

Following with a high sensitivity the adsorption of gases on nanoparticles by indirect nanoplasmonic sensing.

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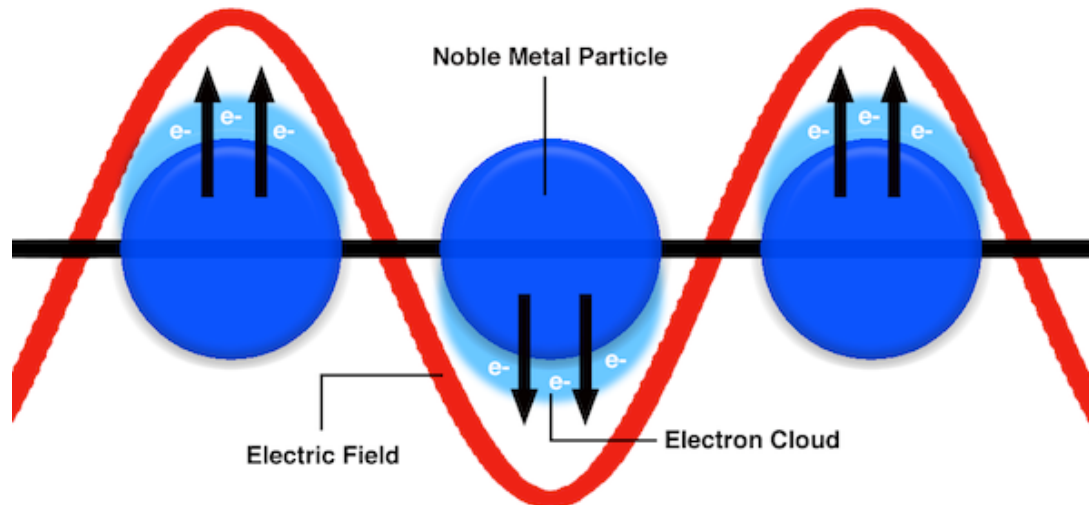
Introduction

Development of chemical and biological nanosensors based on the extraordinary optical properties of noble-metal nanoparticles.

Nanosensors based on localized surface plasmon resonance (LSPR) are sensitive to small local changes in refractive index at the surface of metal nanoparticles during the adsorption/desorption of molecules.

→ These changes induce a shift in the wavelength of the LSPR response.

Variations of the LSPR peak extinction is linked to the collective oscillation of electrons in the metal. The minimum of reflection corresponds to a maximum of absorption.

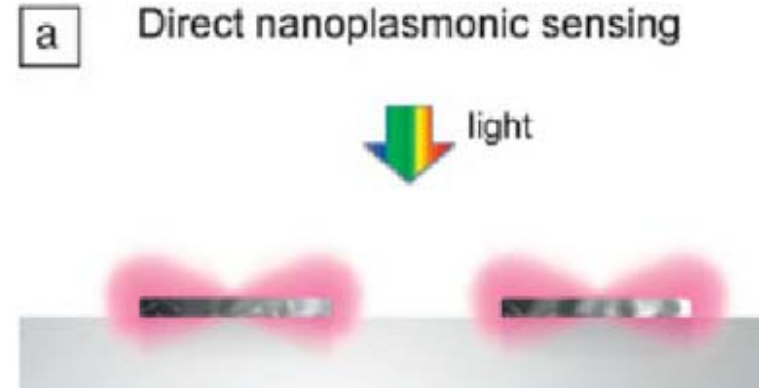


Probing gas adsorption by direct and indirect nanoplasmonic sensing

a) Direct:

Gas adsorption on gold disks modify their dielectric properties

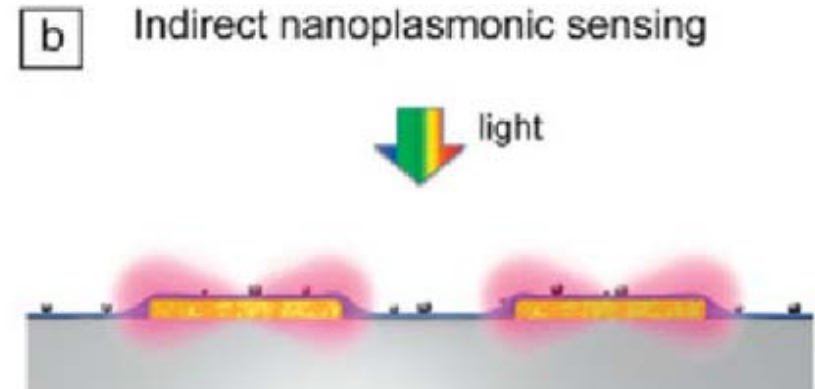
→ a shift in the wavelength of the LSPR response of the gold disk sensor.



b) Indirect:

Gas adsorption on nanoparticles modify the dielectric properties at the surface of the nanoparticles

→ a shift in the wavelength of the LSPR response of the underlying gold disk detector.



Gold nanodisks fabrication: a lift off process

Sample holder = borosilicate glass window, $e = 1$ mm, $\varnothing = 25,4$ mm
Cleaning: acetone + US, then isopropanol + US, EDI rinsing,
oxygen plasma oven at 150°C (300 W during 10 min)

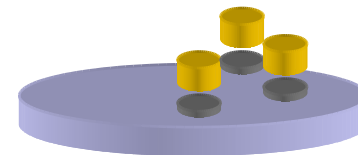
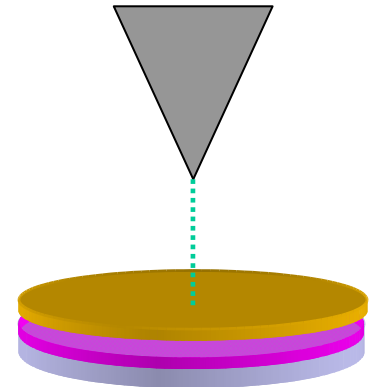
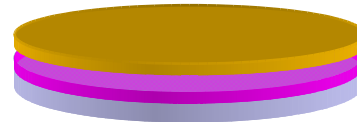
PMMA spin-coating (resin 950 K at 4 %, speed : 4000 rpm, $e = 270$ nm
annealing 10 min at 170°C)

Gold layer deposition (5 nm)
to remove the charges (Edwards 306)

The gold film is irradiated with an electron beam (Raith PIONNEER)
Area of 1×1 mm²

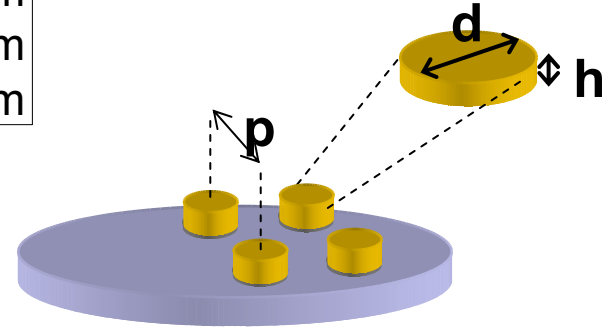
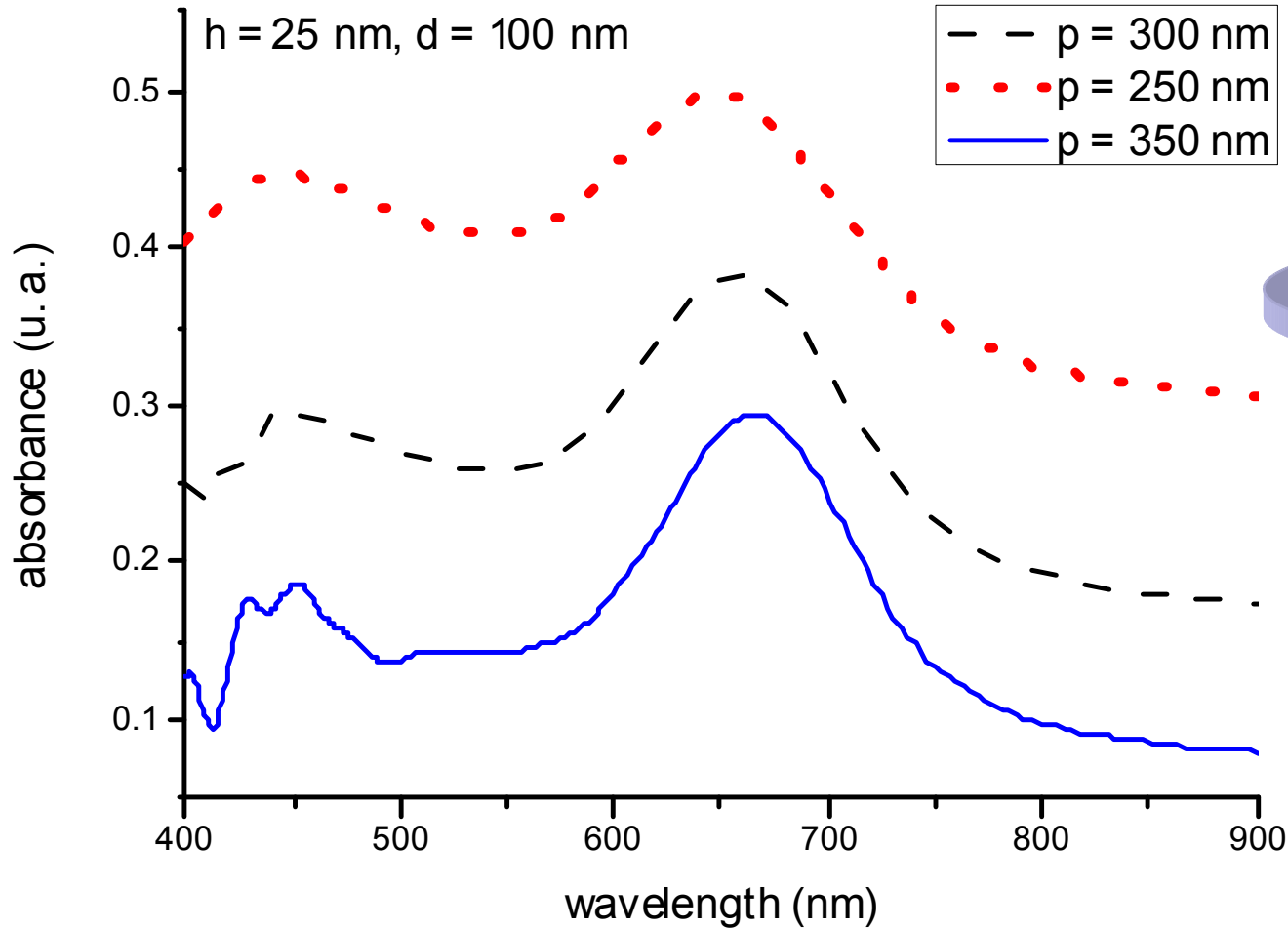
Revelation in acetone (or is removed) then with MIBK/IPA 1 : 3 during 45 s
Then with IPA during 45 s (\rightarrow holes in the resin)

Cr and Au evaporation within the PMMA resin (Edwards 306)
 $e_{\text{Cr}} = 2$ nm, $e_{\text{Au}} = 20$ nm
Lift-off of the resin (acetone + US)



\rightarrow Precise control of the shape, the size and the pitch of gold nanodisks

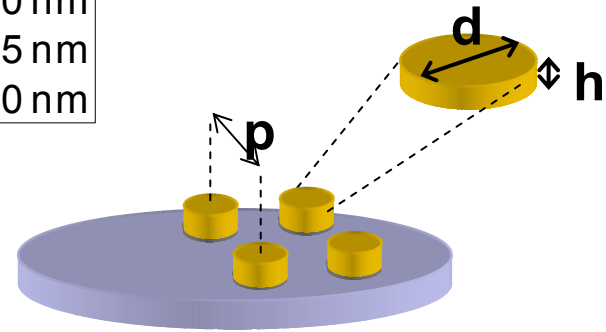
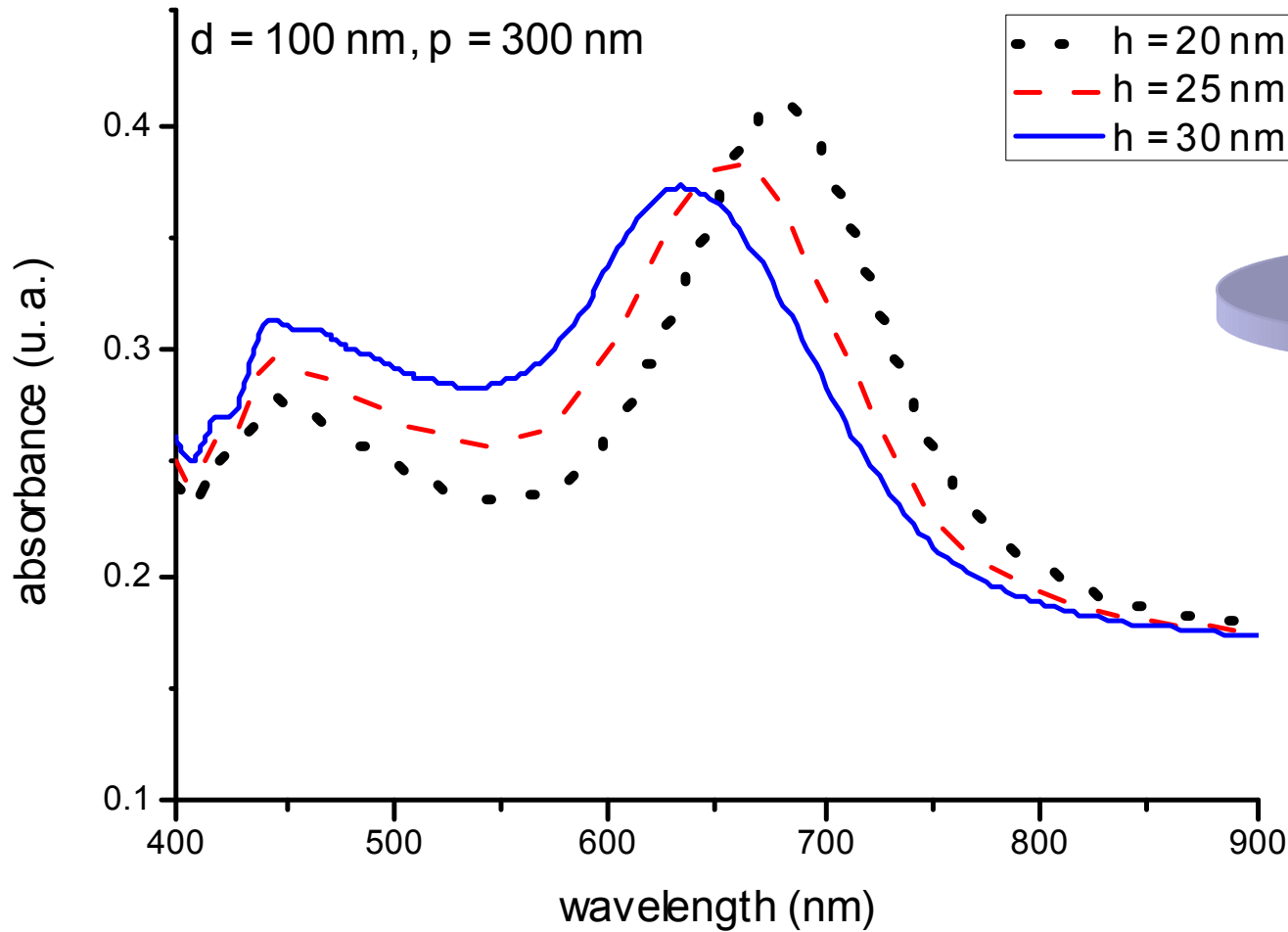
FDTD Simulations → parameters (d , p , h) giving the best theoretical S/N



“OptiFDTD” from Optiwave

d	p	h	λ	$FWHM$
100	250	25	645	95
100	300	25	655	92
100	350	25	663	90

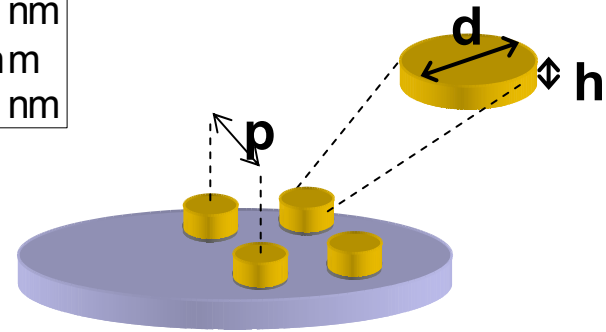
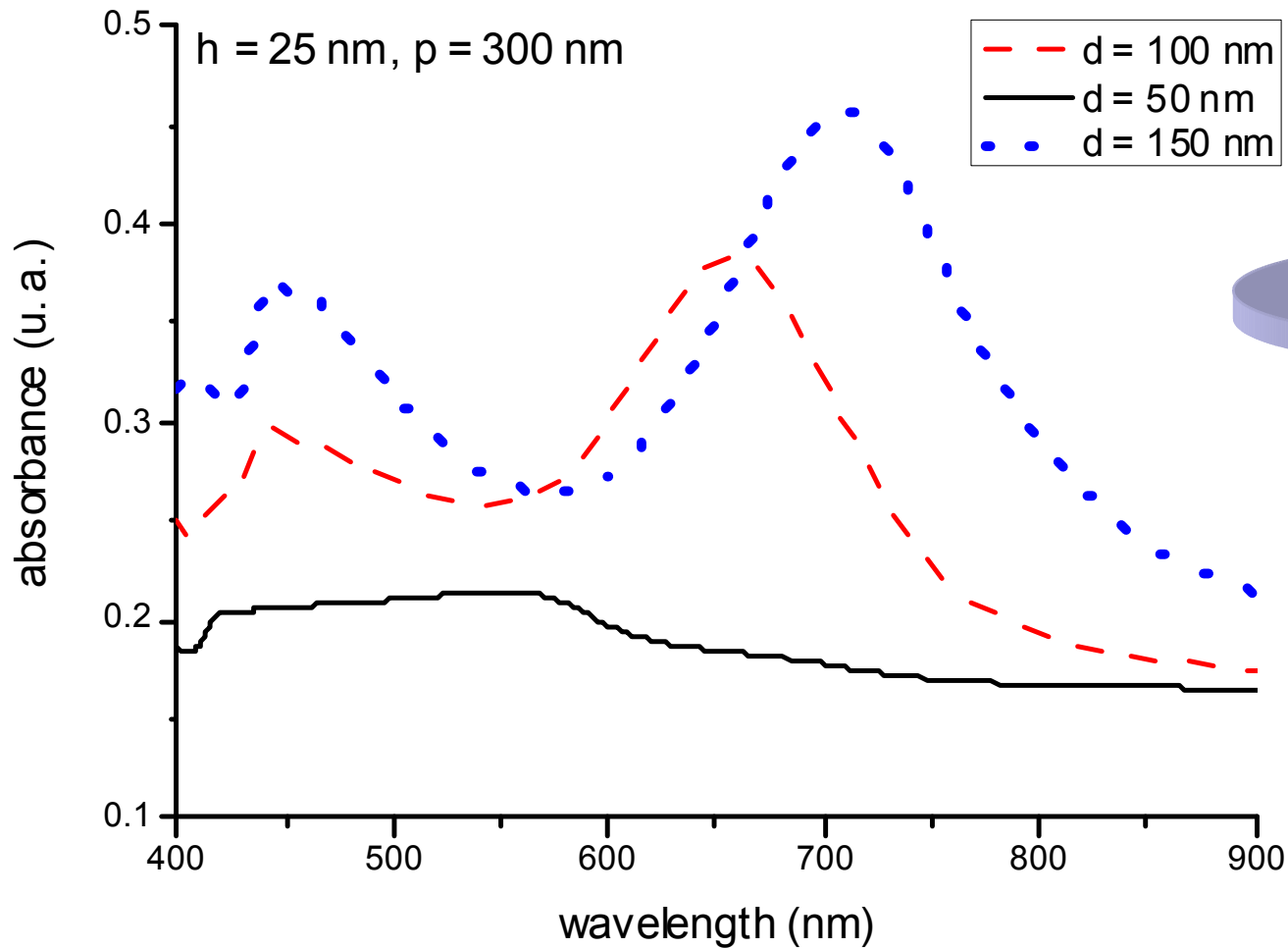
FDTD Simulations



“OptiFDTD” from Optiwave

d	p	h	λ	$FWHM$
100	300	20	677	92
100	300	25	654	96
100	300	30	632	107

FDTD Simulations

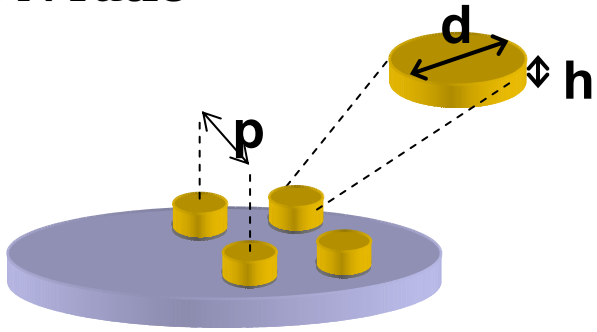
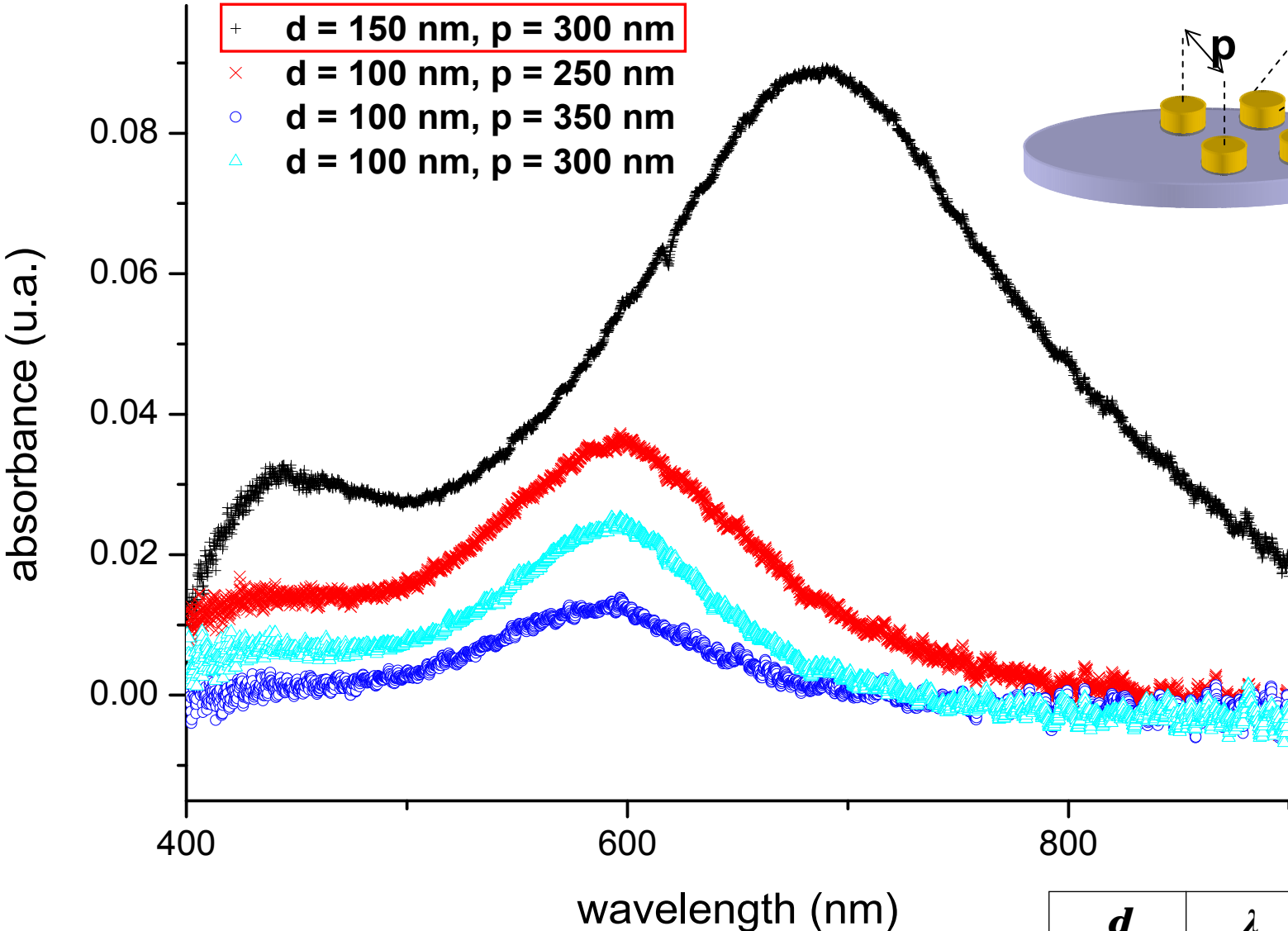


d	p	h	λ	<i>FWHM</i>
50	300	25	538	n.d.
100	300	25	654	96
150	300	25	708	112

Aspect ratio: $d/h = 6$



Parameters (d, p) to obtain the best experimental S/N ratio



$\langle h \rangle = 29 \text{ nm}$
Aspect ratio $d/h \sim 5$

d	λ	$FWHM$
100	585	114
150	678	168

Calibration of our LSPR sensor

The response of LSPR nanosensors follows a simple model described by the group of Campbell:

$$\Delta\lambda = m (n_2 - n_1) [1 - \exp(-2d/l_d)] \quad (1)$$

$\Delta\lambda$: wavelength shift

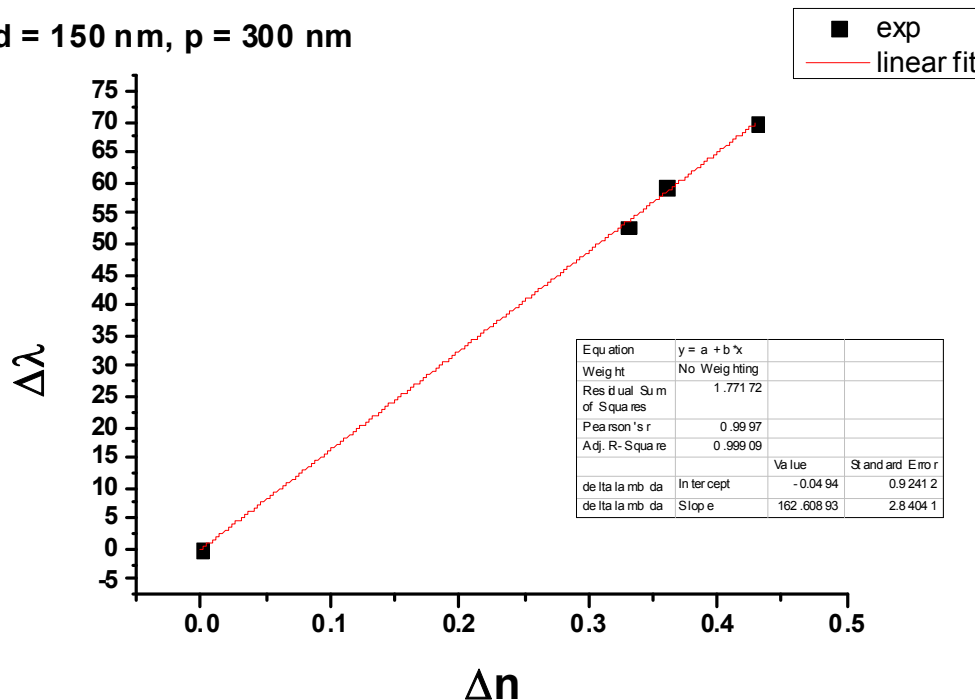
m : sensitivity of the refractive index (RI)

n_2 and n_1 : RIs of different surrounding media

d : effective thickness of the adsorbate layer

l_d : characteristic decay length of the evanescent electromagnetic field

$d = 150 \text{ nm}$, $p = 300 \text{ nm}$



In a liquid medium:

$d \gg 1$

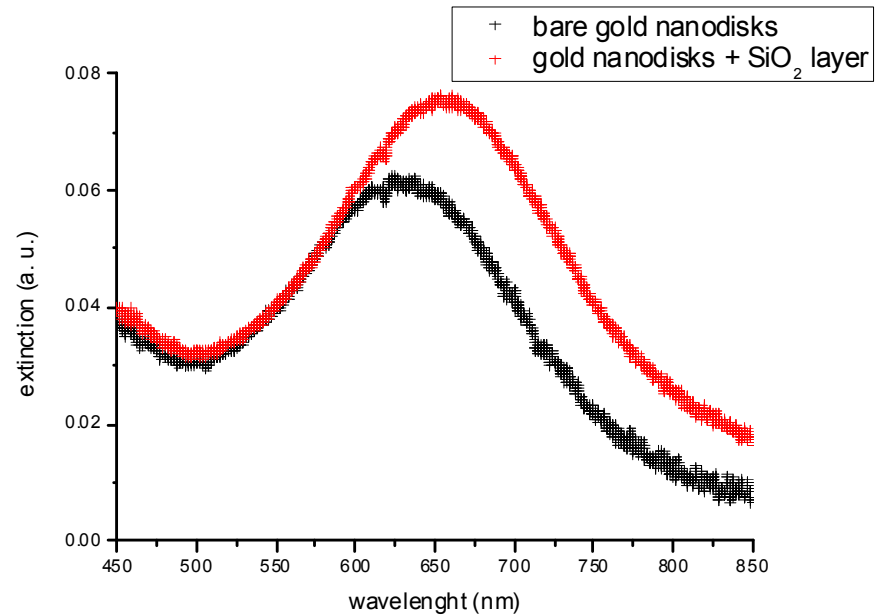
$\Delta\lambda \sim m \Delta n$

$\rightarrow m = 162 \text{ nm} / \text{RIU}$

Deposition of a controlled thickness (8 nm) of SiO₂ layer (magnetron sputtering)

$$\Delta\lambda = 27 \text{ nm}$$

Equation (1) \rightarrow $ld = 36 \text{ nm}$



Aspect ratio (d/h): an important parameter:

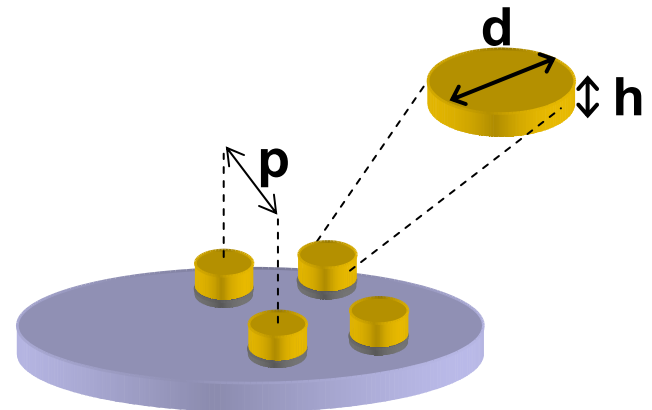
Chen et al. (Nanotechnology, 2009):

$d/h = 4 \rightarrow ld = 39 \text{ nm}, m = 173 \text{ nm/RIU}$

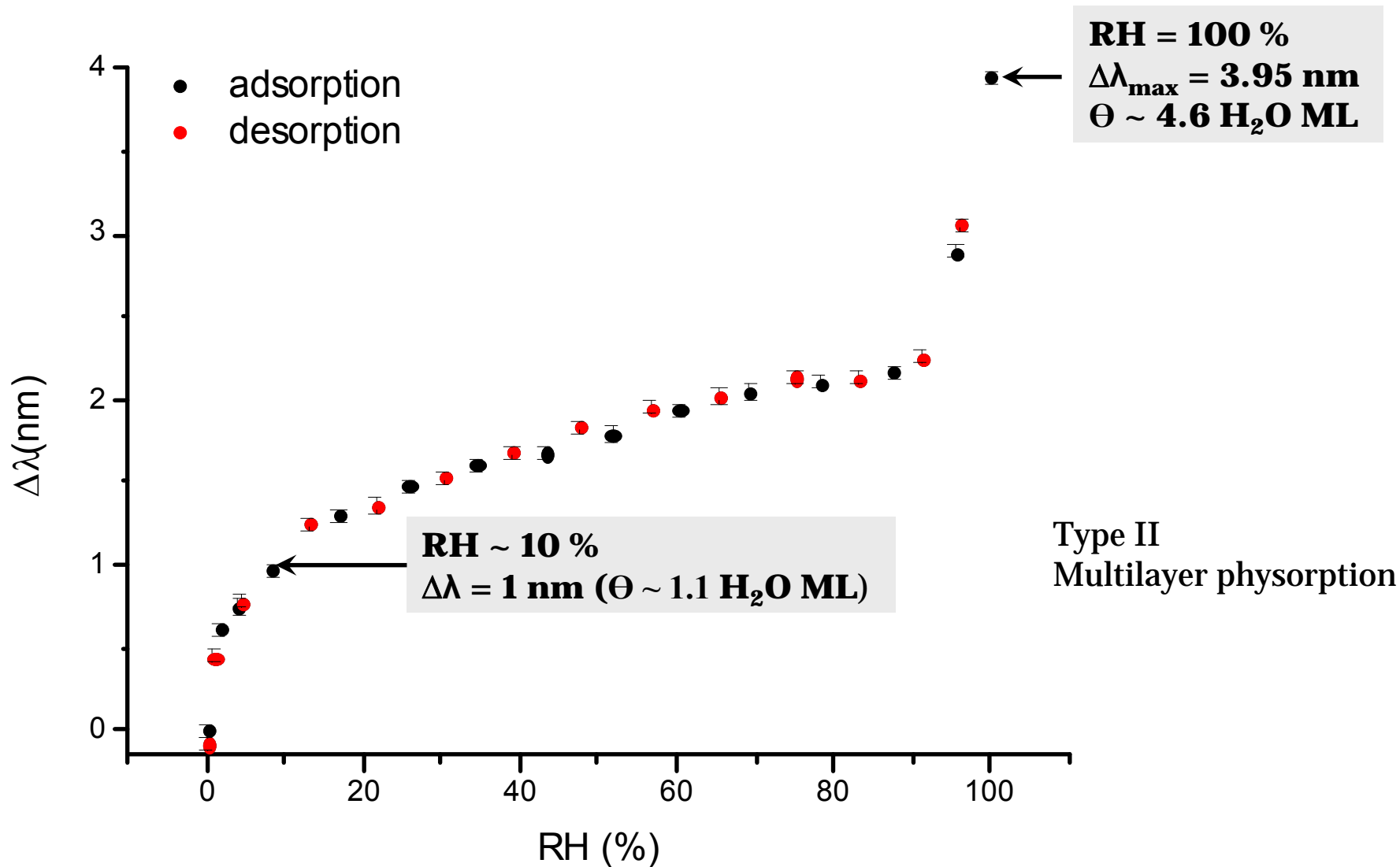
$d/h = 1.43 \rightarrow ld = 28 \text{ nm}, m = 56 \text{ nm/RIU}$

Our work:

$d/h = 5 \rightarrow ld = 36 \text{ nm}, m = 162 \text{ nm/RIU}$



Direct nanoplasmonic sensing: water adsorption isotherms on bare gold nanodisks

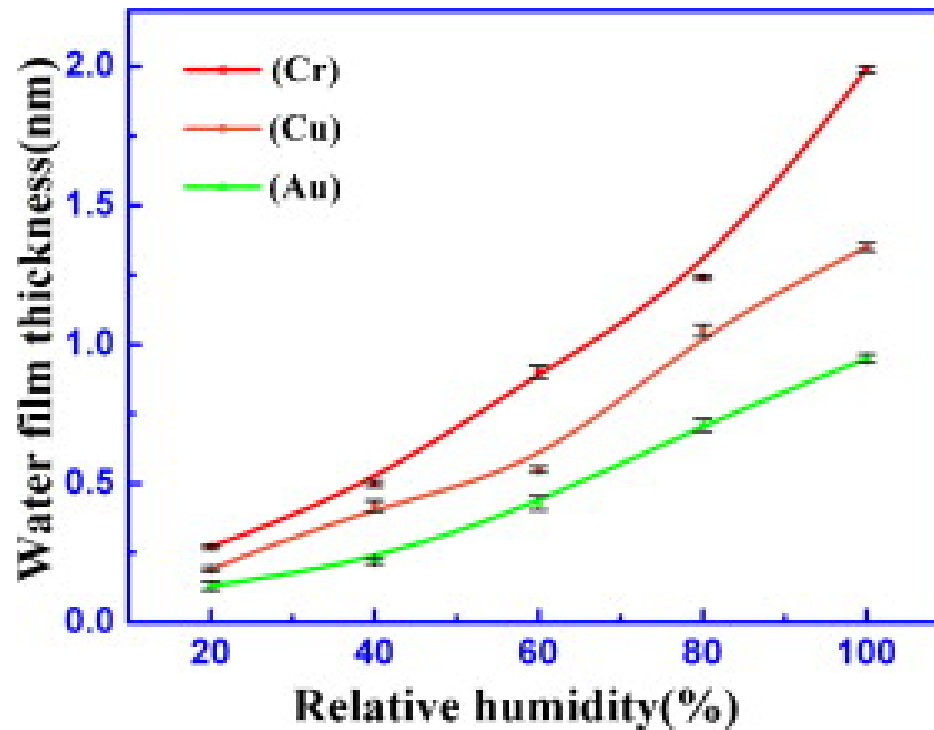


High sensitivity: error bar on $\Delta\lambda \sim 0.04 \text{ nm}$ ($\sim 4/100 \text{ H}_2\text{O ML}$!)

Reversibility: no chemisorption of water on gold (see Heras et al., ZPCNF, 1982)

Water adsorption behavior on metal surfaces and its influence on surface potential studied by *in situ* SPM

Guo et al., Applied Surface Science, 2012



For Au film: $t \sim 1$ nm at RH = 100 %, i.e. about 3.3 H₂O ML

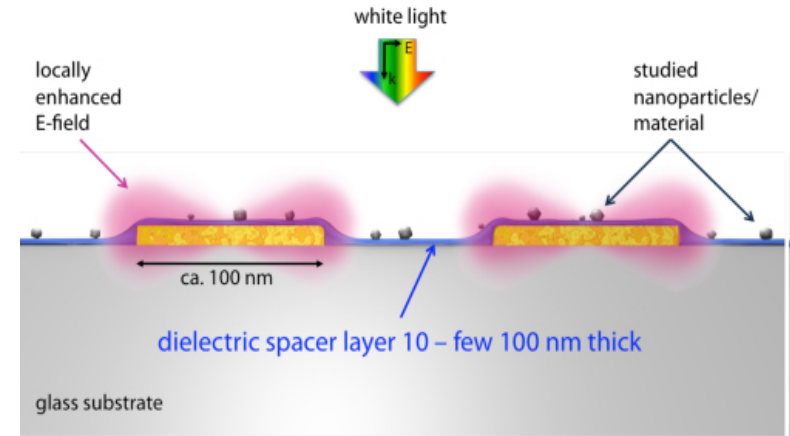
For Cr film: $t \sim 2$ nm at RH = 100 %, i.e. about 6.6 H₂O ML

Indirect nanoplasmonic sensing: water adsorption on soot nanoparticles

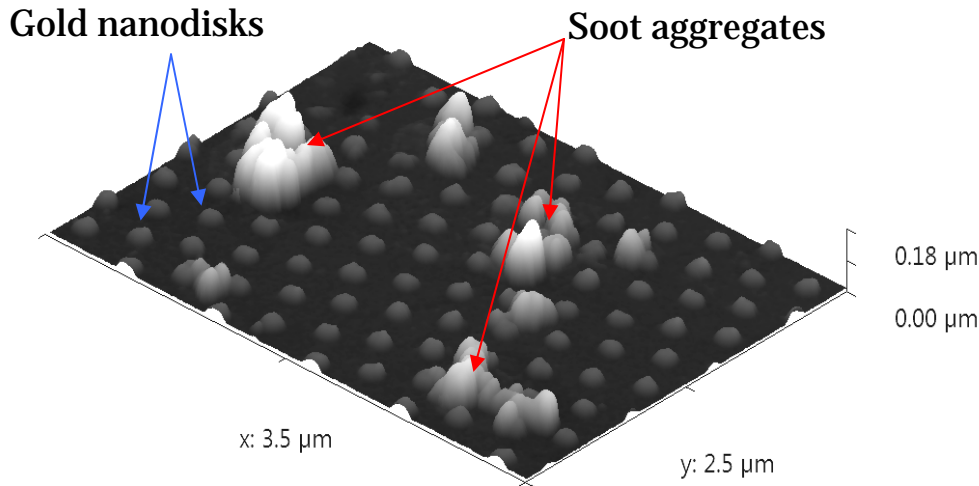
gas/nanoparticles/Au nanodisks

→ insulating layer (SiO_2) on gold nanodisks

1. protects and makes more stable the detection nanostructure at high temperature
2. eliminates the (electronic) interaction NP's / gold nanodisks



<http://www.insplorion.com/technology/indirect-nanoplasmonic-sensing>

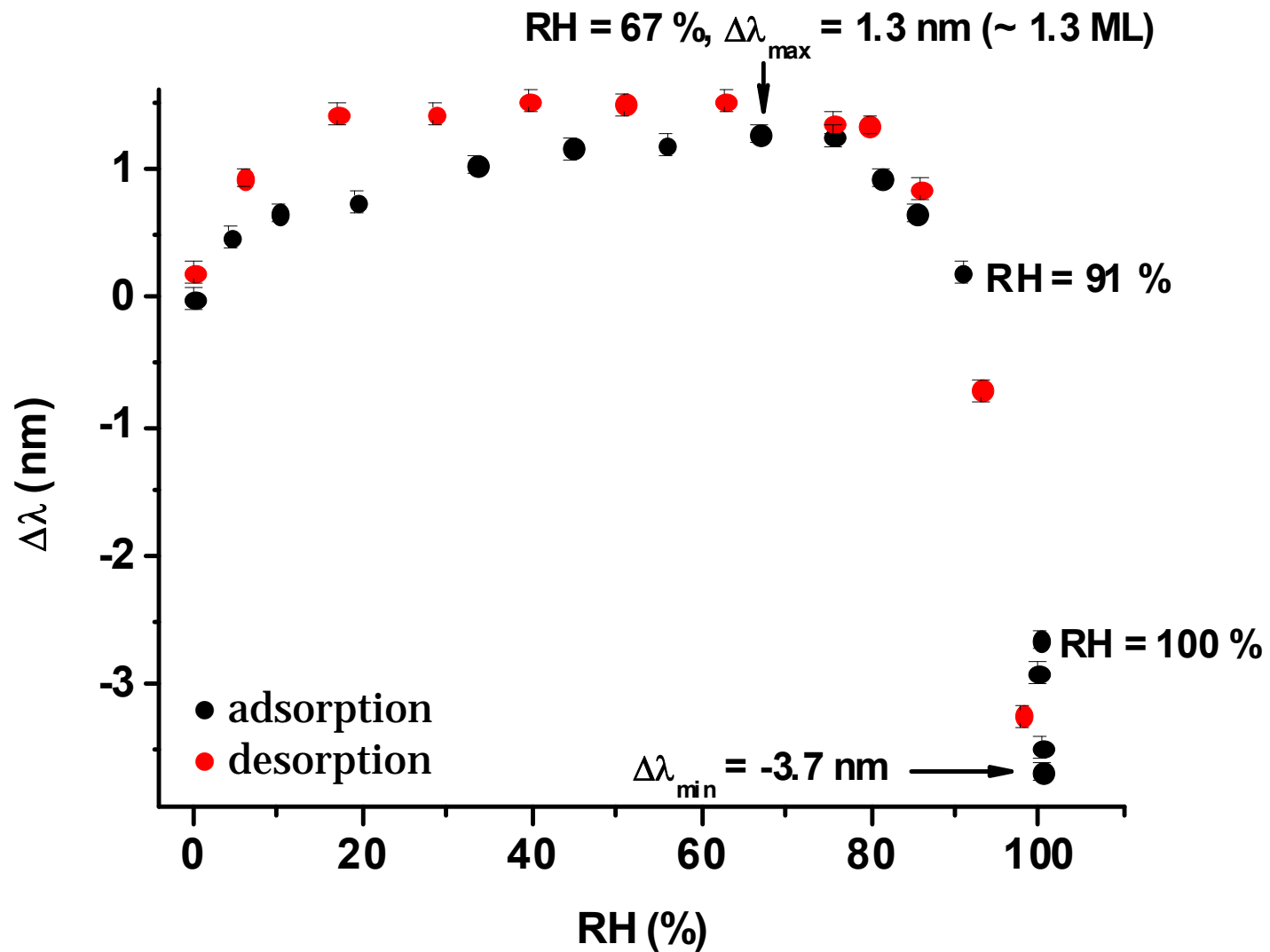


AFM image (tapping mode) - AFM PSIA XE-100

Soot particles are involved in atmospheric process (ice nuclei, contrails formation, radiative forcing, chemi...)

Dilution of soot particles into ethanol + droplet on the gold nanodisks (+ SiO_2)

Water adsorption isotherm on hydrophilic soot



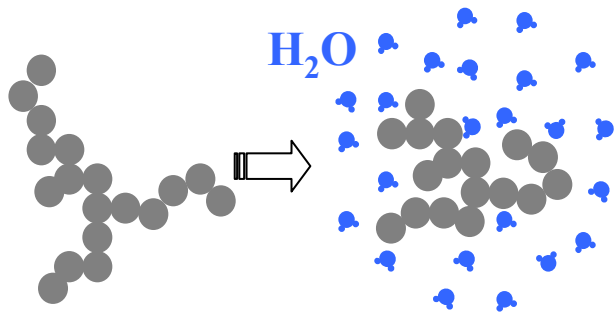
- At RH > 70 % → peculiar blue shift !
- Desorption: small hysteresis → some water molecules do not desorb completely from the soot particles (porosity ...)

Blue shift ?

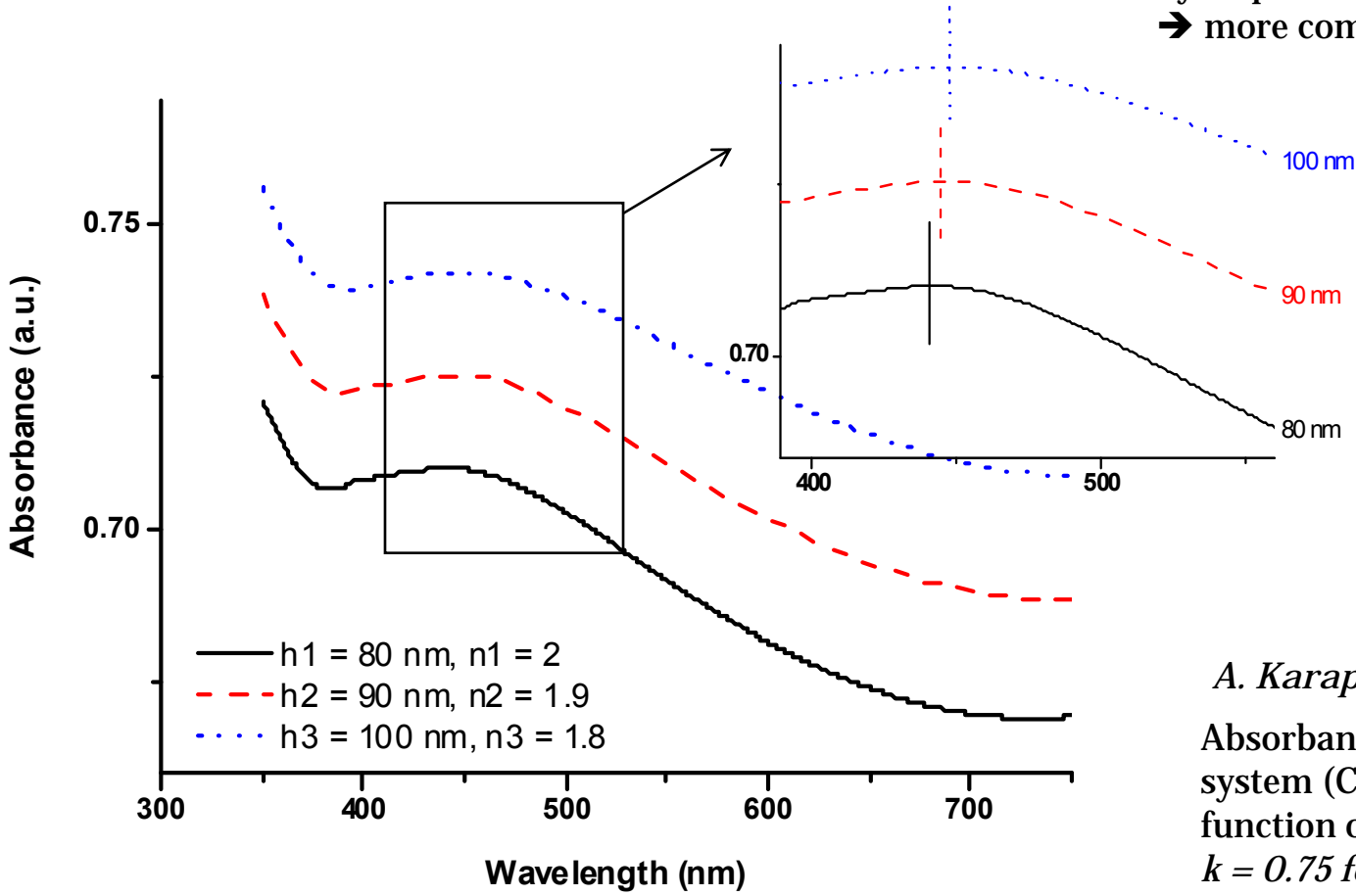
Hydrophilic soot aggregates collapse into + dense structures during RH \nearrow

Mikhailov et al. (JGR, 2006):

- RH = 100 % soot aggregates are more compact
- higher mass fractal dimension Df
- smaller gyration radius
- higher n and k values



capillary forces applied by water molecules adsorbed on surfaces of hydrophilic soot primary particles
 → more compact soot aggregates



From 100 to 90 nm
 → $\Delta\lambda = -4$ nm
 From 90 to 80 nm
 → $\Delta\lambda = -3$ nm

A. Karapetyan

Absorbance of the thin multilayers system (C/SiO₂/gold/glass) as a function of the incident wavelength $k = 0.75$ for the three thicknesses.

Conclusions

High sensitivity sensor (a few hundredths of H₂O ML by DNPS)

Large (P, T) domains of studies

Non destructive probe (compare to e⁻ probes)

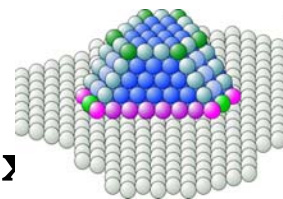
Outlooks

Quantitative measurements with mass spectrometry

Chemical reactivity of gas on nanoparticles

- **Catalysis**

mettalic nanoparticles (Pt, Pd, ...) + CO, O₂ + H₂, NO_x



- **Environmental heterogenous reactions**

Ice nucleation on soot particles

Photochemistry and reactivity NO₂/soot → O₃

