

# Particle surface interactions and molecular selfassembly: an activity overview.

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*\* as of 1st January 2010 : Institute of Molecular Science of Orsay*

*LIFAN, November BA 2009*

# Projected studies

## *Ion/atom interactions:*

+ **Electron transfer on nanoscale metal structures :**

*Au, Pd etc clusters on oxides (*

**Stopping of ions on some meta & organic systems (col. J.Valdes)**

**Negative ion formation: search for efficient yield surfaces (ANR  
ITER-NIS)**

## *Molecular self assembly, nanoparticles, interfaces*

**Self assembly of molecules**

**Growth of metals on SAMs by UHV evaporation**

**Metal nanoparticles on SAMs**

**Growth modes & Electronic structure**

## Collaborations

**Pr. O.Grizzi**, Centro Atomico Bariloche, Argentine (ECOS-Secyt,...)

**Pr. M.Canepa**, Universita di Genova, Italie

**Pr. S.Nannarone**, Université de Modena, Italie

**Pr. R.C.Monreal**, Universidad Autonoma de Madrid, Espagne

**Pr. J.Valdes**, Université de Valparaiso, Chile (ECOS-Sud -Conycit)

**Pr. Y.Yamazaki**, RIKEN institute, Tokyo, Japon

**Pr. E.Goldberg**, Universidad de Santa Fe, Argentine

**Pr. S.Sampath**, Indian Institute of Science, Bangalore, Inde, (ARCUS)

**Pr. G.Kulkarni**, J. Nehru Center for Advanced Scientific Research, Bangalore, Inde (ARCUS)

**Pr. C.S.Bhatia**: SNU, Singapore

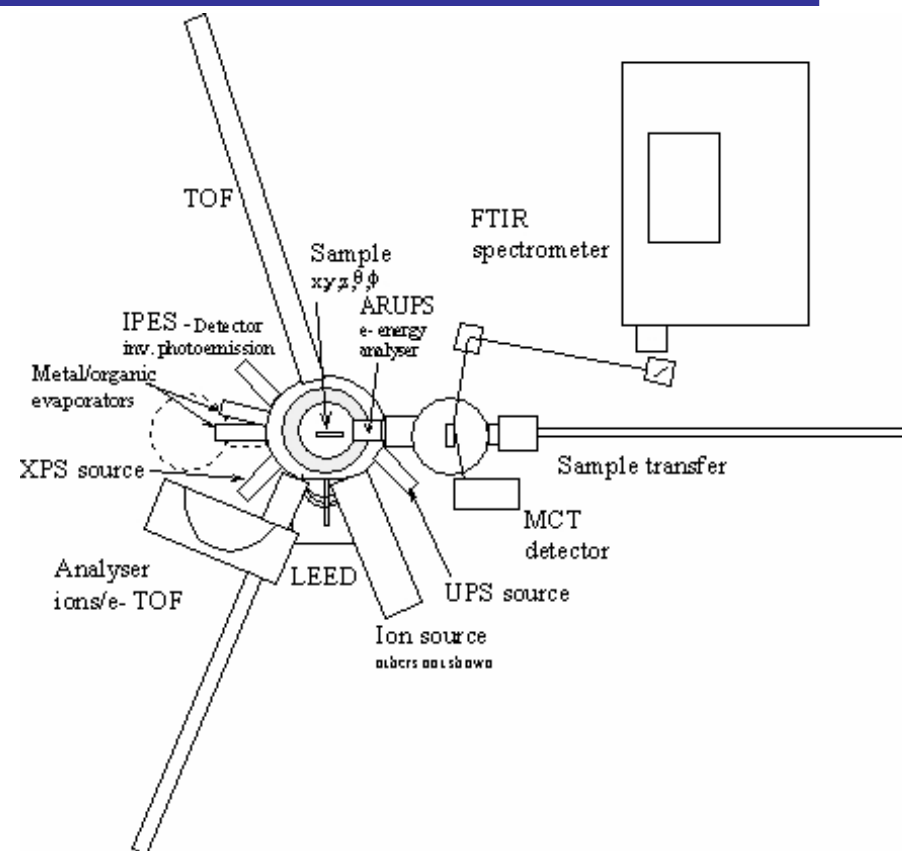
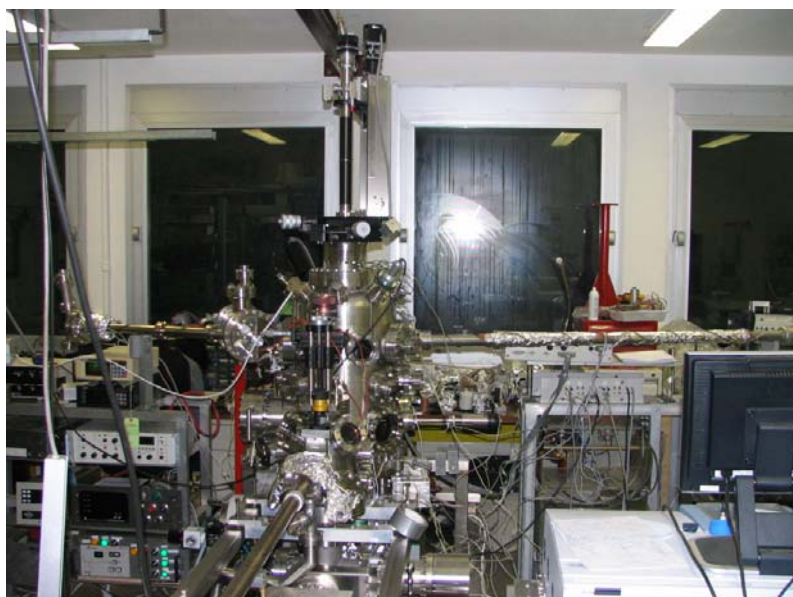
**LCAM**: JP Gauyacq, A.Borissov,

**LPPM**: B.Bourguignon et al SFG experiments

**Pr. P.Cortona**, Ecole Centrale, Palaiseau

**ANR – ITER-NIS (A.Simonin)**

# The Laboratory



*Ion scattering, TOF, AES, LEED, RAIRS (FTIR spectrometer Vertex 70), IPES, ARUPS, metal & organic molecule evaporators*

*Chem lab: Electrochemistry, Controlled atmosphere glove box, Chem hood ...*

## Some illustrations

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● How is electron transfer affected by the presence of adsorbates or on mixed surfaces. Are these “localised” effects

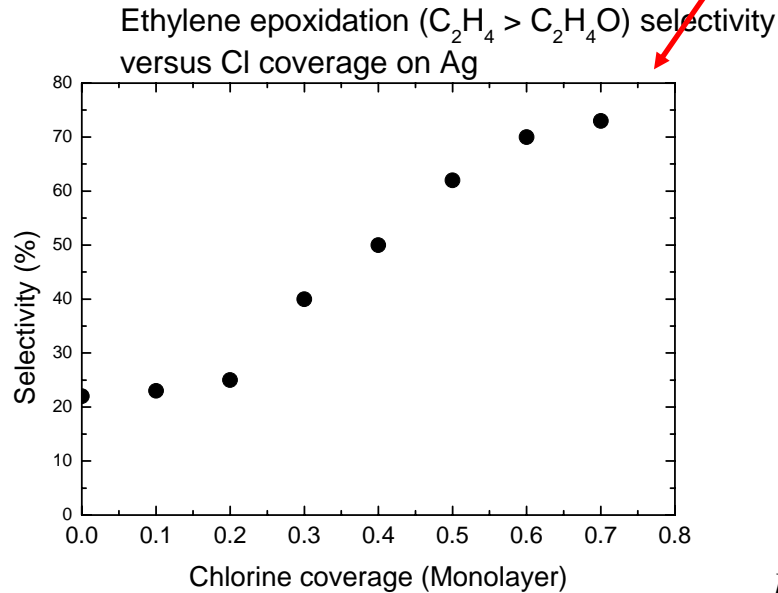
*illustration : F- on Cl covered Ag*

● How are electron transfer processes affected by nanoparticle size (see catalysis)

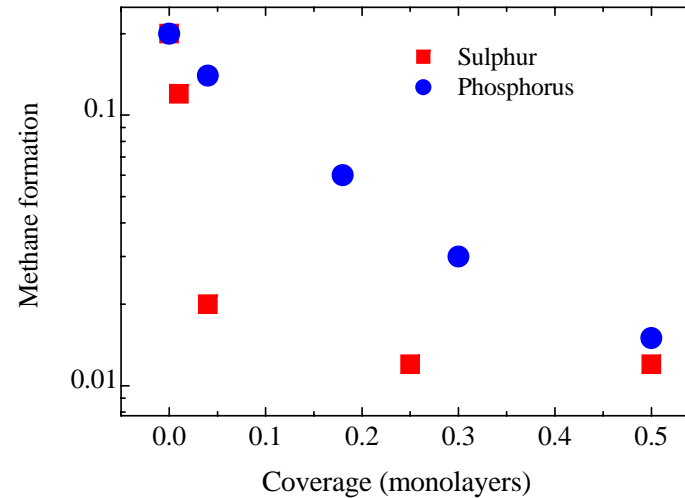
*illustration : Li+ neutralisation on Ag, Au clusters on TiO<sub>2</sub>*

● Ion stopping on surfaces: H<sup>+</sup> scattering on Ag(110)

# Adsorbate effects : promotion or poisoning of reactions at surfaces



Methane formation as a function of S or P coverage



*From R.Lambert ; D.W.Goodman*

What are these effects due to ? Site occupation, workfunction change, electronic structure changes ....

How are electron transfer processes affected at or close to an adsorbate ?

*Induced density of states on Al(111)*

*Electron density*

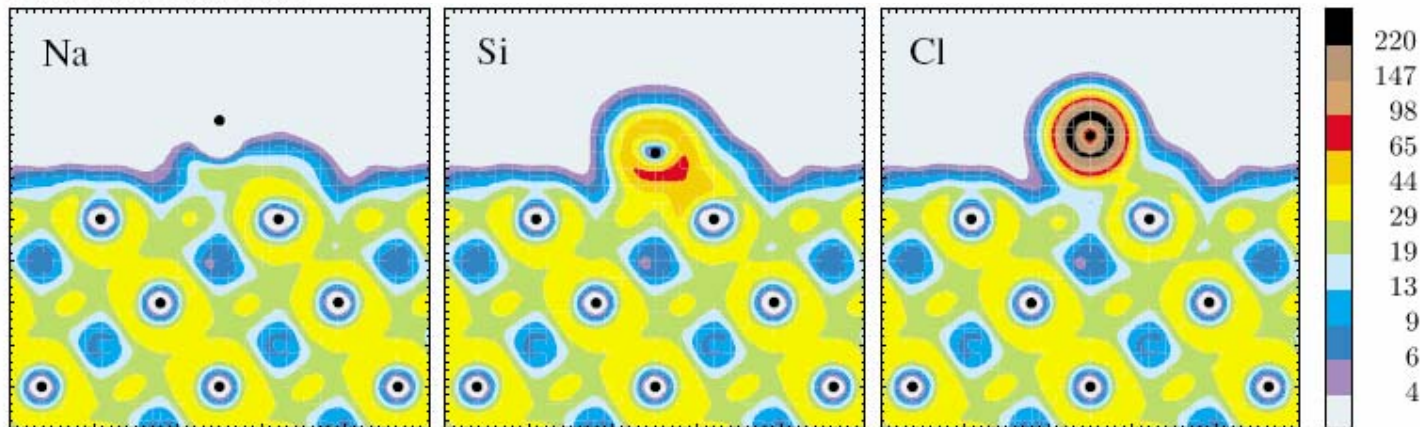
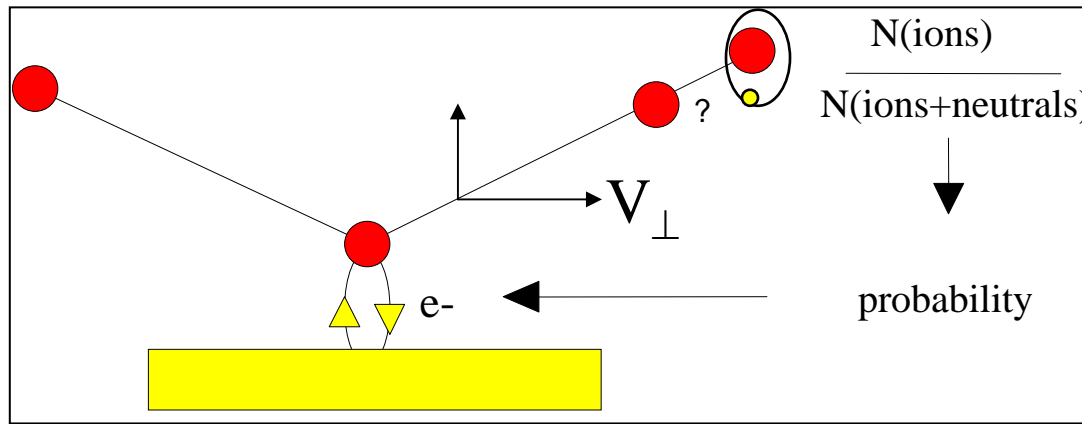


Figure 5.13: Electron density (valence only), cf. Eq. (5.3), for three different adatoms (groups I, IV, and VII of the periodic table) on an Al(111) substrate. We display a cut along the  $(1\bar{1}0)$  plane, perpendicular to the surface. The results are from Bormet et al. (1994a).

# Ion scattering.

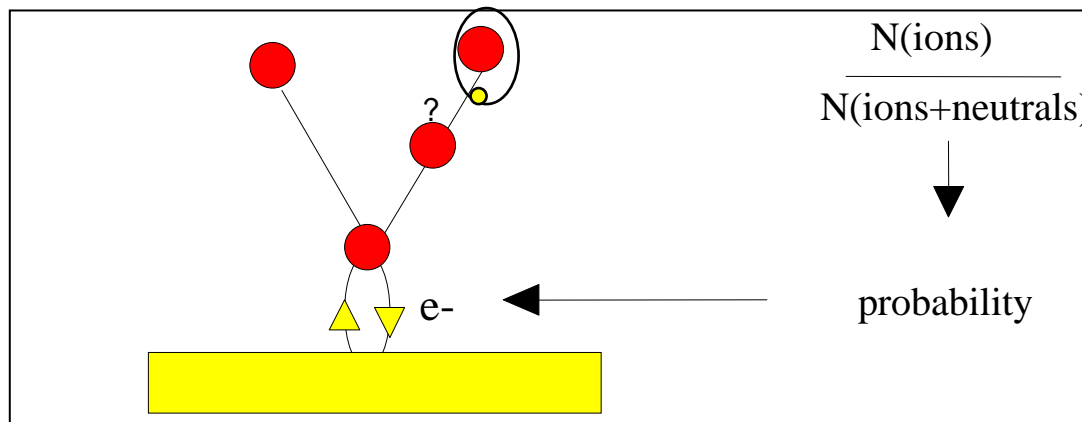
## Scattering configurations



### *Grazing scattering*

#### *Averaged view*

*High ion energy but  
small « perpendicular »  
energy*



### *Large angle scattering*

#### *Localised view – atomically selective*

*Relatively higher  
energies*



# Effect of Cl<sub>2</sub> on F<sup>-</sup> formation on Ag(111)

*Grazing scattering*

*Average over all surface*

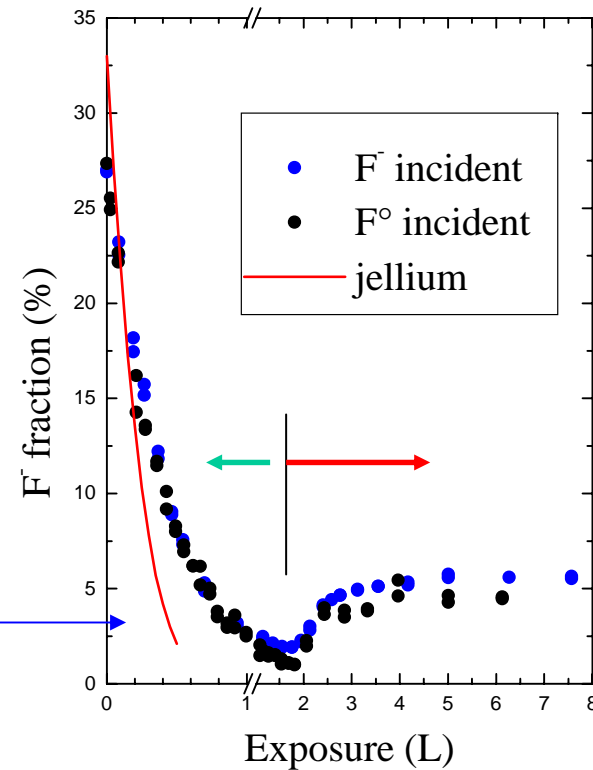
Strong **decrease** in ion fraction for submonolayer (<1.5L) coverage.

Increase at higher coverage corresponding to halide formation

*Less negative ion formation in presence of chlorine.*

Anion fraction not reproduced in *jellium like* calculation including only workfunction changes

*Ion fraction as a function of chlorine coverage*



**Chemisorption Chloride !**

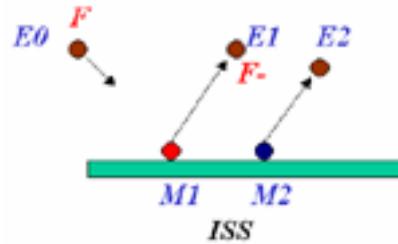
Casagrande et al Surf. Sci. L29, 445, 2000

See also in J.Chem.Phys 113, 2064, 2000

# « Local » versus « non local » effect ?

*Can one describe evrything in terms of a workfunction change ? Can fluorine capture an electron on the chemisorbed Cl ?*

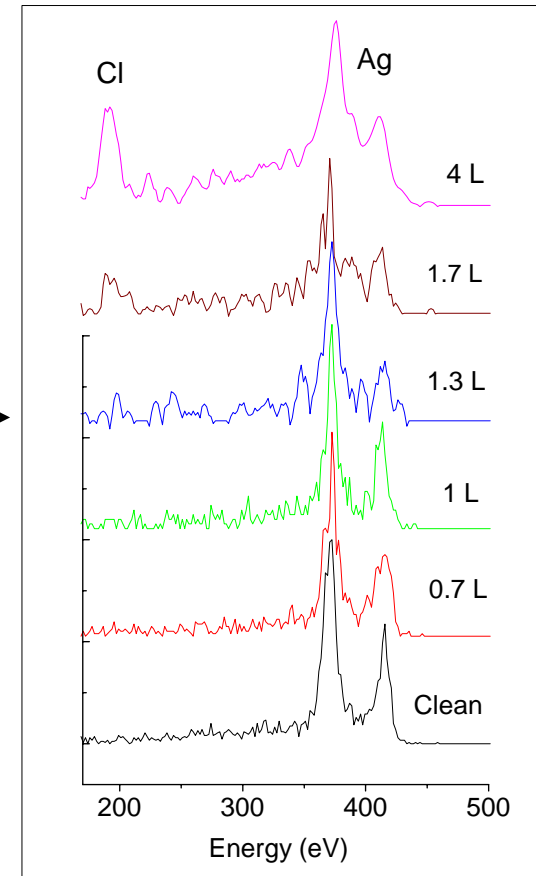
F<sup>-</sup> ISS



F<sup>-</sup> is observed on Cl for AgCl

F<sup>-</sup> *not* observed on chemisorbed Cl (<1.5L)

Chemical environment (*adsorbate/halide*) effects.



# Nanostructures

CO oxidation turnover frequency on Au clusters on TiO<sub>2</sub> – cluster size dependence ( *D.W. Goodman 2002* )

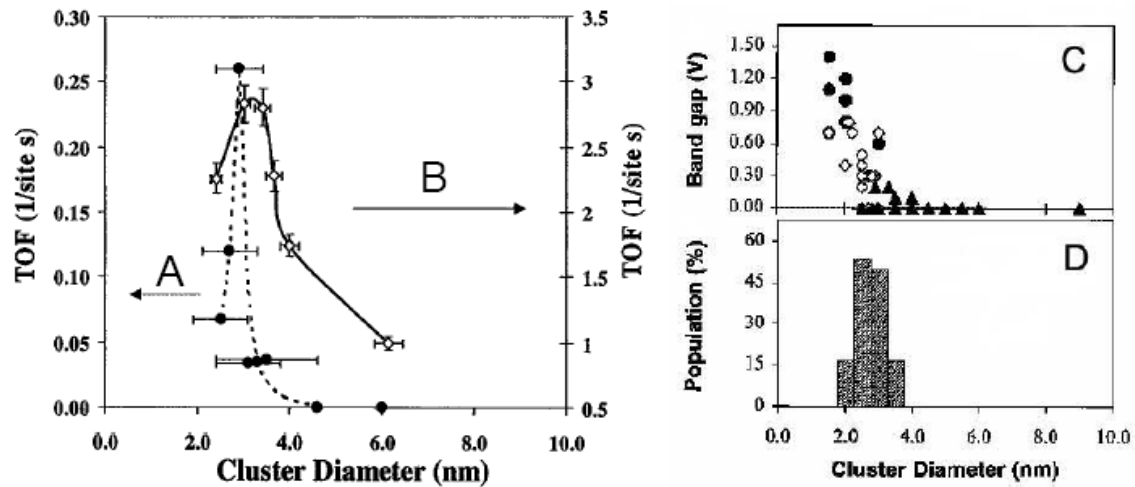
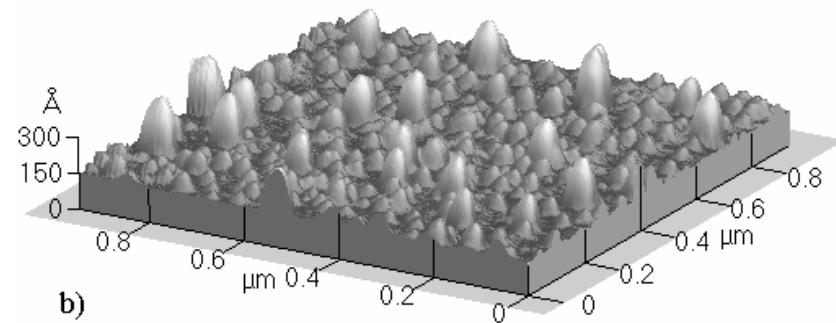
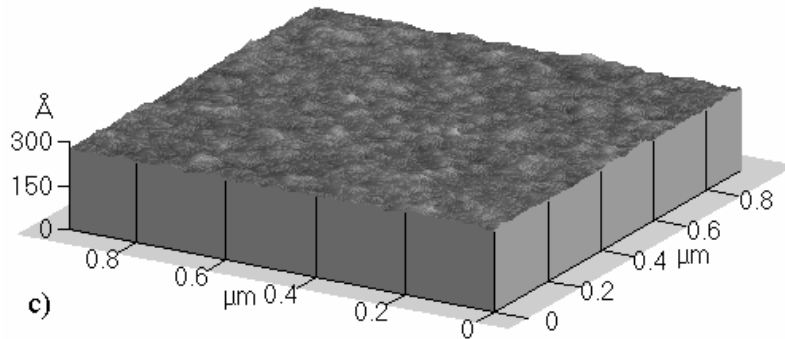


Figure 1: CO oxidation turnover frequency as a function of the Au cluster size supported on TiO<sub>2</sub>: (A) The Au/TiO<sub>2</sub> catalysts were prepared by a precipitation method. (B) The Au/TiO<sub>2</sub> catalysts were prepared by vapor deposition of Au on planar TiO<sub>2</sub> films on Mo(100), where TOF stands for turnover frequency. (C) Cluster band gap measured by STS as a function of the Au cluster size. (●) Two-dimensional (2D) clusters; (○) 3D clusters, two atom layers in height; (▲) 3D clusters with three atom layers or greater in height. (D) Relative population of the Au clusters (two atom layers in height) that exhibited a band gap of 0.2 to 0.6 V as measured by STS. Source: Santra and Goodman (2002).

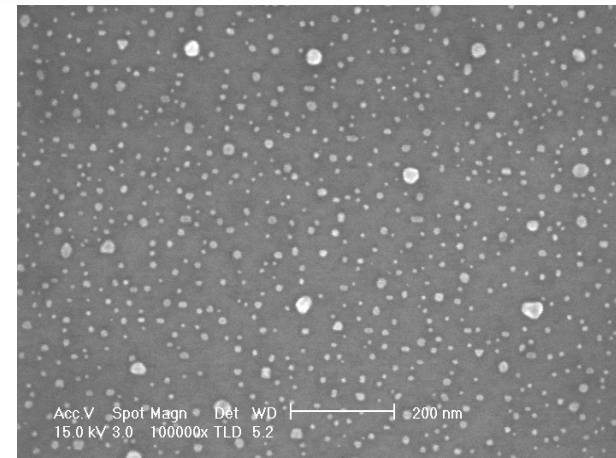
# Li<sup>+</sup> neutralisation on Ag & Au clusters

## *Growth by UHV evaporation*



*Clean surface AFM image*

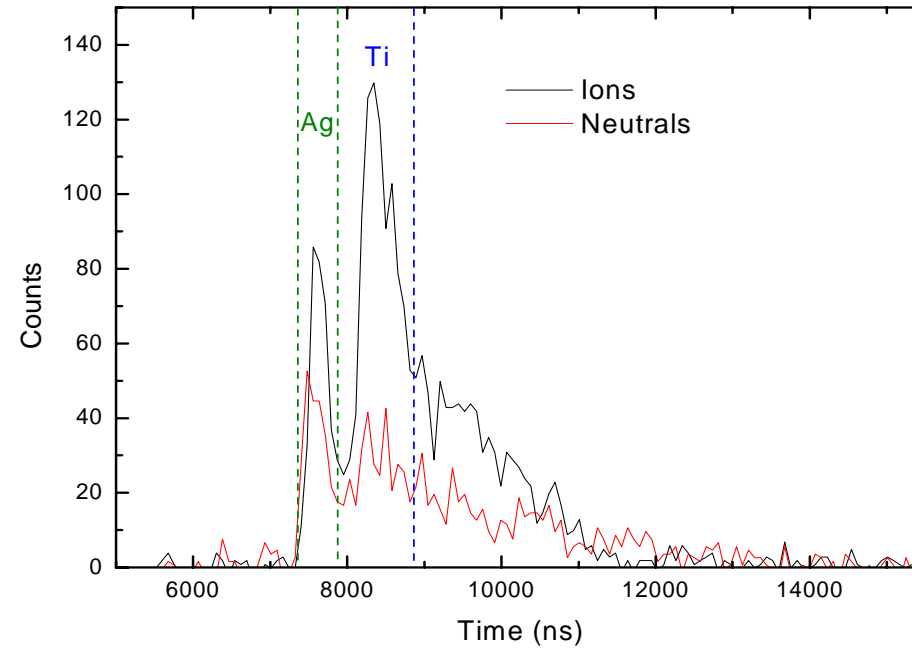
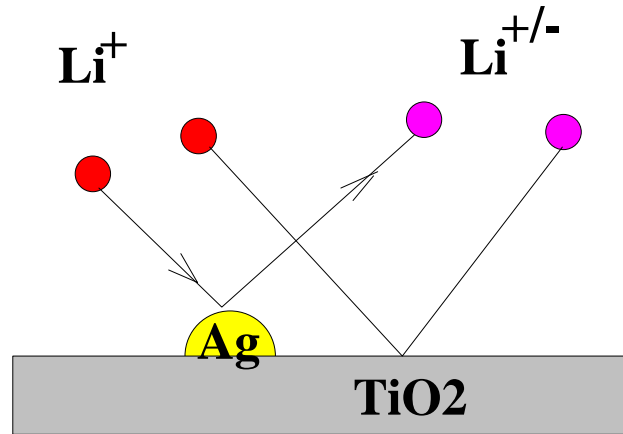
*SEM and AFM images of the TiO<sub>2</sub> with a 0.6 eqML coverage of Ag.*



*Ag cluster sizes varied between about 5nm and 20nm, depending upon evaporation rate.*

*Canario et al Surface Science 547, L887, 2003*

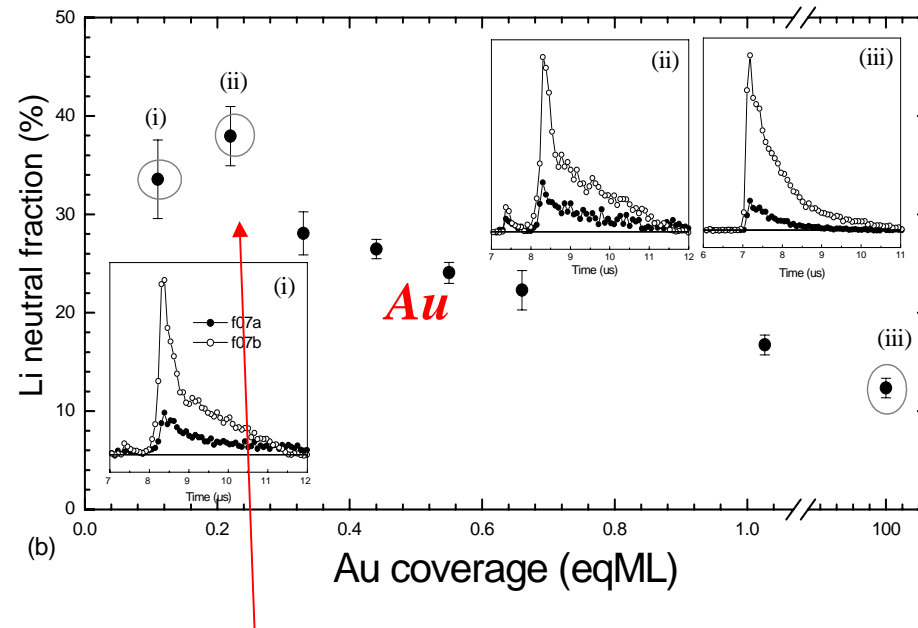
# Li neutralisation



*Time of flight spectra of ions and neutrals used for determining the neutral fraction.*

# Ag & Au clusters on TiO<sub>2</sub>

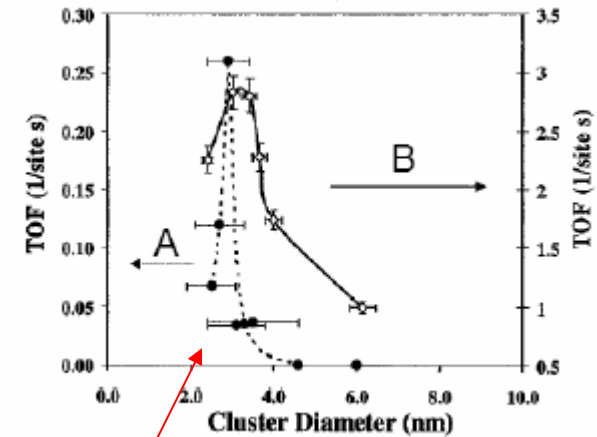
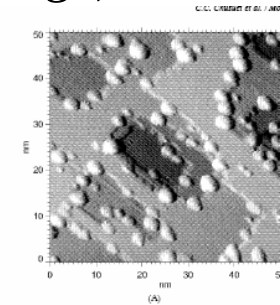
*Li<sup>+</sup> neutralisation : Cluster size dependence (coverage).*



*Goodman*

*Au/TiO<sub>2</sub>*

*CO oxidation*



*Larger neutralisation probability for very small clusters (size between 2-5 nm) same as for catalyst*

## Possible reasons.

1. *Workfunction effect.*
2. *Charging effects – clusters have a charge on TiO<sub>2</sub> (??).*

### 3. *Electronic structure changes.*

*Metallic like clusters may have different electronic structure (surface states etc) than the bulk crystals.*

*In case of smallest non-metallic clusters probably a « more « molecular » model (HOMO-LUMO) should be envisaged*

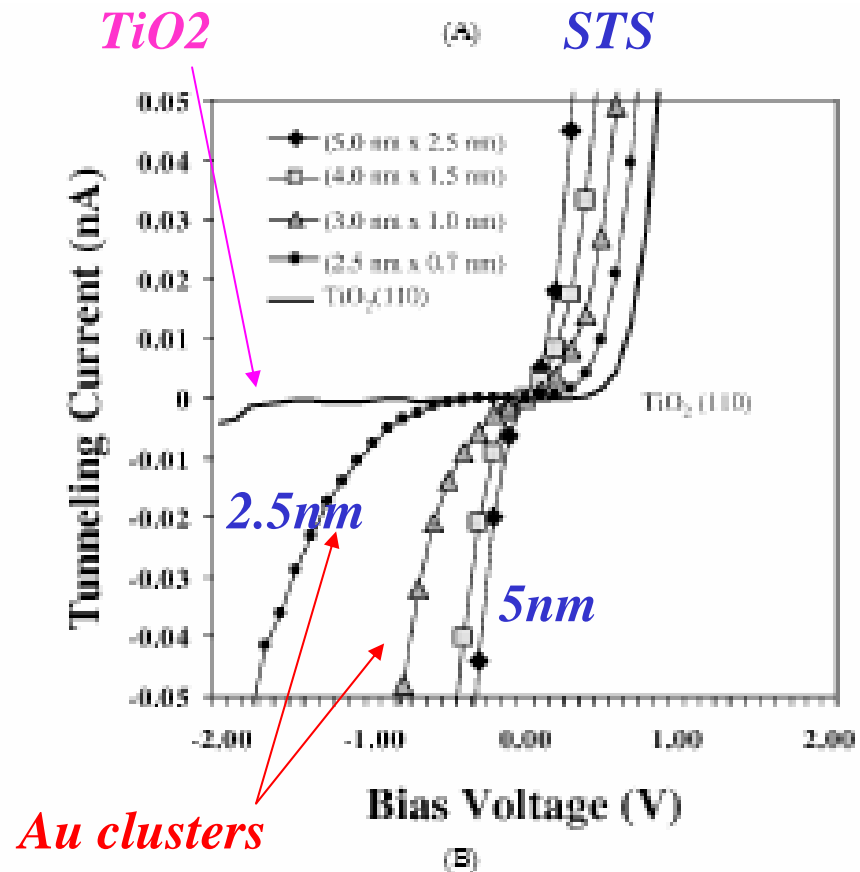


Figure 1. (A) A CCT-STM image of a 0.25 ML Au deposited onto TiO<sub>2</sub>(110)-(1x1) prepared just prior to a CO:O<sub>2</sub> reaction. The sample had been annealed to 830 K for 2 min; (B) STS data acquired for Au clusters of varying sizes on the TiO<sub>2</sub>(110)-(1x1). An STS of the TiO<sub>2</sub> substrate, having a wider band gap than the Au clusters, is also shown as a point of reference.

*Goodman et al*

*Topics in Catalysis Vol. 14, No. 1-4, 2001*

## *Newer projects*

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*Study of organic molecule self assembly on surfaces (FTIR-RAIRS, synchrotron photoemission, ellipsometry, electrochemistry): dithiols, BDMT, EP-PTCDI*

*SAMS as model systems for ion induced damage*

*Metal/nanoparticle deposition on selfassembled organic layers as a way to create metal contacts in molecular electronic devices*

*Assemble « ordered » metallic (magnetic) nanoparticle arrays for plasmonics or magnetic memory applications*

*Collaborations: Argentina, Italy, India, Japan*



# *Molecular self assembly*

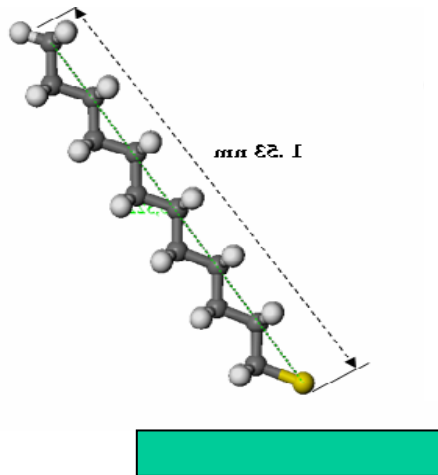
*Experiments by Nuzzo & Allara 1985 on assembly of alkanethiols*



*Make eg an ethanolic solution of these ...  
immerse a gold plate ... and ...*

*obtain a well ordered standing layer of these  
molecules*

*Today a lot of applications : corrosion  
protection, sensors, molecular electronics ...*



*Sounds simple... but ...*

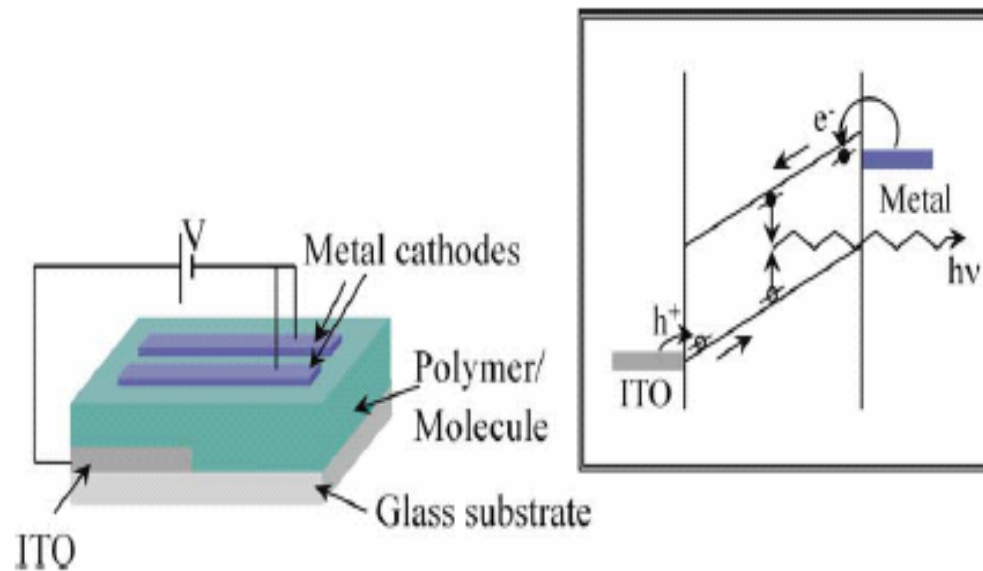
*Questions ?*

*- Assembly conditions, types of ordered structures, effect of solvents, growth from vapour phase, stability etc.*

*- Order in monolayer-multilayer assembly (interesting in some molecular electronics applications for electron transport)*

***Molecular electronics :***

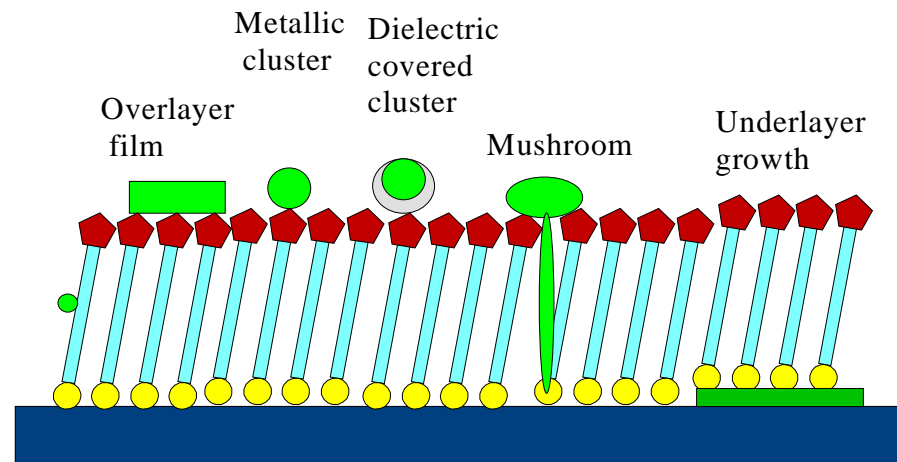
***An active organic layer between two electrodes ( like a light emitting diodes)***



***An important question : how to make an electric contact ?***

*How does a metal « sit » on an organic film ? What happens when you evaporate a metal onto an organic layer ?*

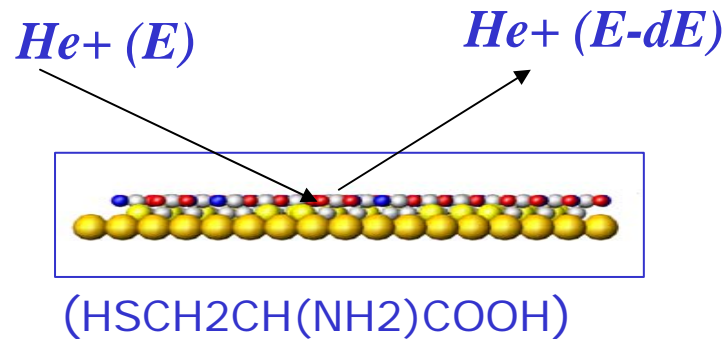
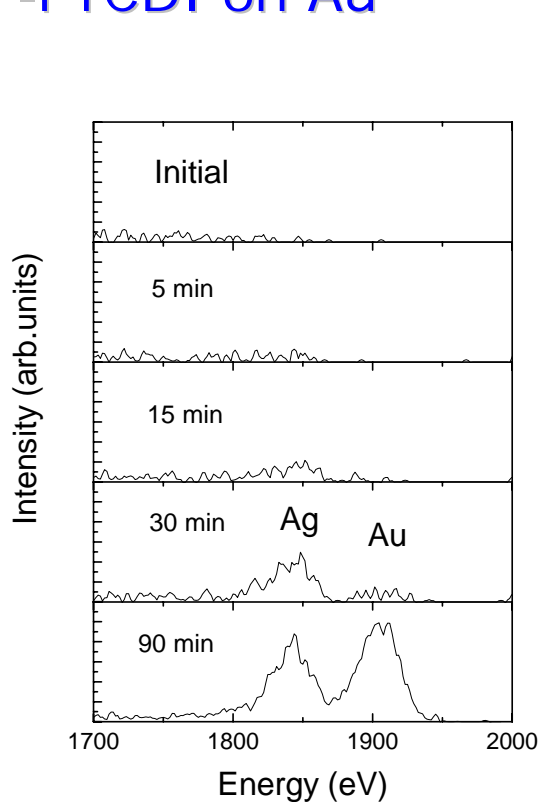
*What type of interface do you get ?*



**Self assembled organic monolayers** : Nice model systems allowing good control of the type of endgroup at the vacuum interface.

A possibility : first stick metallic nanoparticles as a buffer layer

# Metal deposition on self assembled organic monolayers: Ag evaporation onto L-Cysteine-& EP-PTCDI on Au



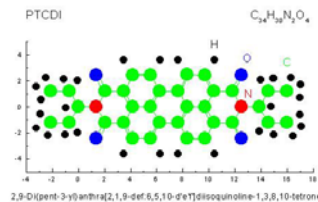
**ISS spectra :**

He<sup>+</sup> backscattering on Ag atoms not observed initially.

First Ag appears, followed by appearance of Au substrate

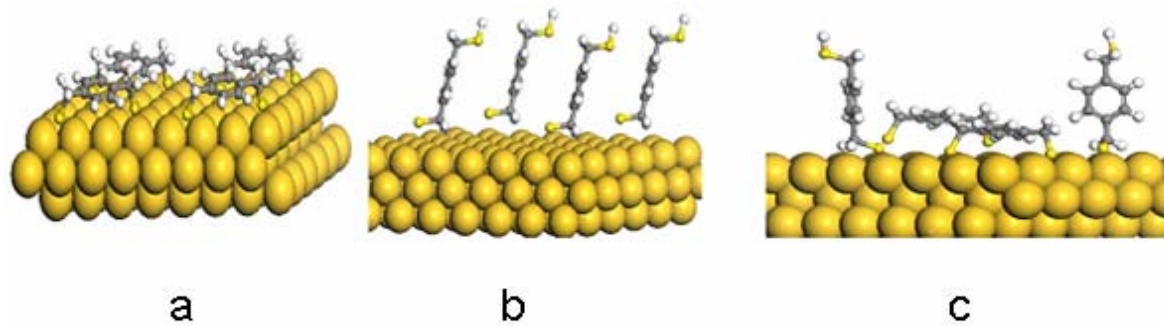
***Metal percolates through SAM layer – no on top film***

***Also on EP-PTCDI***



## 2. Assembly of dithiols on gold

*Dithiol: alkane HS-(CH<sub>2</sub>)<sub>n</sub>-SH or benzene HS-CH<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>)-CH<sub>2</sub>-SH*



*Various possibilities :*

- lying down with both thiol ends attached to surface*
- standing up*
- mixed situation*
- Very controversial in existing literature*

*Question : why would one go from a lying down phase to a standing up one ?*

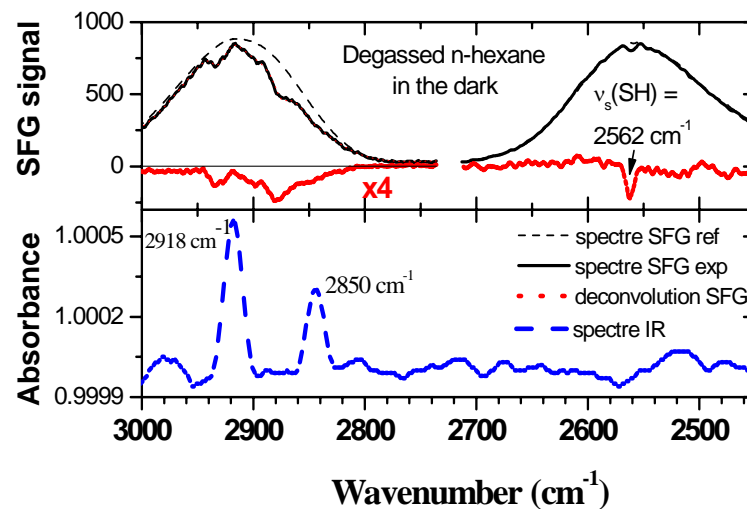
## *Solvent & preparation procedures....*

*(LCAM, LPPM = Orsay + Genova collaboration)*

*Assembly from ethanol : disordred layers*

*Assembly from degassed n-hexane in absence of light: good order*

*RAIRS :Reflection adsorption infrared spectroscopy to detemine order From characteristic positions of peaks in vibrational spectra*



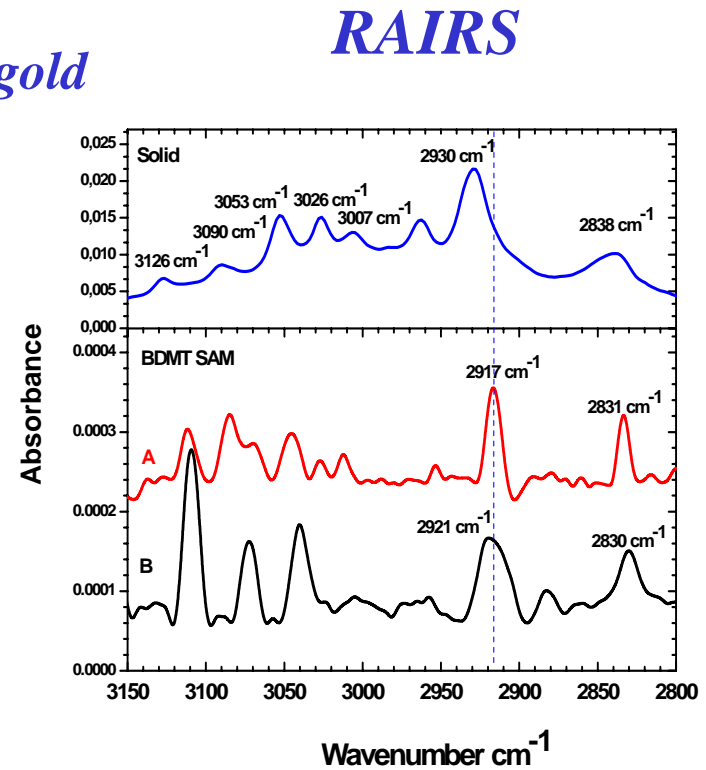
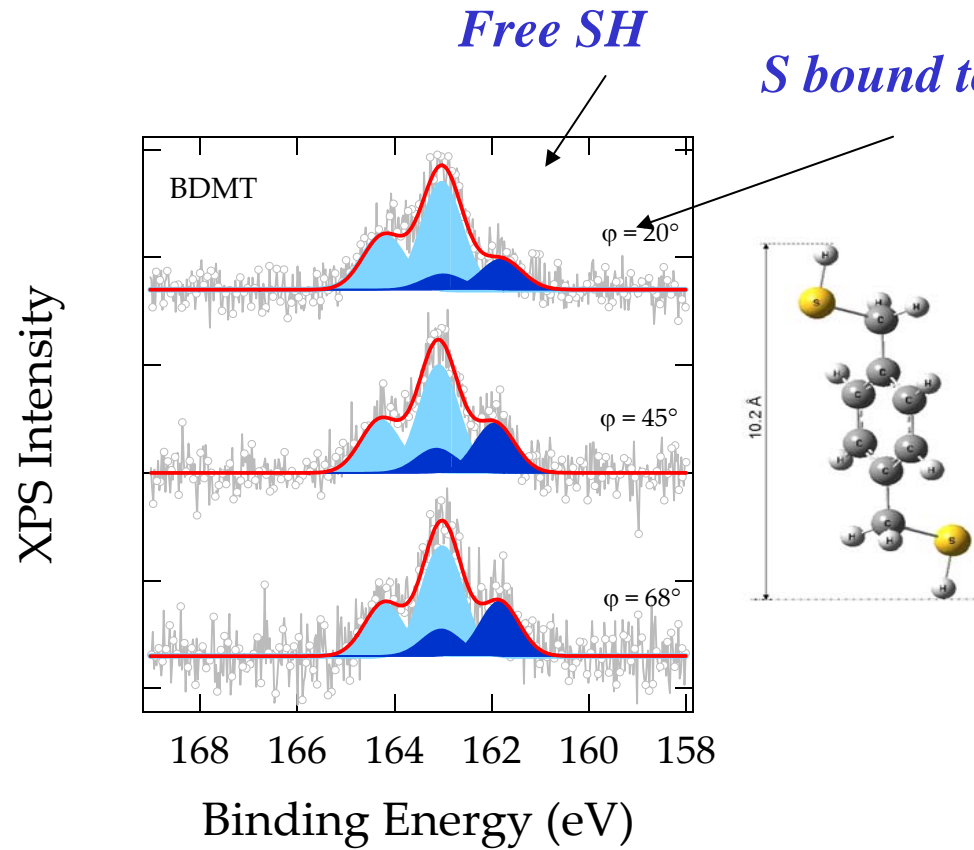
*SFG*

*RAIRS*

*SFG (LPPM) - Sum frequency generation to identify some specific features like presence of free SH groups*

*Spectroscopic Ellipsometry : circa 1nm layer for C9DT*

***BDMT (HS-CH<sub>2</sub>-(C<sub>6</sub>H<sub>4</sub>)-CH<sub>2</sub>-SH) :***



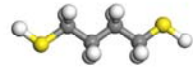
*Standing up molecules*

*XPS : X ray photoelectron spectroscopy (Genova)*



*Question : why would one go from a lying down phase to a standing up one ?*

*Possible reaction : Hydrogen exchange*



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## *Ongoing & Next experiments*

*-Attach metal (Ag) nanoparticles to our dithiol SAMs as a way to create a metal contact*

*-Use dithiols to bind to metal nanoparticles to create ordered structures with variable interparticle distances*

*-- Study other types of SAMs with donor-spacer-acceptor molecular combinations (growth modes & electronic structure)*

*Thank you*