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Control of the environment by surface plasmon resonance optics

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CONTROL OF THE ENVIRONMENT
BY
SURFACE PLASMON RESONANCE

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Winter college on optics in environmental science
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TOPICS

-MOTIVATION

-SURFACE PLASMON RESONANCE

-SURFACE PLASMON RESONANCE FOR SENSING

-SPR FOR CONTROL OF THE ENVIRONMENT

MOTIVATION

-Simple equipment as a sensing devices with high potential for ***research*** and for # ***fields of applications***

- economically attractive

-applications in molecular sensing (high sensitivity, selectivity, fast)

-need moderate training

→ possibility to these sensors to act as portable or "lab-on-chip" devices that can be used by moderately trained individuals outside the laboratory environment .

TOPICS

MOTIVATION

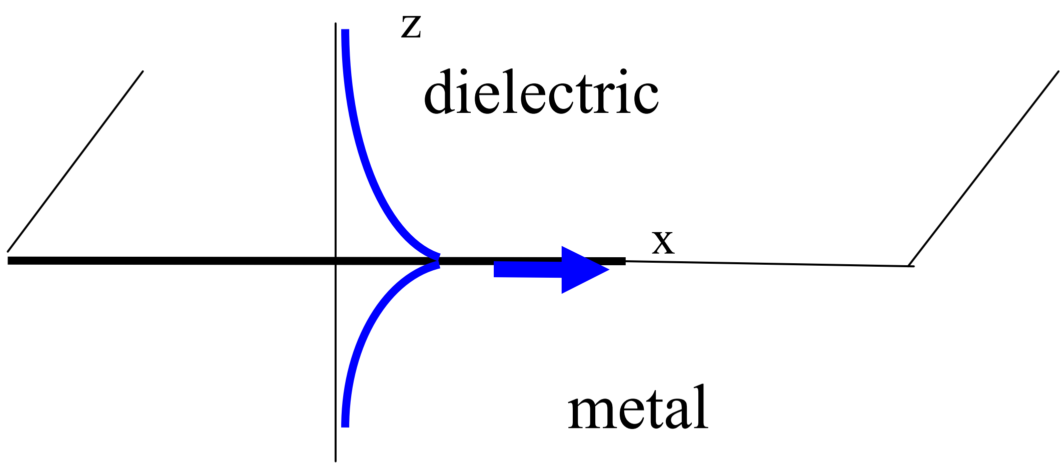
SURFACE PLASMON RESONANCE

SURFACE PLASMON RESONANCE FOR SENSING

SPR FOR CONTROL OF THE ENVIRONMENT

Surface Plasmon Resonance

takes place when we may excite a surface plasma waves



- SPW : collective oscillation of free electrons

 - for some conditions → resonance

 - Basis for a sensing SPR device.

SPR APPLICATIONS

Environment

Agriculture

Medicine

Defense

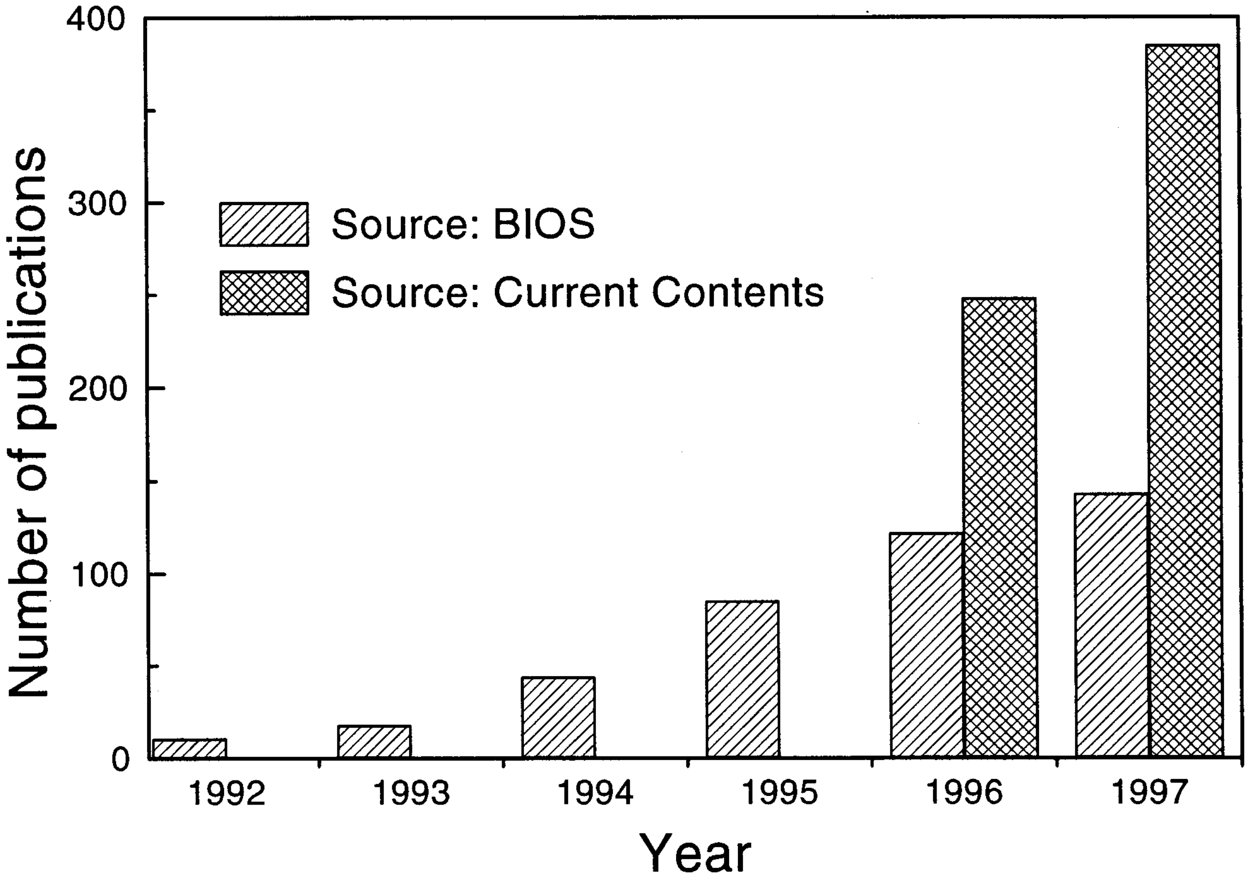
…

SPR research in all area

↓

Increase SPR sensor technology

Great attention
from scientific Community

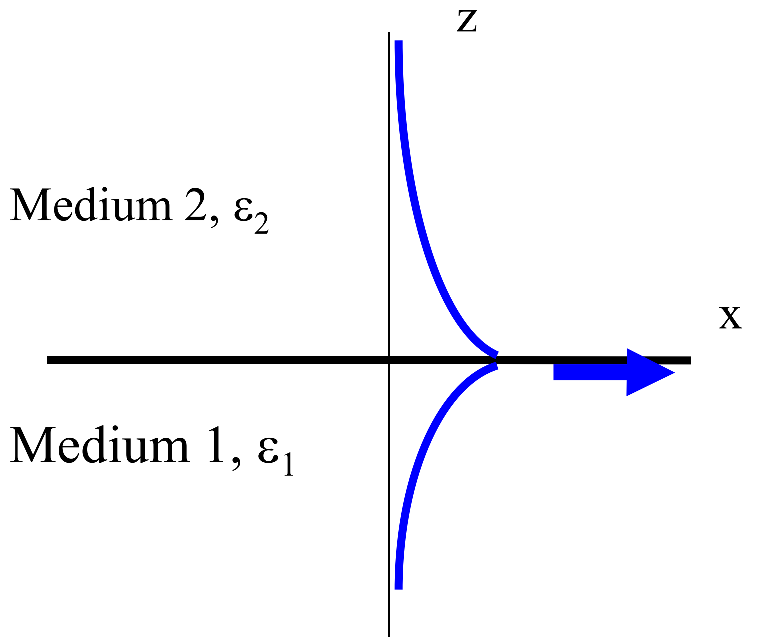


Number of research papers on SPR sensors listed by scientific databases (Homola).

(SPW) is a **TM-polarized wave**

For $\mathbf{k} = (k_x , 0, 0)$

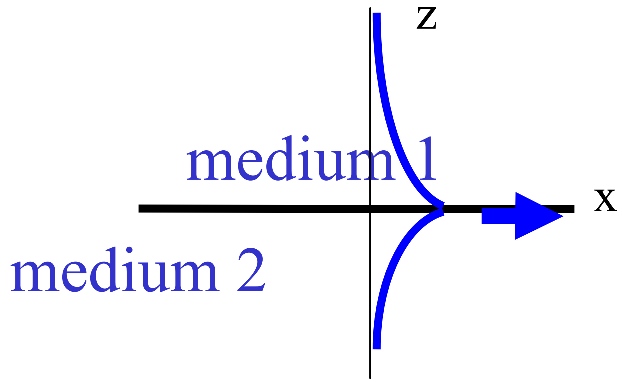
$$H(x, z, t) \left| \begin{array}{c} 0 \\ H_y(z) \exp(j(k_x x-\omega t)) \\ 0 \end{array} \right.$$



$$E(x, z, t) \left\{ \begin{array}{c} E_x(z) \exp j(k_x x-\omega t) \\ 0 \\ E_z(z) \exp j(k_x x-\omega t) \end{array} \right.$$

$H_{y1}(x,z,t) = H_0 \exp(\ q_1 z) \exp j(k_x x - \omega t);$

$(\text{medium } 1, \quad z < 0\ ; \ \ q_1 \text{ (real)} > 0\ )$



$H_{y2}(x,z,t) = H_0 \exp(-q_2 z) \exp j(k_x x - \omega t);$

$(\text{medium } 2, \quad z > 0\ ; \ \ q_2 \text{ (real)} > 0\ )$

<u>Maxwell conditions :</u>

rot (**E**) = -δ**B**/δt   et   rot (**H**) = δ**D**/δt   (D= ε E ;   H = μ B)

$E_{x1} = (q_1 / j\omega\varepsilon_1\ ) H_{y1}(x, z, t) \quad ; \quad E_{x2} = (q_1 / j\omega\varepsilon_2\ ) H_{y2}(x, z, t)$

Continuity Conditions at the interface:

$$- q_1 / q_2 = - \varepsilon_1 / \varepsilon_2 > 0$$

$$- k^2 = (\omega^2 / c^2)\{\varepsilon_1\varepsilon_2/\varepsilon_1 + \varepsilon_2 \} > 0$$

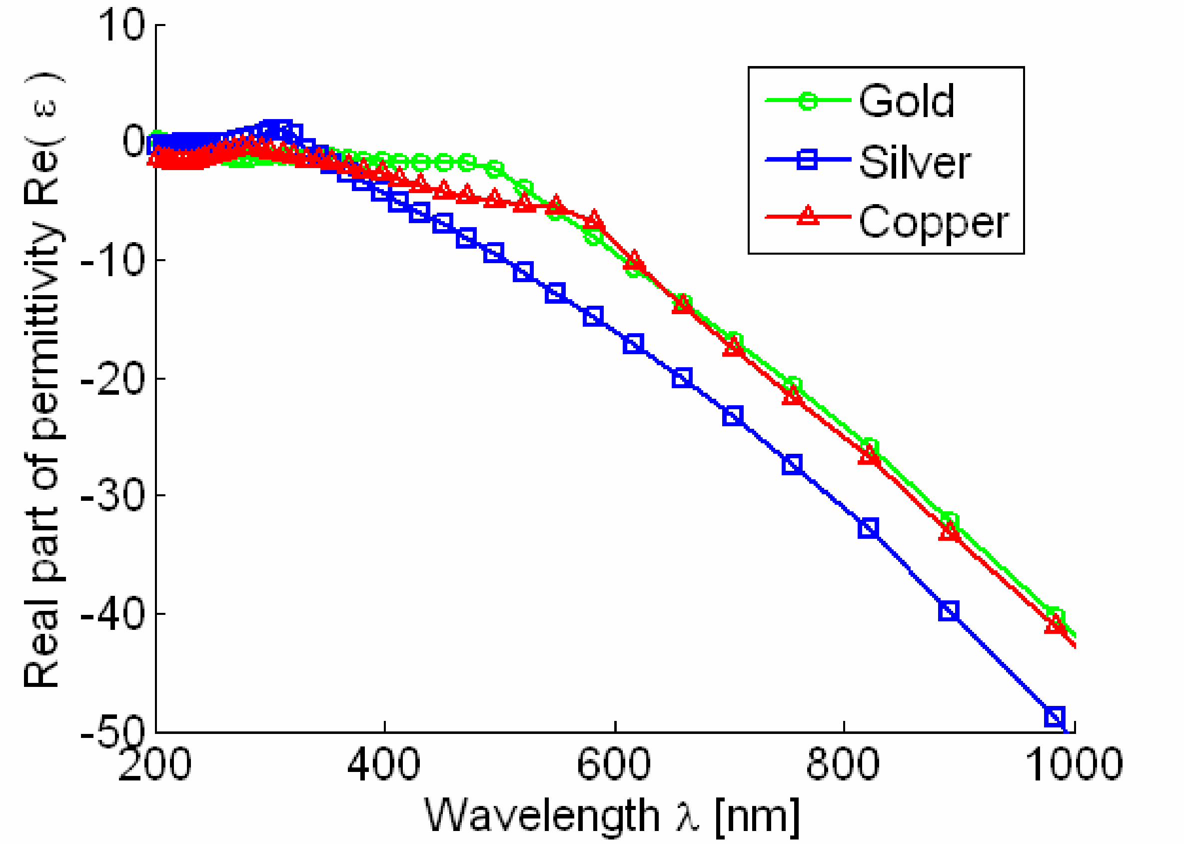
$$\rightarrow (\varepsilon_1 + \varepsilon_2) < 0$$

The real part of ε_1 and ε_2 have opposit sign

→ Mediums: metal, dielectric

the dielectric constant of the metal , ($\varepsilon_m = \varepsilon_{mr} + i\varepsilon_{mi}$)

ε_{mr} , needs to be negative



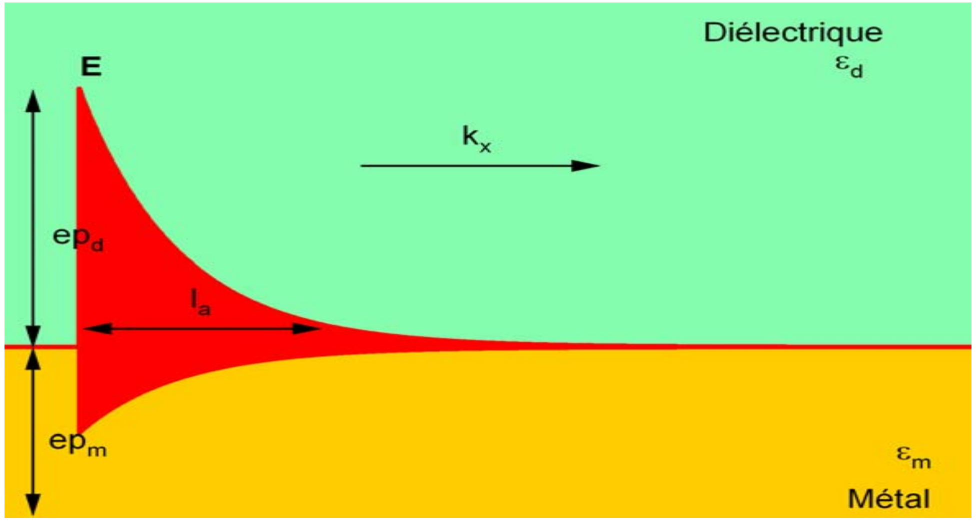
Refraction Index for some dielectric at 660nm ($\varepsilon_d = n^2$)

Glass BK7 n = 1,5142

SF10 n = 1,7205

SF11 n = 1,7756

$\mathbf{E} = E_x(z)\,\mathbf{u}\,\exp j(k_x x - \omega t)$

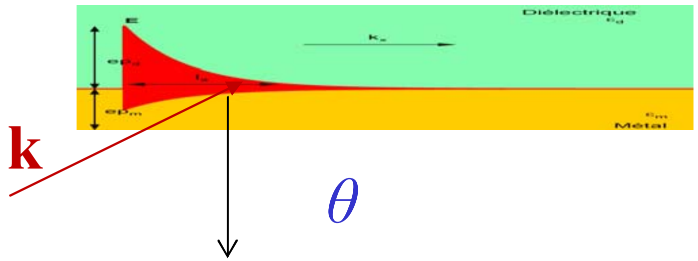


Metal layer supporting SPW	Silver		Gold	
Wavelength	630 nm	850 nm	630 nm	850 nm
Propagation length (mm)	19	57	3	24
Penetration depth into metal (nm)	24	23	29	25
Penetration depth into dielectric (nm)	219	443	162	400
Concentration of field in dielectric (%)	90	95	85	94

Comparison of SPW propagating along the interface between water and a metal layer silver and gold at two distinct wave-lengths in the visible and near-infrared an excitation of SPW by an optical wave: $[(\omega / c), k\,(k_x, k_y, k_z)]$

can lead to resonance if

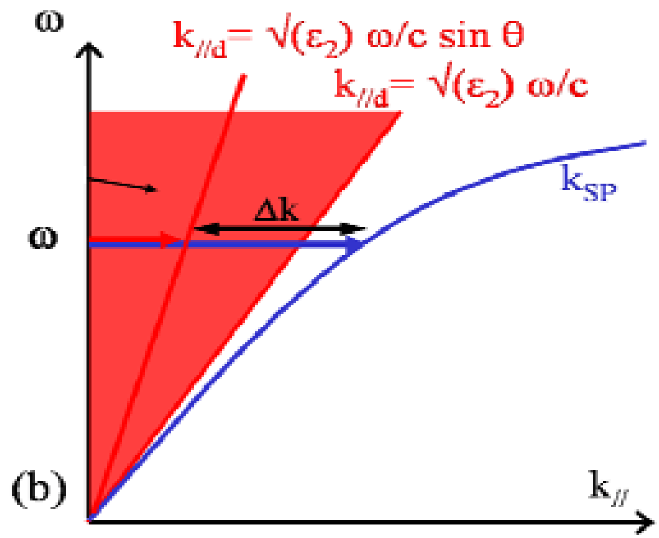
resonant transfer of energy & momentum into the SPW →



(SPR manifests itself by resonant absorption of the energy of the SPW
with matching the requirement

$$\mathbf{k_x = k_{SPW}}$$

k_{SPW} is always h



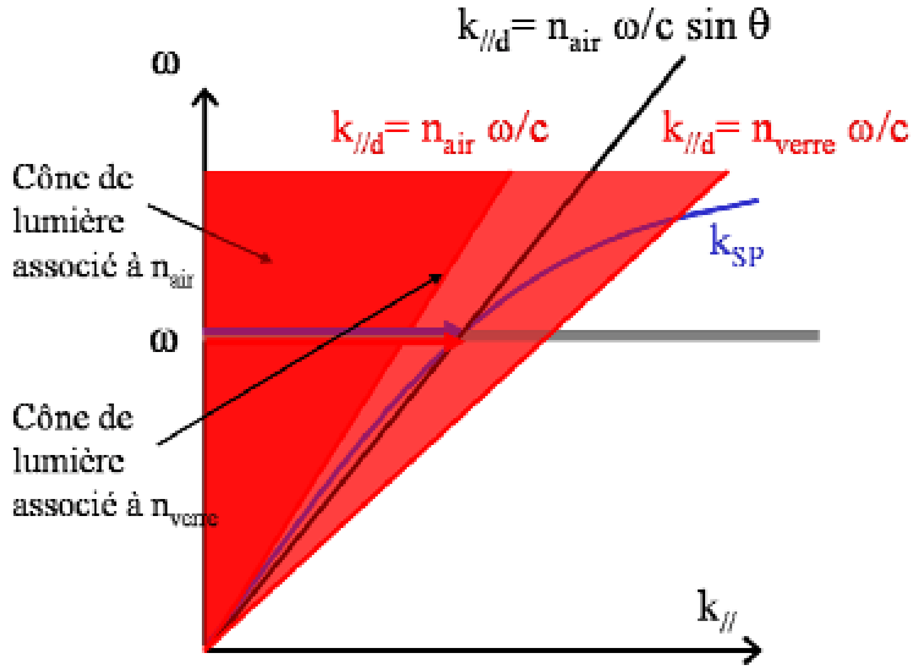
→The SPW cannot be excited directly by an incident optical wave at a planar metal dielectric interface the incident optical wave vector has to be enhanced to match that of the SPW with an increase : $\Delta k = k_{spw} - k_{x,\text{photon}}$

a third insulating substrate layer*, index n,* can be added while launching the incident light at an angle *θ.*

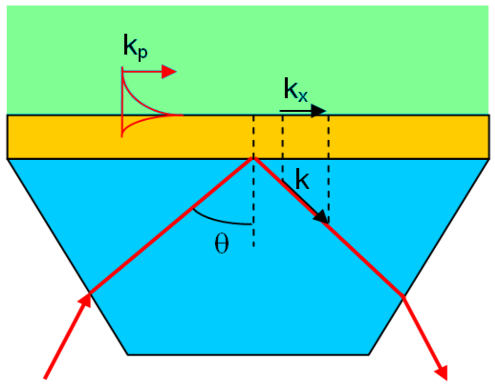
→(multilayer arrangement),

→first configurations:

dielectric-metal-dielectric
& coupling (~1970)

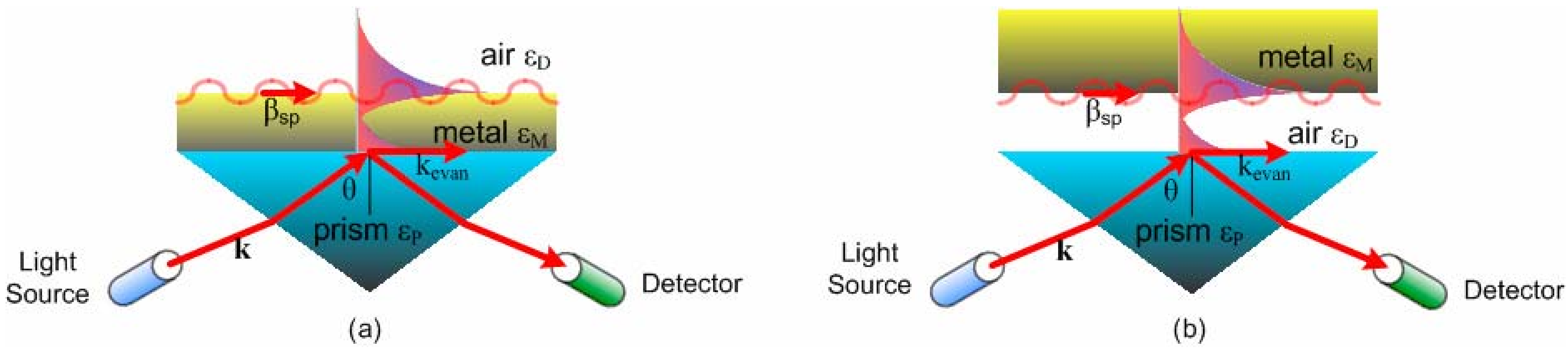


Resonance through Attenued Total Reflexion –ATR- in prism coupler



COUPLING if : $\theta > \theta_{critical.}$

$$(\omega / c).\, n_{prism}.\, \sin\theta = (\omega / c)\; [(\varepsilon_m\, \varepsilon_d\;)/\, (\varepsilon_{m\,+}\, \varepsilon_d)]^{\,½}$$



E.Kretschmann configuration

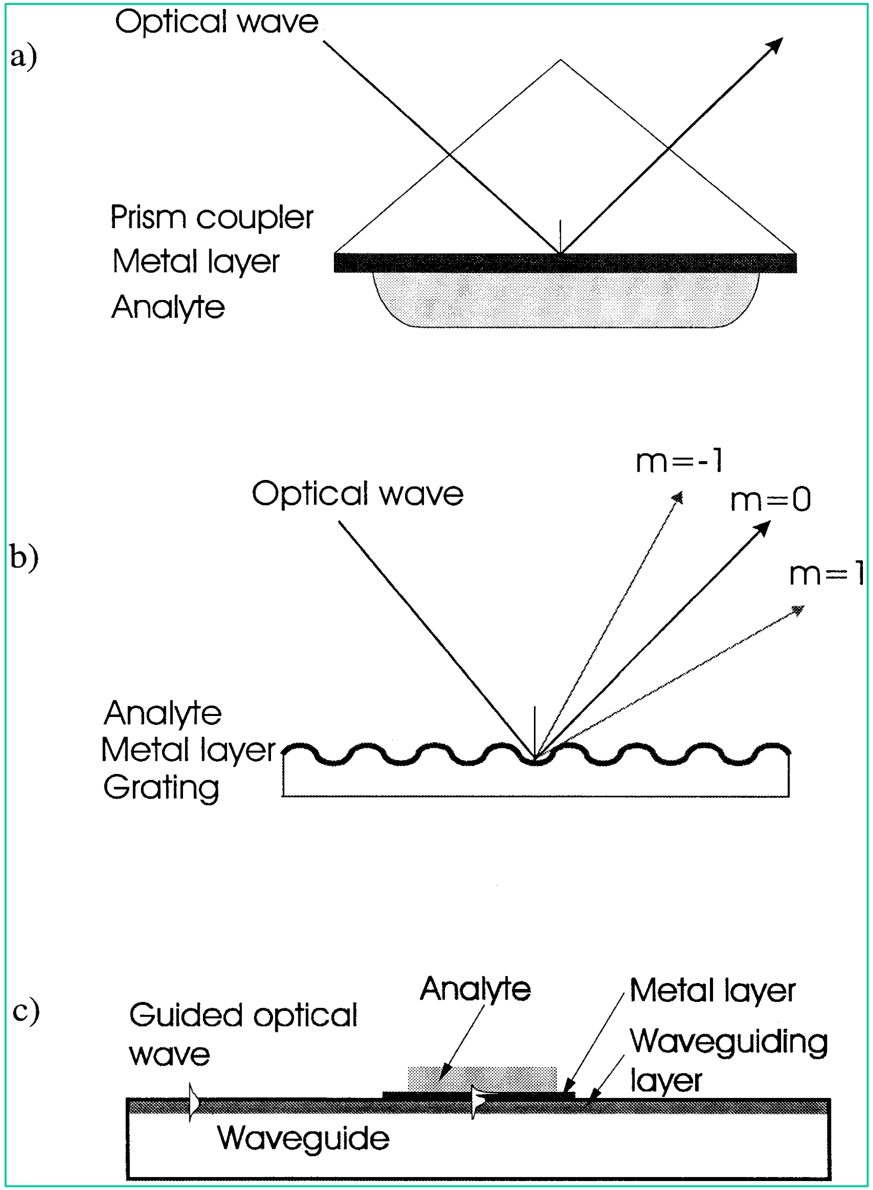
A.Otto configuration

PARTICULAR SPR CONFIGURATIONS

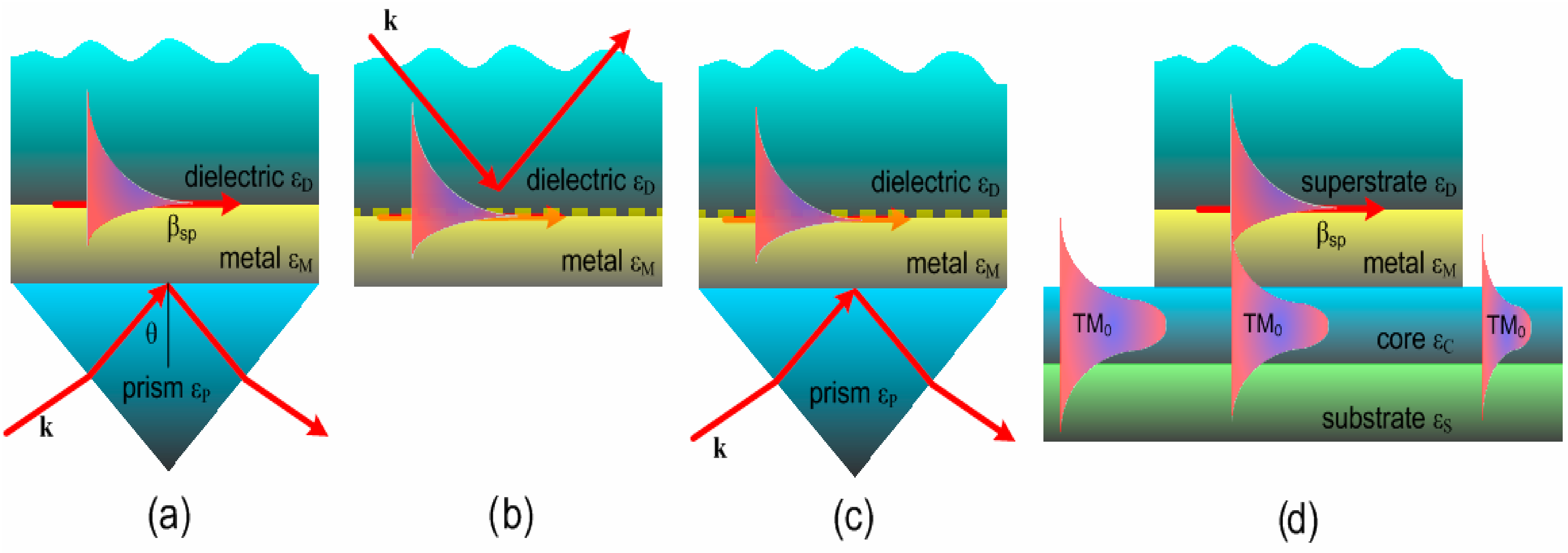
-attenuated total reflection (ATR) **in prism couplers**

-diffraction at the surface of diffraction gratings.

-attenuated total reflection (ATR) **in Optical wave guides**



Different methods to excite surface plasmons



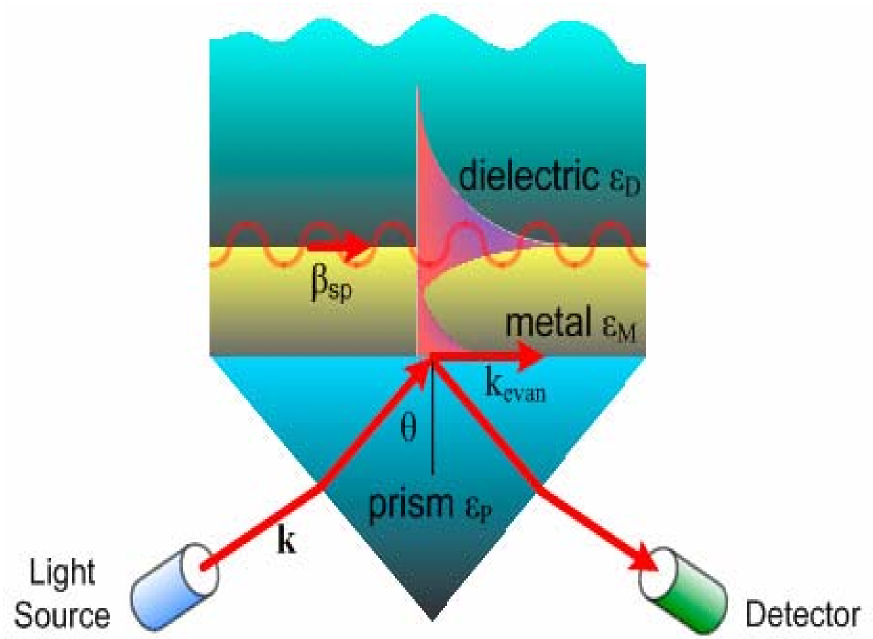
prism coupling

waveguide coupling

direct grating

indirect grating coupling

Common concept for spr optical chemical sensors and biosensors



- **optical system** :

- **transducing medium**

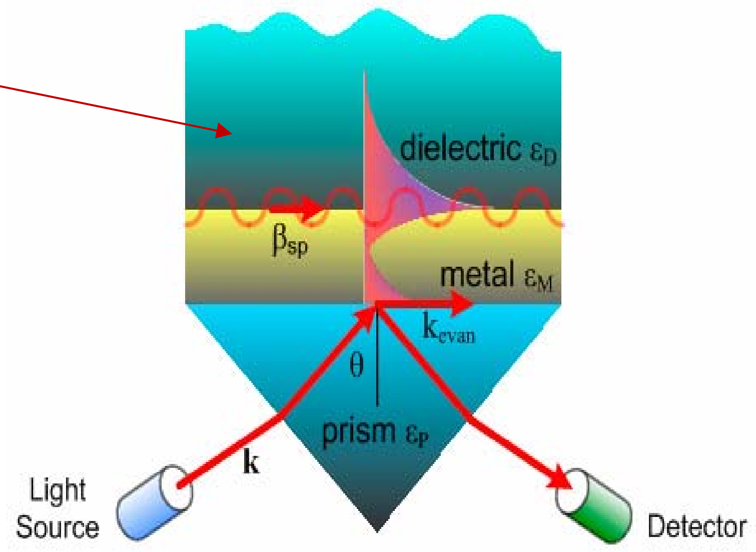
- **electronic system**.

-*The sensor sensitivity, stability, and resolution* depend upon properties of both the optical system (nature, n, T, e_m), the transducing medium & the experimental approach

-*Selectivity and response time of the sensor* are primarily determined by the properties of the transducing medium

SPR Sentivity

SPR **very sensitive to variations in the optical properties of the** transducing medium.



Metal film should be thin enough

→variations in the optical parameters of the transducing medium can be detected by monitoring an interaction between the SPW and the optical wave

→SPR OPTICAL *CHEMICAL SENSORS* AND *BIOSENSORS*

Main detection approaches in SPR sensor

$\mathbf{E} = E_x(z)\,\mathbf{u}\,\exp j(k_x x - \omega t)$

→ **The optical system used to excite the SPW is simultaneously used for the interrogation of SPR.**

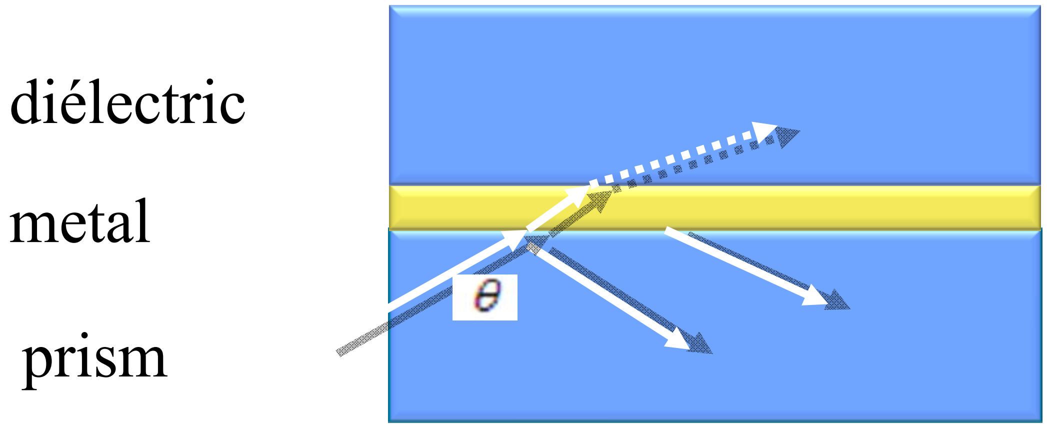
1/. Measurement of the intensity of the optical wave near the resonance

2/. Measurement of the resonant momentum of the optical wave including angular , and wavelength interrogation of SPR

3/. Measurement of changes in phase and polarization

Reflectivity

$$f\,(n_m, n_d, e, \lambda, \theta)$$



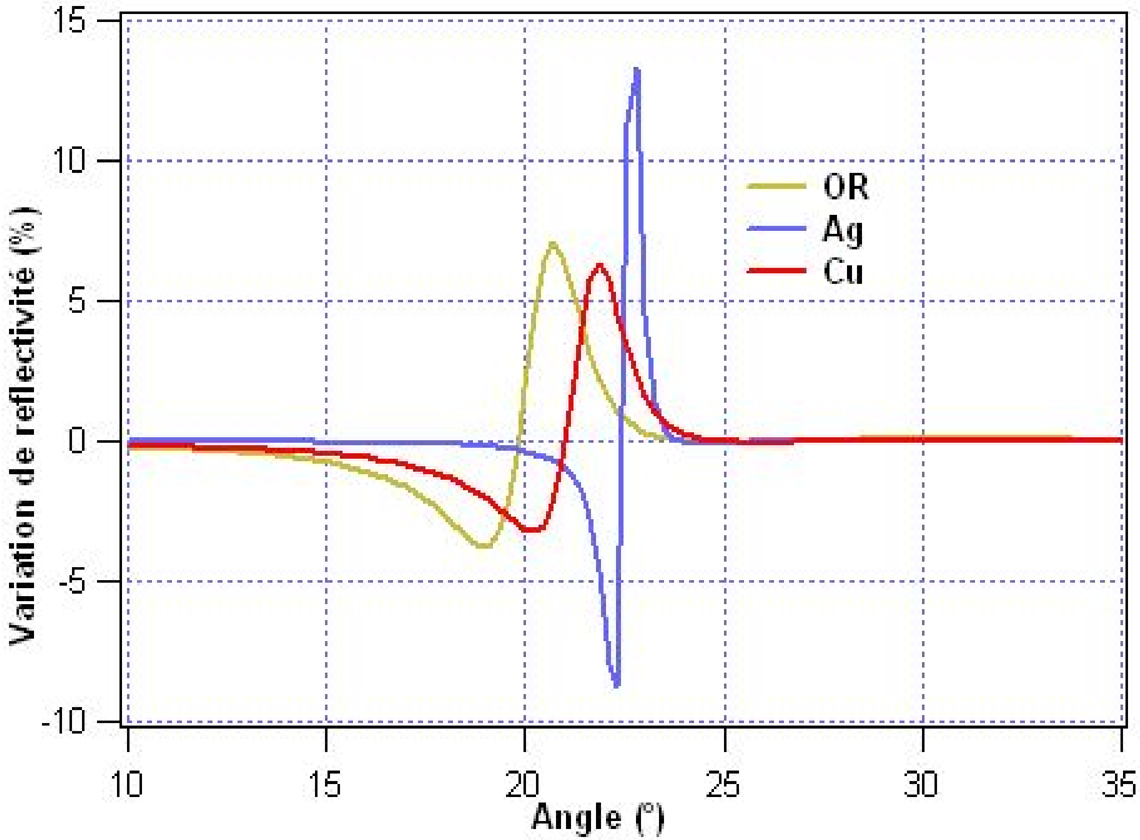
diélectric(n_3)
Metal (e ,n_2)
Prism glass (n_1)

Rouard Method for 3 layers

For 3 layers → $r_2 = \dfrac{r_{1-2} + r_{2-3} e^{2j\varphi_2}}{1 + r_{1-2} r_{2-3} e^{2j\varphi_2}}$

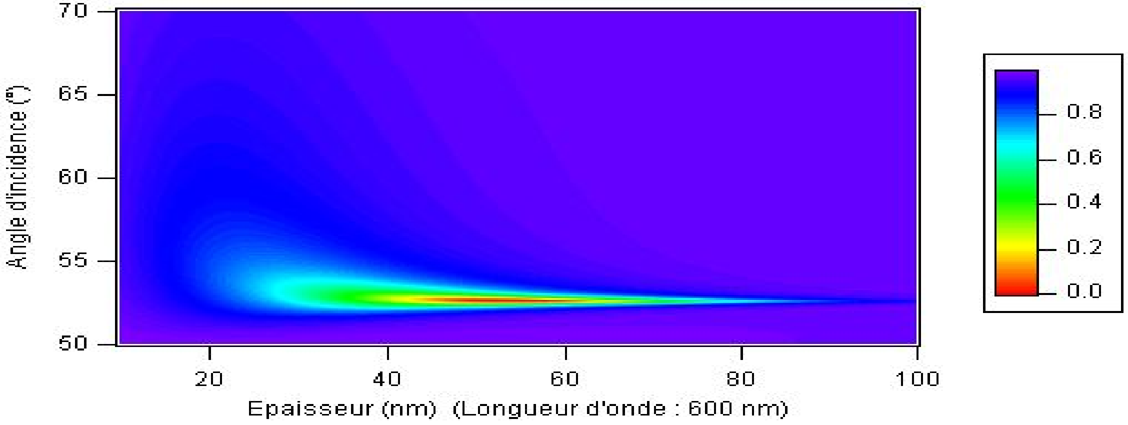
For p layers → $r_{p-2,p} = \dfrac{r_{p-2,p-1} + r_{p-1,p} \cdot e^{j\varphi_{p-1}}}{1 + r_{p-2,p-1} \cdot r_{p-1,p} \cdot e^{j\varphi_{p-1}}}$

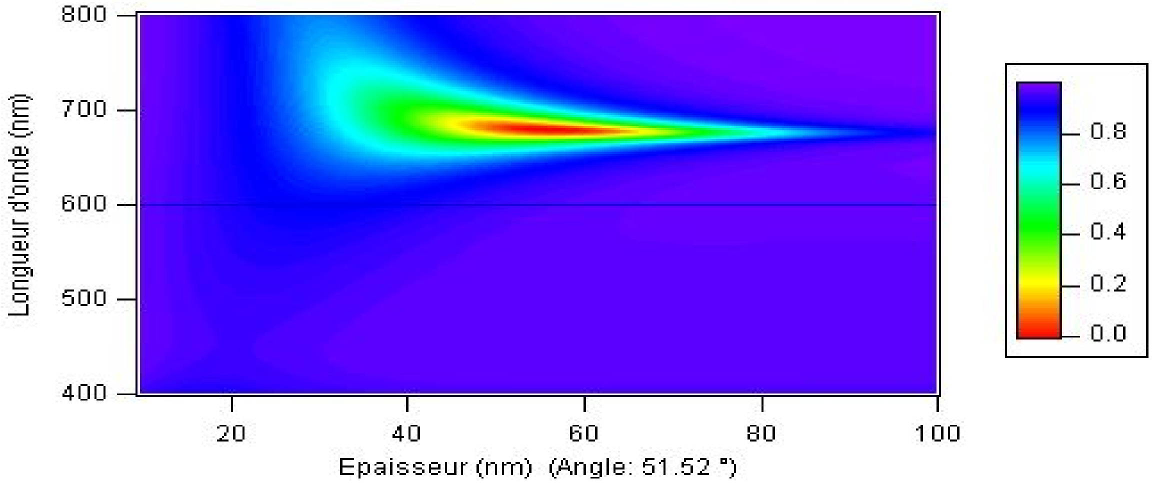
Choice of metal



Silver induces the greatest and sharpeness reflectivity
→ more sensibility

Choice of metal thickness (for Ag , prismSF11)

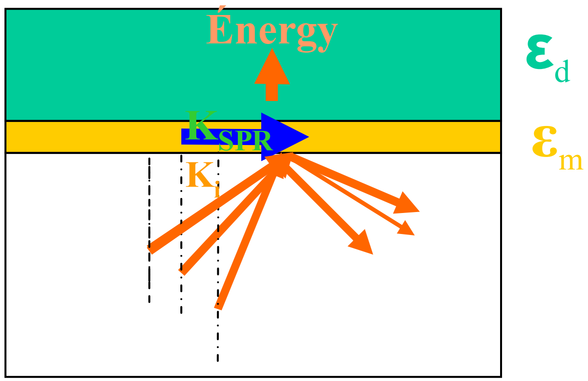




Angular interrogation

$$K_{SPR}(\omega) = \mathrm{Re}\left(\sqrt{\frac{\varepsilon_m(\omega)\varepsilon_d(\omega)}{\varepsilon_m(\omega)+\varepsilon_d(\omega)}}\right)\frac{\omega}{c}$$

$$K_x = \frac{\omega}{c} n_{prism}(\omega) \sin\theta$$



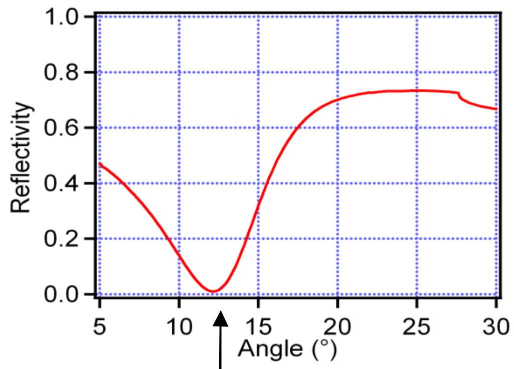
Wavelength contant

↓

ε_d, ε_m and ε_{prism} = Cte

↓

$K_x = K_{SPR}$



Spectral interrogation

$$K_{SPR}(\omega) = \mathrm{Re}\left(\sqrt{\frac{\varepsilon_m(\omega)\varepsilon_d(\omega)}{\varepsilon_m(\omega)+\varepsilon_d(\omega)}}\right)\frac{\omega}{c}$$

$$K_x = \frac{\omega}{c} n_{prism}(\omega)\sin\theta$$

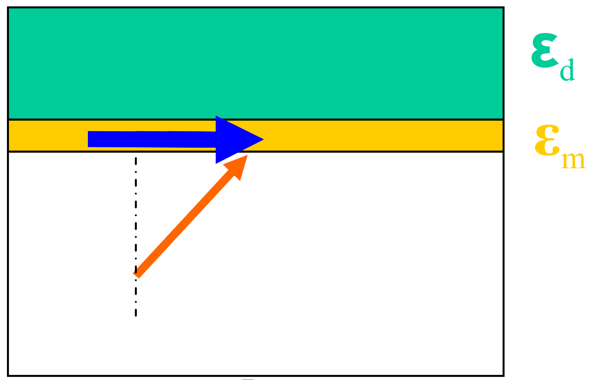
Angle constant

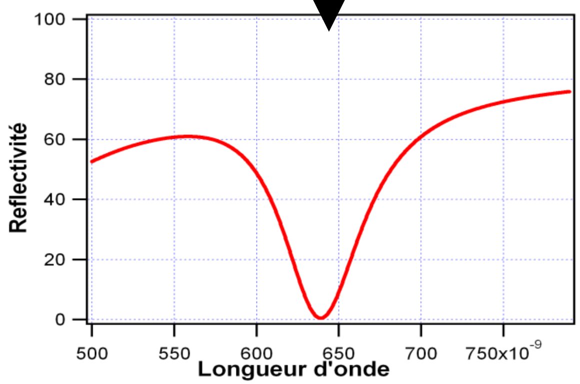
↓

$K_x \approx$ fixe

↓

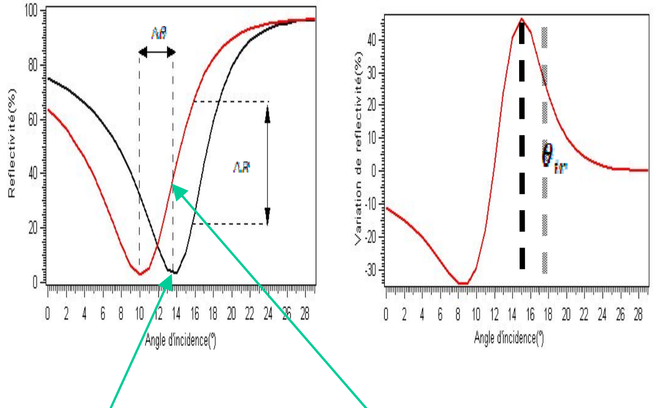
Changing the wavelength
for coupling



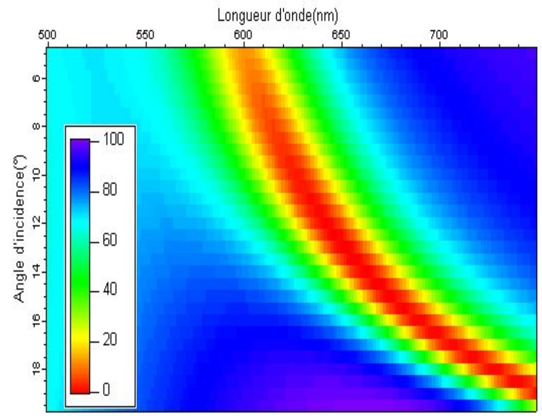


Example of Simulation for DNA (anomaly analysis)

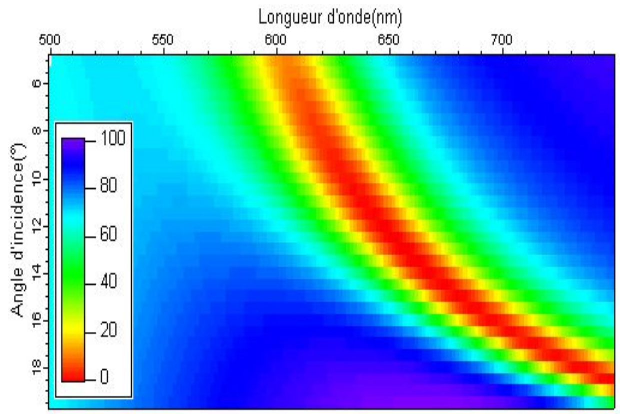
reflectivity & its variation for 3 layers configuration



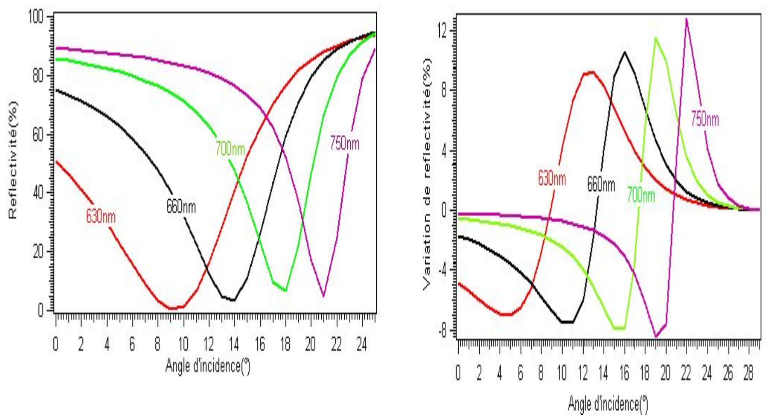
prism BK7; Au(47 nm) water +10 nm dielectric (DNA=1.46)
& prism BK7; Au(47 nm) +water at λ = 660 nm for # angles



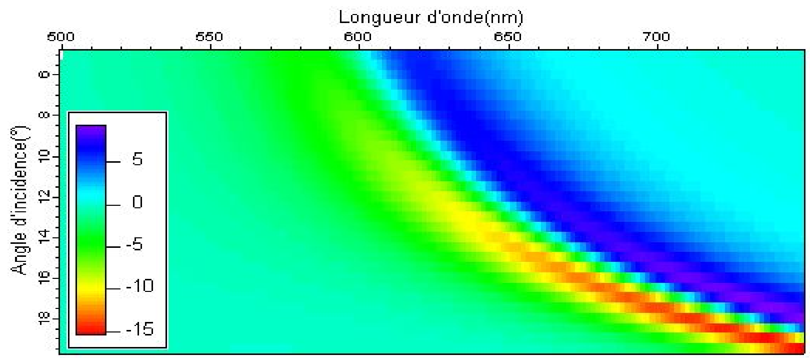
prismBK7+(2nmChr
& 47 nm Au)
+water



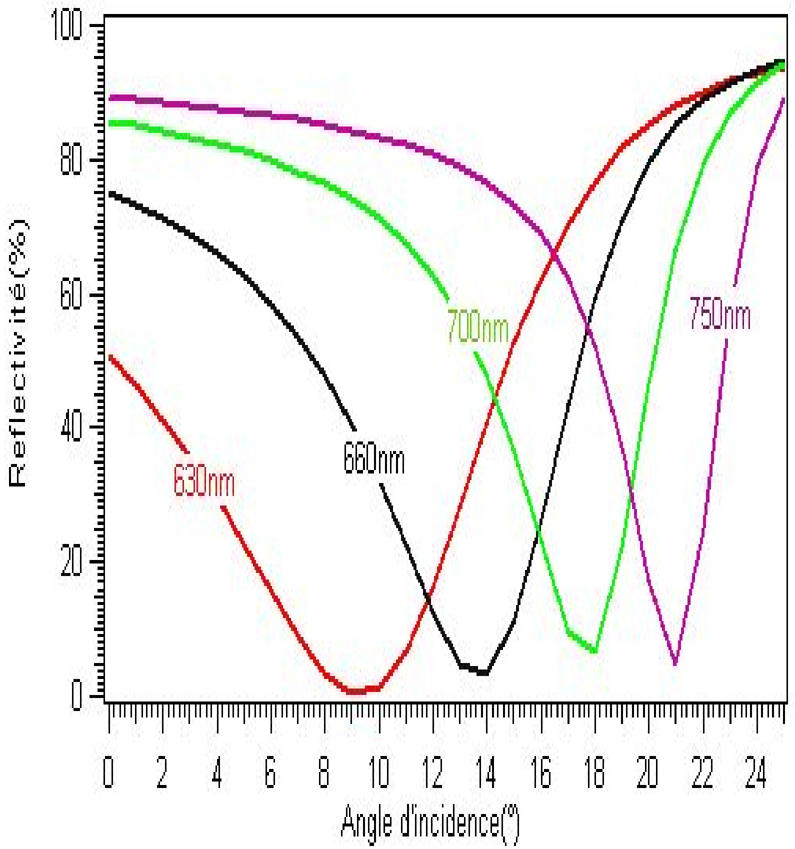
prismBK7+chip(2nmChr
&47 nm Au)+ DNA (2 nm, n=1.46)
+water



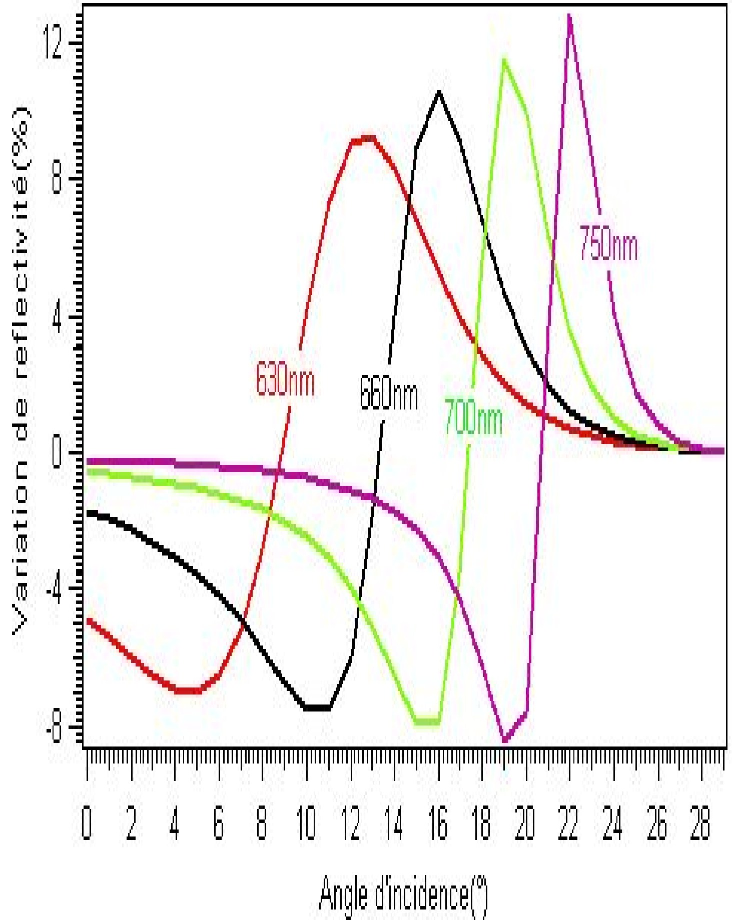
prism BK7; Au(47 nm) water +10 nm dielectric (DNA=1.46)
& water at # λ & for # angles



Difference in reflectivity for addition of the biological layer DNA (e=2 nm , n=1.46)



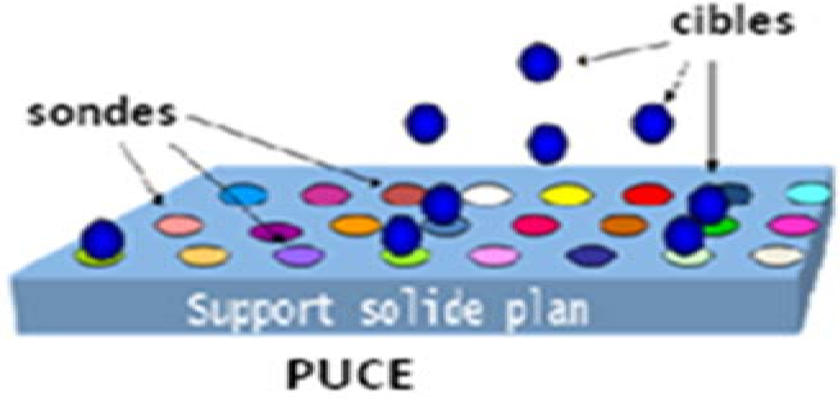
Reflectivité(%)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
18
20
22
24
Angle d'incidence(°)
630nm
660nm
700nm
750nm



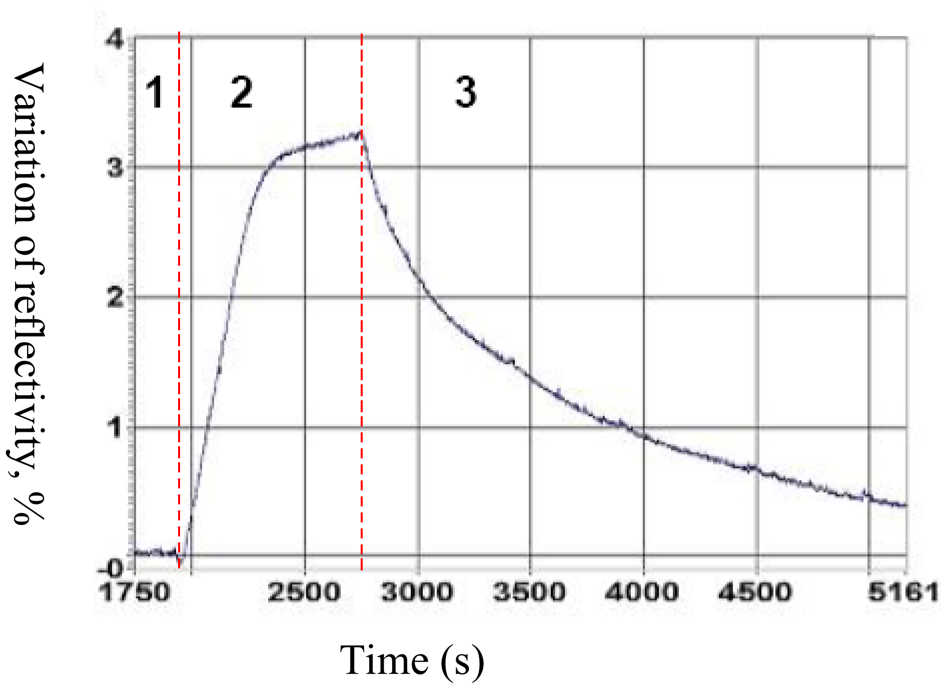
Variation de reflectivité(%)
12
8
4
0
-4
-8
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Angle d'incidence(°)
630nm
660nm
700nm
750nm

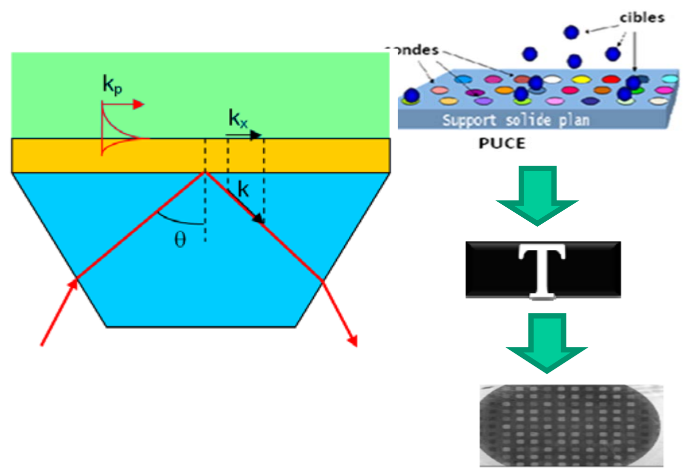
Molecular interaction dynamics

target



ship





Example of Kinetic of reaction ,

I injection of tampon (reference); 2 injection of target with tampon; 3rinsing (dissociation)

TOPICS

MOTIVATION

SURFACE PLASMON RESONANCE

SURFACE PLASMON RESONANCE FOR SENSING

SPR FOR CONTROL OF THE ENVIRONMENT

Measurement of physical quantities

-humidity sensor utilizing humidity-induced refractive index changes of porous thin layers and polymers.

&

-temperature based on the thermo optic effect in hydrogenated amorphous silicon.

Chemical sensing

-Molecular hydrogen

- Hydrocabon gases as benzene, toluene,…

-NO_2 , H_2S, NH_3, …

-- Heavy Metal Ions in water,

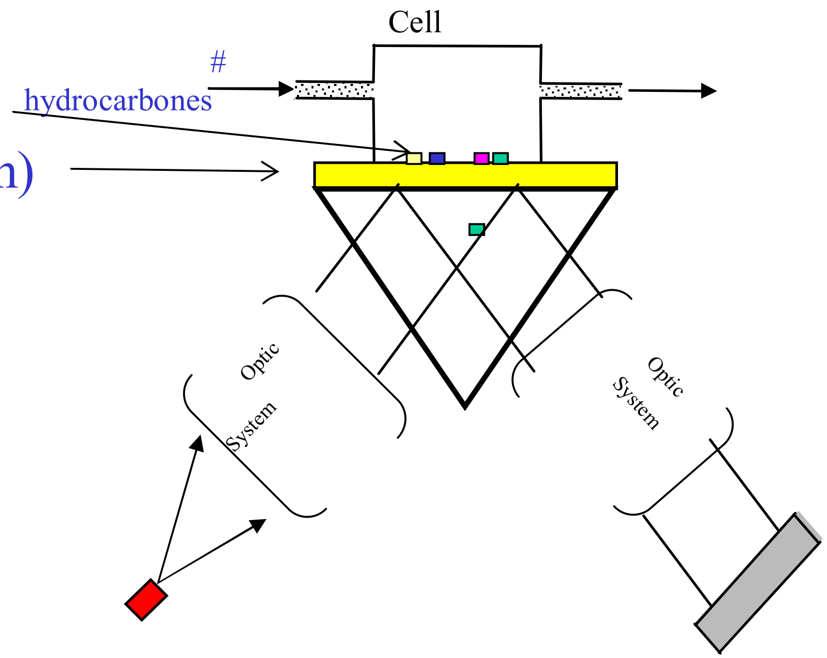
-…..

Sensing for hydrocarbons sensing

(Shozo Miwa et al, Thin solid fim,281-282(1996))

polyethylene glycohol (n=600, e~85nm)

silver (60nm)

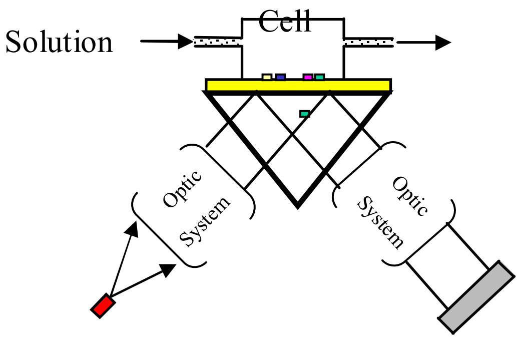


gAngular interrogation resolution: 0,002°,

Alcohols, aldehydes, ketones vapour, and lower hydrocarbon gases mixed in dry air at various concentrations (0.3–29%) were passed through a gas cavity (~ 2.0 cm^3) to displace the air; an inlet and/or outlet plug knob was closed 10 min following the operation.

Sensing for hydrocarbons sensing

(Shozo Miwa et al, Thin solid fim,281-282(1996))



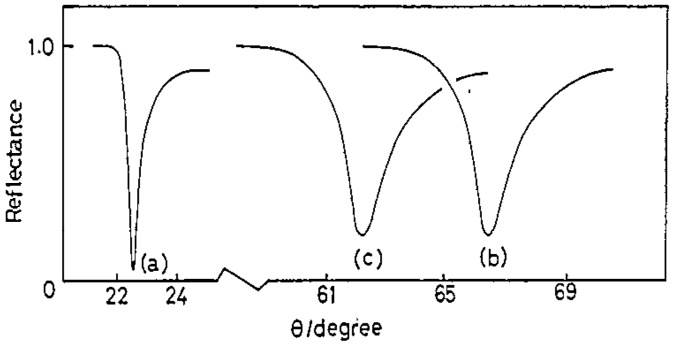


Fig. 1. Resonance curves for: (a) a silver thin film in air, (b) a coated polyethylene glycohol film, and (c) the curve produced on the introduction of methanol vapour over a polyethylene glycohol film.

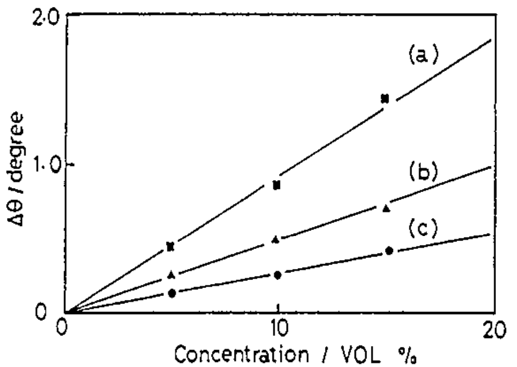


Fig. 4. Calibration plots of the vapour of aldehydes: (a) $CH_3(CH_2)_2CHO$ (13.4), (b) CH_3CH_2CHO (18.5), (c) CH_3CHO (21.1). The values in parentheses are the dielectric constants.

In all cases the shift of the incident angle increase with the increase of the number of carbones

Detection limit 77 ppm , comparable to chromatography detection apparatus

Sensing for hydrocarbons sensing

(Shozo Miwa et al, Thin solid fim,281-282(1996))

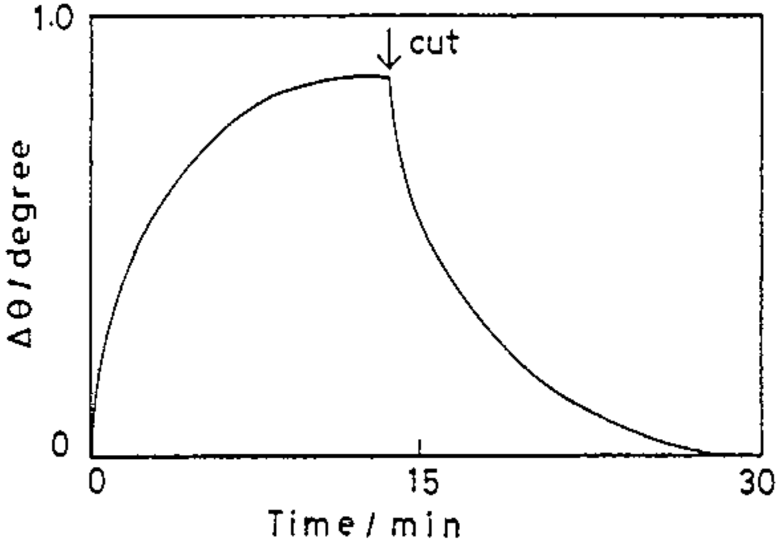
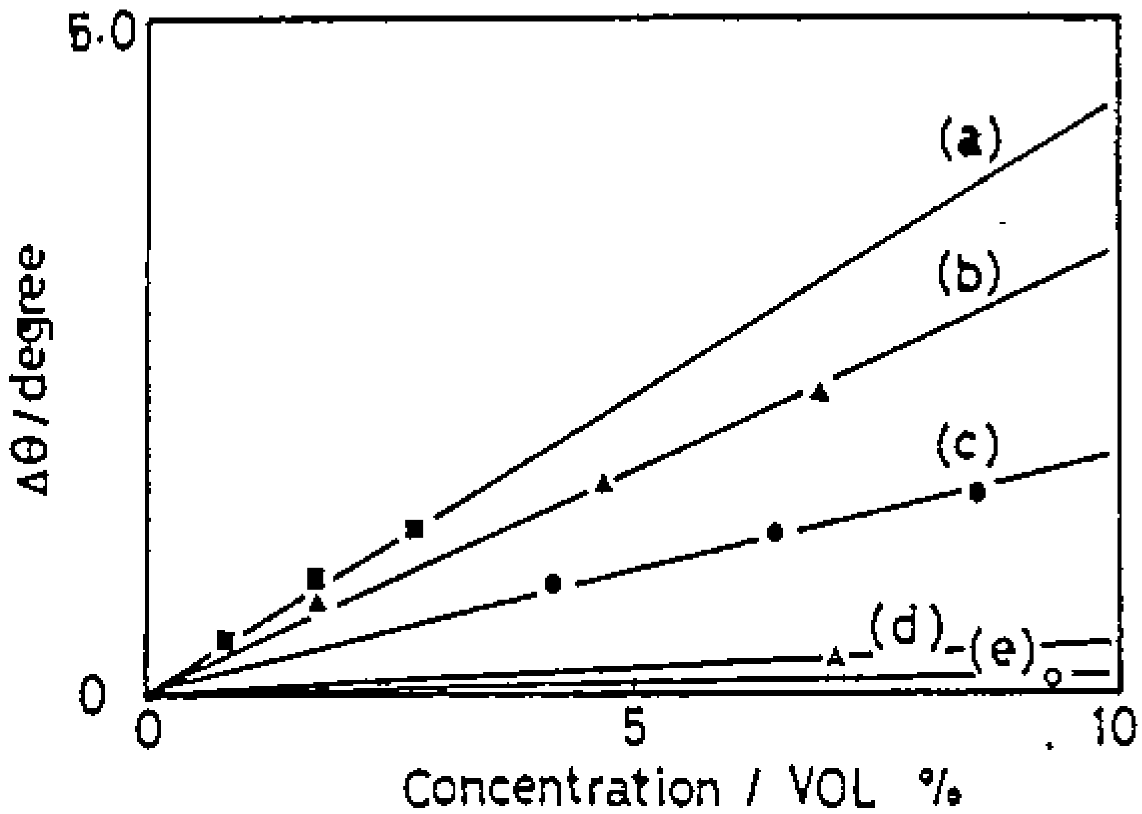


Fig. 5. The time response of the incident angle shifts upon exposure of the polyethylene glycohol film to CH_3OH vapour (5 vol.%).

kinetic studies

(Shozo Miwa et al, Thin solid fim, Japan(1996))



Calibration plots for gaz adsorbing organic material :

(a)C_3H_7OH (20.3), (b)C_2H_5OH (24.6), →device sensor

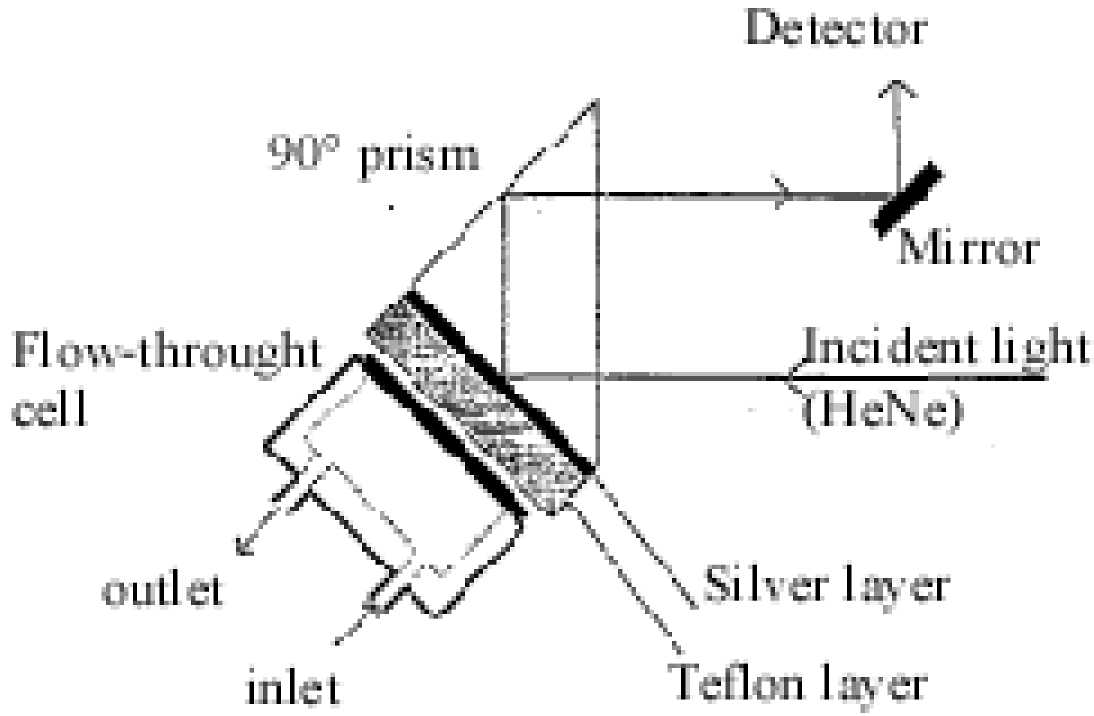
(d)$(C_2H_5)_2O$ (4.3),

(e) n- C_6H_{14} (1.9),

( ) dielectric constants

Gaz sensing -benzene,toluene, xylene - & process dynamic analysis

(R.P.Podgorsek et al- Germany - Sensors & Actuators B (1997)

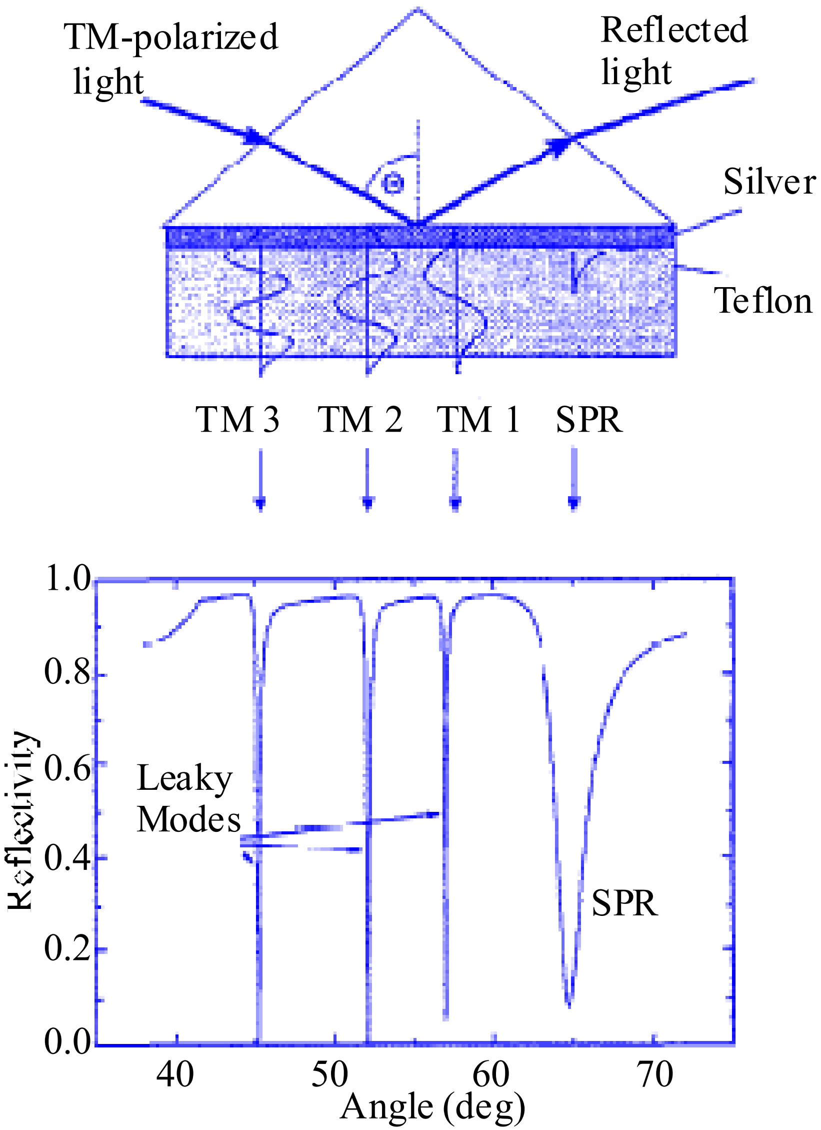


Set up for ATR leaky mode spectrum of a polymer film on exposure to a vapour atmosphere

The SPP resonance occurs at the metal-polymer interface with a penetration depth of 10 to 100 nm. Thus the vapour molecules have to diffuse through the polymer until the SPP sphere of influence is reached and the position of its resonance is shifted

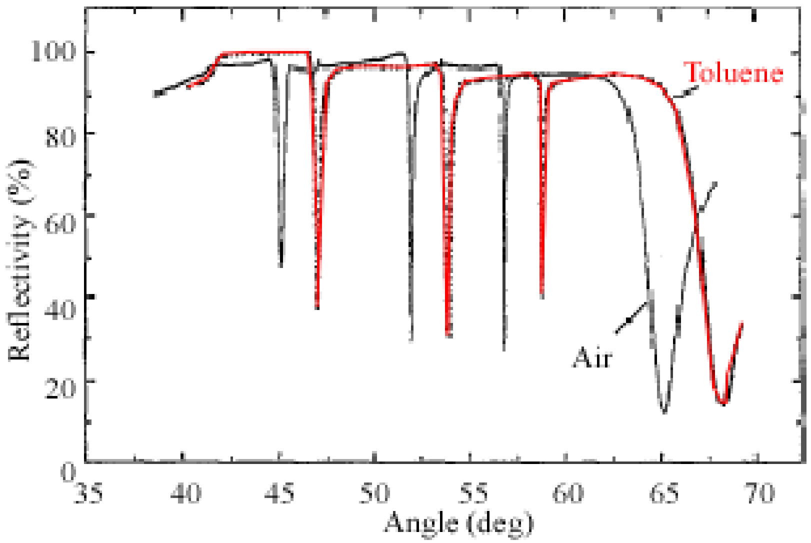
Gaz sensing -benzene,toluene, xylene - & process dynamic analysis

(R.P.Podgorsek et al- Germany - Sensors & Actuators B (1997)

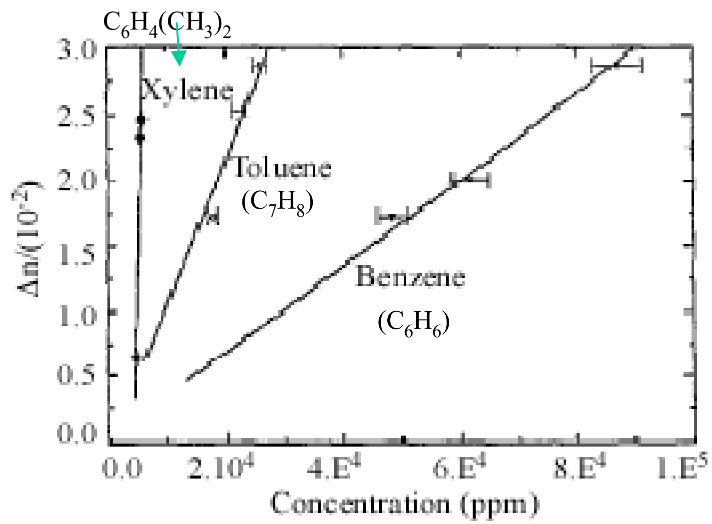


Beside the SPR resonance, the leaky mode resonance of the polymer film appear in the spectrum.

Concentration analysis



Shift of the whole spectrum under a toluene atmosphere.



refractive-index change of a 1- 3 µm Teflon film for different vapour concentration of xylene, toluene and benzene

Analyte	Xylene	Toluene	Benzene
Sensitivity (Δn/ppm)	1.51×10^{-5}	1.41×10^{-6}	2.96×10^{-7}

Sensitivity values for different analytes

→ the smaller is the molecule the lower the time constant -

Dynamic process Analysis

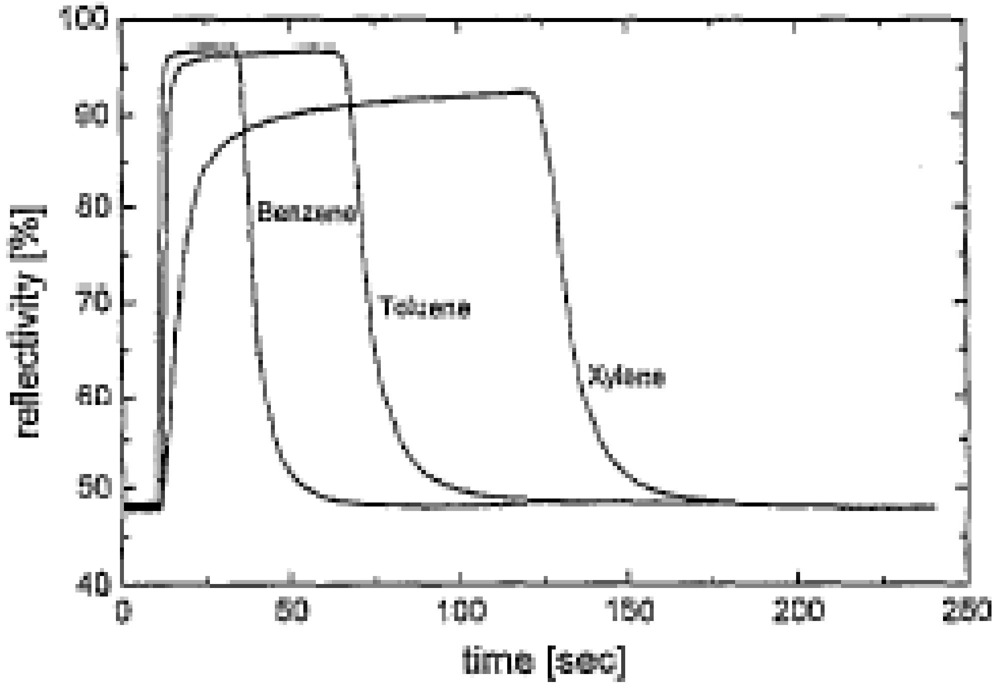


Fig. 6. Change of reflectivity measured on the angle of the SPP resonance for saturated BTX vapours.

Table 2
Response times for different analytes

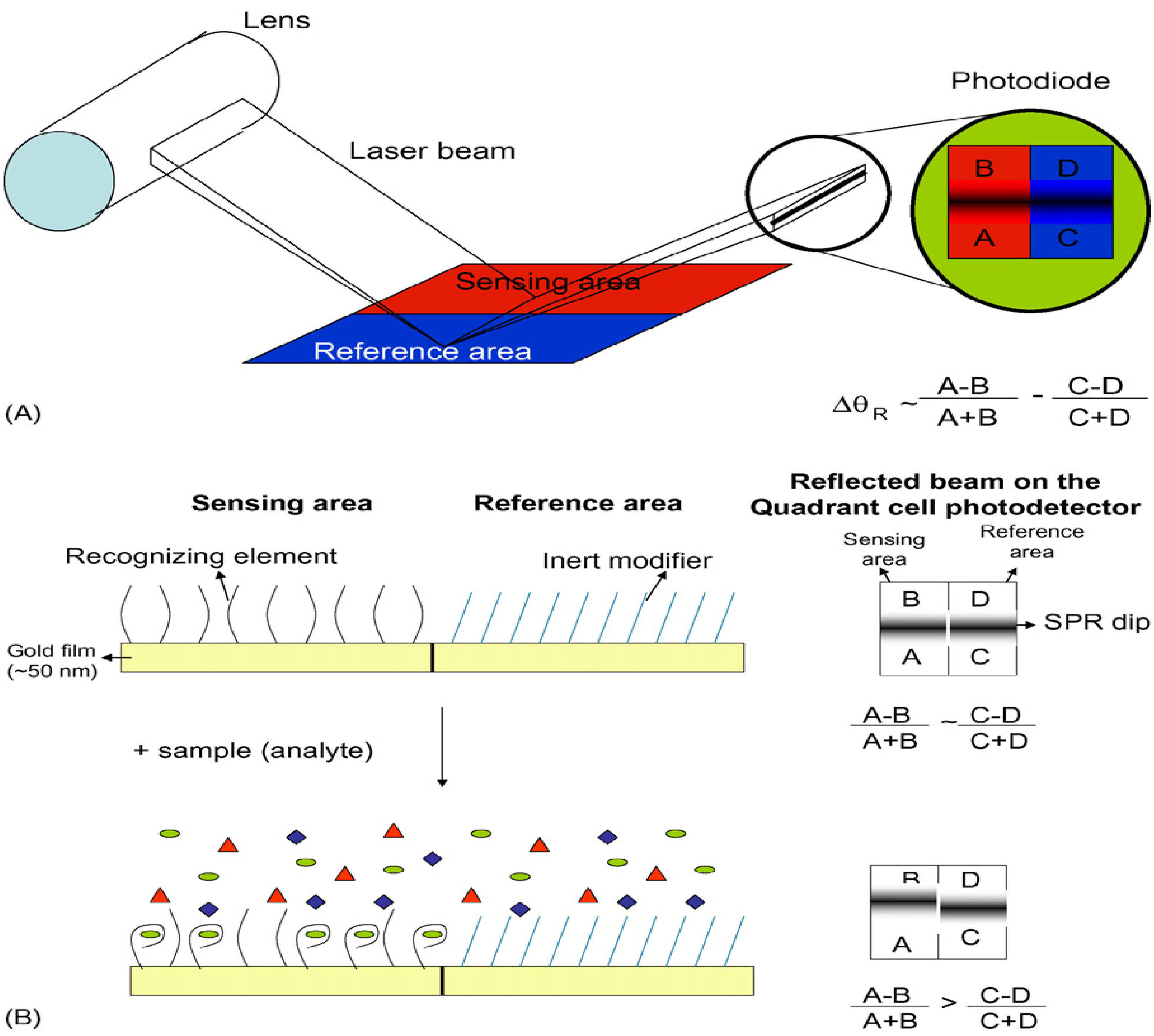
Analyte	Xylene	Toluene	Benzene
Response time (s)	8.3	2.0	1.3

the smaller is the molecule,
the lower are the time constants.

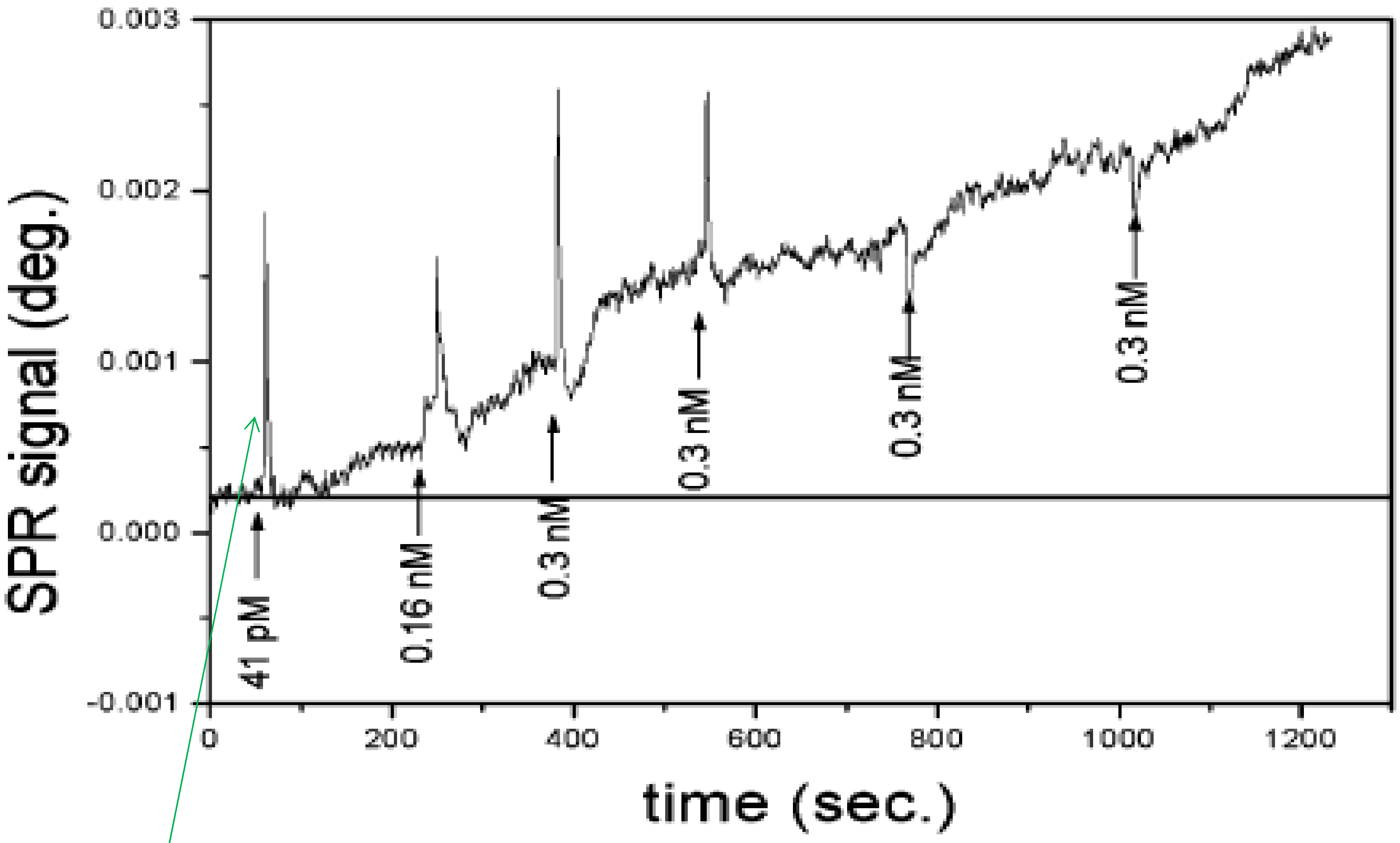
HEAVY METAL ION DETECTION WATER

Heavy Metal Ions in Drinking Water *(Er i c a s . Fo r z a n i et al, Environ. Sci. Technol. 2005)*
Arsenic in groundwater *(Erica S. Forzani a et al-Sensors and Actuators B (2007)*

Selective detection of Cu^{2+} and Ni^{2+} and arsenic in the ppt-ppb range was obtained using differential surface plasmon resonance (SPR).



Lens
Laser beam
Photodiode
B
D
A
C
Sensing area
Reference area
(A)
$\Delta\theta_R \sim \frac{A-B}{A+B} - \frac{C-D}{C+D}$
Sensing area
Reference area
Reflected beam on the Quadrant cell photodetector
Recognizing element
Inert modifier
Sensing area
Reference area
Gold film (~50 nm)
B
D
A
C
SPR dip
$\frac{A-B}{A+B} \sim \frac{C-D}{C+D}$
+ sample (analyte)
B
D
A
C
$\frac{A-B}{A+B} > \frac{C-D}{C+D}$
(B)



Detection of the specific binding of Ni^{2+} in real time from solution concentrations as low as 41 pM (2.4 ppt)

SURFACE PLASMON RESONANCE BIOSENSING

The first application of SPR to biosensing was demonstrated in 1983.

Survey on real-time biospecific interaction analysis with # methods

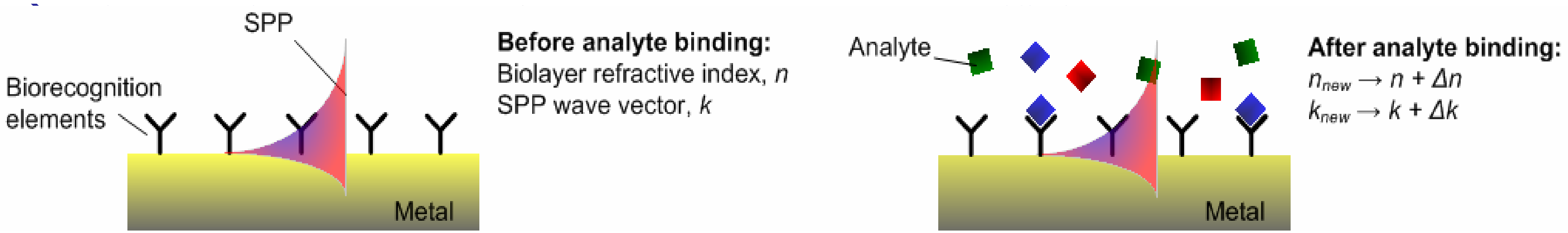
-examination of kinetic and thermodynamic constants of biomolecular interactions.

-Analyte quantification by direct detection of the binding reaction,

ex: - Examination of protein–protein or protein–DNA interactions

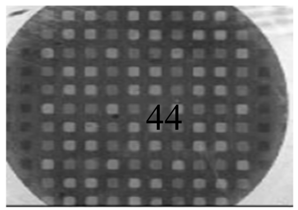
- Detecting conformational changes in an immobilized protein .

Analysis of biomolécule's interactions

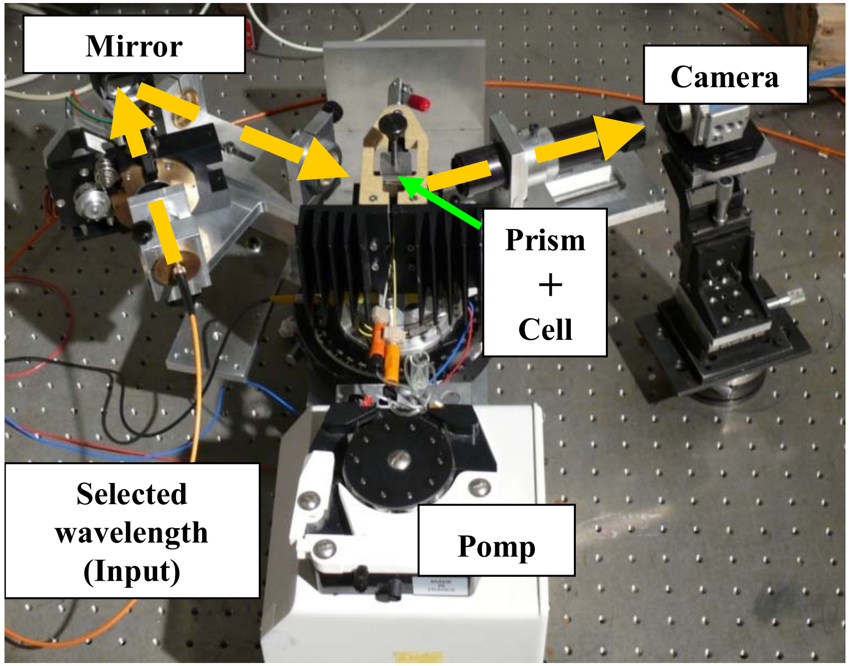


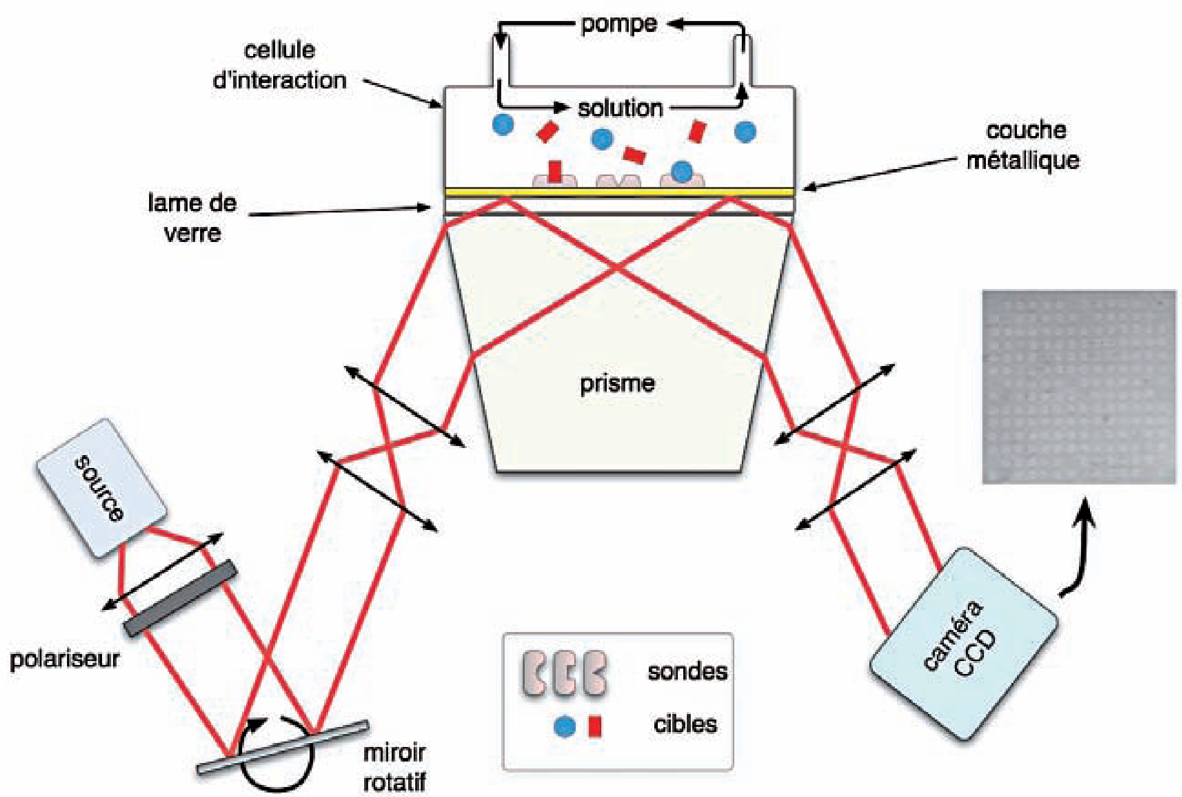
Transductor

Detection & quantification



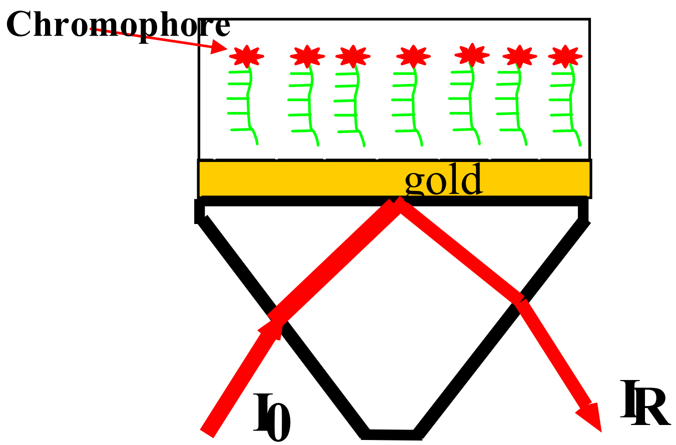
Set up used for biomolecule's interaction-(case of DNA-DNA)

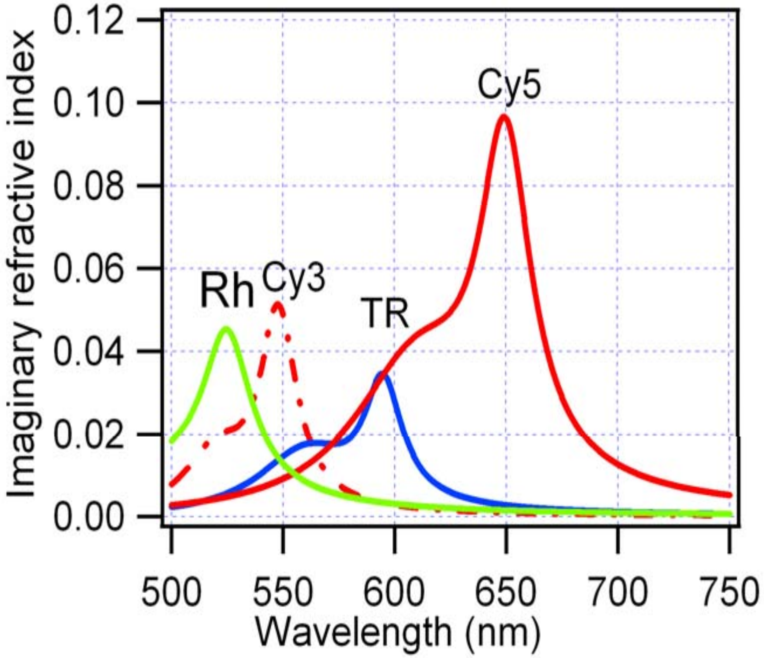


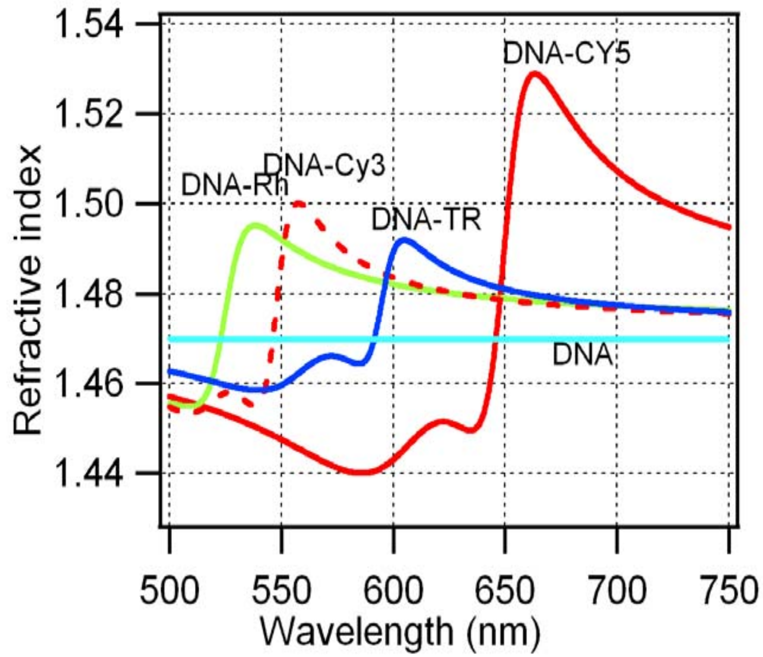


Enhancing of refraction index by addition of chromophores

Chromophores	Excitation (nm)
Rhodamine 6G	525
Cy3	548
Texas Red (TR)	595
Cy5	650

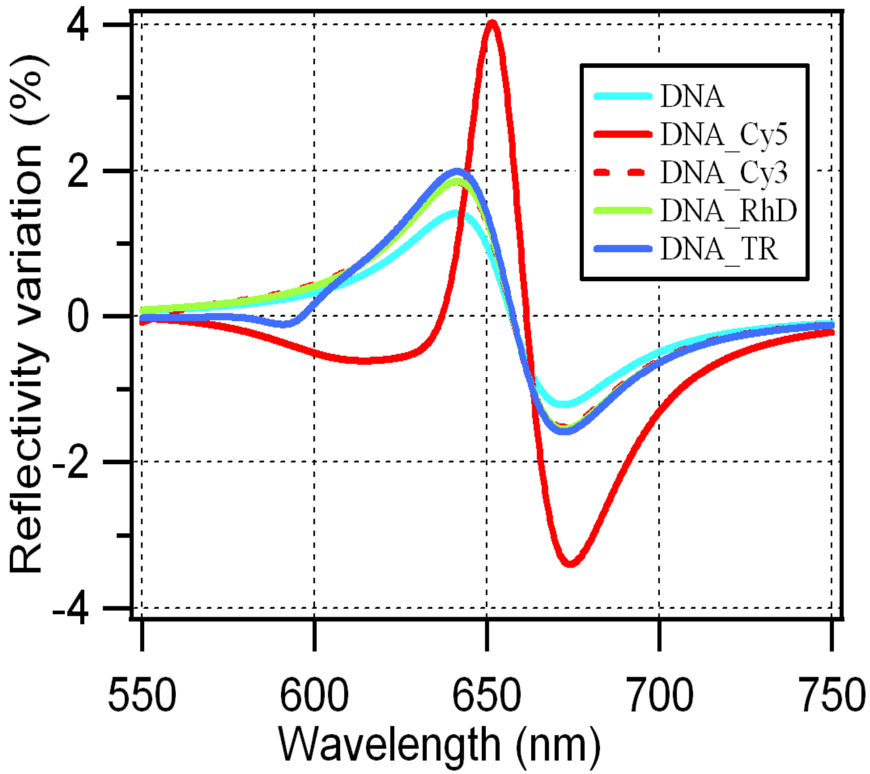




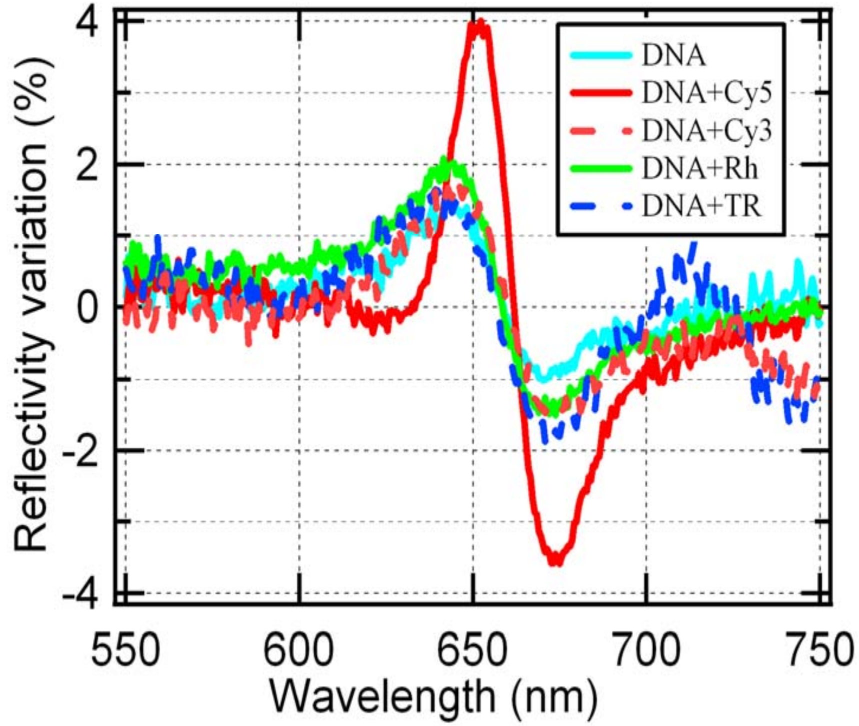


Enhancement of Reflectivity at 650 nm with DNA-**Cy5**

Simulation

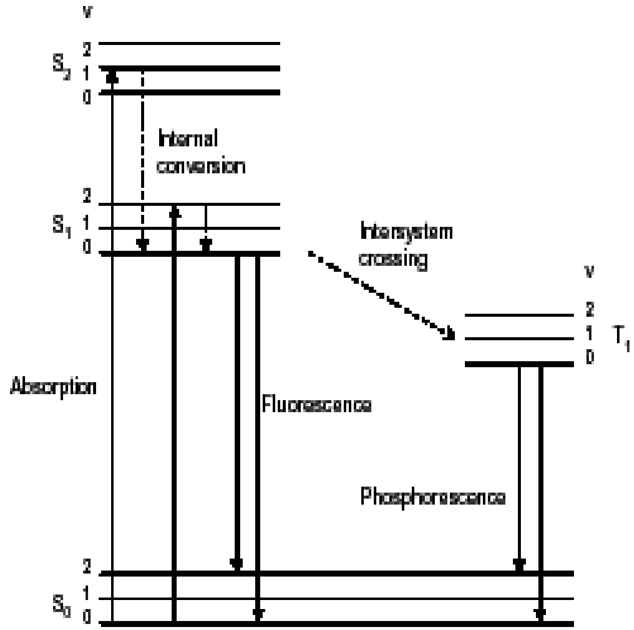


experimental



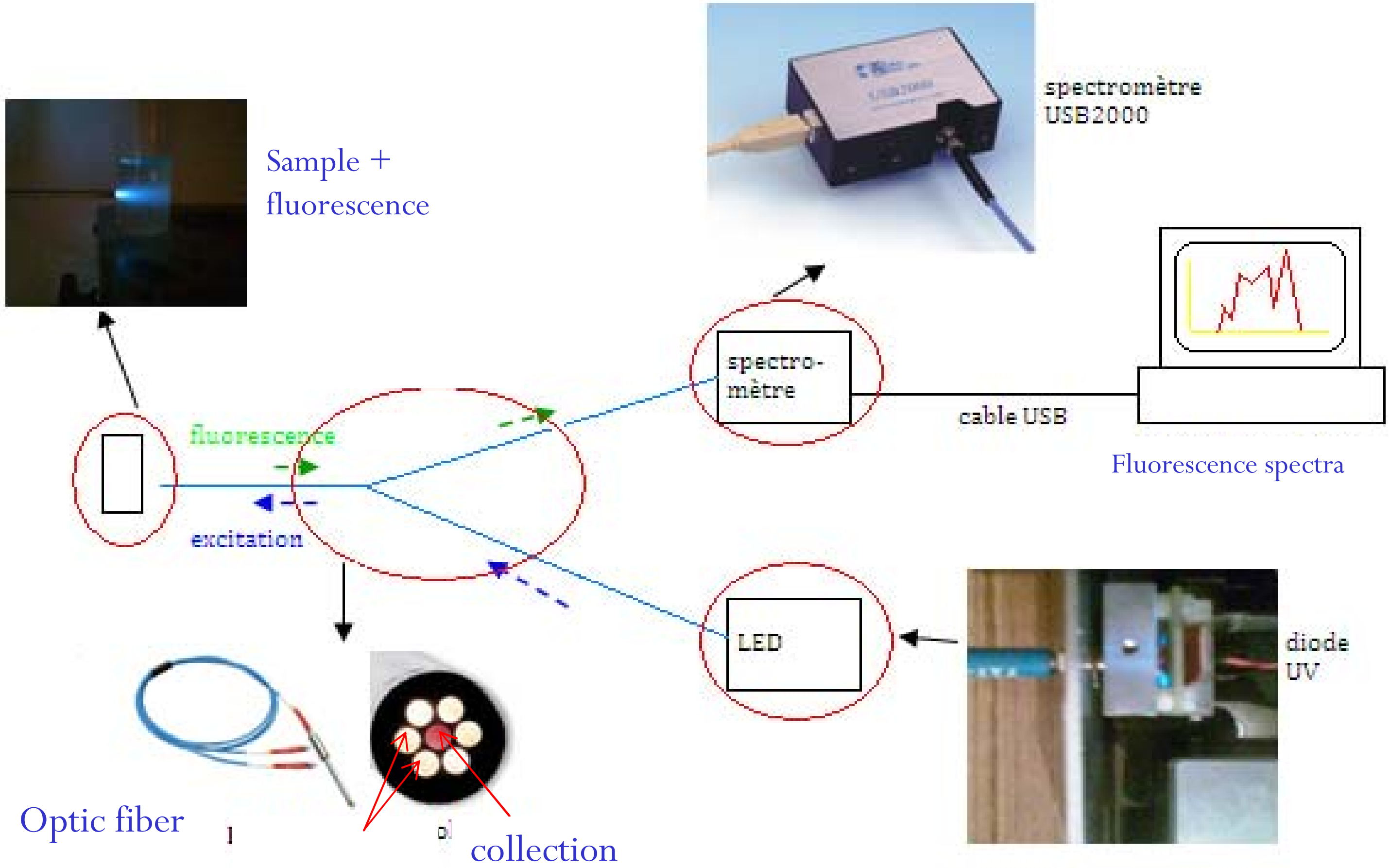
Characterization and quality control of vegetable oils
-by fluorescence spectroscopy
-by SPR

by fluorescence
spectroscopy



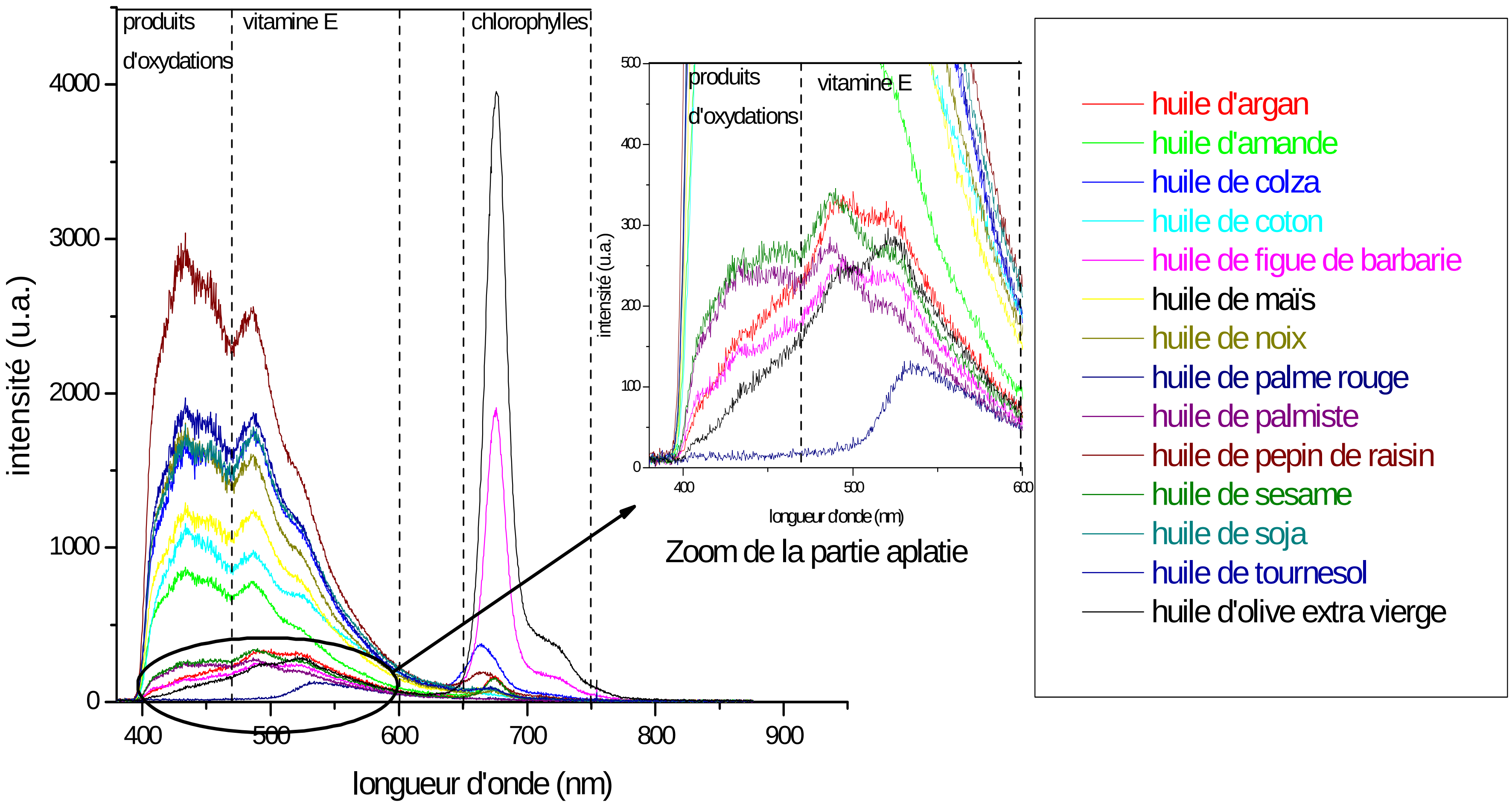
Yvon G. MBESSE KONGBONGA
Hassen Ghalila
Workshop biophotonique,16 - 17 Janvier 2009 Faculté des Sciences de Tunis

Experimental setup

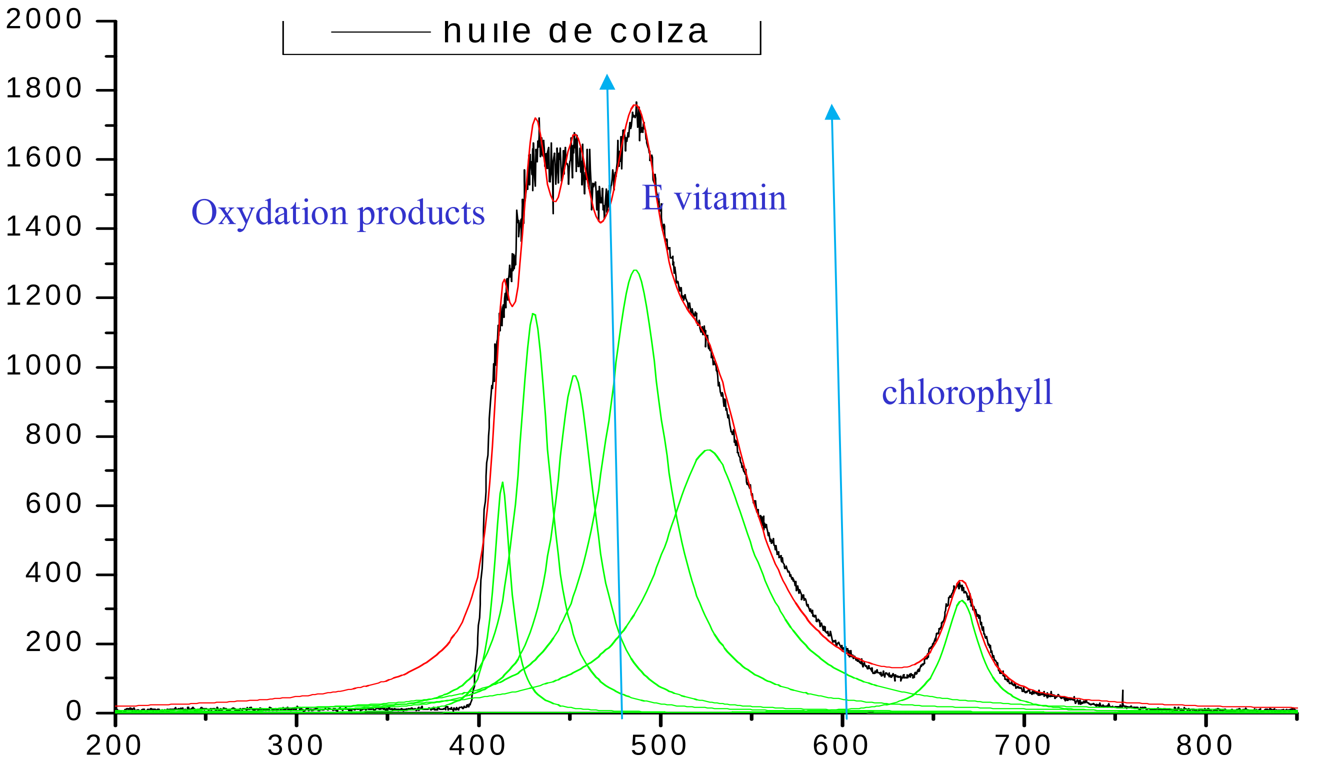


Oil fluorescence spectra analysis

Several varieties of vegetable oils from different regions (Cameroon, France, Italy, Morocco,Tunisia) were analyzed in the same conditions.

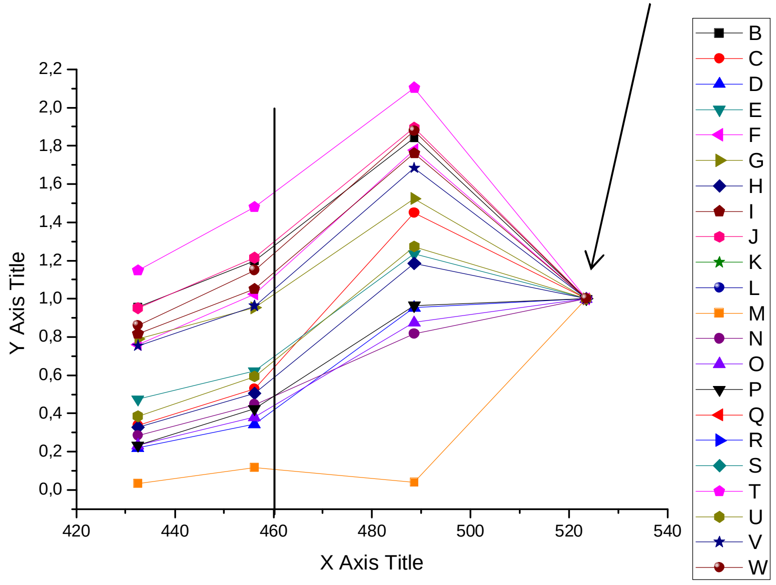


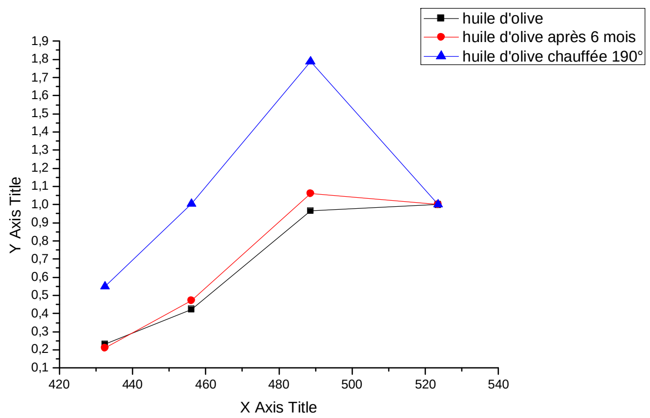
Deconvolution → -431nm and 453nm are products of oxidation,
-480nm to 600nm vitamin E,
-670nm and 730nm - Chlorophyll

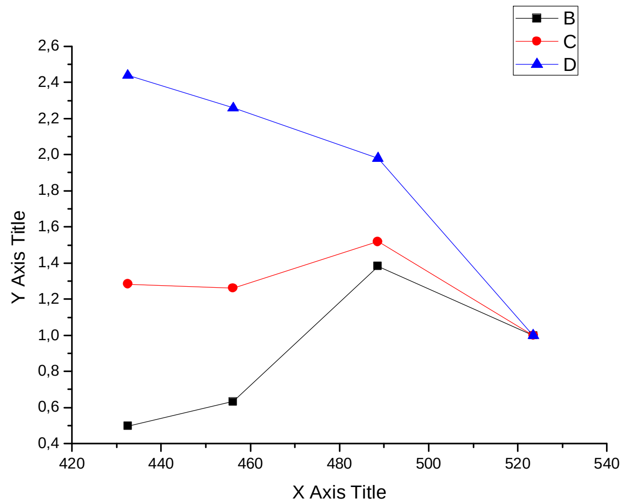


Quality controle – degradation (Effect of T, of time,..)

Vitamin E





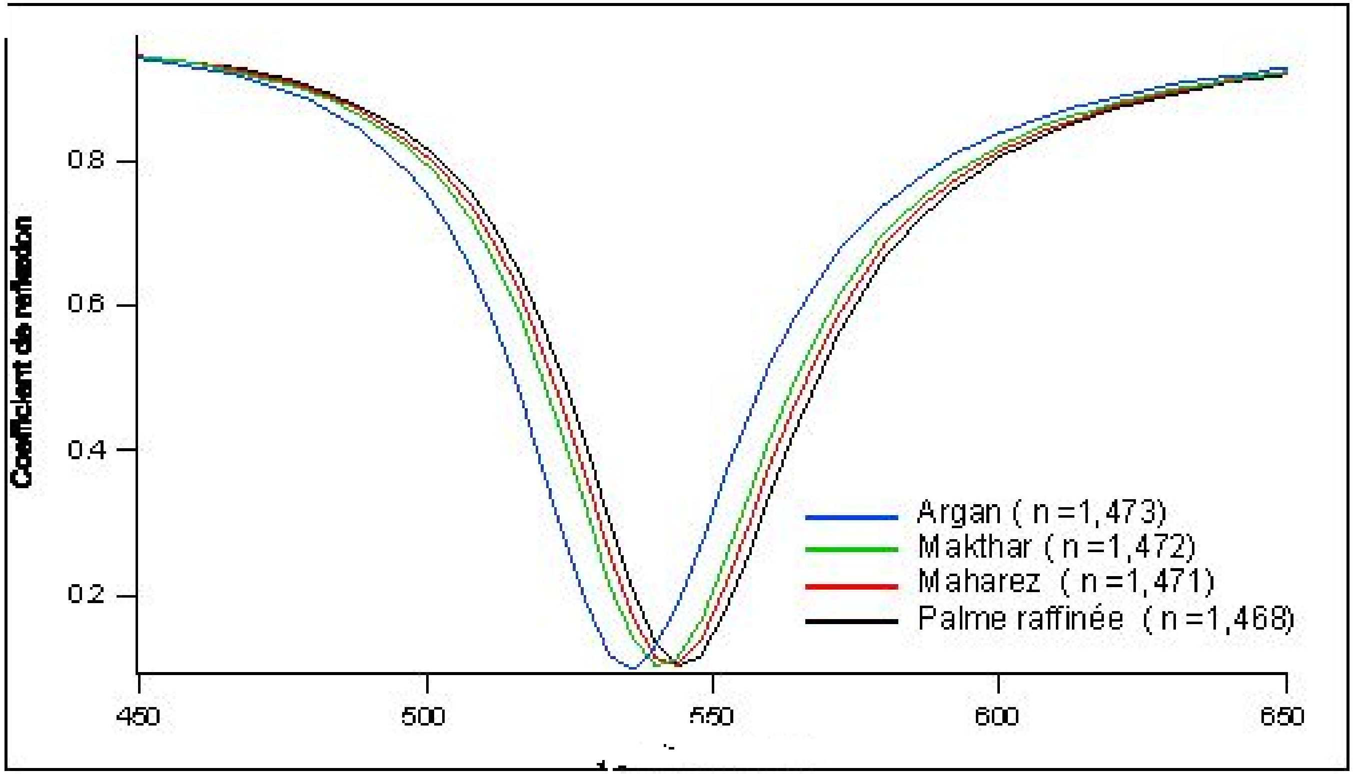


Refractive index of different oils

oils ;fatty acids,can be saturated or unsarturated, depending ofn double bonds,and differ in length

Palmioleic acid: $CH_3(CH_2)_5$**CH=CH**$(CH_2)_7COOH$

Oleic acid: $CH_3(CH_2)_7$**CH=CH**$(CH_2)_7COOH$



Wavelwength (nm)

Technology today

System can detect 9600 protein on DNA simutaneously-

(D.L.Shenkenberg, Biophotonics-Dec.2008)

FUTURE

-Dynamic of biomolecular bindings → to detect, for ex. biomarkers of Sepsis.

-Increase the sensitivity of the flat metallic surface in the 2D SPR sensor

- surface plasmon resonance (LSPR) on metal-nanospheres *surface plasmons localized on small spheres*-

-investigation of plasmonic waveguides→ ultra dense data storage, sensing, metamaterials

-..

FUTURE

-Dynamic of biomolecular bindings

-Increase the sensitivity of the flat metallic surface in the 2D SPR sensor

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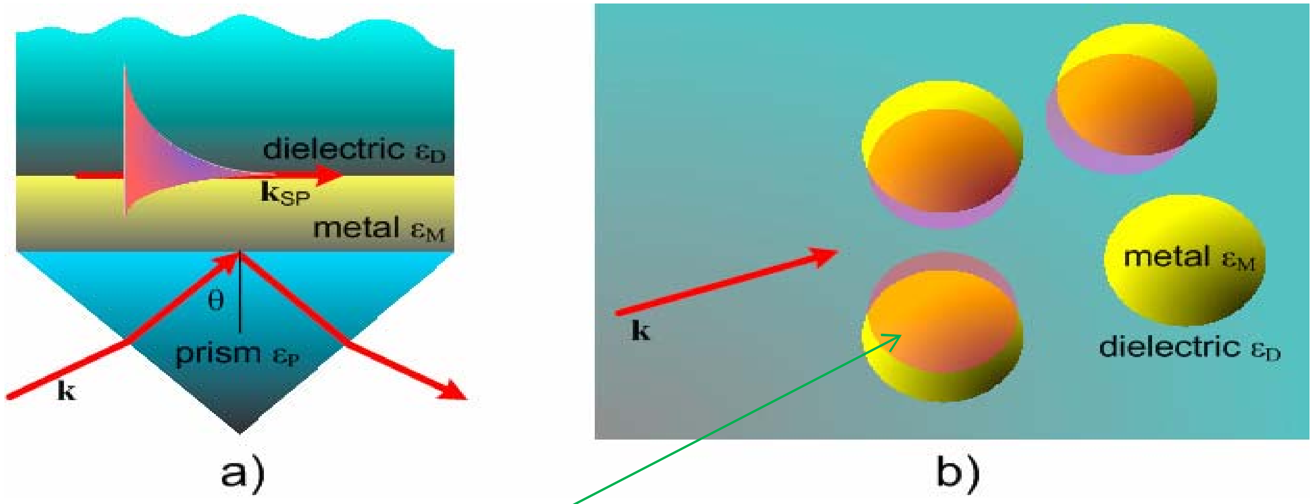

localized SPR supported on metallic nanospheres for molecular fingerprinting

(electric fields can be enhanced in gold nanoparticle assemblies by an order of 450 in nanometer volumes)

ACKOWLEDGEMENTS

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-Hassen Ghalila

LSAMA-LIA-Tunis-Tunisia

-Maha Chamtouri

LSAMA-LIA-Tunis-Tunisia

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- Detection of arsenic in groundwater using a surface plasmon resonance sensor *(Erica S. Forzani a et al- Sensors and Actuators B 123 (2007) 82–88)*.
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Thank you