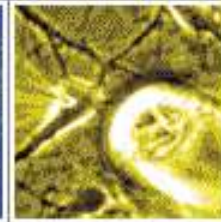




Nanostructured Interfaces and Surfaces
Centre of Excellence



Università di Torino

International Summer School for young scientists

Nanotechnology: from fundamental research to innovations

August 26 - September 2, 2012, Bukovel, Ukraine

Raman Lab at "NIS-Centro dell'Innovazione"
in Torino

Alessandro Damin

Advances in Resonant Raman and SERS
for surface characterization





The University of Torino in brief



- The oldest among the four Piedmont Universities (established in 1404)
- 13 Faculties (in the fields of Humanities, Social Sciences, Medicine and Life Sciences, Science)
- 9 Interfaculty Schools (e.g. Biotechnology)
- 1 School for Advanced Studies
- approx 70.000 students, approx 2.200 Faculty staff



distinguished students:
Nobel laureates in Medicine
R. Dulbecco and R. Levi-Montalcini



The Research System

- 35 Departments (15 in Science and Technology)
- 4 PhD Schools (2 in S&T, 25% foreign students)
- in 2009: 1350 PhD students, 600 Post Docs,
700 technicians
- Overall funding: approx. 73 M€
- 3 National Centres of Excellence:
 - *Molecular Imaging*
 - *CEBIOVEM (Plant and Microbial Biosensing)*
 - *NIS (Nanostructured Interfaces and surfaces)*

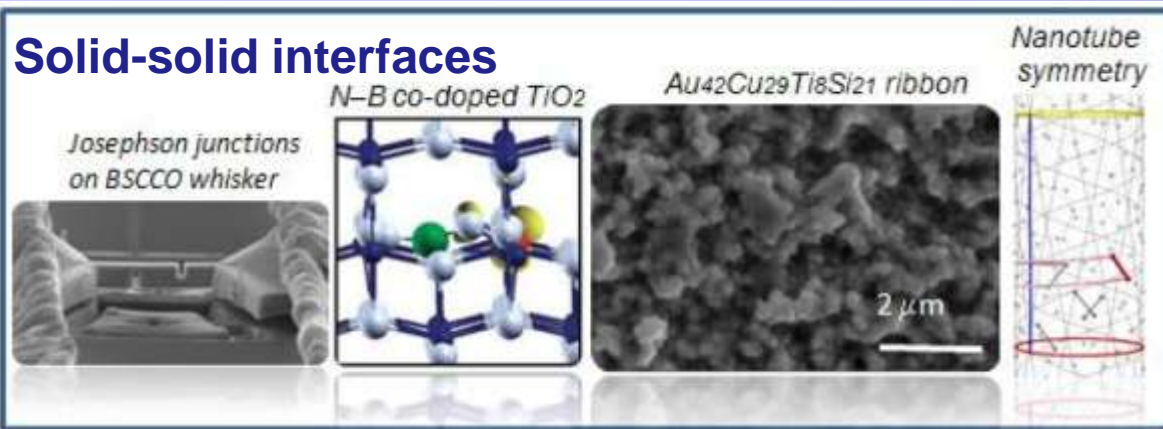
Research in Nanoscience and Nanotechnology



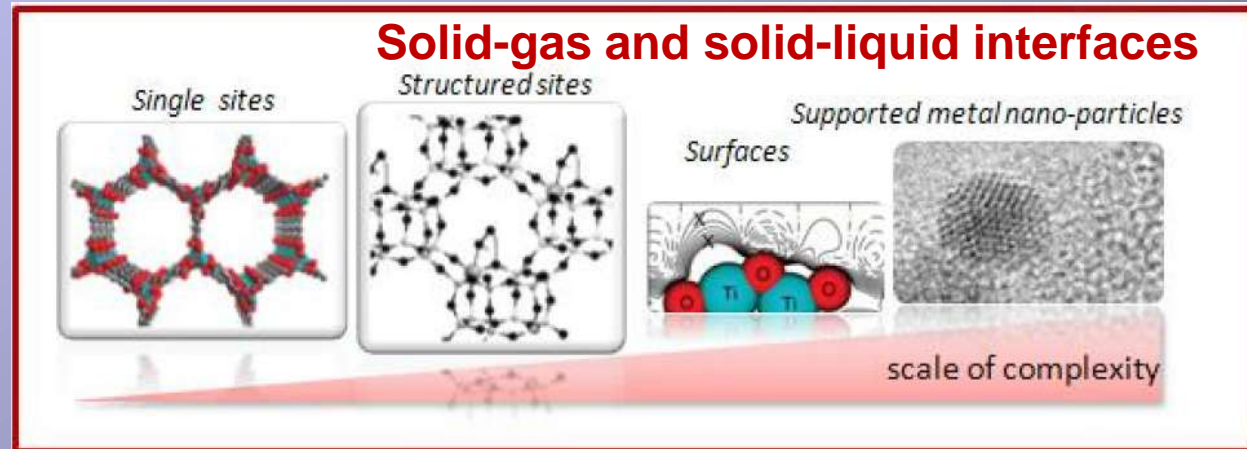
The “Nanostructured Interfaces and surfaces” (NIS) Centre of Excellence (Est. 2003)

- Inter-disciplinary character: Physics, Chemistry,
Biology, Neuroscience
- 80 permanent researchers, approx 60 young researchers
- supports departmental laboratories and manages common interdisciplinary laboratories

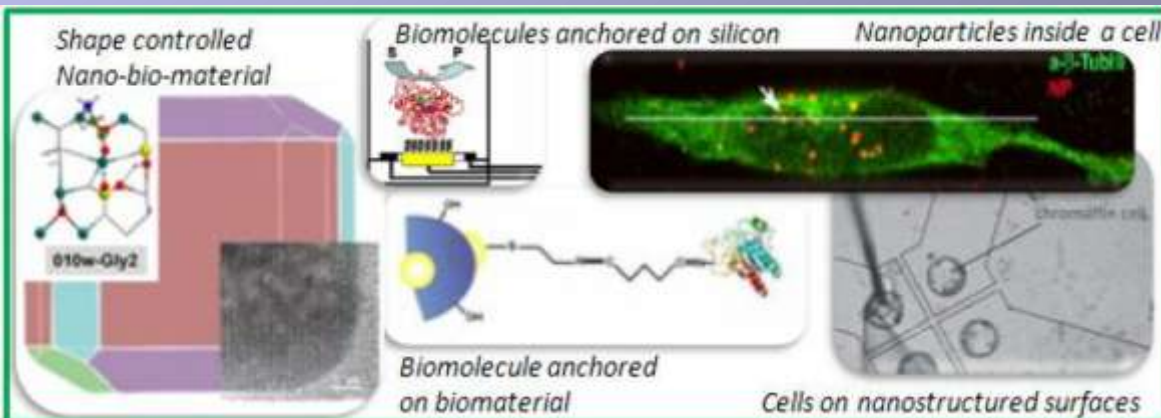
Solid-solid interfaces



Solid-gas and solid-liquid interfaces



Nanobiointerfaces



785 nm

514 nm



442 nm

325 nm



244 nm



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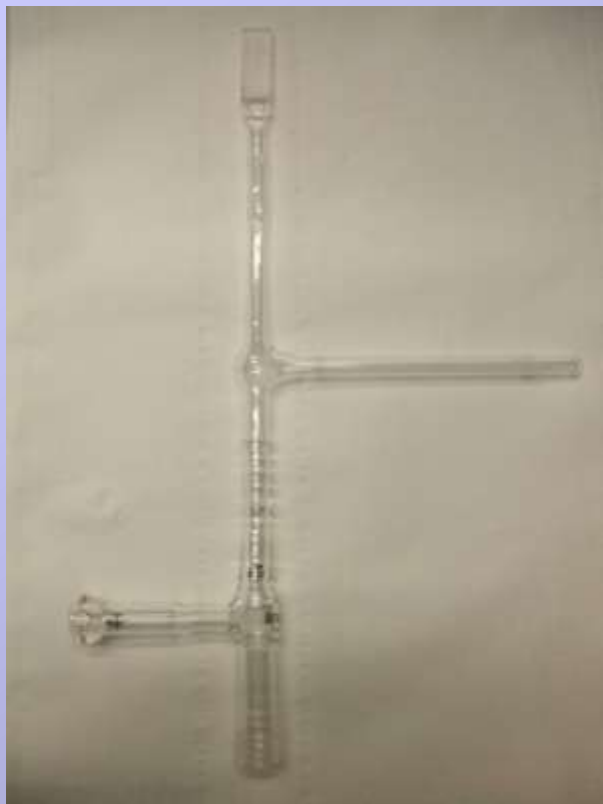
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C. Bianco *et al.*, Penetration of Ag nano-particles in human skin, in progress.

Measurements on activated samples and in controlled atmosphere



E. Groppo *et al.*, New strategies in the Raman study of Cr/SiO₂ Phillips catalyst: observation of molecular adducts on Cr(II) sites, *Chem. Mater.* **2005**, 17, 2019-2027.

F. Bonino *et al.*, Vibrational properties of Cr(II) centres on reduced Phillips catalyst highlighted by resonant Raman spectroscopy, *Chem. Phys. Chem.* **2006**, 7, 342-344.

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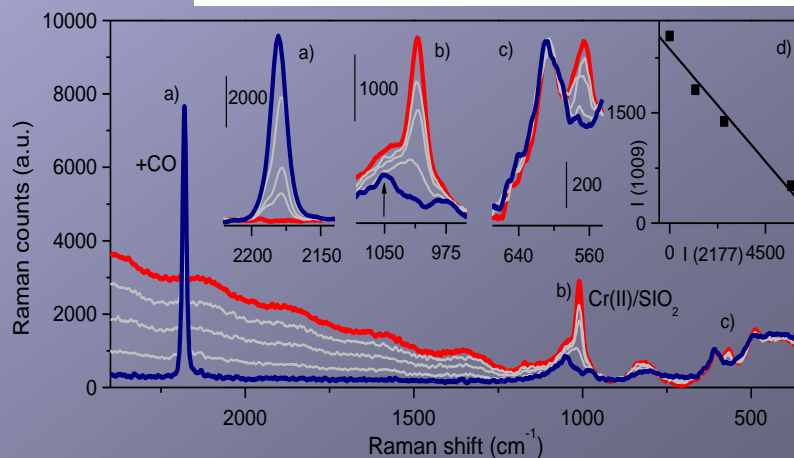
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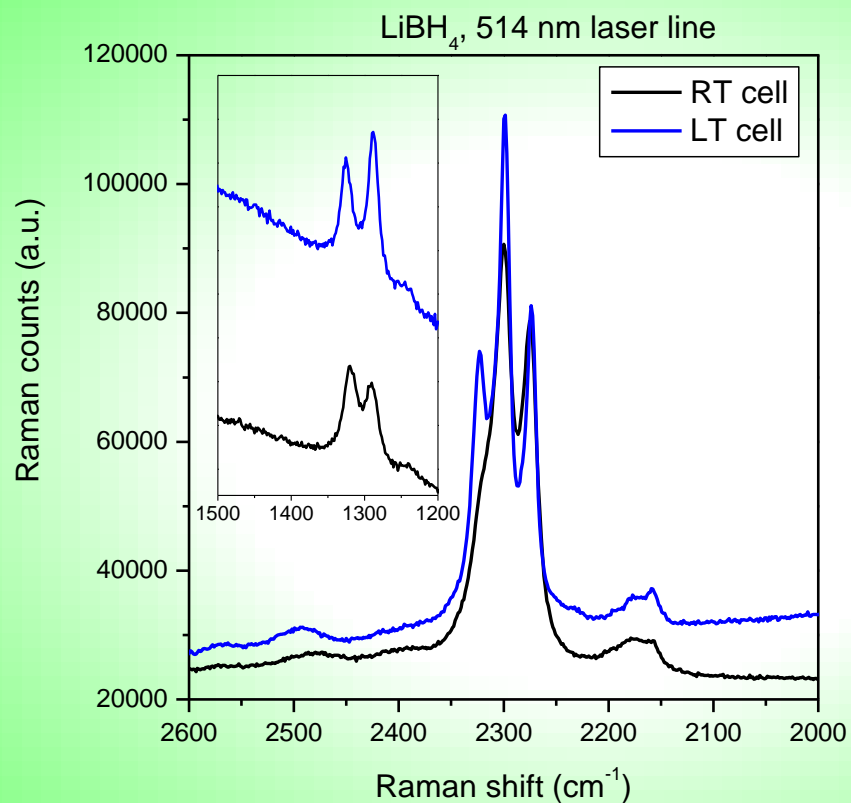
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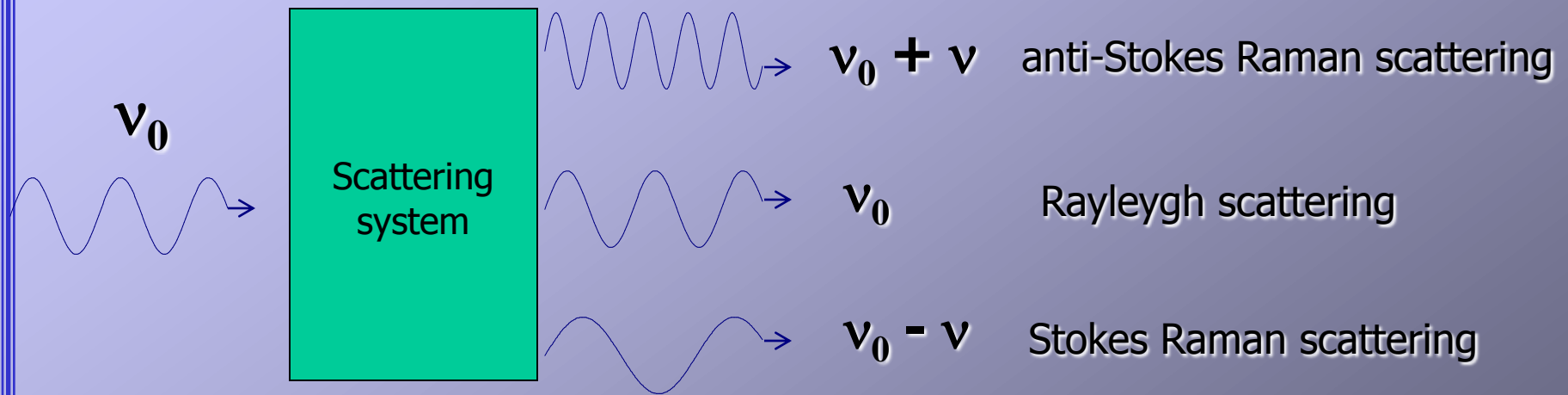


Raman study of Phillips catalyst and its interaction with CO

Measurements at LT on activated samples and in controlled atmosphere



RAMAN spectroscopy is originated by the scattering of the light (electromagnetic wave, EMW) by a system containing electrons, *e.g.* a molecule. In the scattering process the electrons of the system are interacting with the oscillating electric vector of EMW and are forced to oscillate, becoming new emitting sources of EMW, that is the scattered light. Experimentally, three type of EMW are observed to overcome:



From experiments,
the scattering
efficiency is
proportional to ν_0^4

Which is the origin of
the Raman scattering?

A classical view

If a **molecule interacts with an EMW**, the oscillating electric field of photons will exert oppositely directed forces on the electrons and the nuclei, **inducing an electric dipole moment**. The induced dipole moment is **proportional to the electric field** and to a **property of the molecule** called the **polarizability** α (tensor):

$$\bar{\mu} = \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} \text{ induced dipole}$$

$$\bar{\mu} = \alpha \bar{E}$$

$$\bar{E} = \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \text{ electric vector of the incident EMW}$$

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \text{ polarizability of the molecule}$$

Each component of the induced dipole can be obtained accordingly to:

$$\mu_\rho = \sum_{\sigma=x}^z \alpha_{\rho\sigma} E_\sigma$$

is an oscillating vector, each of its components
By considering that \overline{E} can be related to the ν_0 frequency of the incident EMW by the relation:

$$E_{\sigma} = E_{\sigma}^0 \cos 2\pi \nu_0 t$$

Consequently, the induced dipole is an oscillating vector also and each of its components can be now obtained by the relation:

$$\mu_{\rho} = \sum_{\sigma=x}^z \alpha_{\rho\sigma} E_{\sigma}^0 \cos 2\pi \nu_0 t$$

As like as an emitting radio-antenna of an AM station, **such oscillating dipole will emit EMW of ν_0 frequency**. For a simple case of a x polarized light and $\alpha_{\rho\sigma} = 0$ for $\rho \neq \sigma$, the induced dipole will have only the x component, defined as:

$$\mu_x = \alpha_{xx} E_x^0 \cos 2\pi \nu_0 t \longrightarrow \mu_x^0 = \alpha_{xx} E_x^0 \longrightarrow \mu_x = \mu_x^0 \cos 2\pi \nu_0 t$$

$$\overline{\mu} = \begin{pmatrix} \mu_x \\ 0 \\ 0 \end{pmatrix} \quad \mu = \mu_x$$

and the average intensity of the emitted EMW of ν_0 frequency can be defined as:

$$I(\theta)_{av} = \frac{(\mu_x^0)^2 \nu_0^4}{A r^2} \sin^2 \theta$$

θ is the angle between the induced dipole and the direction of propagation of the EMW

For a molecular system however $\alpha_{\rho\sigma}$ is **dependent** upon the **position of the nuclei**. So, **the 3N-6 (3N-5) vibrational modes have to be expected to induce a variation in this quantity**. For a diatomic molecule with the single normal coordinate Q_1 , the dependency of $\alpha_{\rho\sigma}$ on Q_1 is expressed as a series expansion:

$$\alpha_{\rho\sigma} = \alpha_{\rho\sigma}^0 + \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_1} \right)_0 Q_1 + \dots \quad \alpha_{\rho\sigma}^0 \text{ equilibrium value of the polarizability.}$$

The position of the nuclei is time dependent because the molecule is vibrating with frequency ν . This motion can be expressed as:

$$Q_1 = Q_1^0 \cos 2\pi\nu t \quad \text{where } Q_1^0 \text{ is the maximum vibrational amplitude}$$

So, $\alpha_{\rho\sigma}$ oscillates with the vibrational frequency ν also

By keeping only the first two terms of the series expansion, the components of the induced dipole can so be redefined as:

$$\mu_{\rho}(Q_1) = \sum_{\sigma=x}^z \alpha_{\rho\sigma}^0 E_{\sigma}^0 \cos 2\pi\nu_0 t + \frac{1}{2} \sum_{\sigma=x}^z E_{\sigma}^0 Q_1^0 \left(\frac{\partial \alpha_{\rho\sigma}}{\partial Q_1} \right)_0 \left[\cos 2\pi t(\nu_0 + \nu) + \cos 2\pi t(\nu_0 - \nu) \right]$$

Rayleigh

anti-Stokes Raman

Stokes Raman

If the incident EMW is polarized along the x direction and $\alpha_{\rho\sigma}=0$ for $\rho \neq \sigma$, then:

$$\mu_x(Q_1) = \alpha_{xx}^0 E_x^0 \cos 2\pi\nu_0 t + \frac{1}{2} E_x^0 Q_1^0 \left(\frac{\partial \alpha_{xx}}{\partial Q_1} \right)_0 \left[\cos 2\pi t(\nu_0 + \nu) + \cos 2\pi t(\nu_0 - \nu) \right]$$

Such oscillating induced dipole will emit 2 types of EMWs:

- a) Scattered EMW unshifted in frequency (Rayleigh scattering)
- b) Scattered EMW red-shifted (**Stokes**) and blue-shifted (**anti-Stokes**) of ν if vibration mode induce a variation in α_{xx} , i.e.

$$\left(\frac{\partial \alpha_{xx}}{\partial Q_1} \right)_0 \neq 0$$

For a given vibrational mode, the Raman scattering total intensity will be defined as:

$$I(\theta)_{av} = B(\nu_0 \pm \nu)^4 I_0 \left(\frac{\partial \alpha_{xx}}{\partial Q_1} \right)_0^2 \sin^2 \theta$$

I_0 is the intensity of the incident EMW

From the above reported relation, it clearly appears that:

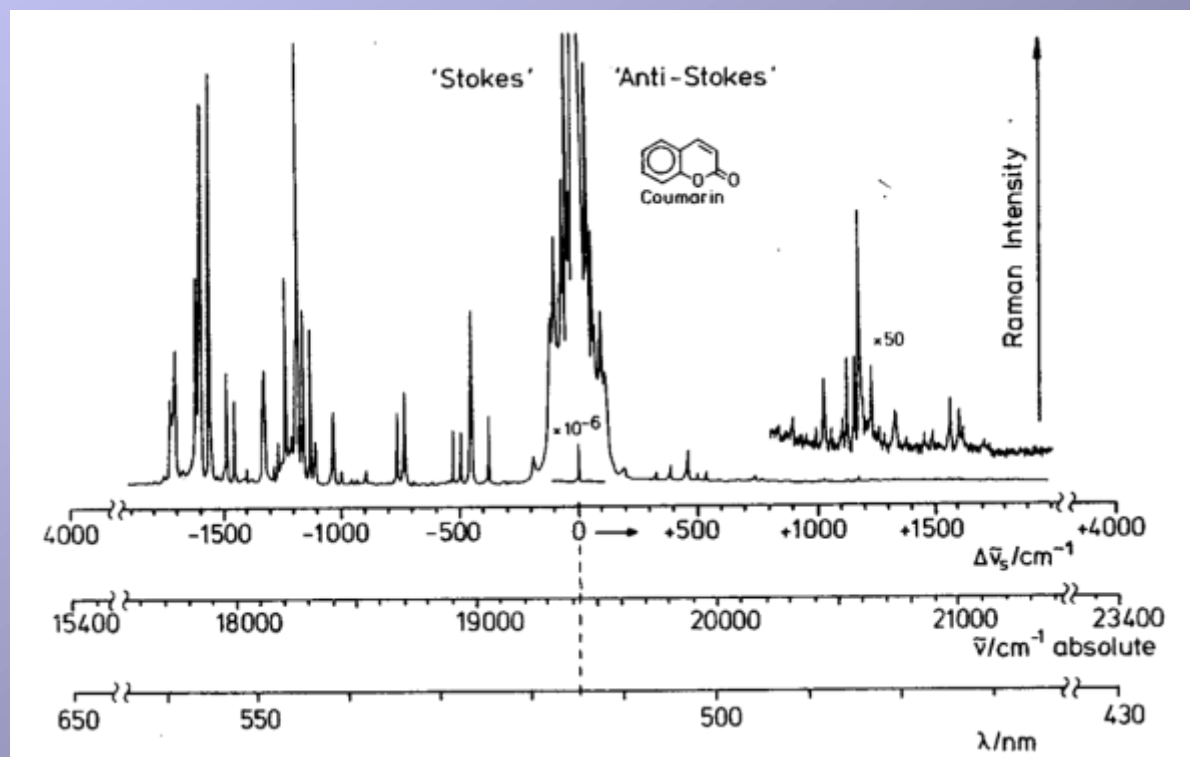
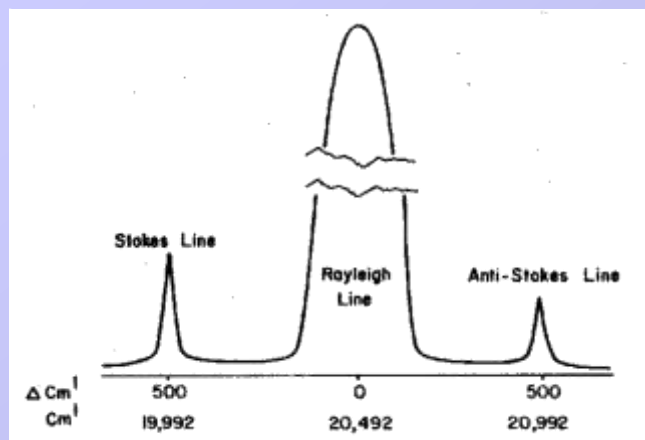
a) The Raman scattering intensity is proportional to

b) The Raman scattering intensity is proportional to the fourth power of $(\nu_0 \pm \nu)$

c) The intensity of the incident EMW

$$\left(\frac{\partial \alpha_{xx}}{\partial Q_1} \right)_0^2$$

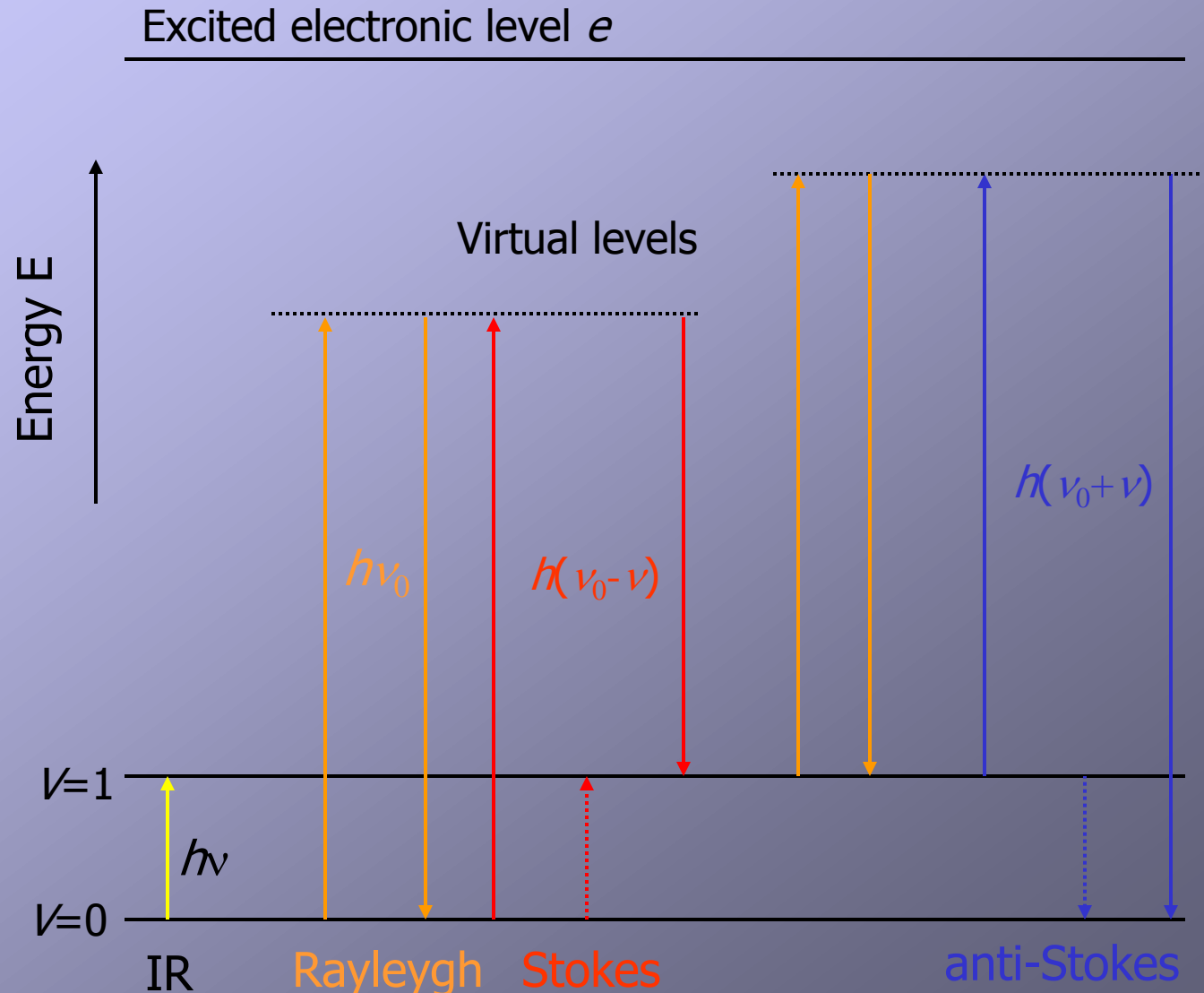
Experimental Raman spectra show that anti-Stokes signals are less intense than the Stokes ones. This observation is not properly taken into account from the classical description.



Quantum-mechanical description of the Raman scattering

The quantum-mechanical description of the scattering process of a EMW with ν_{exc} frequency by a molecule can be schematized as follows:

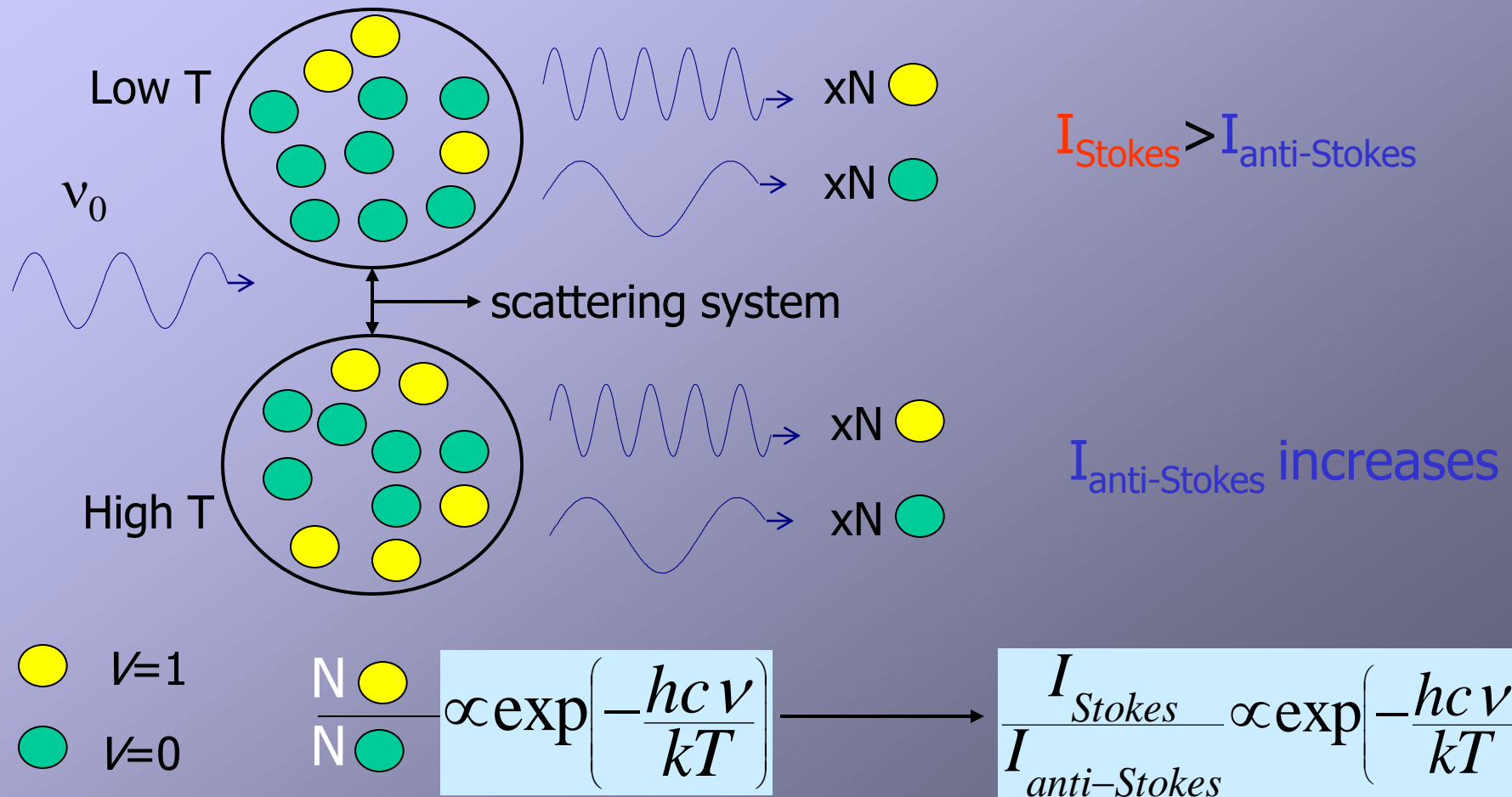
In this case
 $\hbar\nu_{\text{exc}} \neq E_e - E_g$



The final effect of the Raman scattering is a **transition between the vibrational levels ν of the electronic ground state** of the molecule

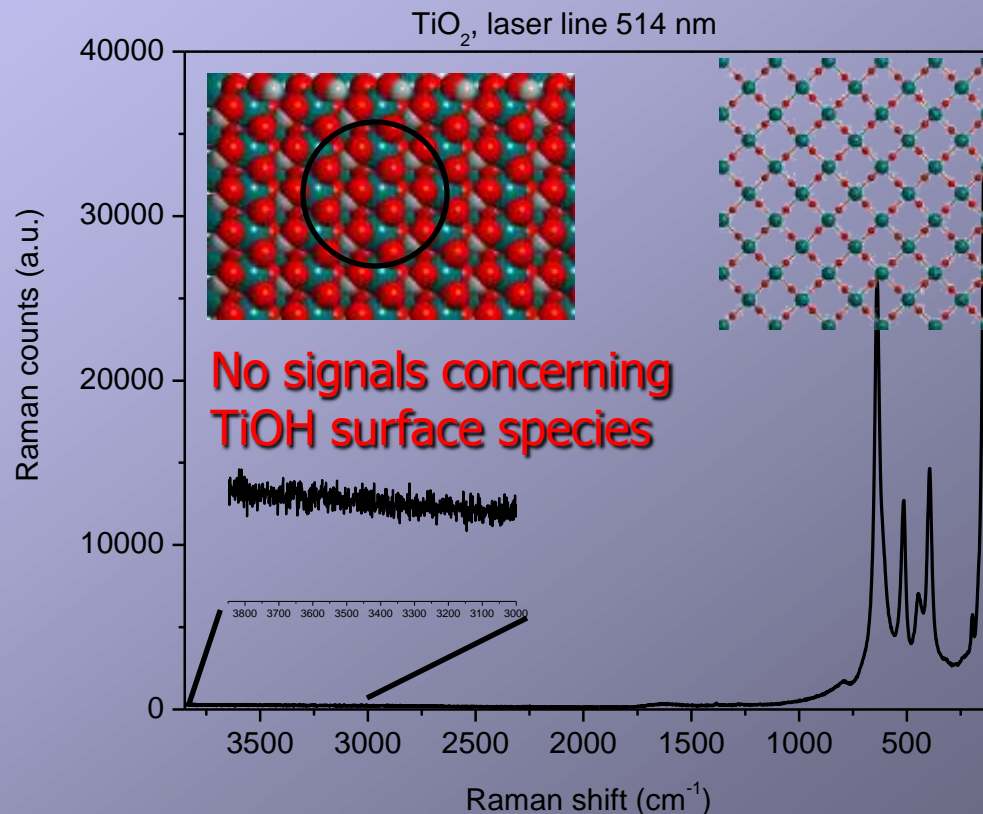
a) Stokes: $\nu=1 \leftarrow \nu=0$ (absorption of a photon with energy $h\nu$)

b) anti-Stokes: $\nu=0 \leftarrow \nu=1$ (emission of a photon with energy $h\nu$)



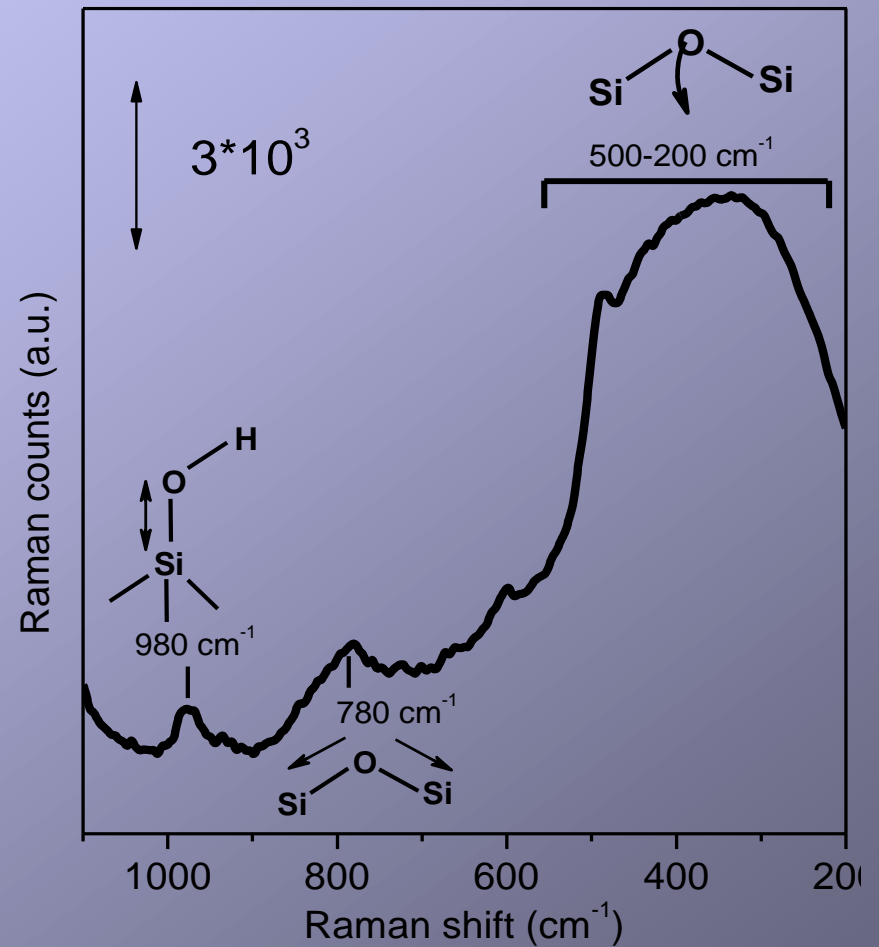
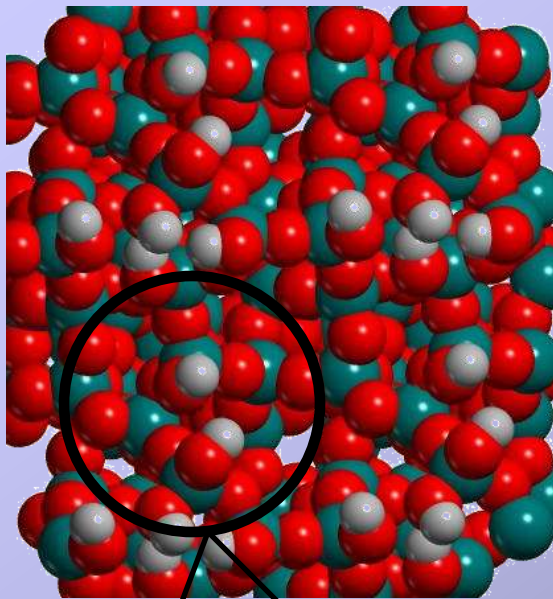
powerful technique to study bulk properties (like phase transitions) of heterogeneous catalysts

Raman spectroscopy



low sensitivity towards very diluted species as surface (active) groups are

Laser line 785 nm

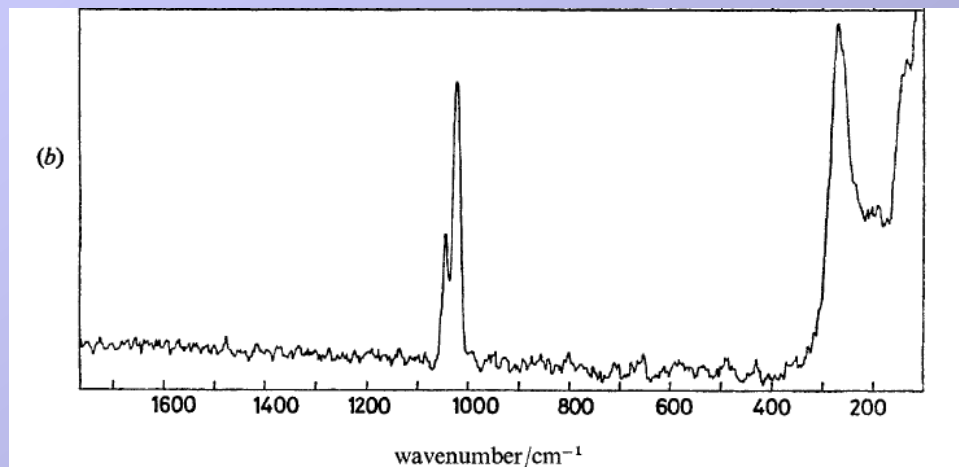


How nanotechnology can help in increasing Raman sensitivity?

SERS (Surface Enhanced Raman Spectroscopy)

Discovered in the '70 (pyridine on silver electrodes)

Gold and silver colloids work too (Creighton *et al.*, J. Chem. Soc. Faraday Trans. II 1978, 75, 790) to enhance pyridine (Py) Raman signals



Raman Py signals of a 10⁻³M Py solution in presence of gold nanoparticles (prepared by red. with NaBH₄) appear 3 times more intense than those in 0.1 M Py solution

Intensity of Py signals increases as exciting laser line is approaching the peak at higher wavelength appearing in the optical spectrum of Py/Gold system

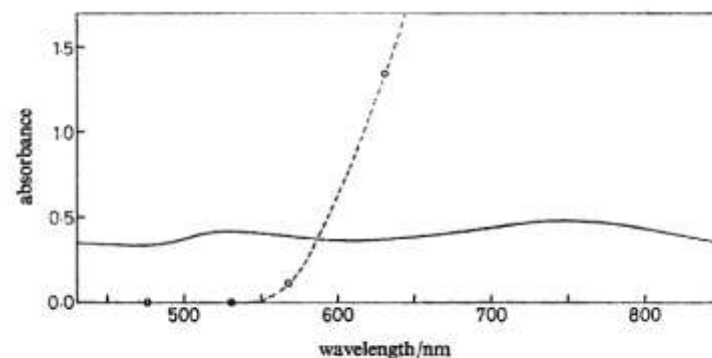
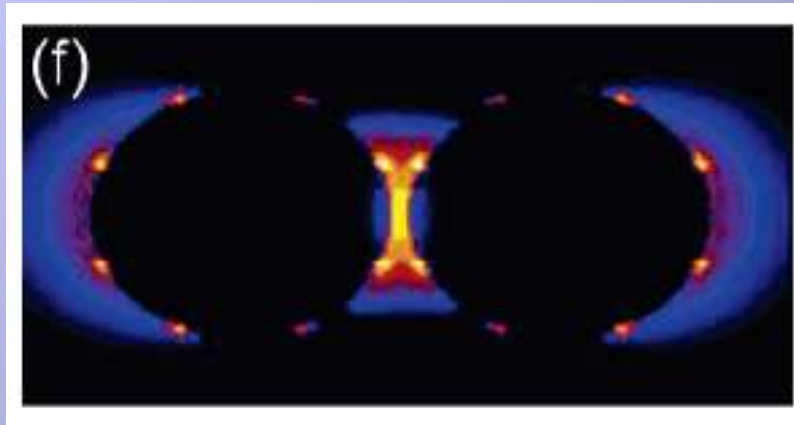
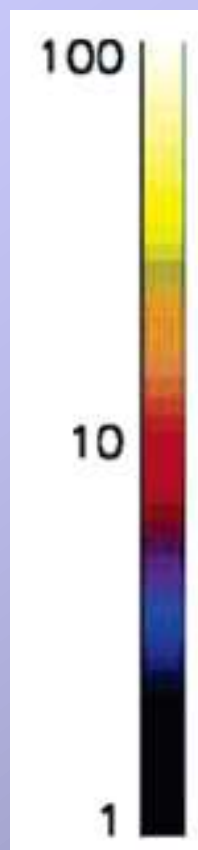
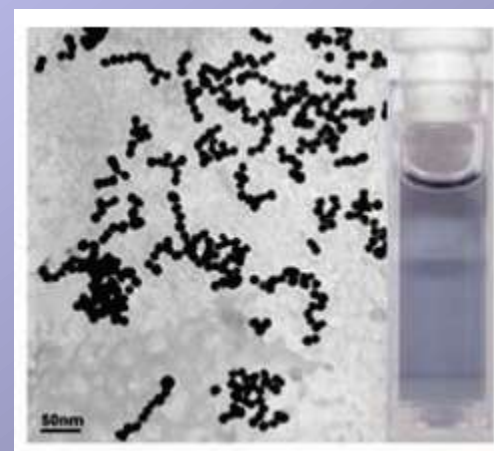
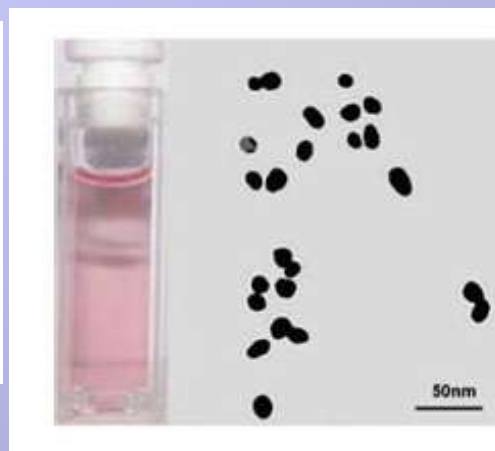
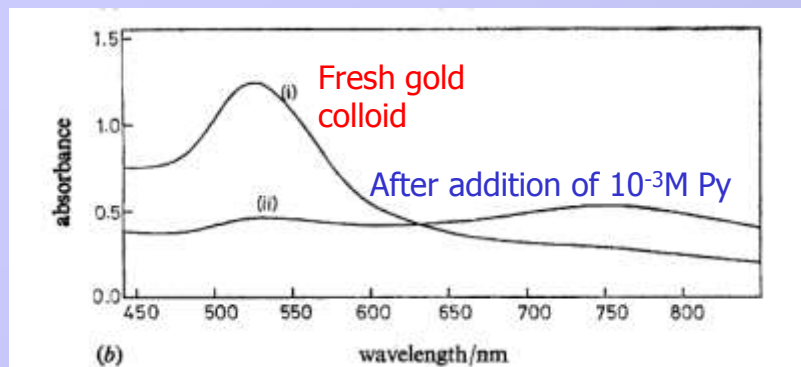


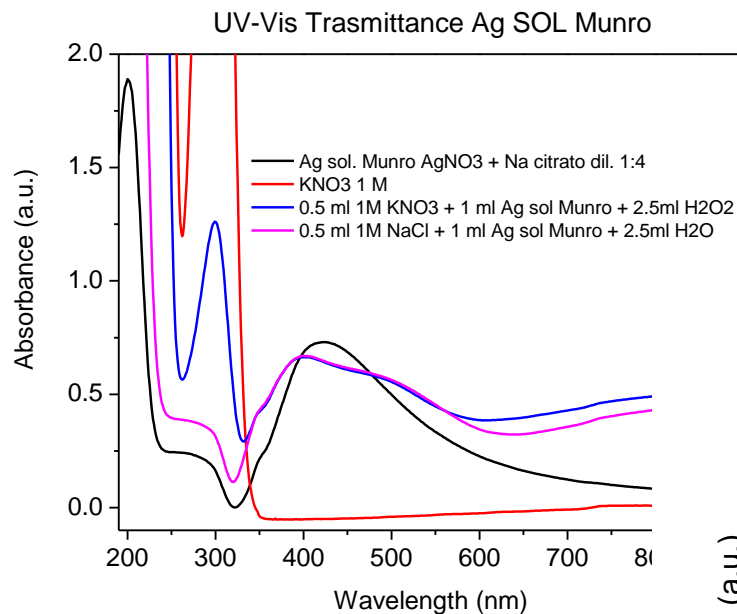
FIG. 4.—Absorbance (—) and Raman excitation profile (---) for gold sol with added pyridine. ○ denotes the experimental points (arbitrary linear intensity scale) for the 1014 cm⁻¹ Raman band of adsorbed pyridine.



E field enhancement computed at $\lambda = 630$ nm for 30 nm gold particles dimer

Py molecules which are located in the lighter region of the dimer (**hot spot**) are subjected to higher electric field than that coming from the exciting laser line: so their Raman signals will be enhanced ($|E|^4$), as μ_{ind} is proportional to the applied electric field. This is the so called electromagnetic enhancement (EMe) component of SERS. However it has been also observed that the stronger is the interaction mol/gold interaction, the higher is the enhancement (chemical enhancement, CHE)

SERS of Py on Ag colloid (liquid phase measurements)

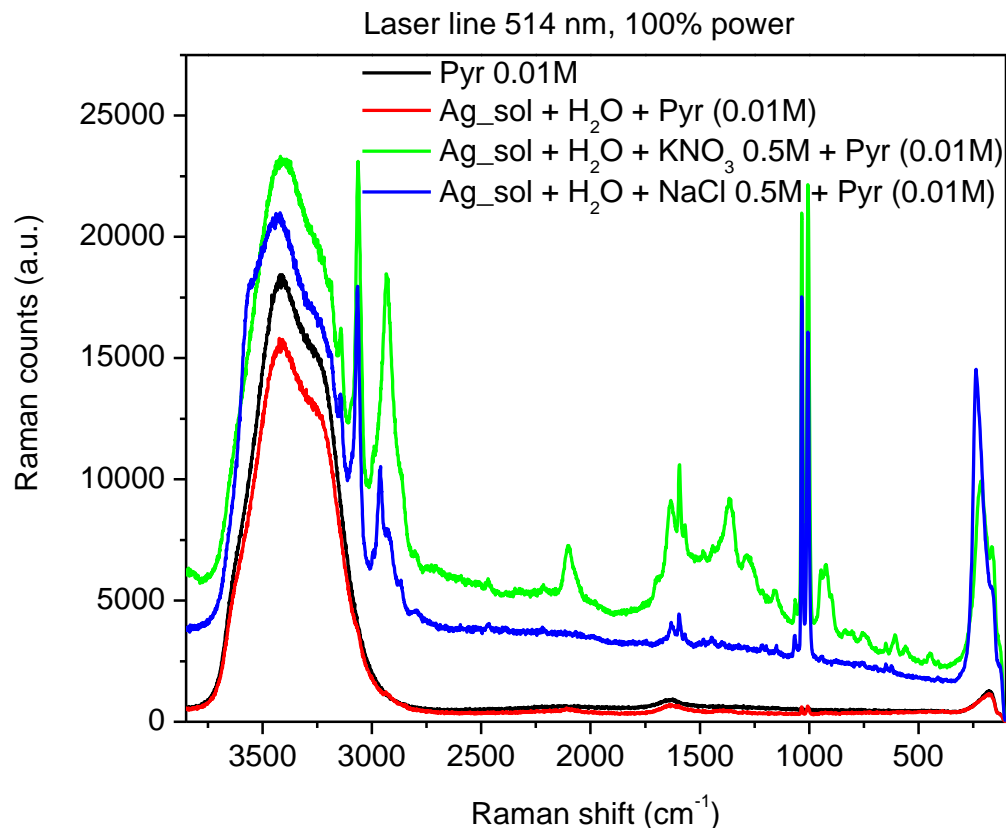


Ag sol prepared by reduction of AgNO₃ with trisodium-citrate.

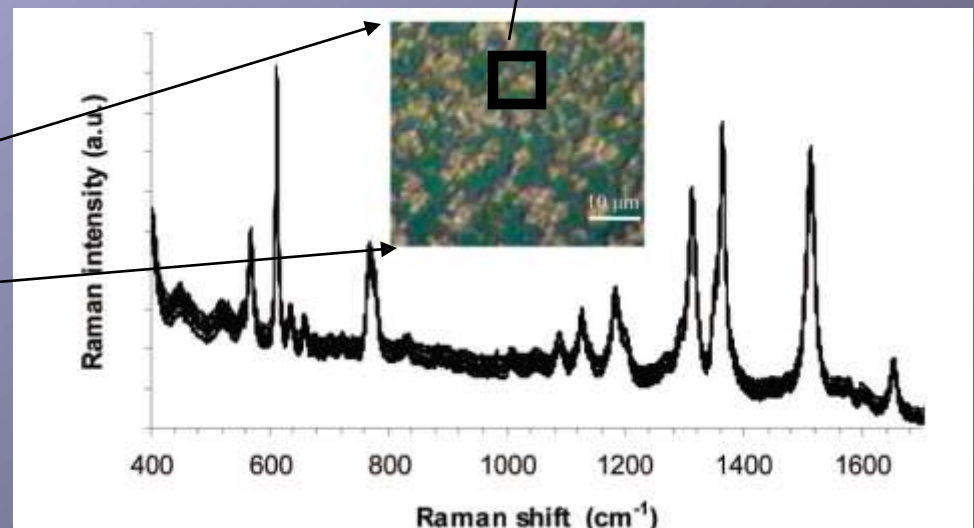
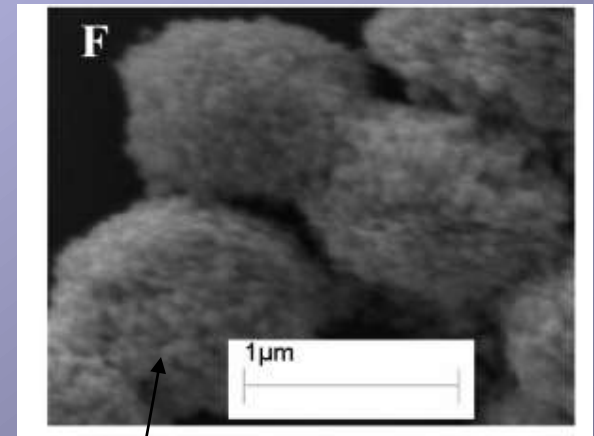
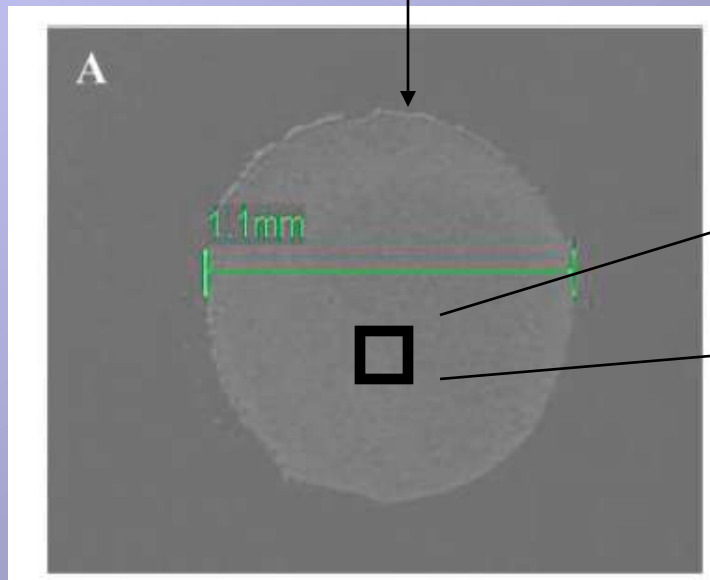
Ag nano-particles capped by citrate groups

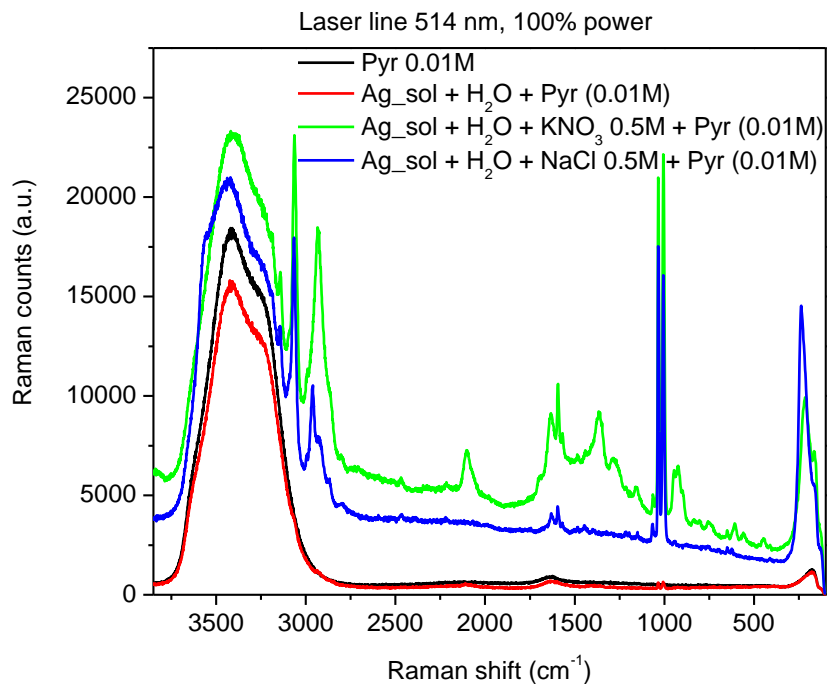
Py is not able to give aggregation in such prepared colloid.

NaCl or KNO₃ have to be used.

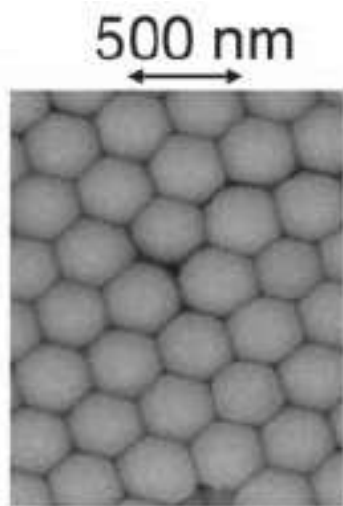


SERS measurements in solution are strongly affected by low reproducibility of the signal, probably due to an ill-defined aggregation state. **To overcome this, SERS measurements are typically performed on substrates obtained by depositing drops of aggregated colloidal solution (containing already the analyte) on glass-slides and evaporating the solvent.**





SERS from colloids could be affected by serious problems of contamination coming from chemicals (citrate, NO₃⁻, Cl⁻) adopted for reduction/aggregation



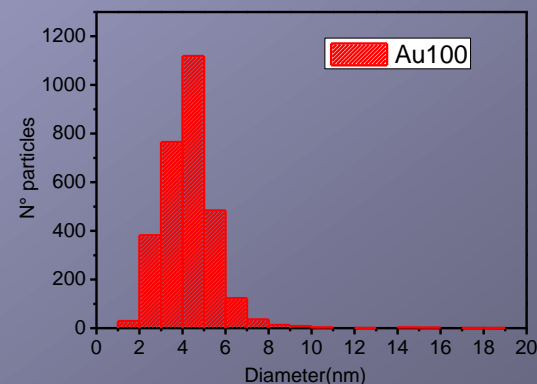
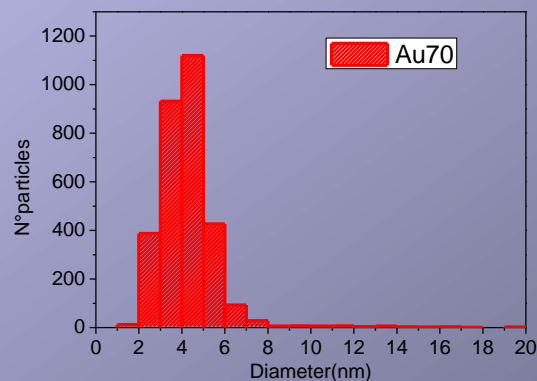
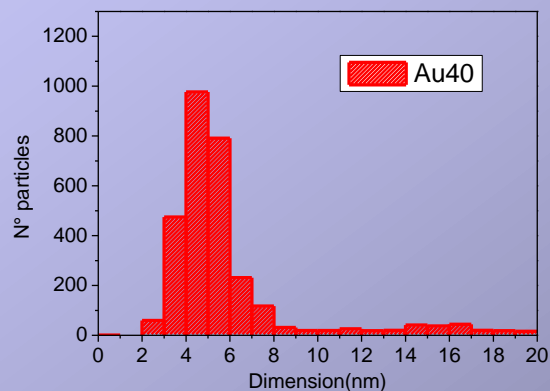
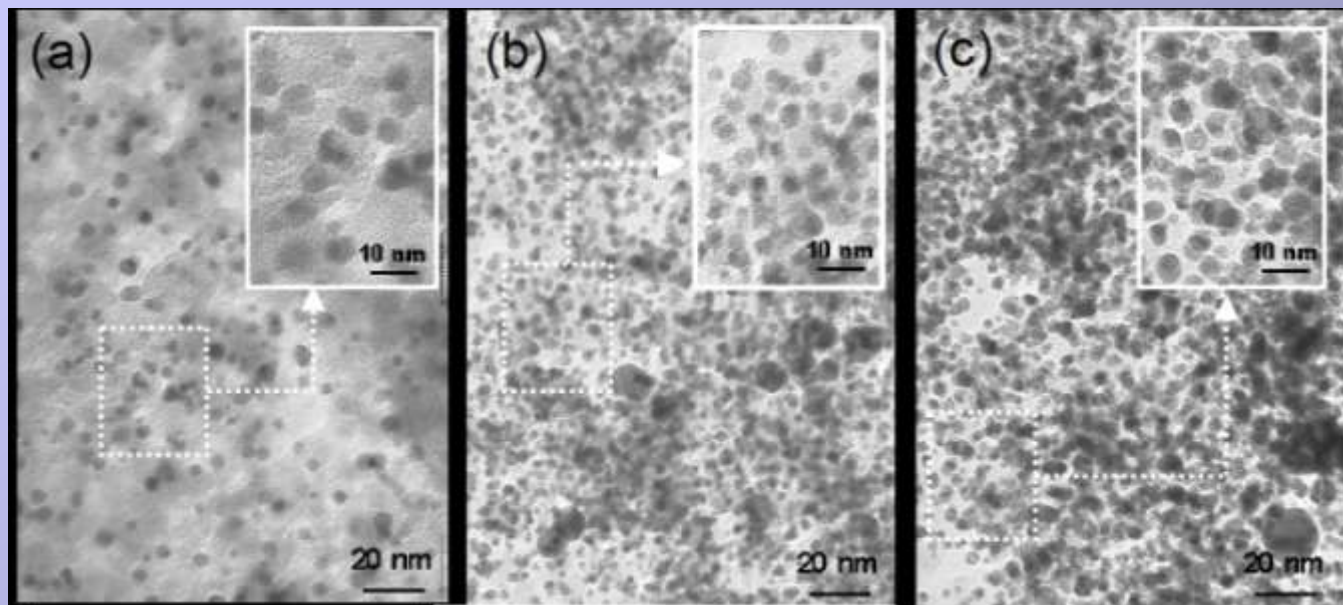
More clean SERS active substrates can be obtained by metal sputtering on nano-spheres (as in the case of AgFON)...

...or by applying synthesis procedure coming from Au catalysts preparation...

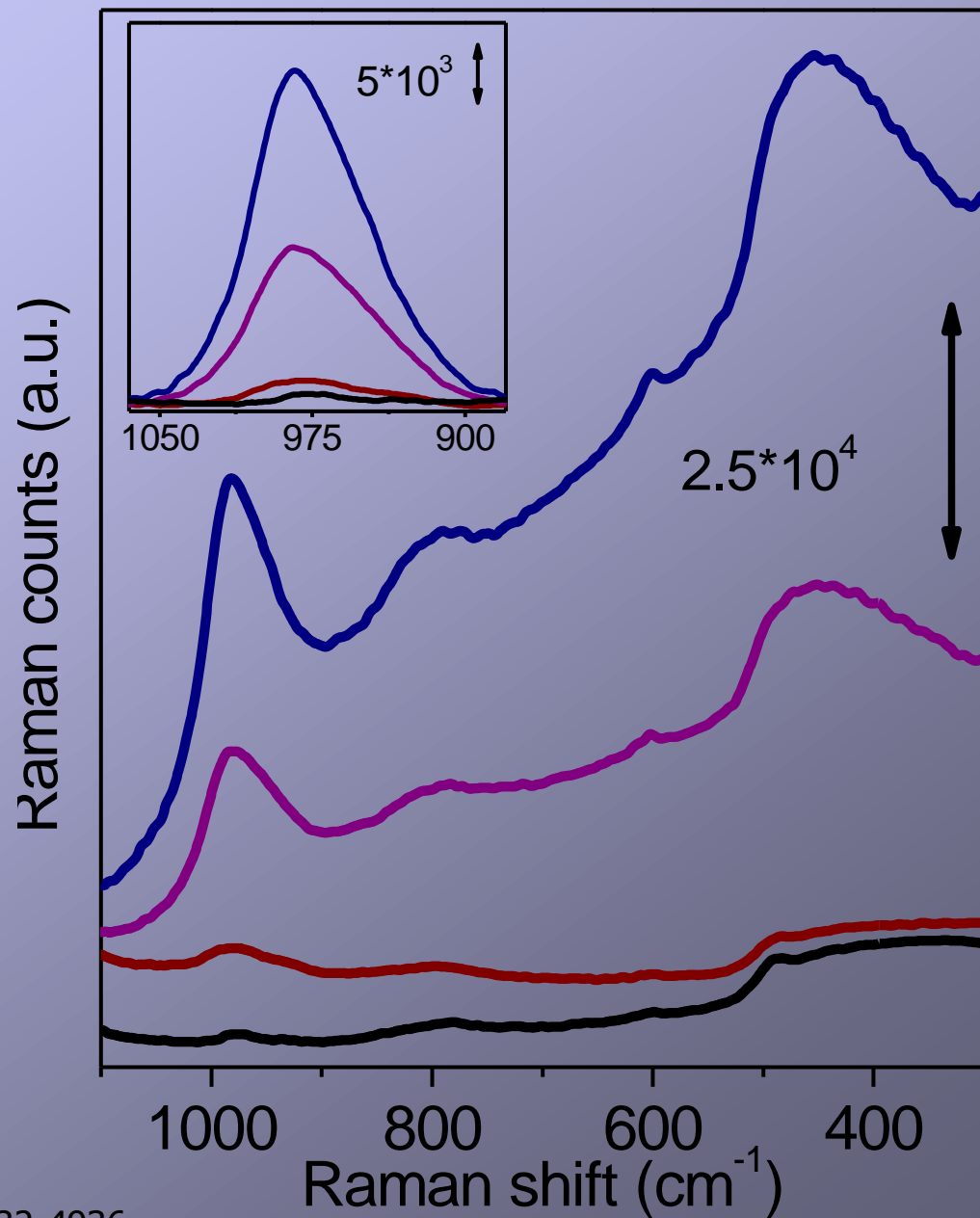
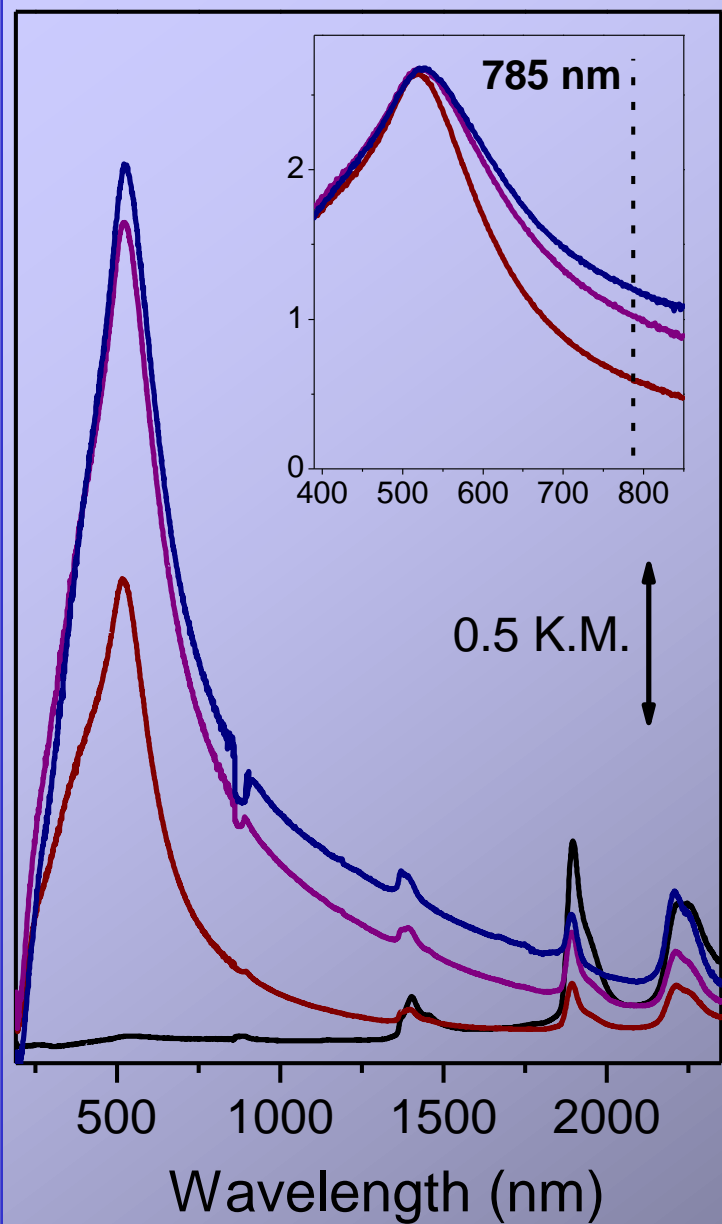
Synthesis of SiO₂ supported Au gold nanoparticles

- a) Impregnation of SiO₂ (Aerosil 300, surface area 300 m²/g) with **x** amount of HAuCl₄•3H₂O (pH = 9.5)
- b) Impregnated samples (yellow powders) were rinsed with distilled water and dried overnight at 333 K
- c) Dried powders were re-washed three times with diluted solution of 30% water ammonia
- d) Finally the so obtained powders were calcined at 673 K for 4 hours and then reduced in H₂ at 573 K for 2 hours

x = 0 (Au0, reference sample), 40wt% (Au40), 70wt% (Au70) and 100wt% (Au100) of Au



Increasing loading does not affect the dimensions and the shape of the Au nano-particles, but instead their aggregation state

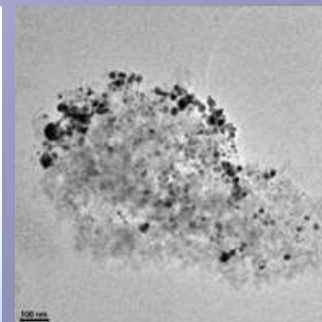


Synthesis of SiO₂ supported Au gold nanoparticles: a simplified procedure

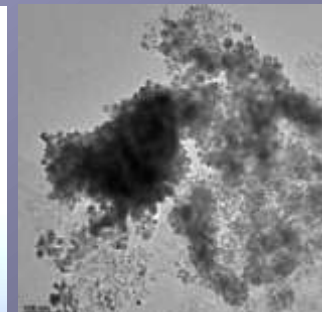
Aux

- Impregnation of SiO₂ (Aerosil 300, surface area 300 m²/g) with **x = 16 and 50 wt%** of Au (Au precursor: HAuCl₄ x 3H₂O)
- Impregnated samples (yellow powders), after drying at room temperature, were rinsed with ammonia solution (30 wt%, 10 ml in 100 ml of water), rinsed with distilled water, and dried overnight at 333 K
- The so obtained powders were calcined at 673 K for 4 hours, after a pre-treatment at 190 °C for 20 mins

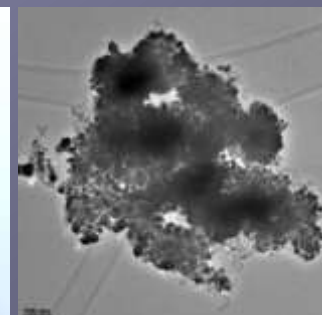
Au5wt%

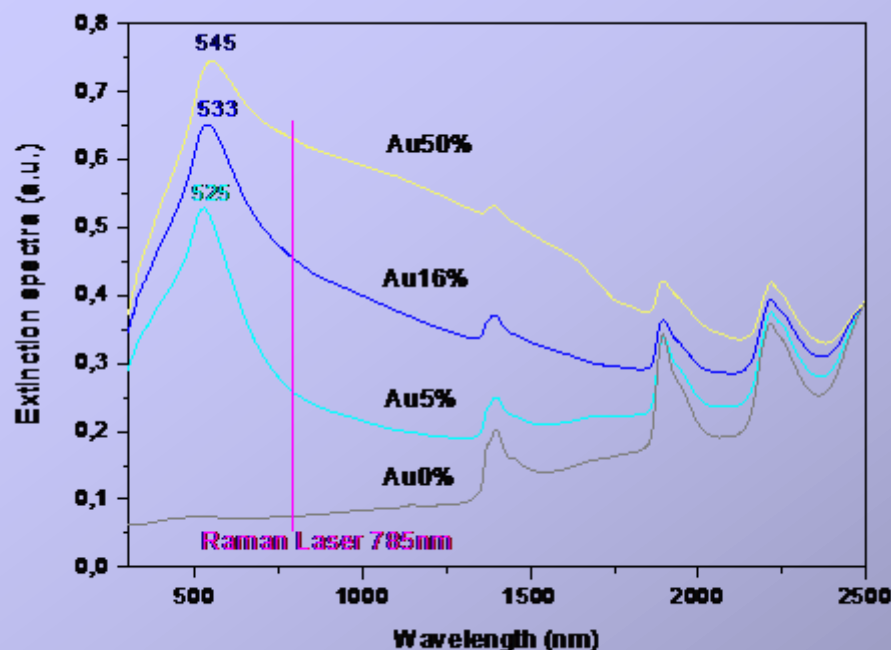


Au16wt%

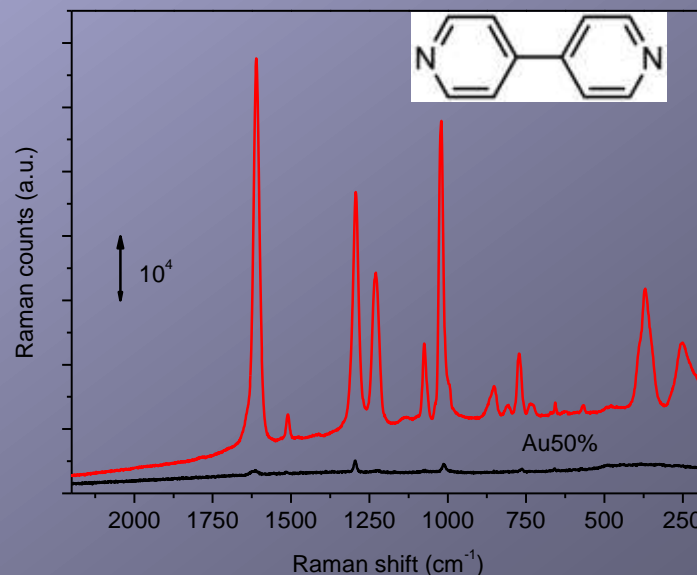
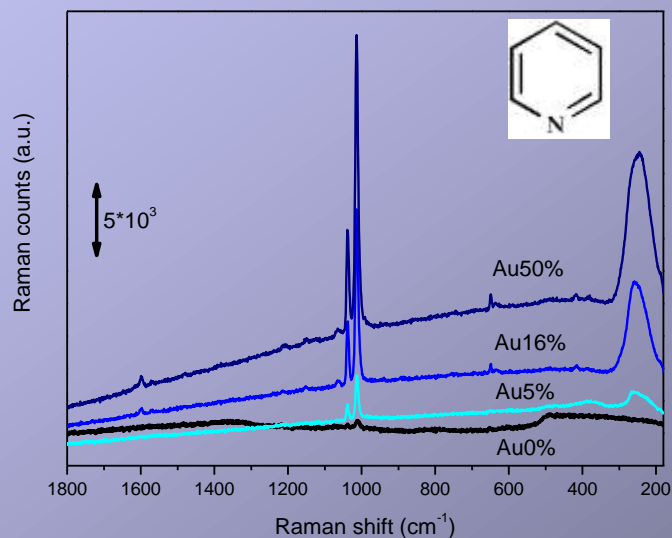


Au50wt%





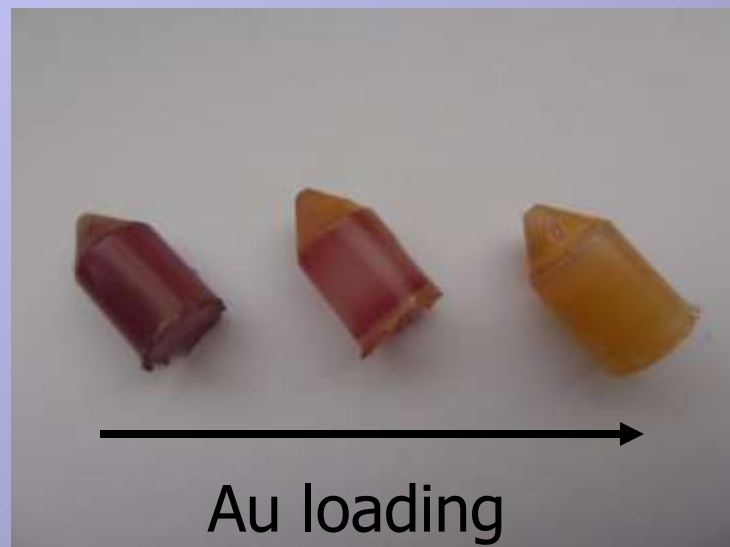
When compared to pure Aerosil300, $\langle EF \rangle$ of 10^3 is obtained for pyridine (dosed from the vapour phase). SERS is more effective for molecules.





Sol-gel synthesis allows to obtain high surface area microporous and transparent SiO₂ monoliths.

Once properly doped with Au, or Ag, they could work as very effective substrates for SERS.



One pot synthesis of Au doped (0.02-2 wt%) monoliths has been tried.

Up to now no good results are obtained. In particular no control of Au aggregation state: this means no control on the plasmonic properties of the materials. Work is in progress.

Cr doping



Cr doping (0.5 wt%) leads to microporous glass with properties, when properly activated, very similar to Cr/SiO₂ Phillips catalyst.

Ti doping



2mol%



5mol%



10mol%



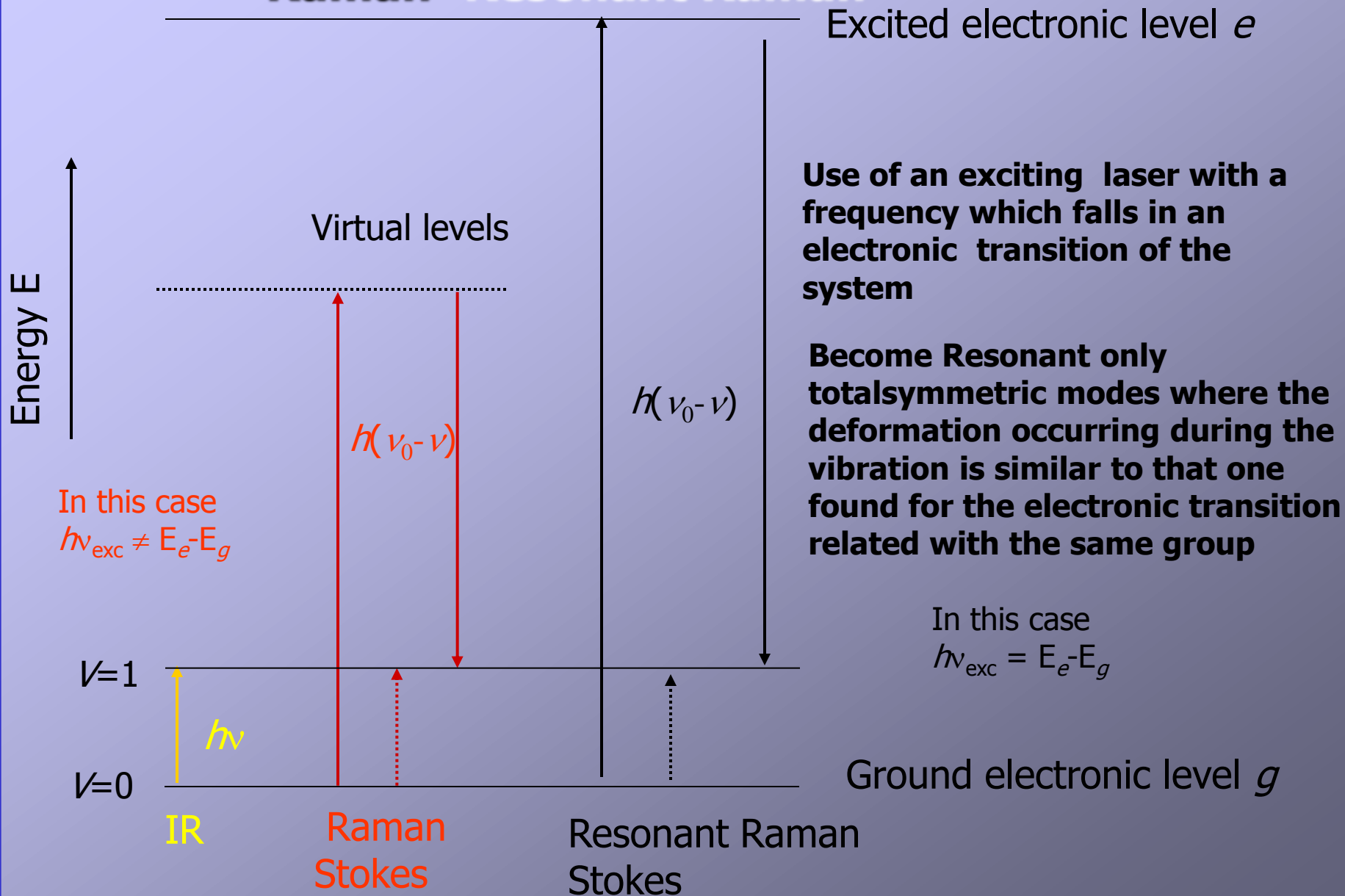
20mol%

Ti is prevalently present as TiO₂ nanoparticles

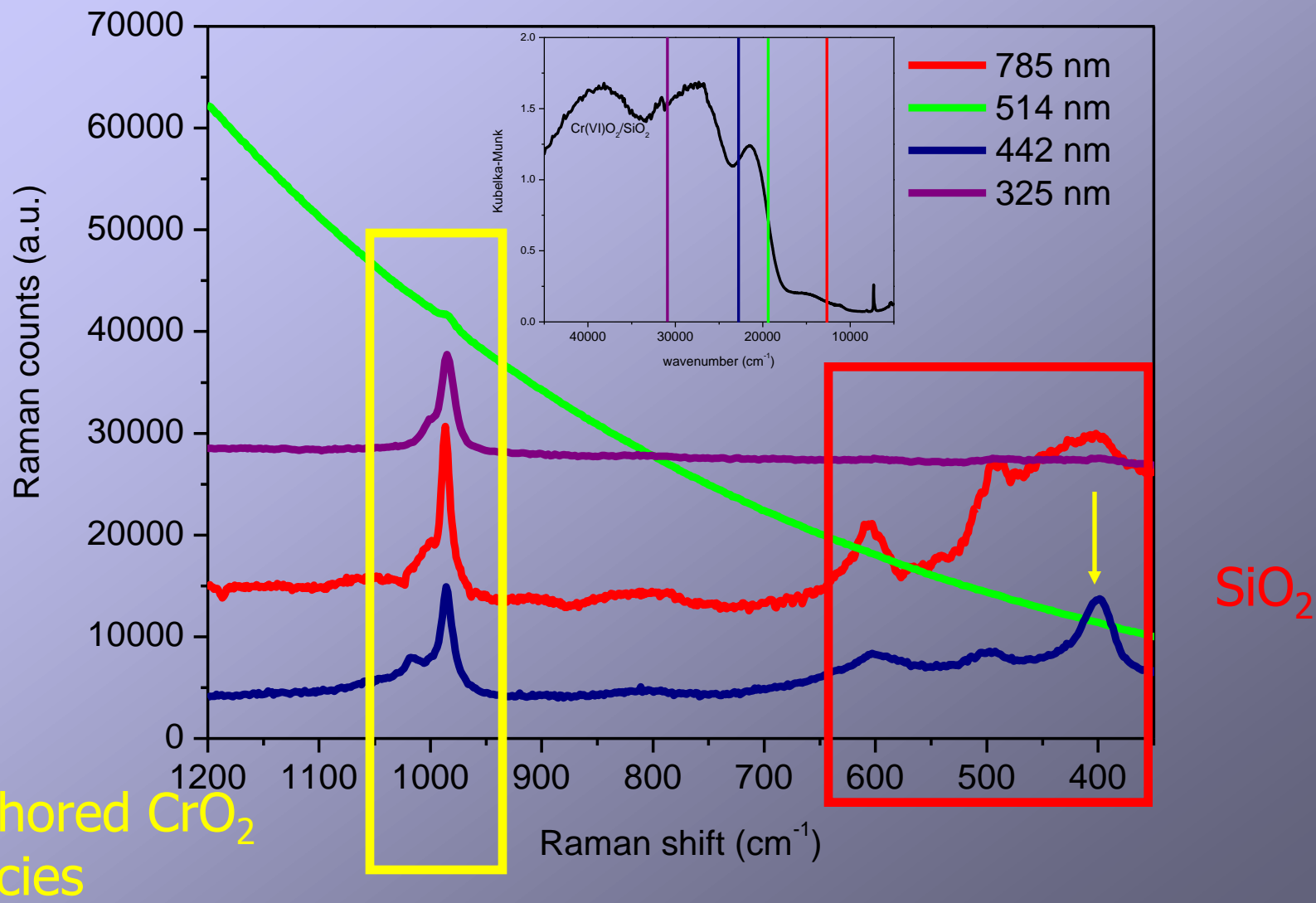
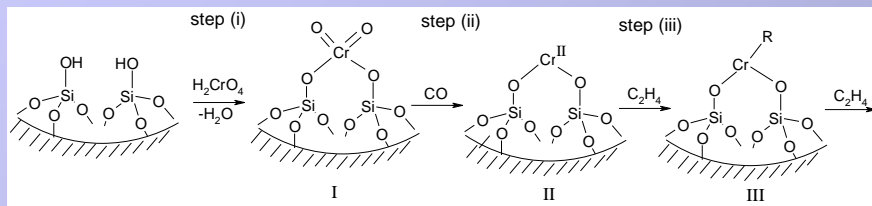
Does Ti isomorphously substitute Si as in Ti-zeolites?

Can Raman be employed to get informations about so diluted species?

Raman Resonant Raman

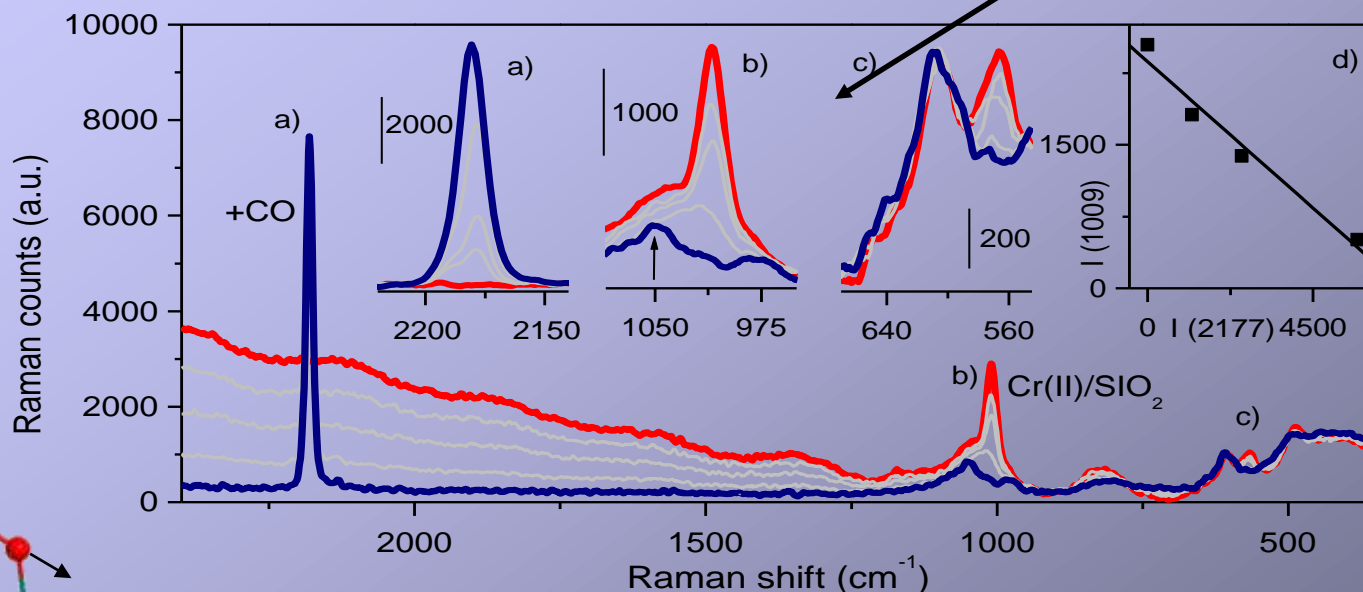
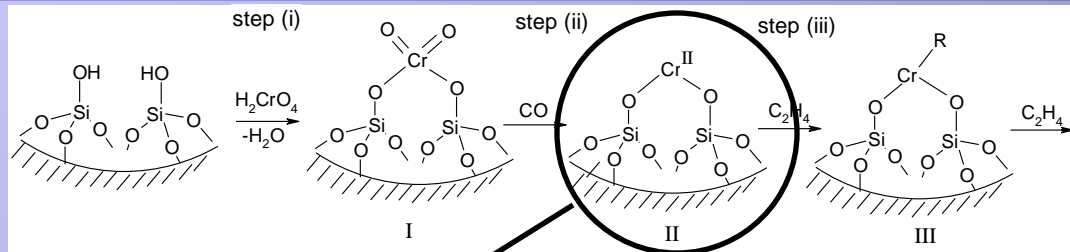


Phillips catalyst



Phillips catalyst

Damin *et al.*,
ChemPhysChem, 2006, 7,
342

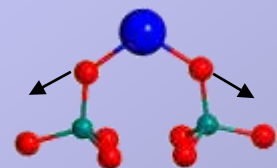


442 nm
laser
line

CO adsorption causes:

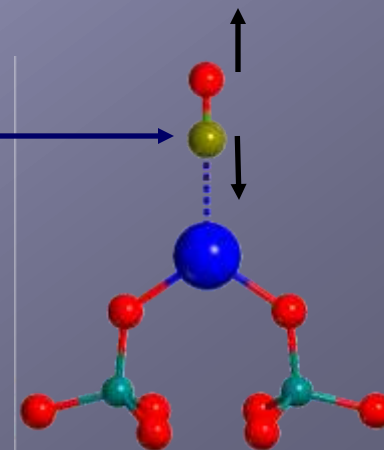
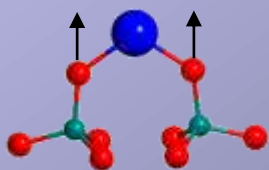
The **erosion** of the 568 and 1009 cm^{-1} bands

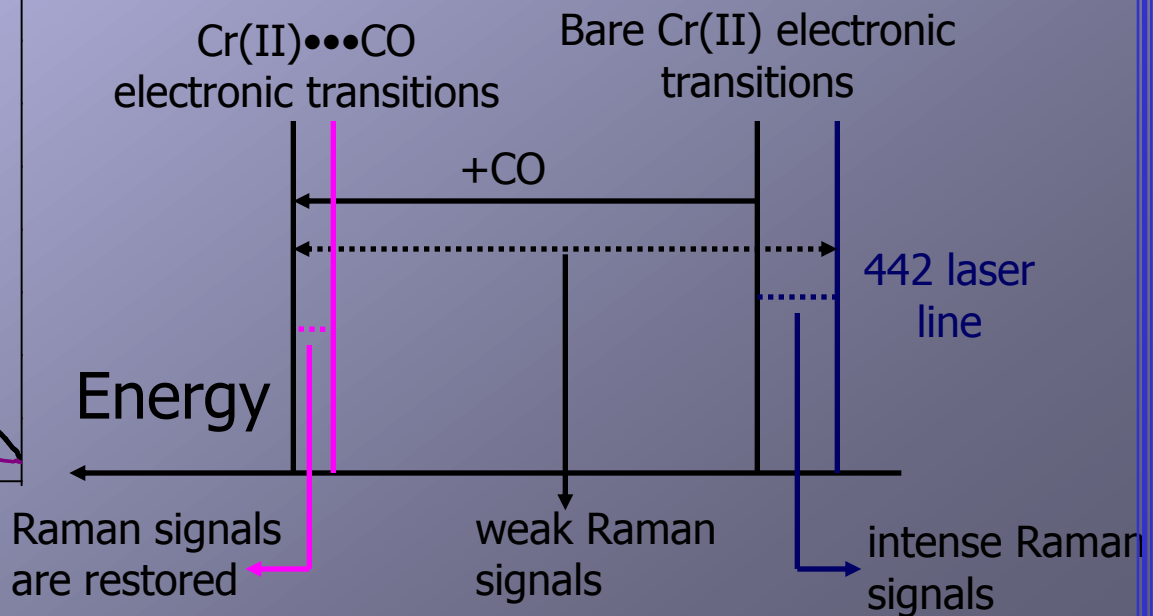
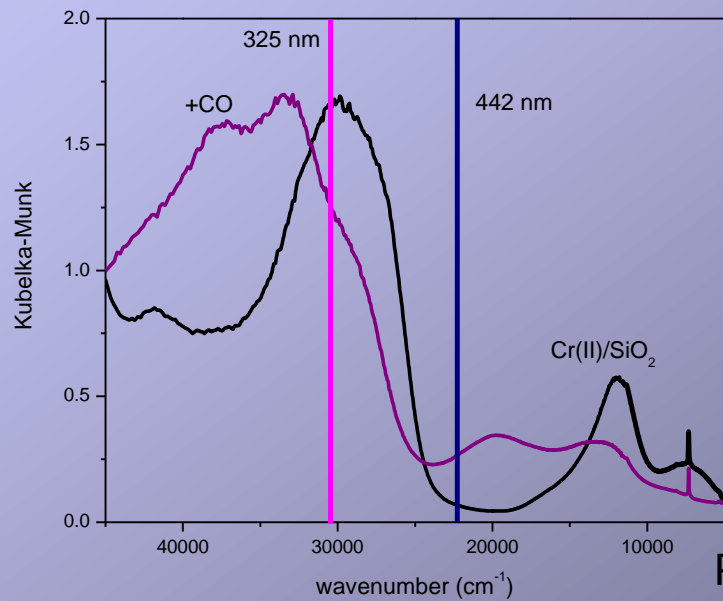
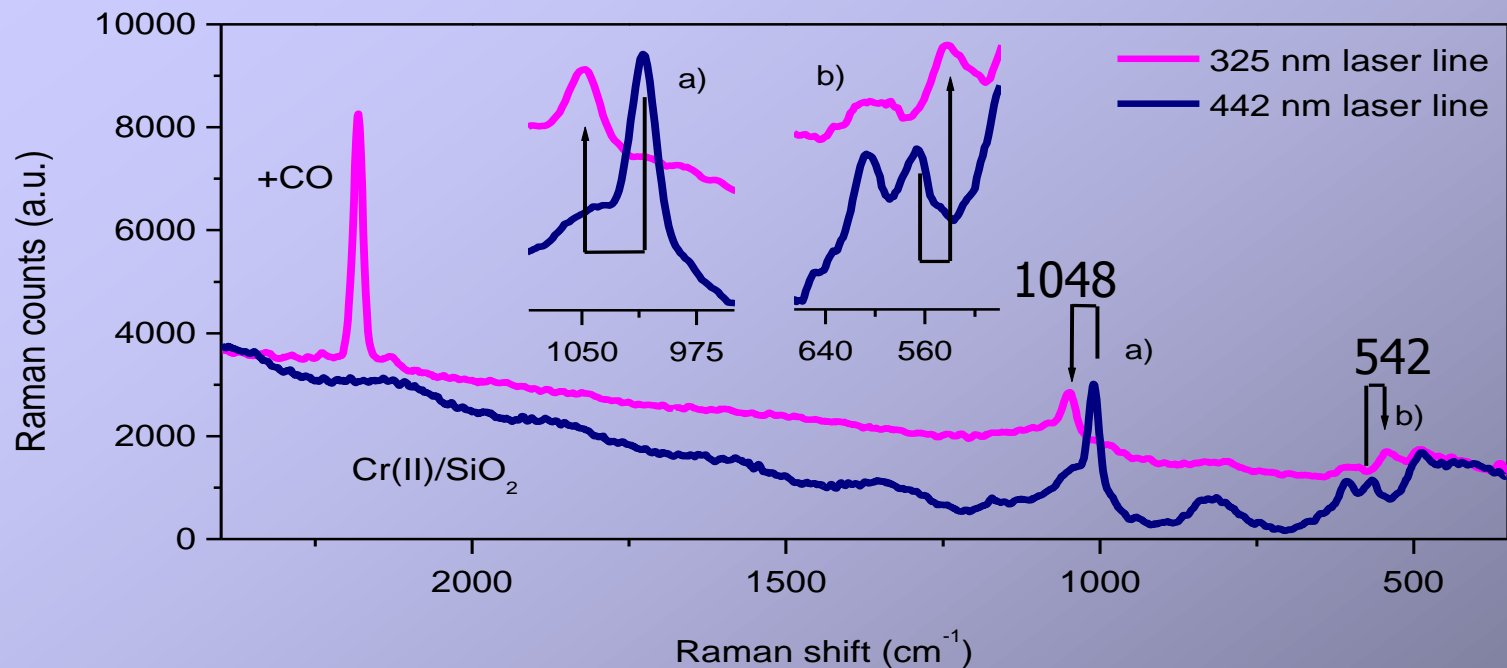
The **appearance** of a strong signal in the 2177-2189 cm^{-1} range ascribable to



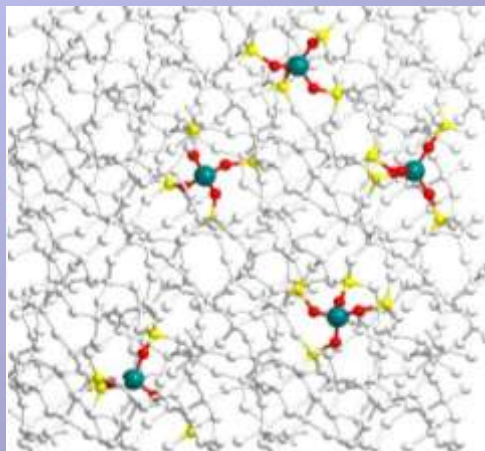
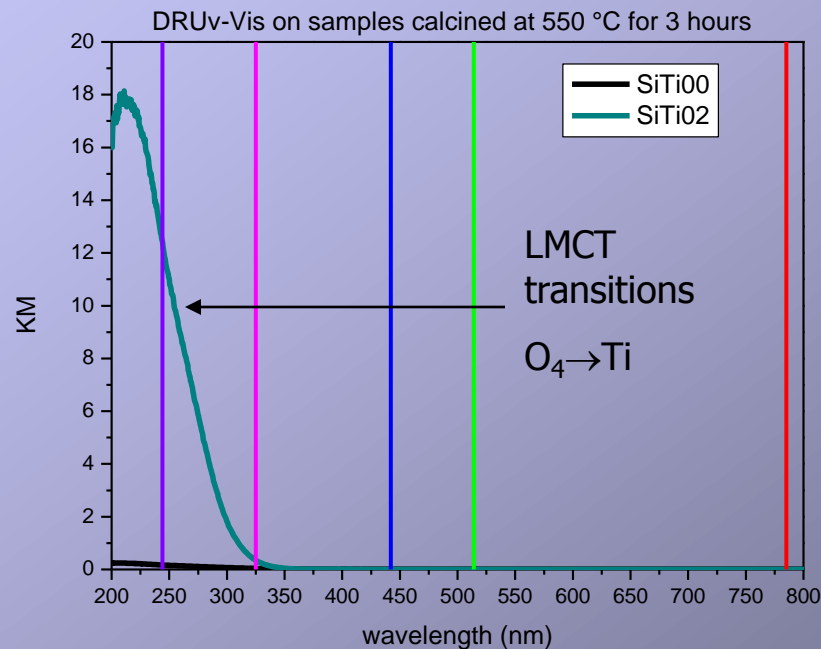
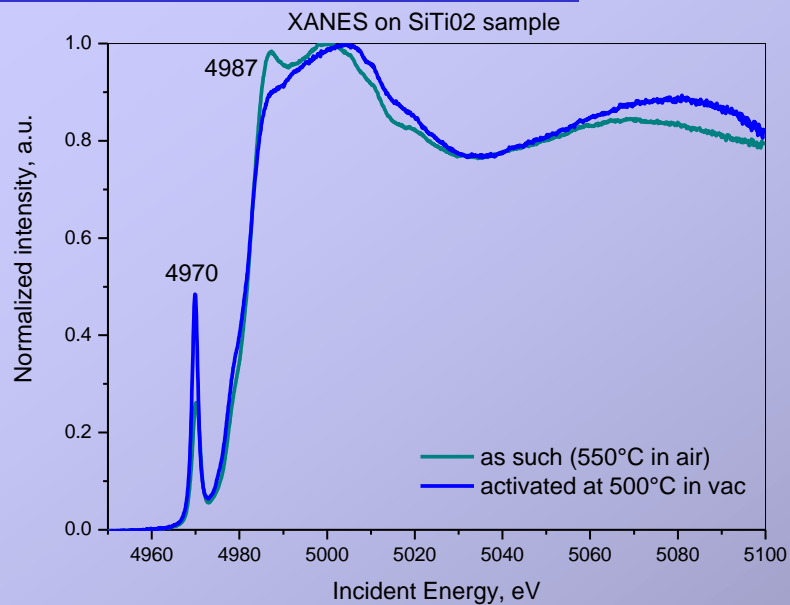
568 cm^{-1}

1009 cm^{-1}

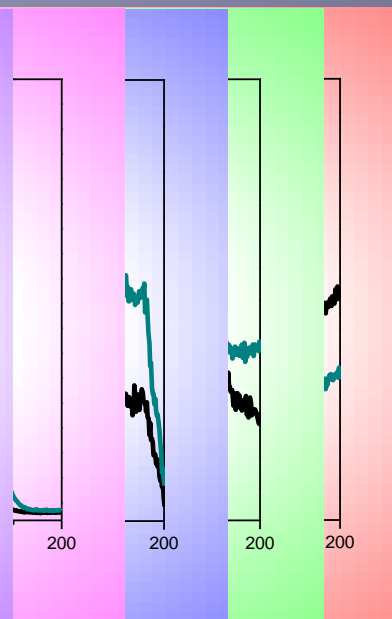
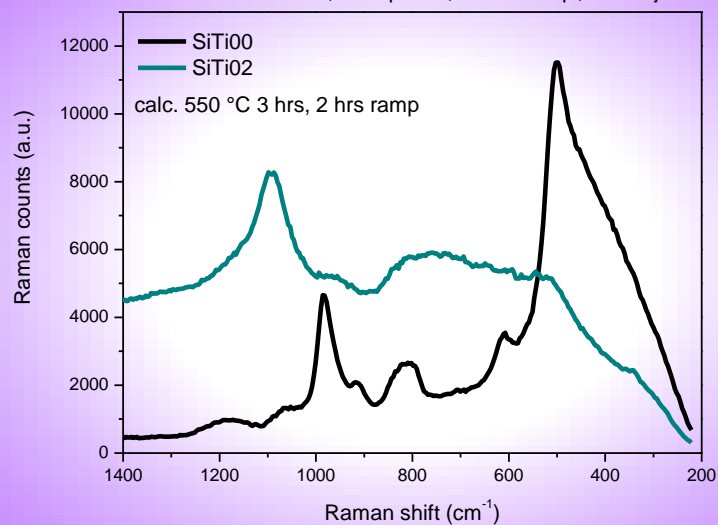




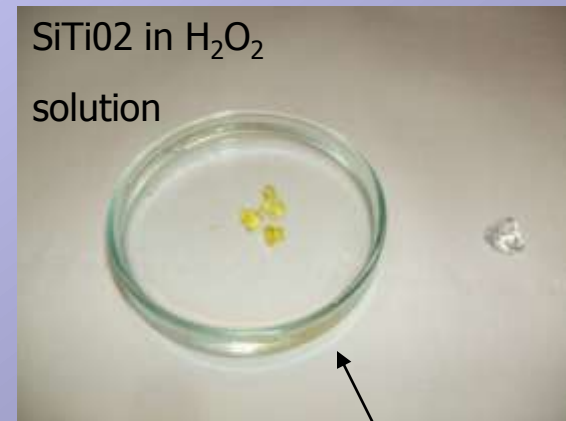
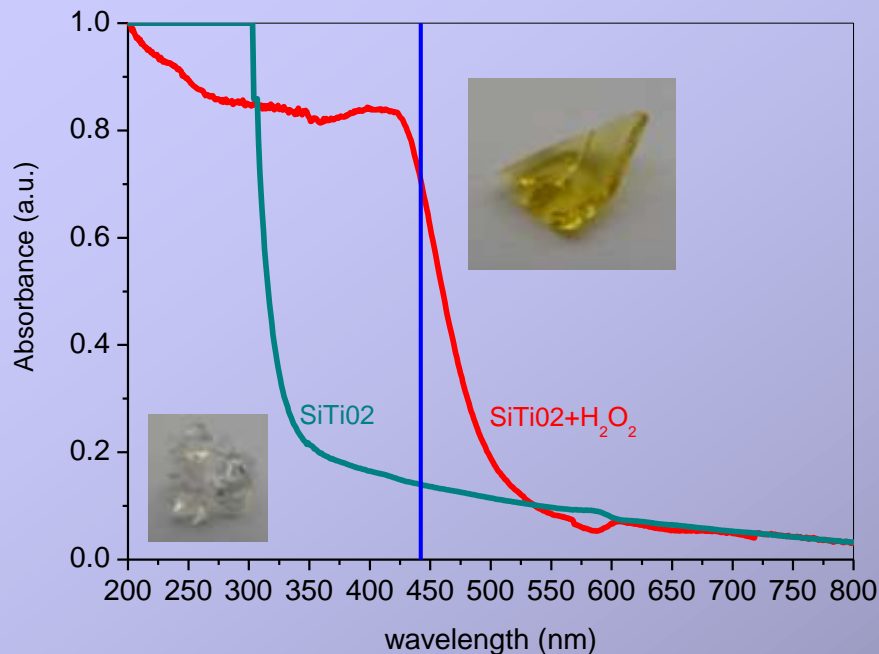
Ti containing glass



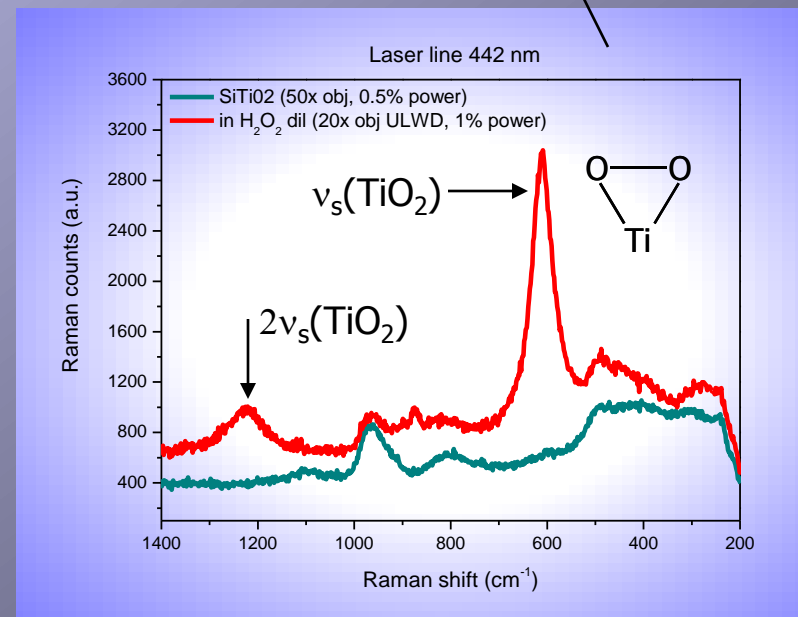
Laser line 244 nm, 25% power, 50x40" acqs, 15x obj



Interaction with H_2O_2



Resonant Raman spectroscopy is effective in studying very diluted species, becoming atomically selective too.



Acknowledgements

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NIS Centre of Excellence

All of you for the kind attention