Surface Plasmon Resonance

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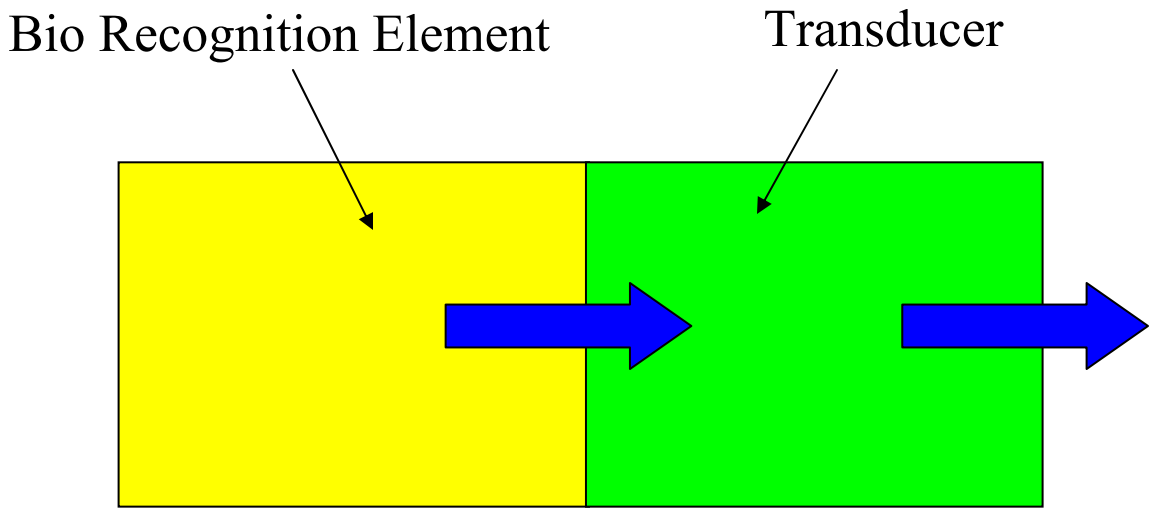
Biosensor



Requires:
Sample
Immobilization

Enzymes;
Antibodies;
Receptors;
Whole
cells...

Electrochemical

Optical

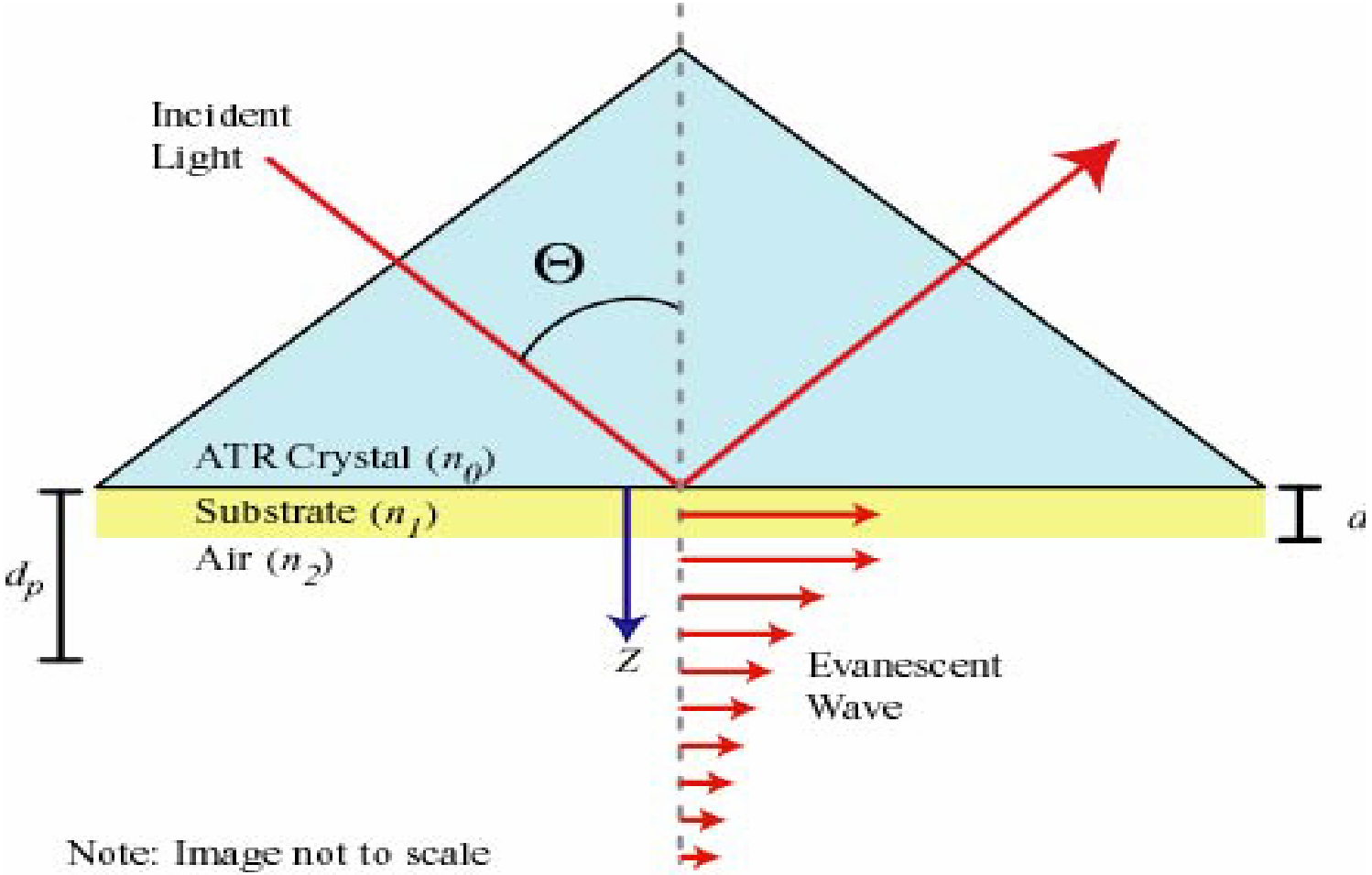
Requires:

Simple read out and data interpretation;

Easy to use;

Quick response.

Evanescent Wave



Evanescent wave

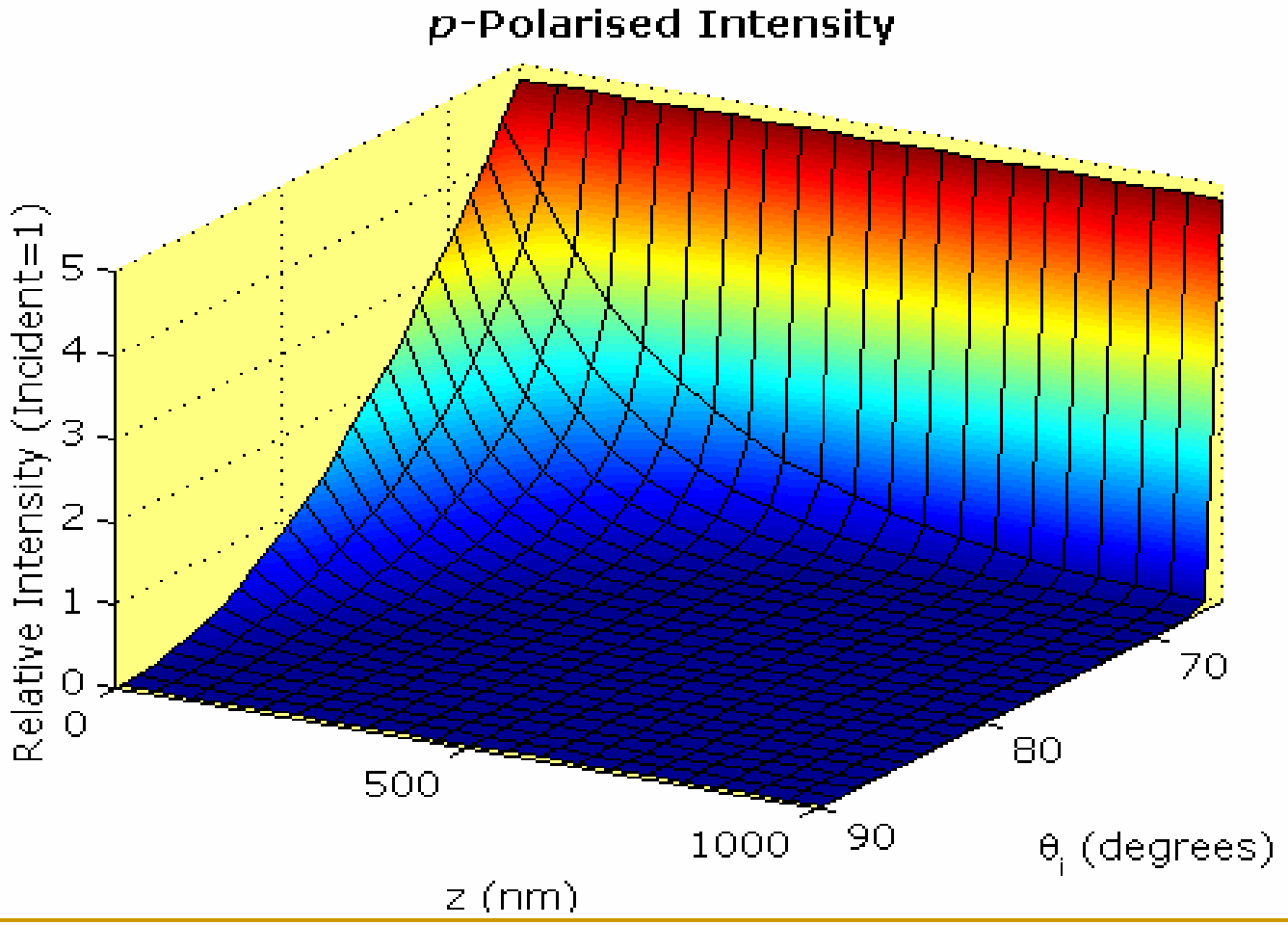
- Evanescent wave: a few hundred nanometers
- Decays exponentially over a fraction of the wavelength
- Evanescent wave and the resonance angle depend on the refractive index in the interface.

Penetration depth

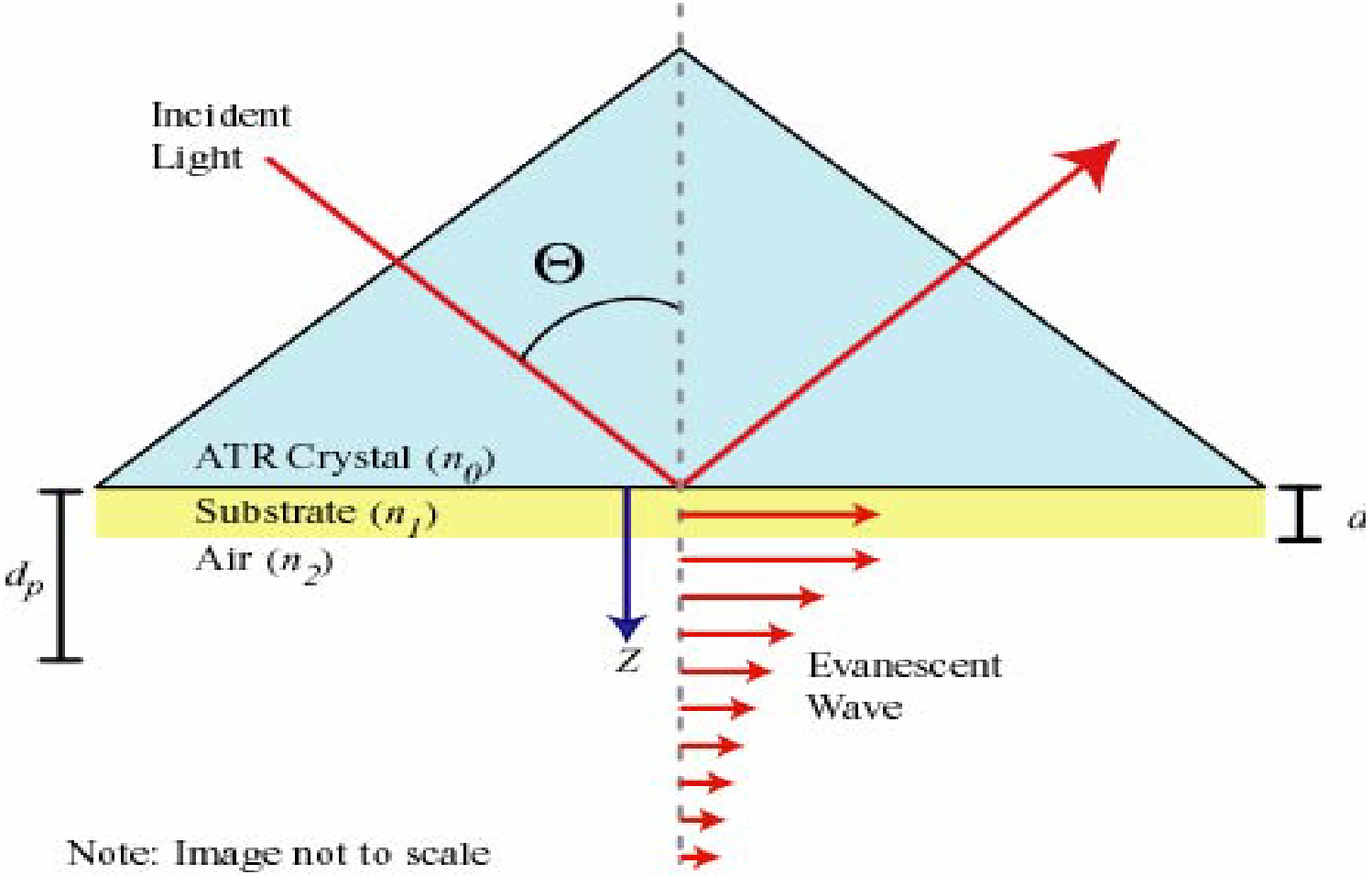
$$d_p = \frac{\lambda}{2\pi(n_{co}^2 \sin^2\theta_1 - n_{cl}^2)^{1/2}}$$

- where $\theta 1$ is the internal incident ray angle with the normal to the core/cladding interface
- Penetration depth provides a spatial separation between the fluorescent complexes bound to the core and those free in solution
- Highly specific antibody binding event
- Eliminates the need for the washing step

Intensity for 532 nm light at a quartz-water interface



Evanescent Wave



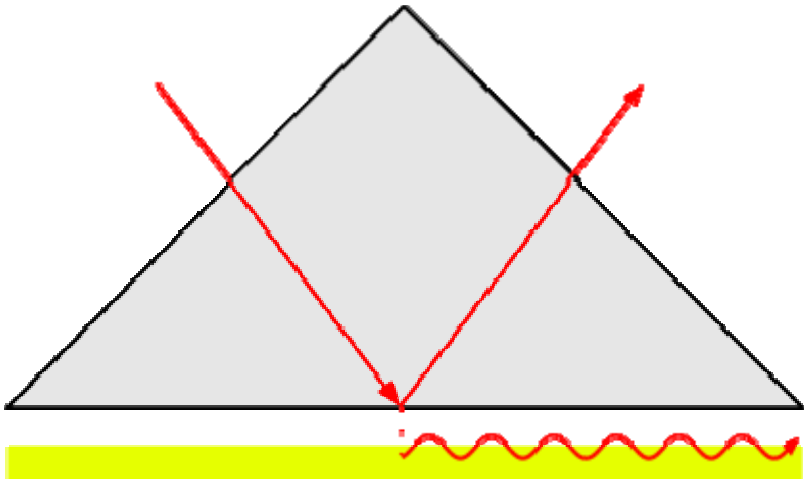
Surface Plasmon Resonance

- Interface: high refractive index; thin layer wit good electric conductivity; a medium of low refractive index
- Evanescent wave interacts with free electrons in the conductive layer
- Give rise to “plasmons”
- Energy is lost from the reflected light
- Results in a minimum of the reflected intensity at the resonance angle.

Surface plasmons

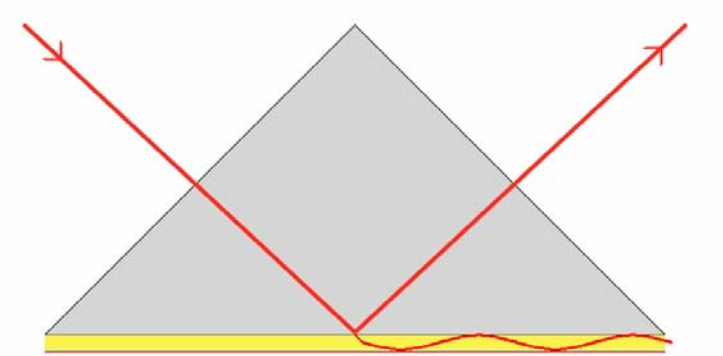
- Surface electromagnetic waves
- Propagate parallel along a metal/dielectric interface
- Very sensitive to any changes of this boundary

Two configurations



Otto setup, the light is shone on the wall of a glass block, typically a prism, and totally reflected. A thin metal (for example gold) film is positioned close enough, that the evanescent waves can interact with the plasma waves on the surface and excite the plasmons.

- Typical metals: silver and gold.



Kretschmann configuration, the metal film is evaporated onto the glass block. The light is again illuminating from the glass, and an evanescent wave penetrates through the metal film. The plasmons are excited at the outer side of the film. This configuration is used in most practical applications.

Biosensing

- Measure refractive index changes due to the absorption of material to the sensor surface
- Refractive index changes are proportional o the mass of the molecules that enter the interfacial layer

Biosensing

- Metal/dielectric interface
- Truly reagentless sensor (label-free)
- Antibody is immobilized on the surface of the metal at which the surface wave is generated.
- On binding a large analyte the refractive index within the region of the surface plasmon evanescent field changes
- Matching requirements for surface plasmon generation are correspondingly altered
- Change in the angle of the incident light required to achieve resonance

Commercial instrument

- BIAcore from Pharmacia Biosensor AB in 1990
- Autosampler
- Integrated fluid-handling system
- High-resolution sensor on top of a microflow chamber
- Temperature-stabilized environment
- Become a standard technique in many biological and medical research areas.

Schematic of SPR setup

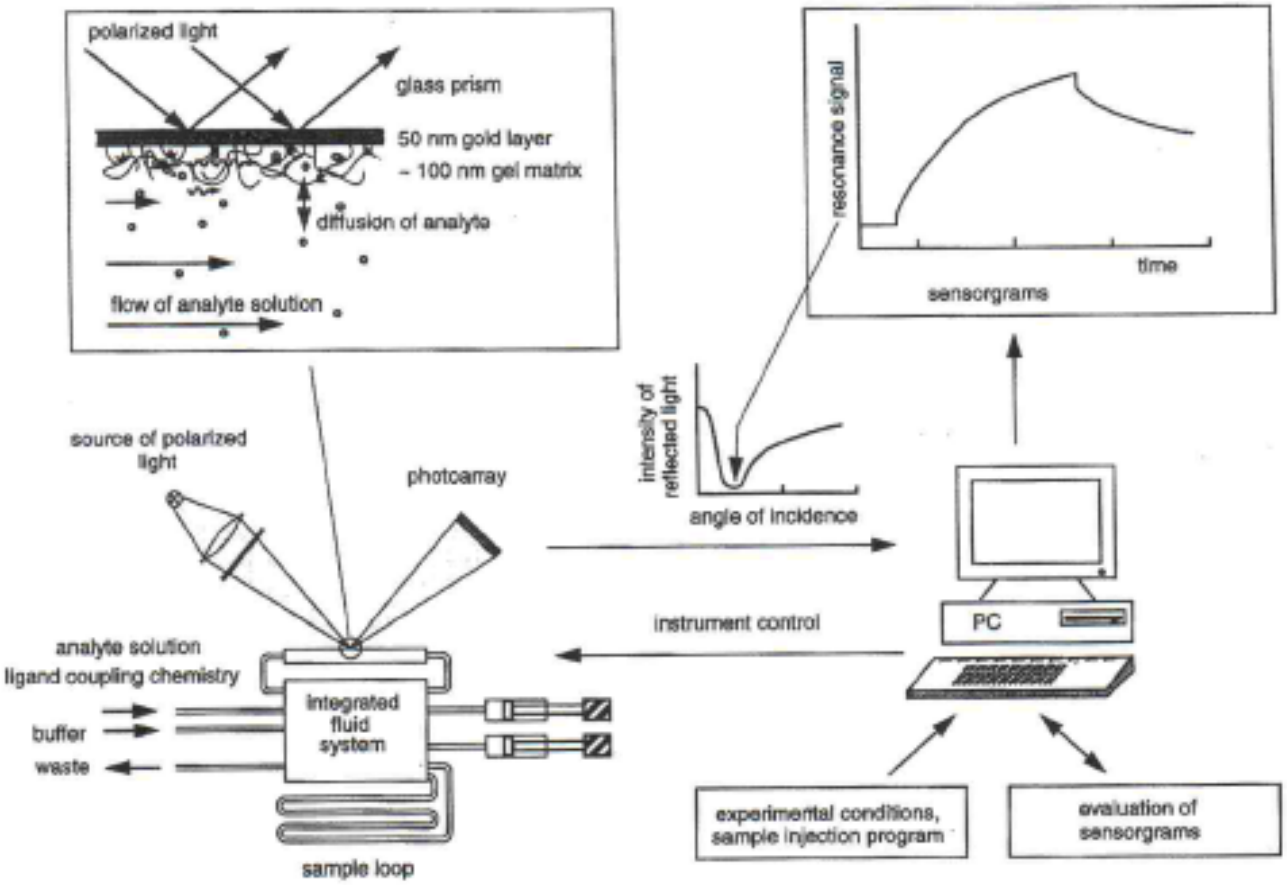


Figure 11.1. Basic scheme of surface plasmon resonance measurements in a BIAcore

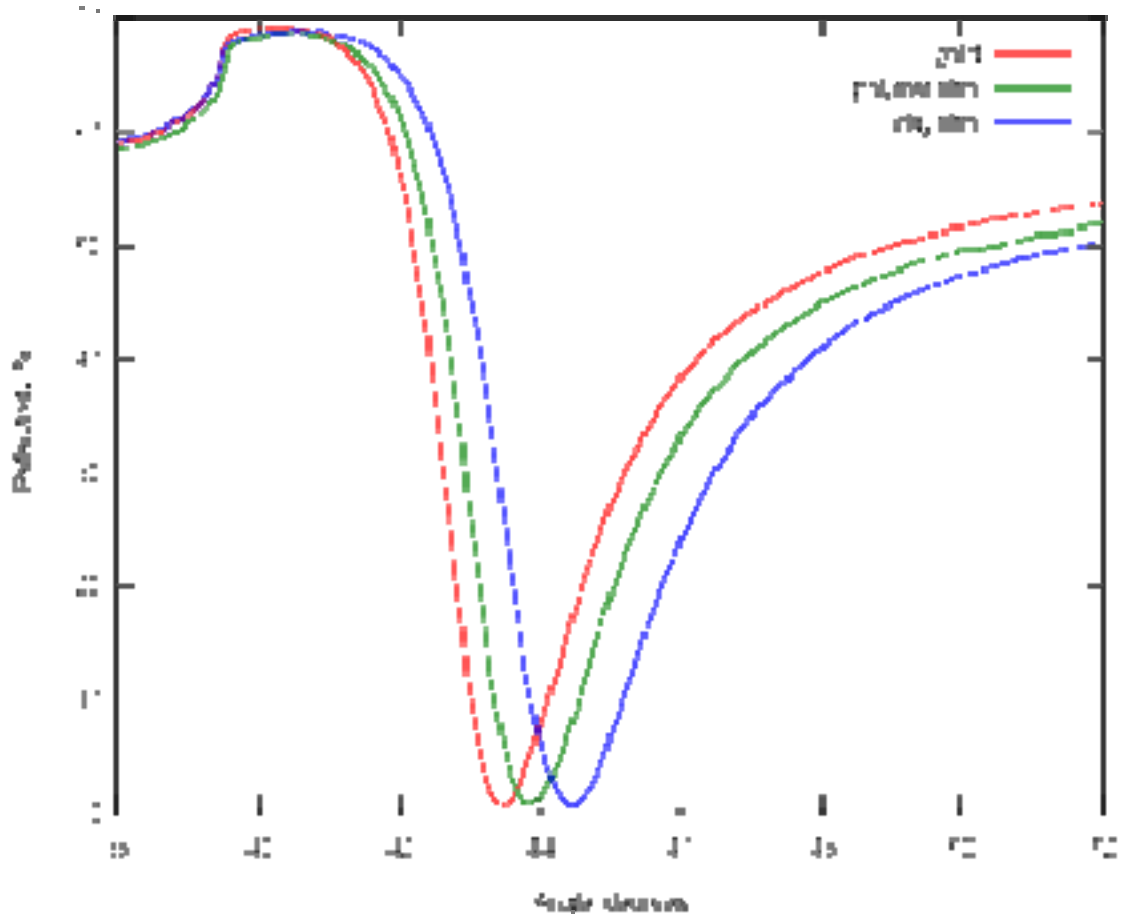
Another commercial instrument

- IBIS; Intersens, Amersfoort, Netherlands
- Only a few users
- Fiber-optic -> remote sensing
- Light intensity is measured as a function of wavelength instead of angle of incidence

Applications

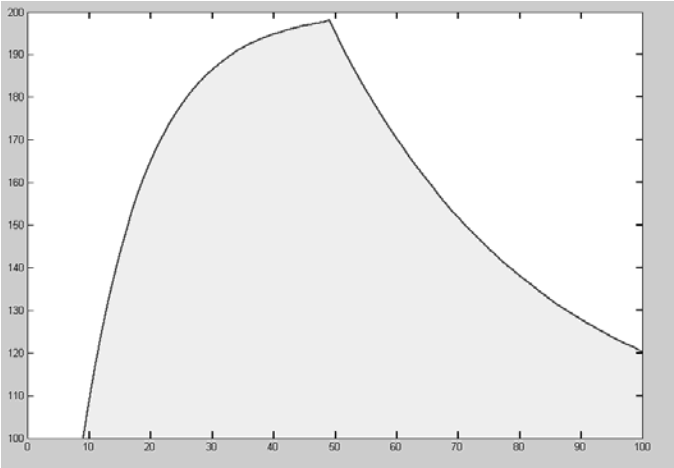
- Linear relationship between resonance energy and mass concentration
- Analyte and ligand association and dissociation ; rate constants; equillibrium constants can be calculated.

Examples: measurement of film thickness

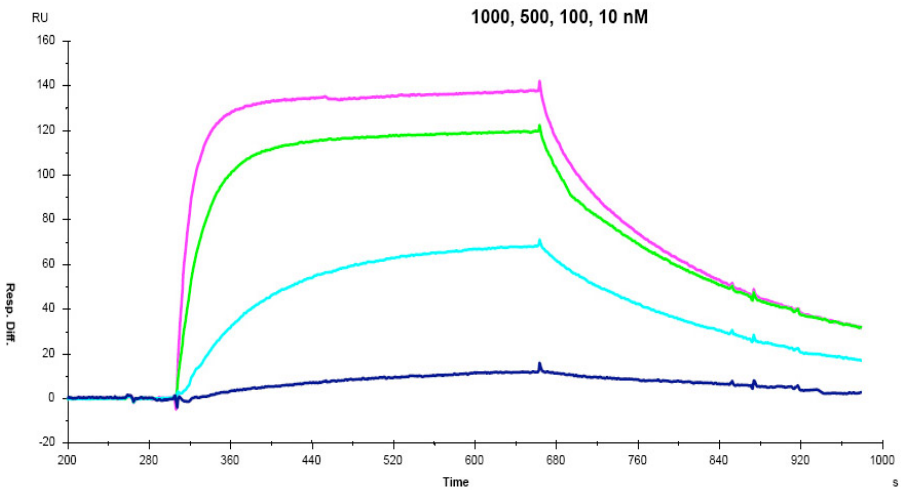


Example: Binding constant determination

- Binding constant -> affinity of two ligands
- Association rate divided by the dissociation rate
- Prey lignad; bait layer; a solution without the prey -> microflow system



Association and dissociation signal



Output from Biacore

Combined with other sensing methods

- Fluorescence
- Raman scattering
- Surface plasmon resonance imaging (surface is patterned with different biopolymers)
- Michelson Interferometer

Michelson Interferometer

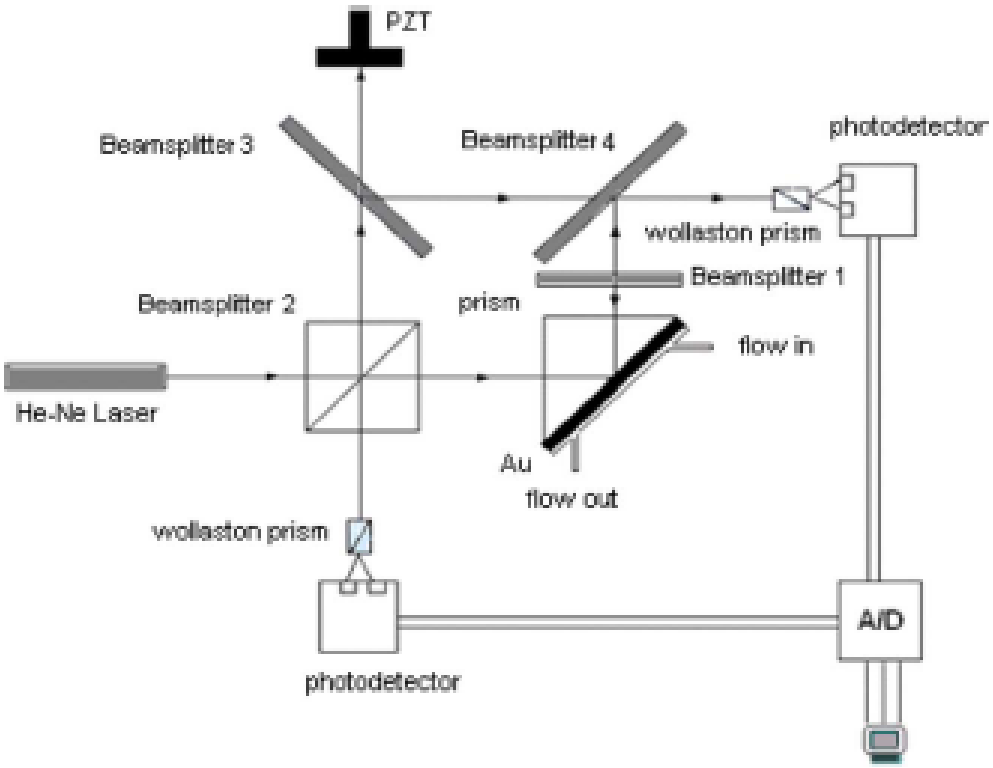


Fig. 1. Experimental setup combining Mach–Zehnder and Michelson interferometer configurations for real-time differential phase measurement and comparison.

Localized surface plasmon resonance (LSPR)

- Nanometer-sized metallic structures
- Extraordinary optical properties of noble metal nanoparticles
- Nanoscale chemosensors and biosensors
- Nanoparticles of noble metals exhibit strong UV-Vis absorption bands

Advantages

- Ag nanoparticle
- Ultrasensitive biodetection
- Extremely simple
- Small
- Light
- Robust
- Low-cost instrumentation
- Less than one picomolar up to micromolar concentrations
- Medical diagnostics, biomedical research, and environmental science

Principle

- Transducing small changes in refractive index near the noble metal surface into a measurable wavelength shift response

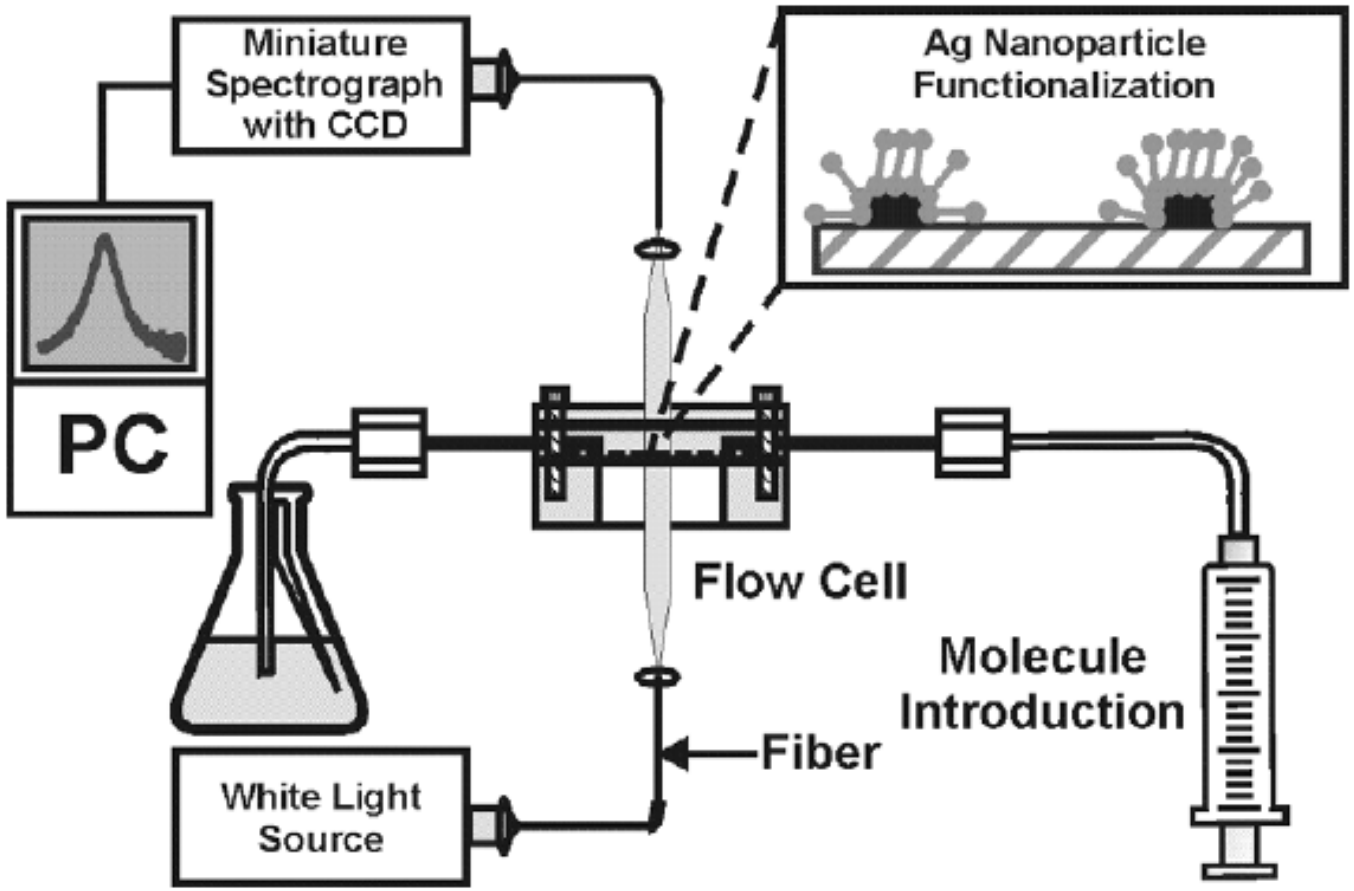
$$\Delta R_{max} = m(n_{adsorbate} - n_{blank})\left[\exp\left(-\frac{2d_{adsorbate}}{l_d}\right)\right]\left[1-\exp\left(-\frac{2d_{adsorbate}}{l_d}\right)\right]$$

- where m is the refractive index sensitivity of the sensor, $n_{adsorbate}$ and n_{blank} are the refractive indexes of the desired adsorbate and bulk environment prior to the sensing event, respectively, $d_{adsorbate}$ is the effective thickness of the adsorbate layer, and l_d is the characteristic electromagnetic field decay length associated with the sensor.

Comparison

- Flat surface SPR sensors have a large refractive index sensitivity, ~2x106 nm/RIU
- LSPR nanosensors have a modest refractive index sensitivity, ~2x102 nm/RIU.
- SPR sensors have a decay length on the order of ~200 nm
- For the nanoparticles and the corresponding LSPR nanosensor, a much shorter electromagnetic field decay length (~6 nm)
- This short decay length gives rise to the large sensitivity of the LSPR nanosensor

Instrumental diagram for the LSPR nanosensor experiment



Results

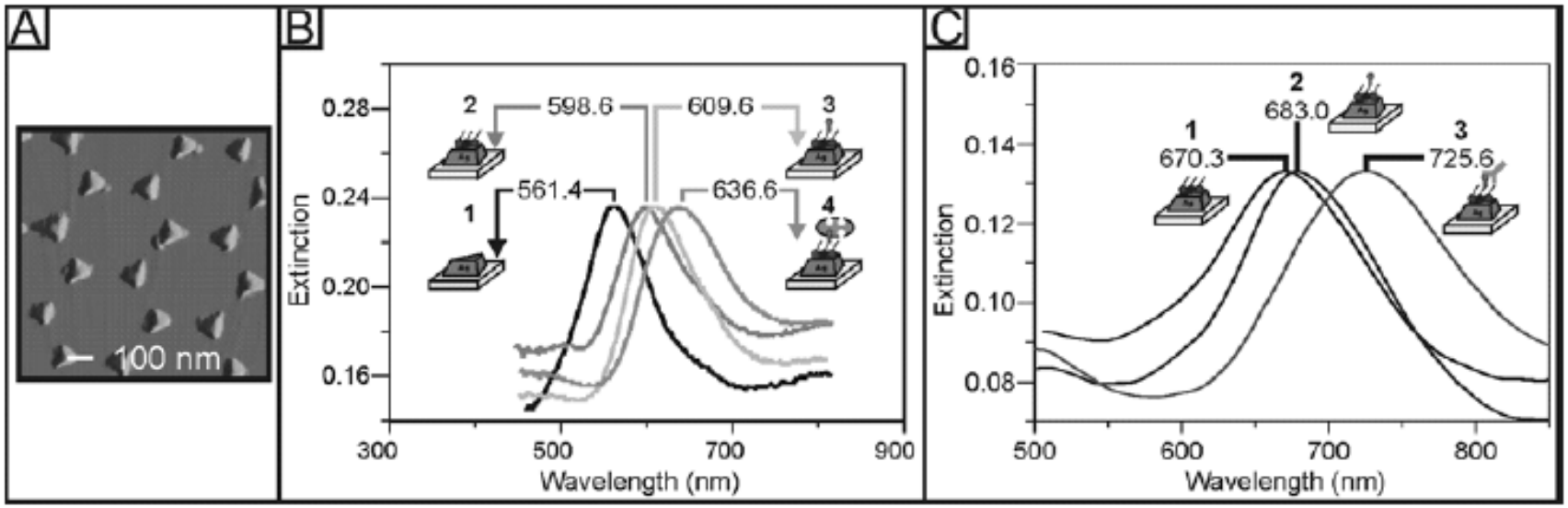
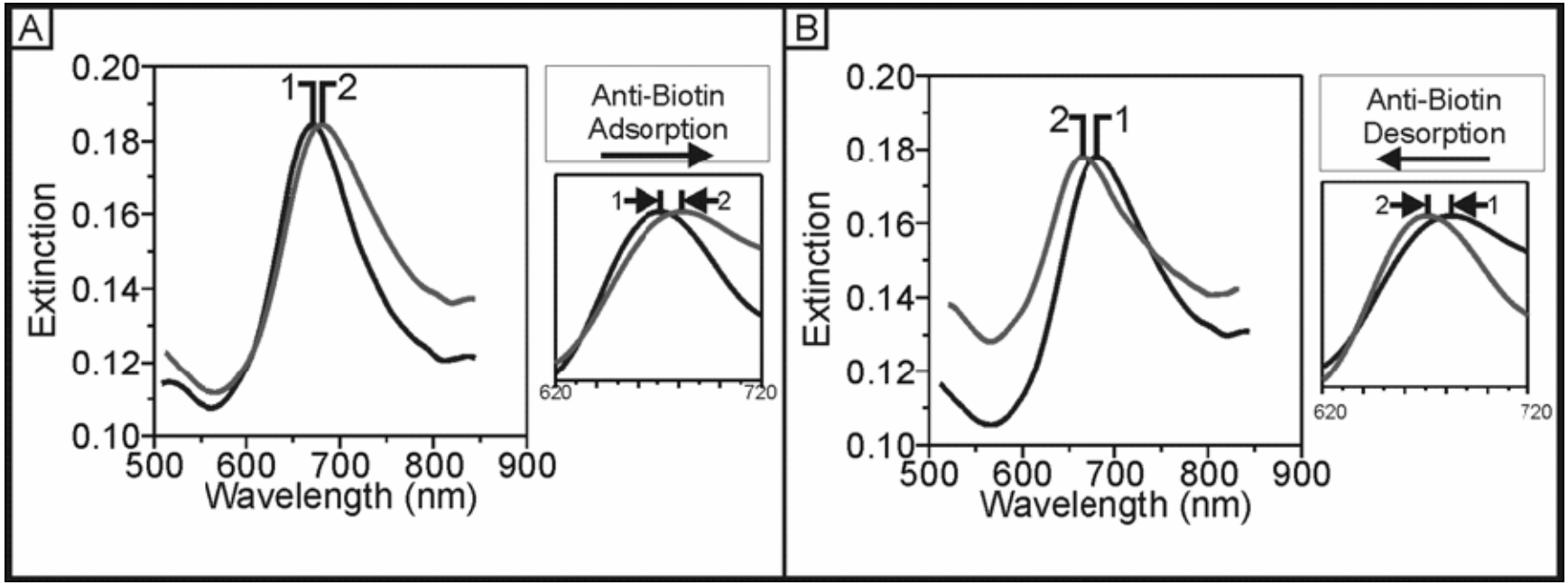


Figure 2. (A) Tapping mode AFM image of Ag nanoparticles. (B) LSPR spectra of each step in the surface modification of NSL-derived Ag nanoparticles to form a biotinylated Ag nanobiosensor and the specific binding of streptavidin. (C) Smoothed LSPR spectra for each step of the preparation of the Ag nanobiosensor, and the specific binding of anti-biotin to biotin.

Adsorption/Desorption



Performance

- Time scale for these events appears to be less than a minute
- Binding of DNA and proteins
- Future work: miniaturization of the sensor, linkage of the sensor to drug delivery chips, and biocompatibility

References

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