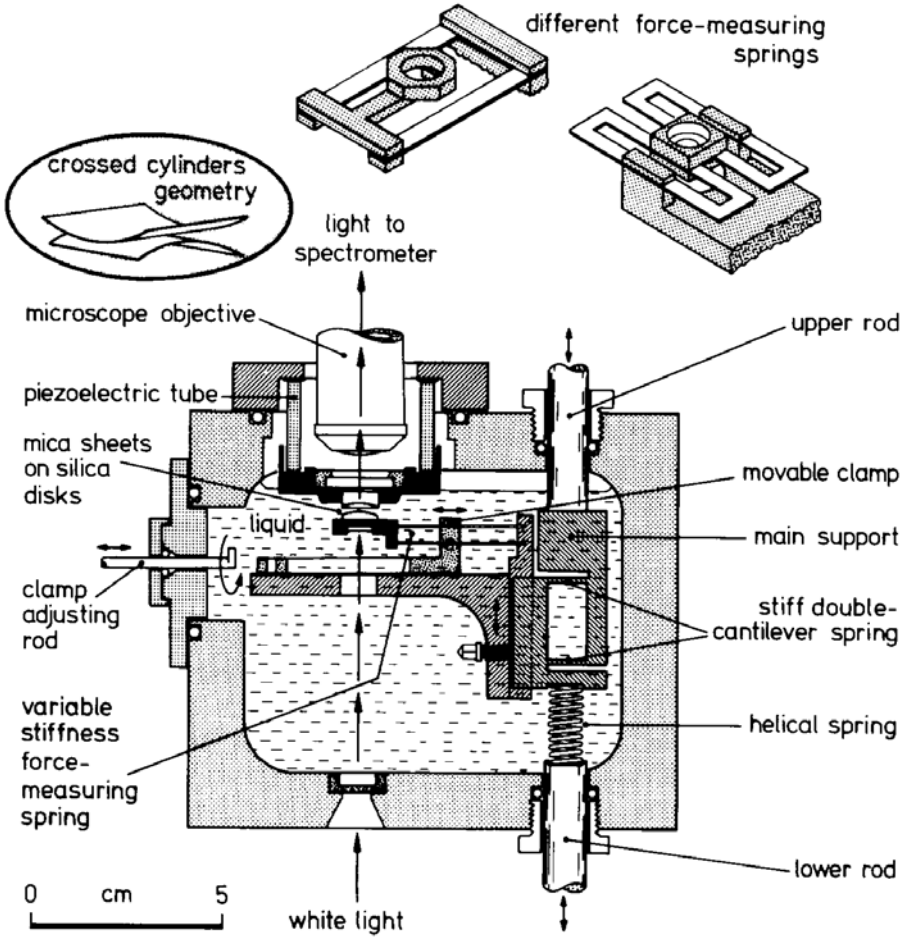
measurement of adhesion forces and interfacial energy can be analyzed by JKR (Johnson, Kendal, Roberts) theory for large soft objects, or DMT (Derjaguin, Muller, Toporov) for small hard objects

JKR:

$$F_{adhesion} = 3\pi\gamma R$$

DMT:

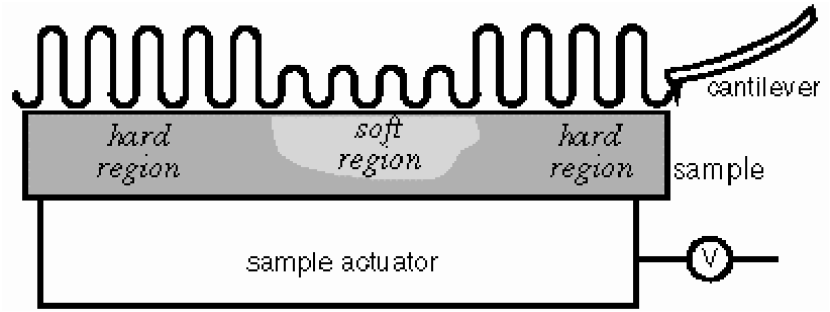
$$F_{adhesion} = 4\pi\gamma R$$

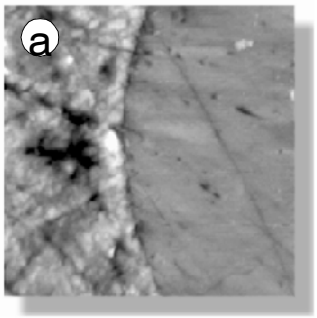


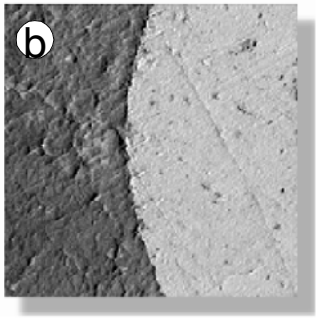
Force Measurement: SFM / AFM

force modulation microscopy: damping of cantilever oscillation due to energy dissipation in sample surface is correlated to elastic properties of surface (compare also phase modulation)

→ hard surface: weak damping, soft surface: strong damping



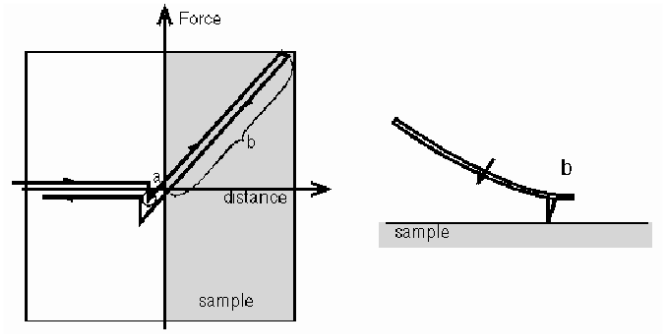




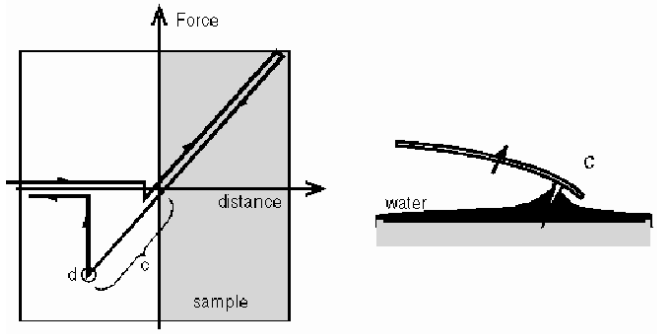
a) contact mode AFM of carbon fiber (right half) in polymer matrix (left half)

b) force modulation mode image of a)

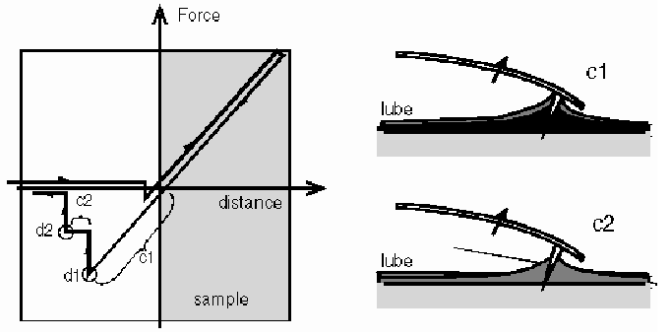
force *versus* distance curves: vertical deflection of cantilever is measured with respect to acting force over a spot on the sample surface → provides information on adhesive forces



in vacuum: primarily vdW interactions of tip and surface



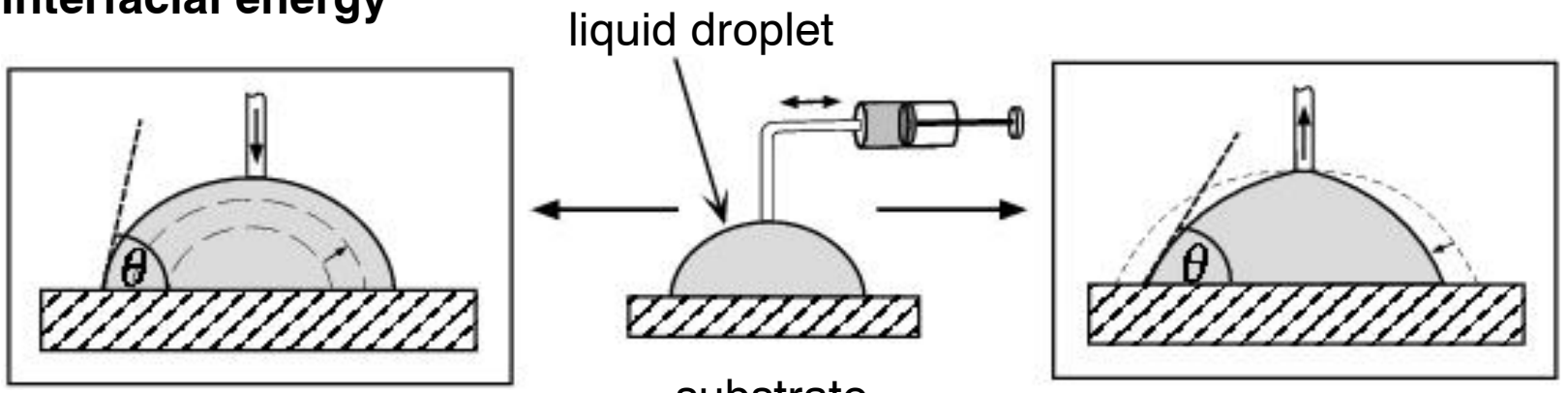
in clean air: thin water film on surface, capillary forces



in ambient air: thin contamination / lubrication film (+/– H_2O)

Contact Angle Goniometry

contact angle of **liquid** on **substrate** in **air** is measured to give idea about **surface** / **interfacial energy**



advancing contact angle θ_a

receding contact angle θ_r

opt. microscopy of water droplet

Young equation: macroscopic description of contact angle θ formed by a liquid with surface tension γ_l on a flat solid surface with surface energy γ_s and interfacial energy γ_{ls} between solid and liquid

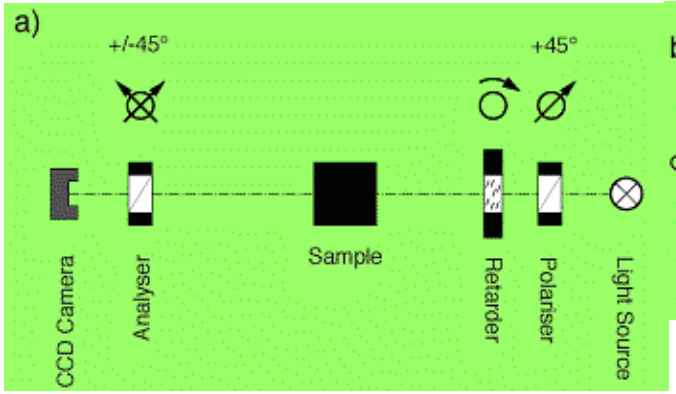
$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl}$$

real contact angle is influenced by 1) surface roughness, 2) surface inhomogeneities, and 3) restructuring of surface upon contact with water

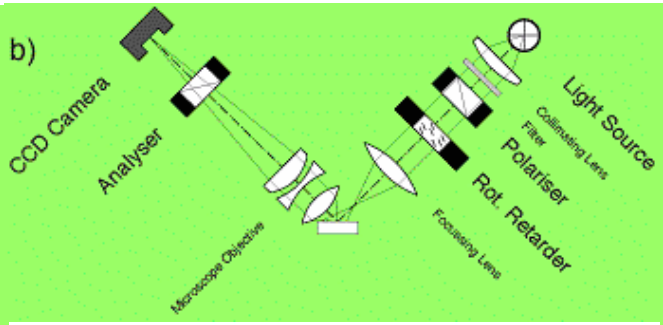
contact angle hysteresis $\Delta\theta = \theta_a - \theta_r$: difference between advancing θ_a and receding contact angle θ_r → dynamic ($\Delta\theta$ relevant) versus static (absolute value of θ relevant) hydrophobicity, dewetting behavior (small $\Delta\theta$ and large θ result in effective dewetting)

Ellipsometry

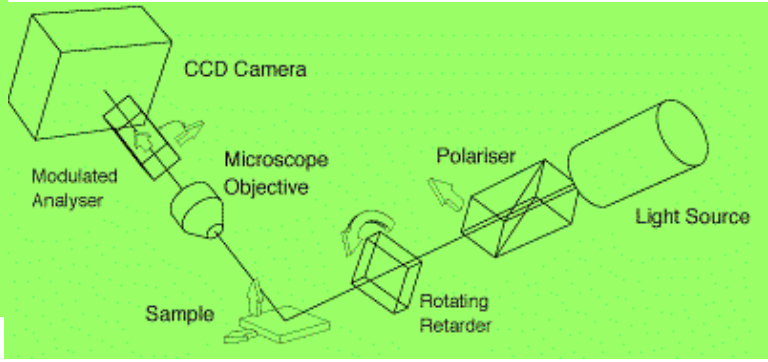
ellipsometry can be used to measure the **thickness** (and / or refractive index) of a **thin film** / **monolayer** on a solid substrate by **reflection** of **polarized light** (before and after film deposition)



top view



side view

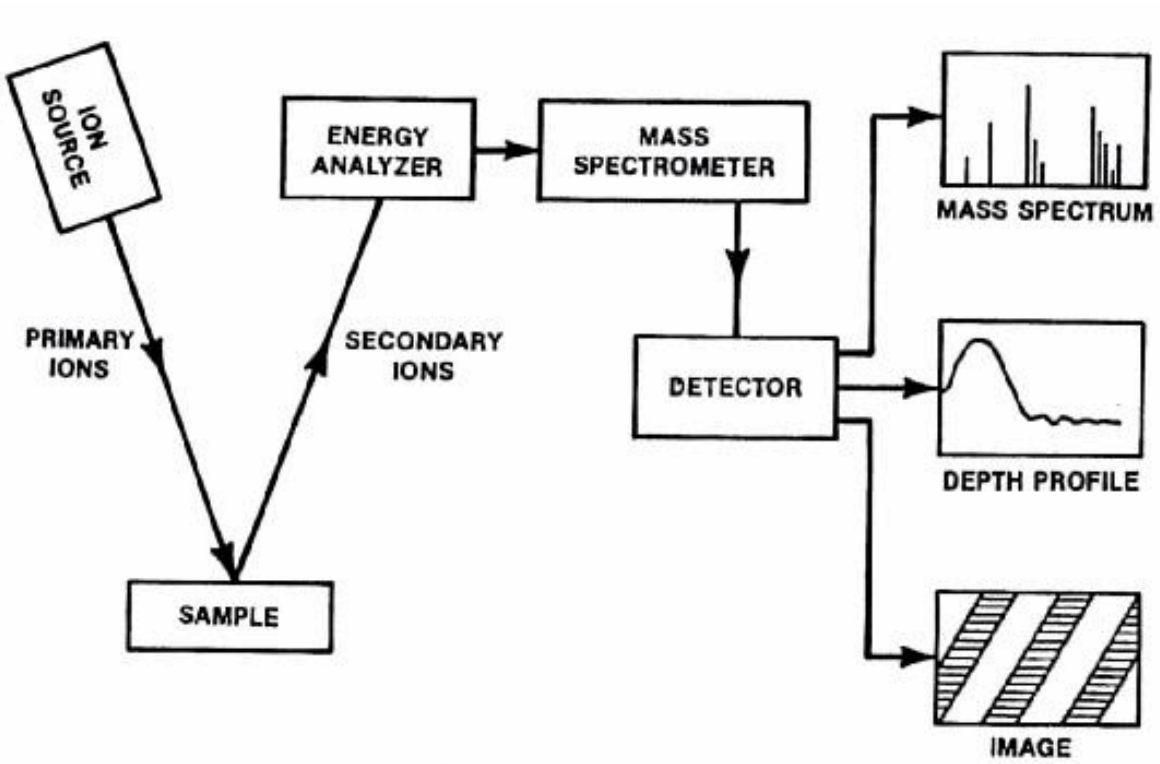


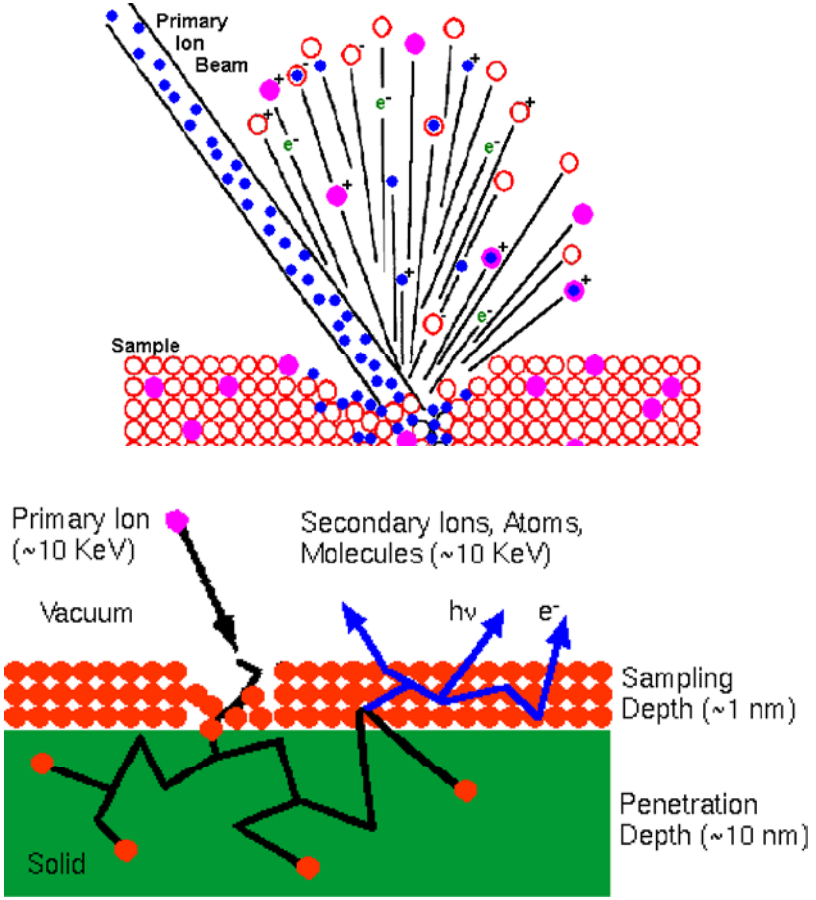
3D view

A linear polarized monochromatic light beam (from source & polarizer) is passing through retarder / compensator in +/– 45° orientation and then impinging on the substrate surface with equal polarization component parallel (s) and perpendicular (p) to the surface. After reflection the light is elliptically polarized due to different interaction of s– and p–component with the surface. By setting the polarizer and analyzer so that no light is passing (null ellipsometer) the relative phase change Δ and relative amplitude change ψ can be calculated. If the refractive index of the thin film (n_D =1.45 – 1.5 for hydrocarbons) is known the thickness can be calculated from Δ and ψ with angstrom resolution (→ molecular monolayers).

Secondary Ion Mass Spectrometry (SIMS)

SIMS: mass spectrometric characterization of surface and near surface regions, the sample in ultra high vacuum (10^{-9}–10^{-10} torr) is bombarded with neutral or charged ions (primary ions, Cs^+, O_2^+, O^- → reactive, Ar^+, He^+, Ne^+ → inert), which eject ions from the sample (0.5–30 keV, secondary, or sputtered ions), these ions are then analyzed with a spectrometer, which detects their mass to charge (m/z) ratios allowing identification of the elements in the material (→ depth profiling)

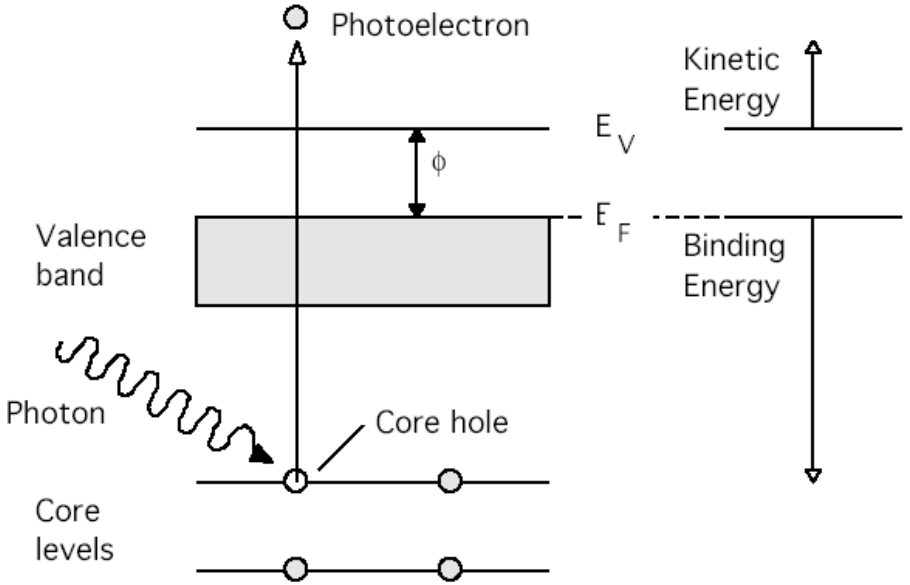


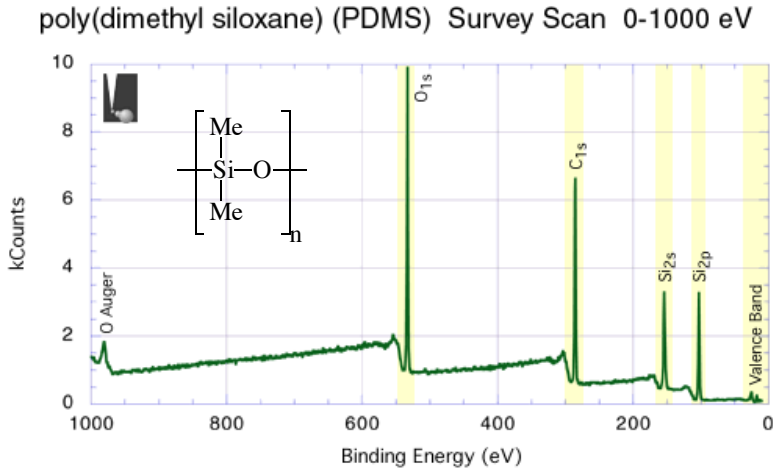


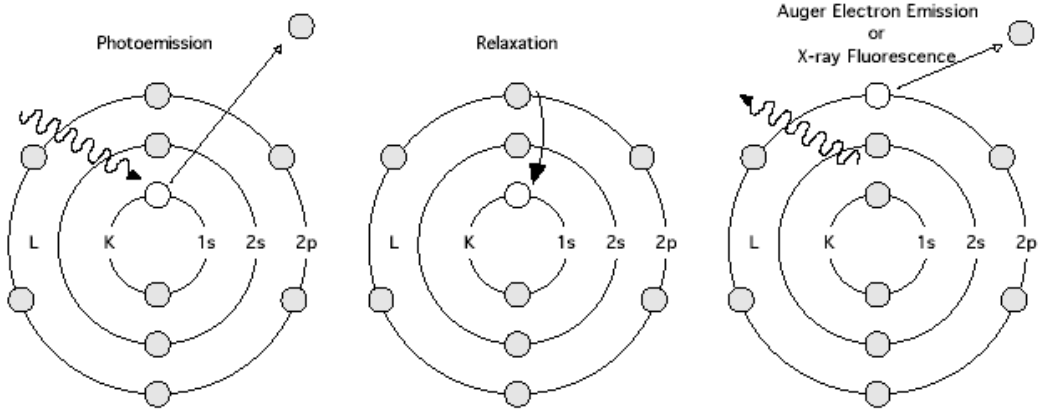
X–Ray Photoemission Spectroscopy (XPS / ESCA)

surface is irradiated with x–rays, core electrons in surface atoms are ejected and their energy is measured (element specific, often binding state specific), valence electrons can fall into core hole and emit characteristic photons (→ x–ray fluorescence) or secondary electrons of lower energy (Auger electrons)

- non destructive (...limited to organic material)
- quantitative method for elemental composition
- sensitive (0,1% ML)
- chemical shifts give information about:
  - oxidation state
  - chemical environment
- sampling depth 10–100 Å (depth profiling)
- possibility of imaging

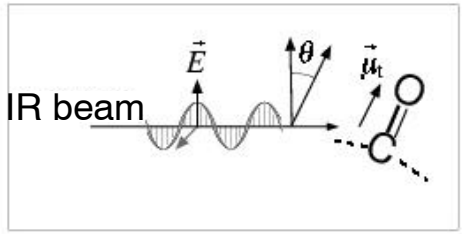


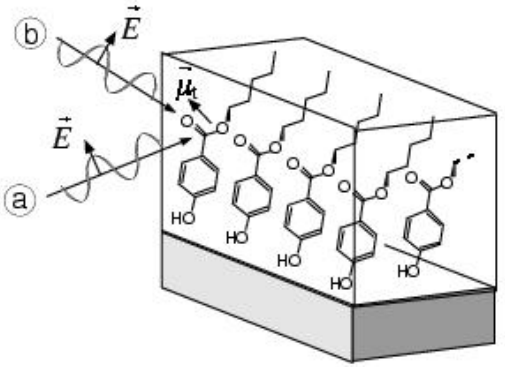


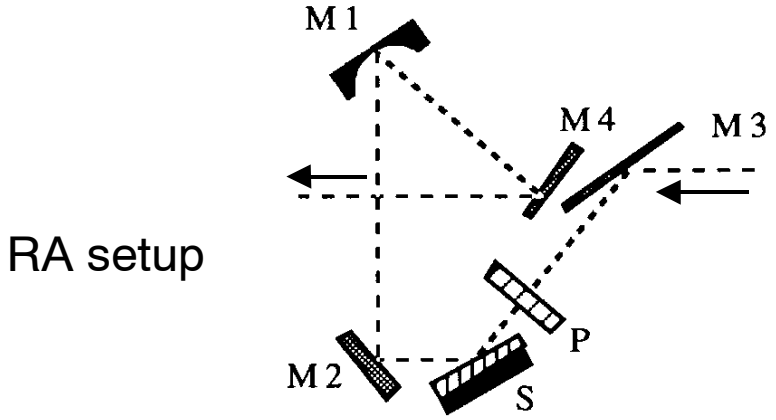


Fourier Transform Infrared Spectroscopy (FTIR)

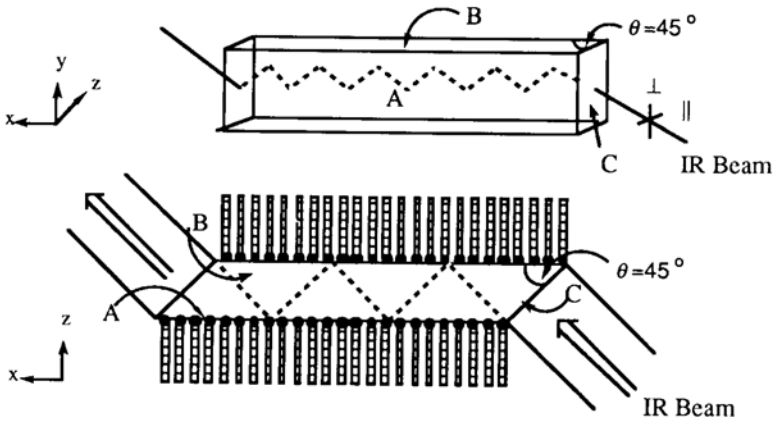
polarized IR in reflection absorption (RA) can detect **orientation** of molecules in **anisotropically** oriented **sample**, in attenuated total reflection (ATR) higher signal–to–noise ratios can be obtained



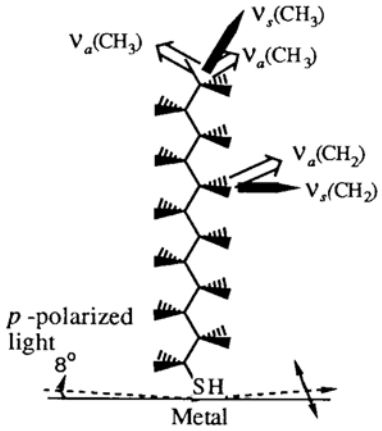


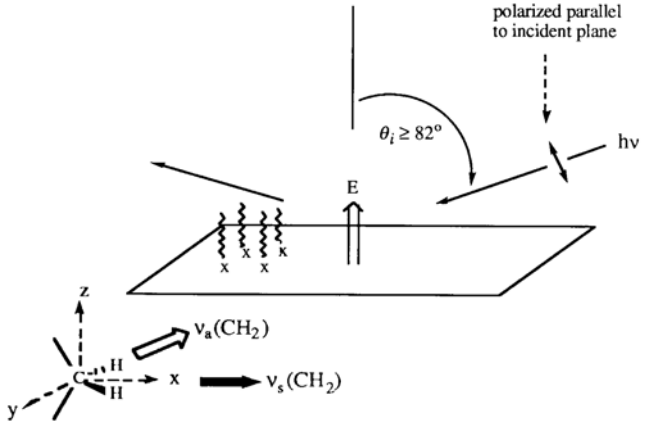


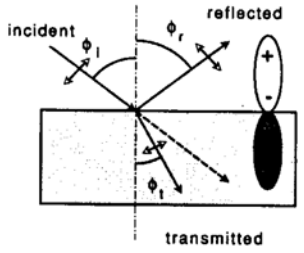
RA setup



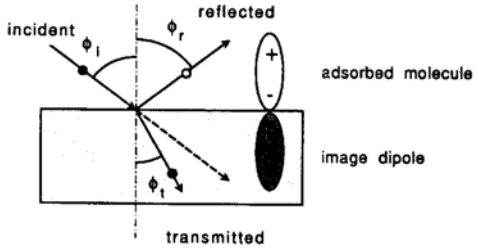
ATR setup







reflection of p-polarized light plane of polarization parallel to plane of incidence, electric field normal to surface



reflection of s-polarized light plane of polarization perpendicular to plane of incidence, electric field parallel to surface

Small Angle X–Ray Scattering (SAXS)

x–ray reflectivity / diffraction or small angle x–ray scattering (SAXS) provides information on **film thickness** / **layer spacing** by diffraction at the film planes / periodic layer spacings parallel to the substrate plane according to **Bragg's law**: $n\lambda = 2d \sin\theta$

n: order of reflex (n = 1, 2, 3,...); λ: wavelength of x–ray; d: layer spacing; θ: angle of x–ray to surface plane

Bragg peaks (large angle): periodic layer spacing

Kiessig peaks (small angle): overall film thickness