Diffusion Raman exaltée de surface (DRES) ou Surface enhanced Raman scattering (SERS)

Principes, quelques exemples

Nordin FELIDJ
Laboratoire ITODYS, Université Paris Diderot
Email: nordin.felidj@univ-paris-diderot.fr

Molecular Plasmonic team – ITODYS

J. Aubard, Pr. Em.

L. Boubekeur-Lecaque
Researcher CNRS

N. Felidj, Pr.

J. Grand
Ass. Professor

S. Lau-Truong
Ingenior CNRS

G. Lévi
Invited researcher

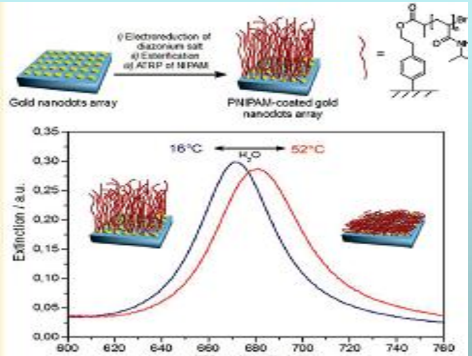
SERS

MOLECULAR PLASMONICS

MOLECULAR PLASMONICS

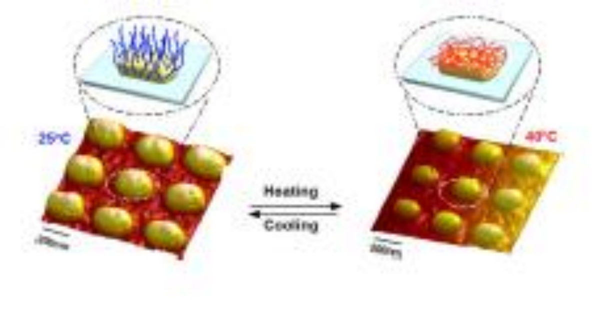
La plasmonique moléculaire est l’étude des interactions locales entre particules présentant des résonances plasmon et systèmes moléculaires pourvues de propriétés et de fonctionnalités variées (polymères photochromes, photosensibles, thermosensibles, conducteurs, cristaux liquides…).

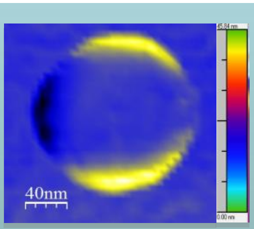
Molecular systems to modify the optical properties of the plasmonic structures

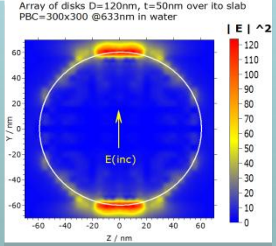


J. Phys. Chem. Lett., 2011

Plasmonic structures to modify, induce or/and probe the chemical (or physical) reactions or properties of molecular systems







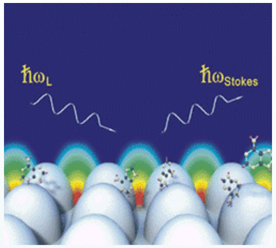
ACS Photonics, 2015,
Mater. Chem., 2016,
Nanoscale, 2016

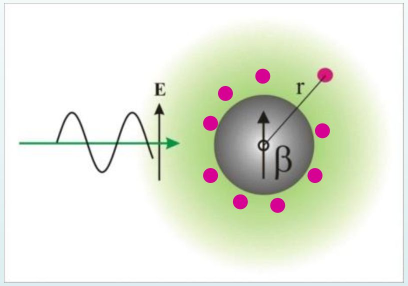
Coll. C. Mangeney, ITODYS

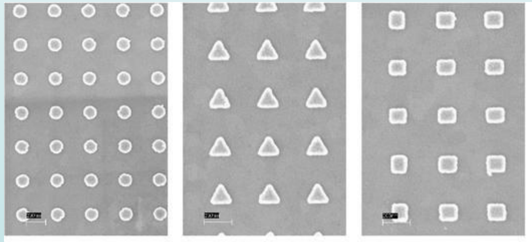
Plan

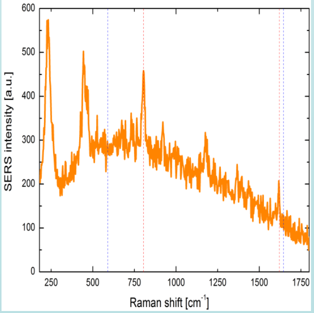
Effet SERS (Diffusion Raman exaltée de surface)

- Définition, historique, enjeux
- Mécanismes d'exaltation
- Définitions du gain Raman
- Quelques caractéristiques
- **Points chauds et détection de la molécule unique**









Raman spectroscopy

This was simultaneously discovered by Raman & Krishnan and Mandelstam & Landsberg (in the USSR the phenomenon is called *combination scattering*)

SIR CHANDRASEKHARA V. RAMAN

The molecular scattering of light
Nobel Lecture, December 11, 1930

In the history of science, we often find that the study of some natural phenomenon has been the starting-point in the development of a new branch of knowledge. We have an instance of this in the colour of skylight, which has inspired numerous optical investigations, and the explanation of which, proposed by the late Lord Rayleigh, and subsequently verified by observation, forms the beginning of our knowledge of the subject of this lecture. Even more striking, though not so familiar to all, is the colour exhibited by oceanic waters. **A voyage to Europe in the summer of 1921 gave me the first opportunity of observing the wonderful blue opalescence of the Mediterranean Sea. It seemed not unlikely that the phenomenon owed its origin to the scattering of sunlight by the molecules of the water. To test this explanation, it appeared desirable to ascertain the laws governing the diffusion of light in liquids, and experiments with this object were started immediately on my return to Calcutta in September, 1921.** It soon became evident, how-ever, that the subject possessed a significance extending far beyond the special purpose for which the work was undertaken, and that it offered unlimited scope for research. It seemed indeed that the study of light-scattering might carry one into the deepest problems of physics and chemistry, and it was this belief which led to the subject becoming the main theme of our activities at Calcutta from that time onwards.

Diffusion Raman spontanée

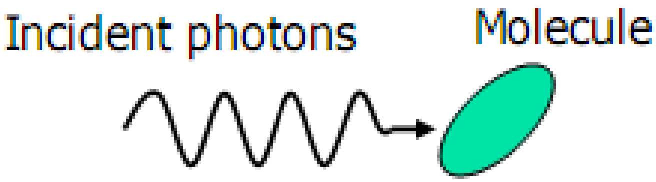
$$P = \alpha \overline{E}$$

$$\overline{E} = E_o \cos(2\pi\nu_o t)$$

$$P = \alpha E_o \cos(2\pi\nu_o t)$$

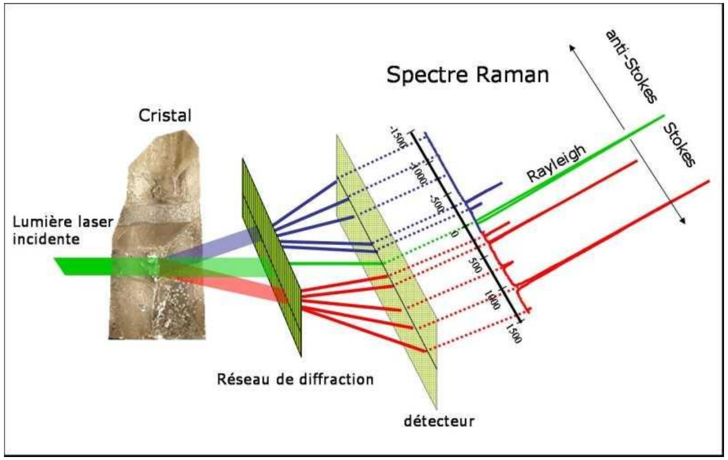
$$\alpha = \alpha_o + \frac{\partial \alpha}{\partial Q} dQ$$

$$dQ = Q_o \cos(2\pi\nu_{vib} t)$$

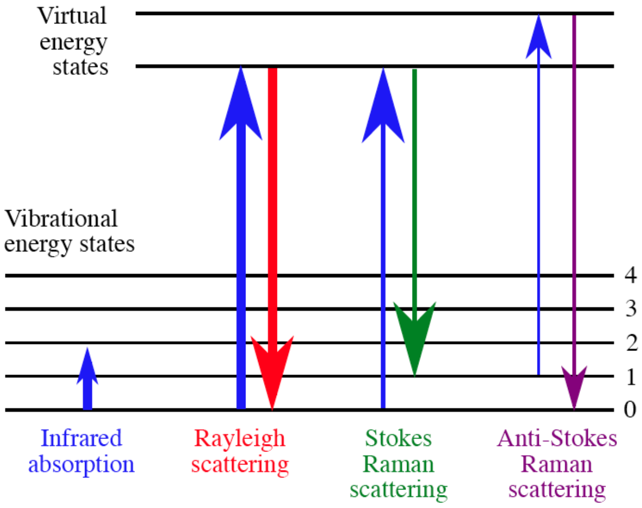


- **Pour une molécule diatomique:**

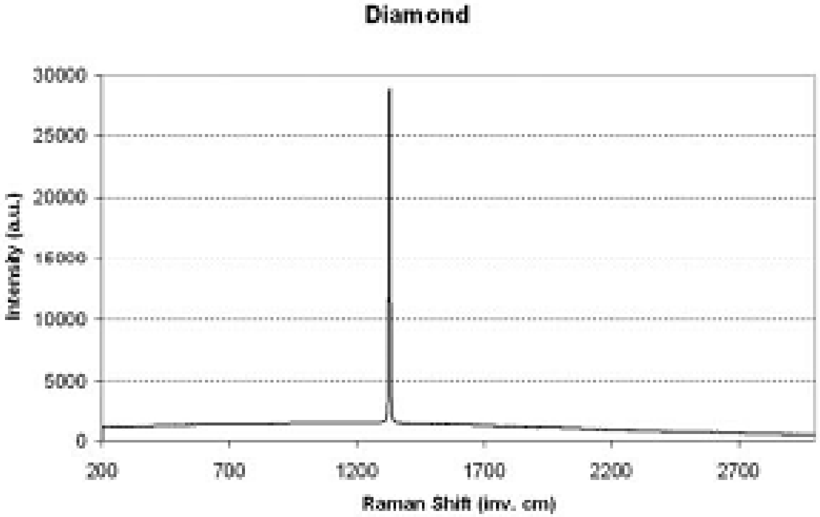
$$\vec{p} = \vec{\alpha}_0 \vec{E}_0 \cos(2\pi\nu_0 t) + \left(\frac{\partial \vec{\alpha}}{\partial q}\right)_0 \frac{q_0 \vec{E}_0}{2} \left[\cos(2\pi(\nu_0 + \nu_v)t) + \cos(2\pi(\nu_0 - \nu_v)t)\right]$$



$$\left(\frac{\partial \vec{\alpha}}{\partial q}\right) \neq 0$$

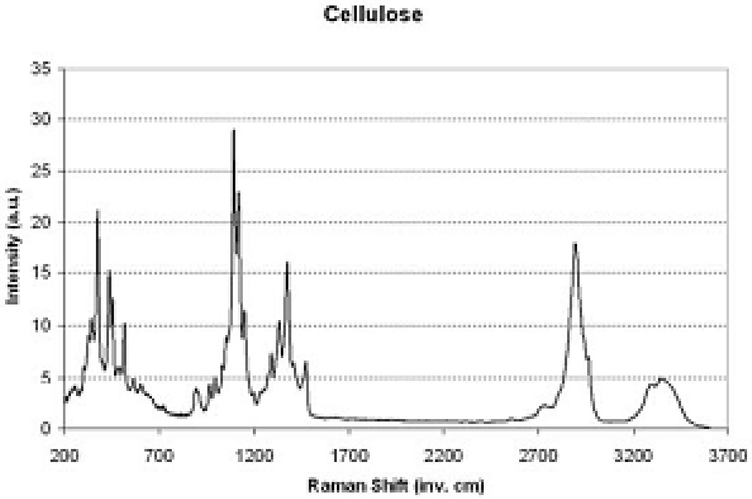


Sample Raman Spectra



Diamond:

- C-C lattice
- Only one bond type
- One Raman band

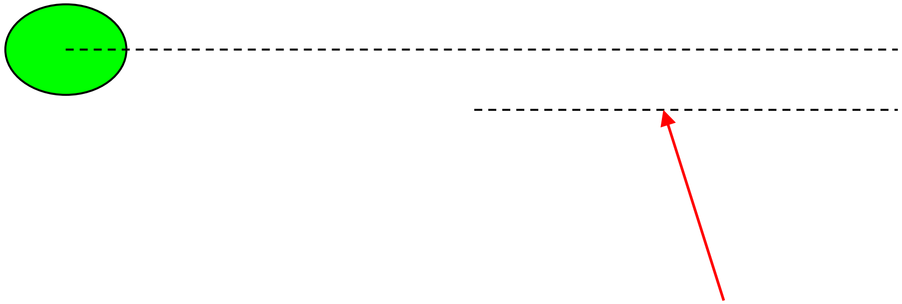


Cellulose ($C_6H_{10}O_5$):

- Organic molecule
- Many bond types
- Several Raman bands

- **Raman signal: fingerprint of the molecule**

Raman scattering: excitation of vibrational modes

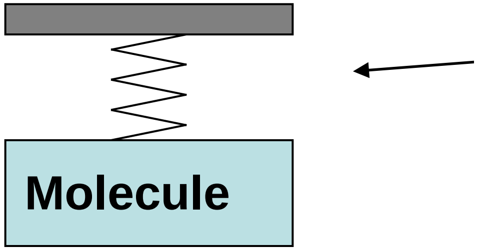


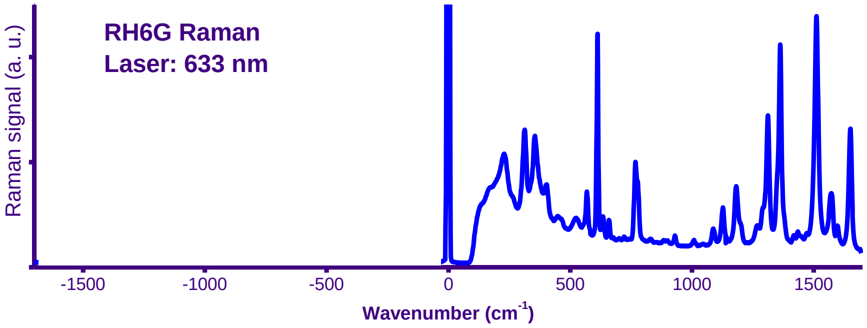
photon Stokes

ΔE < 0

$$I_S = N \sigma_S I_{\mathrm{laser}}$$

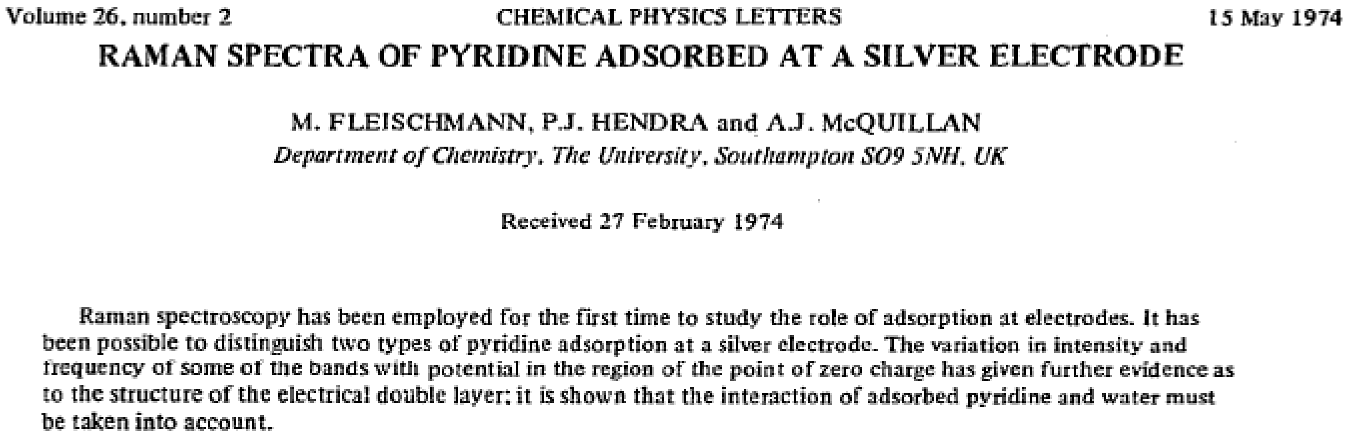
$\sigma_S \approx 10^{-29}$ cm^2 (non-resonant) – 10^{-23} cm^2 (resonant)





Inconvenients

- Raman scattering is a weak effect
  - Raman scattering cross section ~10^{-30} cm^2
- If we can increase the local fields we can obtain a larger *effective* scattering cross section
  - More Raman scattering (higher signal)
  - Lower detection limits
- How can we increase the local fields?
  - Plasmon excitation produces induced fields
  - Fields can be localized and intense



Volume 26, number 2 CHEMICAL PHYSICS LETTERS 15 May 1974

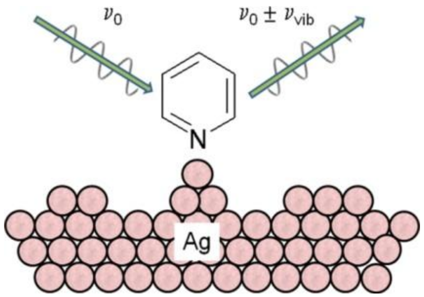
RAMAN SPECTRA OF PYRIDINE ADSORBED AT A SILVER ELECTRODE

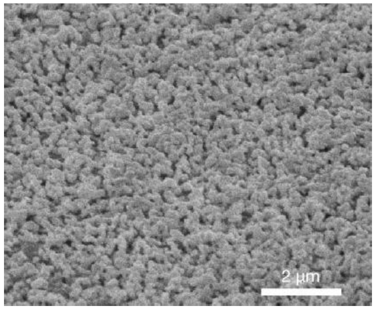
M. FLEISCHMANN, P.J. HENDRA and A.J. McQUILLAN
Department of Chemistry, The University, Southampton SO9 5NH, UK

Received 27 February 1974

Raman spectroscopy has been employed for the first time to study the role of adsorption at electrodes. It has been possible to distinguish two types of pyridine adsorption at a silver electrode. The variation in intensity and frequency of some of the bands with potential in the region of the point of zero charge has given further evidence as to the structure of the electrical double layer; it is shown that the interaction of adsorbed pyridine and water must be taken into account.

Les premières observations d’un spectre Raman exalté de surface ont été faites au milieu des années 70, par Fleischman et ses collaborateurs, dans l’étude de la pyridine adsorbée à la surface d’une électrode d’argent soumise à des cycles d’oxydo-réduction. Quelques années plus tard un phénomène analogue a été mis en évidence par Creighton *et al.* dans des solutions de nanoparticules colloïdales d’argent et d’or agrégées.





A. Kudelski / Vibrational Spectroscopy 39 (2005) 200–213

Hypothèse 1

<u>Fleishmann en 1974:</u>

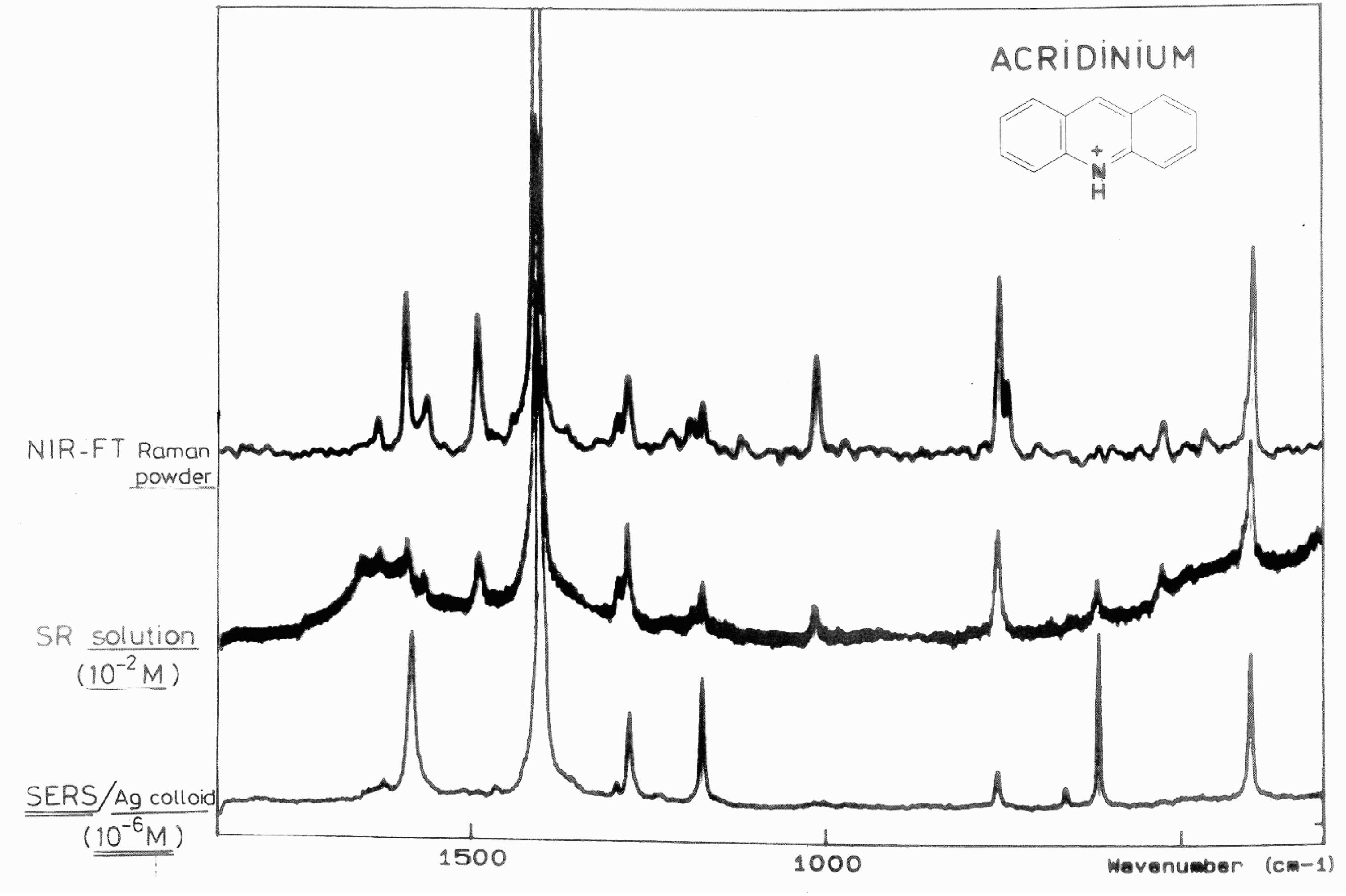
Grande surface spécifique des électrodes rugueuses qui piègent les molécules

Hypothèse 2

<u>Jeanmaire & Van Duyne en 1977:</u>

Plasmons de surface à l’origine de l’exaltation du signal Raman

Surface Enhanced Raman Scattering (SERS)



Dans une expérience SERS classique : G_{SERS} ~ 10^5 -10^6

SERS: première définition

- **SERS = Surface-Enhanced Raman spectroscopy – spectroscopie Raman exaltée de surface**

- **<u>Spectroscopie Raman</u> : Spectre Raman de molécules : la technique consiste à mesurer les spectres Raman de molécules. Permet d'accéder à la structure chimique des composés.**

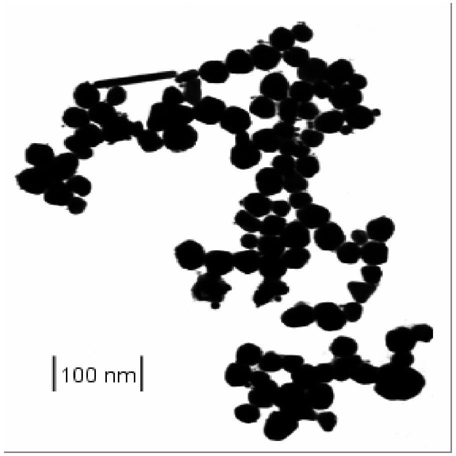
- **<u>Exaltée</u>: Gain grâce au phénomène de résonances de plasmon de surface localisé en présence d'un substrat SERS (nanostructures métalliques*): le facteur d'exaltation est engendré par l'excitation des plasmons de surface localisés.***

- **<u>de Surface</u> : Molécules sur une surface métallique : le SERS est une technique de surface. Les molécules doivent être adsorbées ou à proximité de la surface**

Nanoparticules pour le SERS

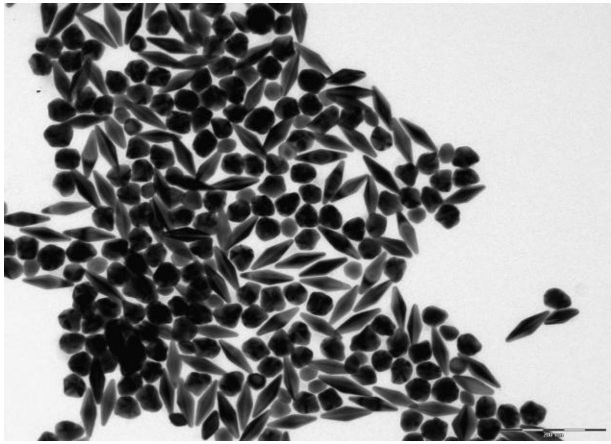
- Fortes résonances plasmon

colloides d'or

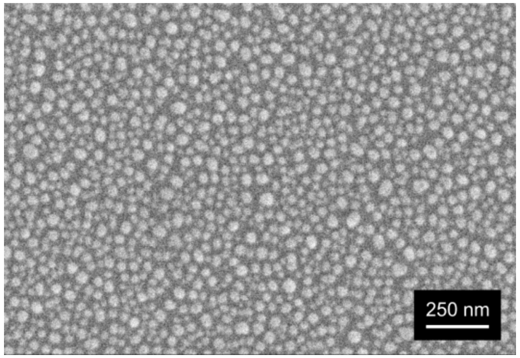


- Premières expériences SERS

- Détection de la molécule unique (points chauds)



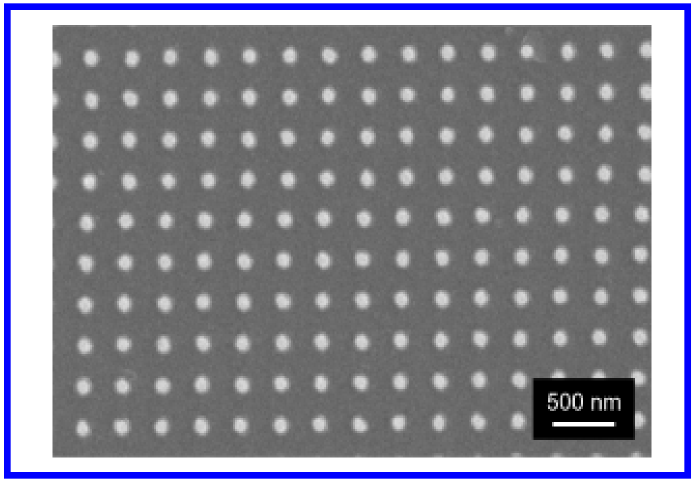
- Films d'argent



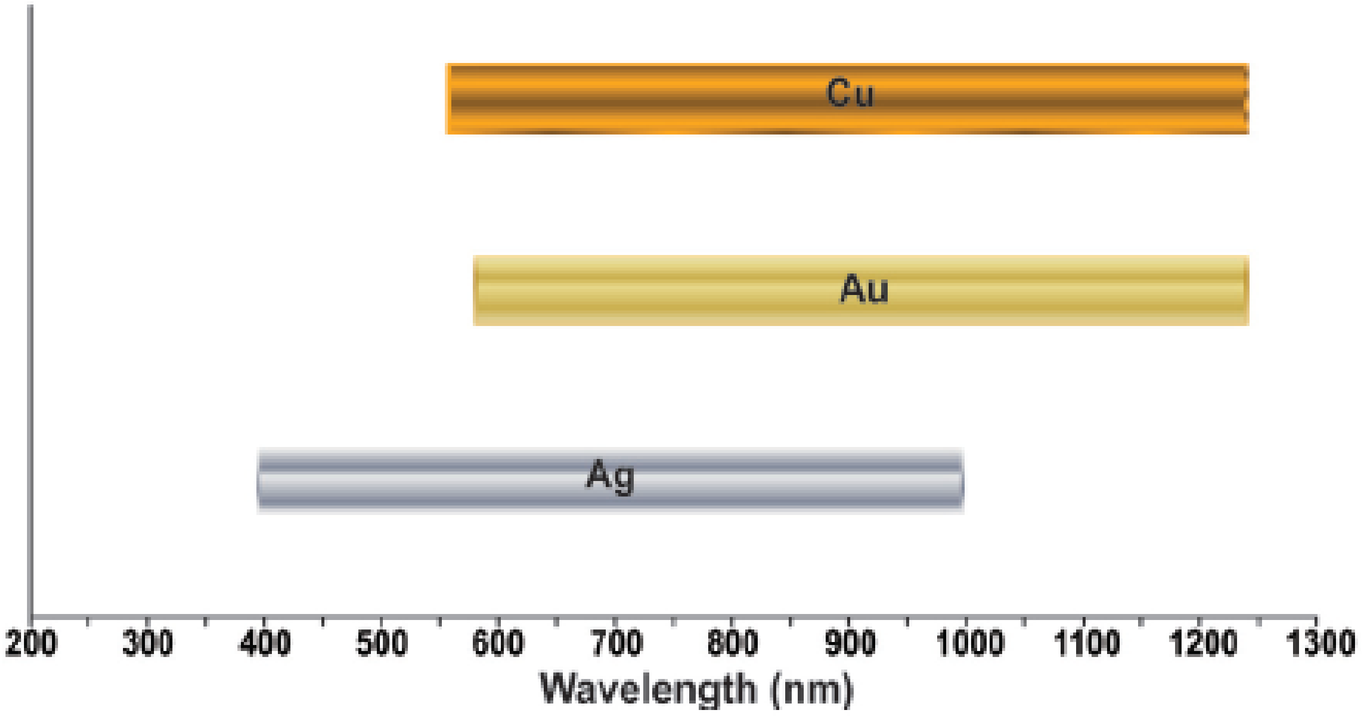
- Avec les progrès sur le plan instrumental: nouveau type de structures organisés

- Meilleure compréhension du phénomène SERS

- Réseau lithographique de NPs d'or



Les métaux bien adaptés et caractérisés pour le SERS sont:



- Performances optiques remarquables (faible partie imaginaire de ε)
- Résonances plasmon dans le visible et proche infra-rouge
- Longueurs d’onde laser principalement dans le visible

ENJEUX

Détection de molécules à l'état de traces

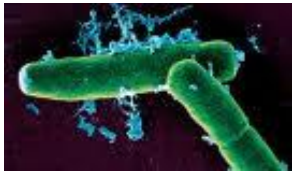
- ***Quels sont les besoins ?***

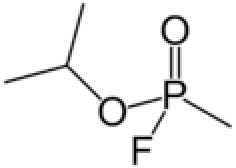
- Domaine bio-médical:

détection de maladies (cancers, maladie d'Alzheimer, de Parkinson…)

- Domaine de la défense :

vecteurs d'attaque chimique et biologique (gaz sarin, anthrax) ; explosifs (TNT, Semtex) ; stupéfiants…

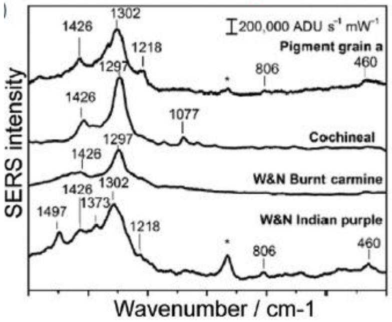




- Domaine de l'art:

Identification de pigments prélevés sur des tableaux de maîtres (restauration)

Avant



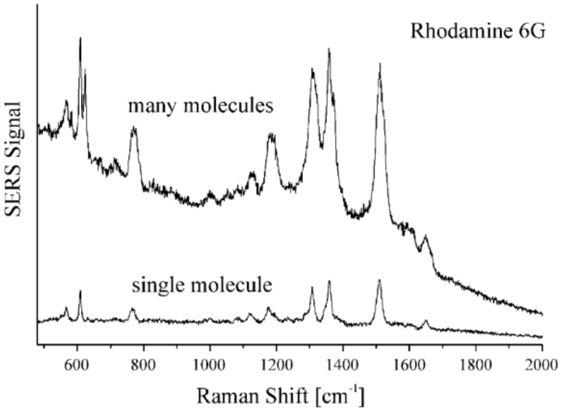
Après

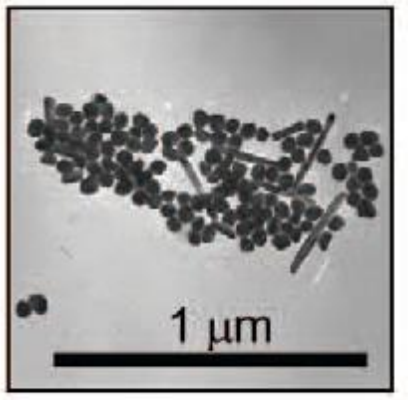
Winslow Homer « for to be a farmer'boy »

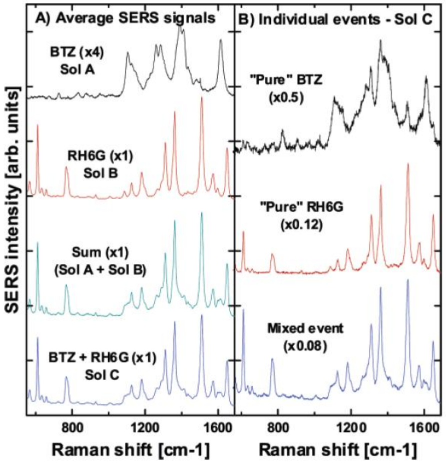
R. Van Duyne et al., Materials Today, vol. 15, 16, 2012

ENJEUX

Détection de molécules à l'état de traces:
Vers la détection de la molécule unique ?



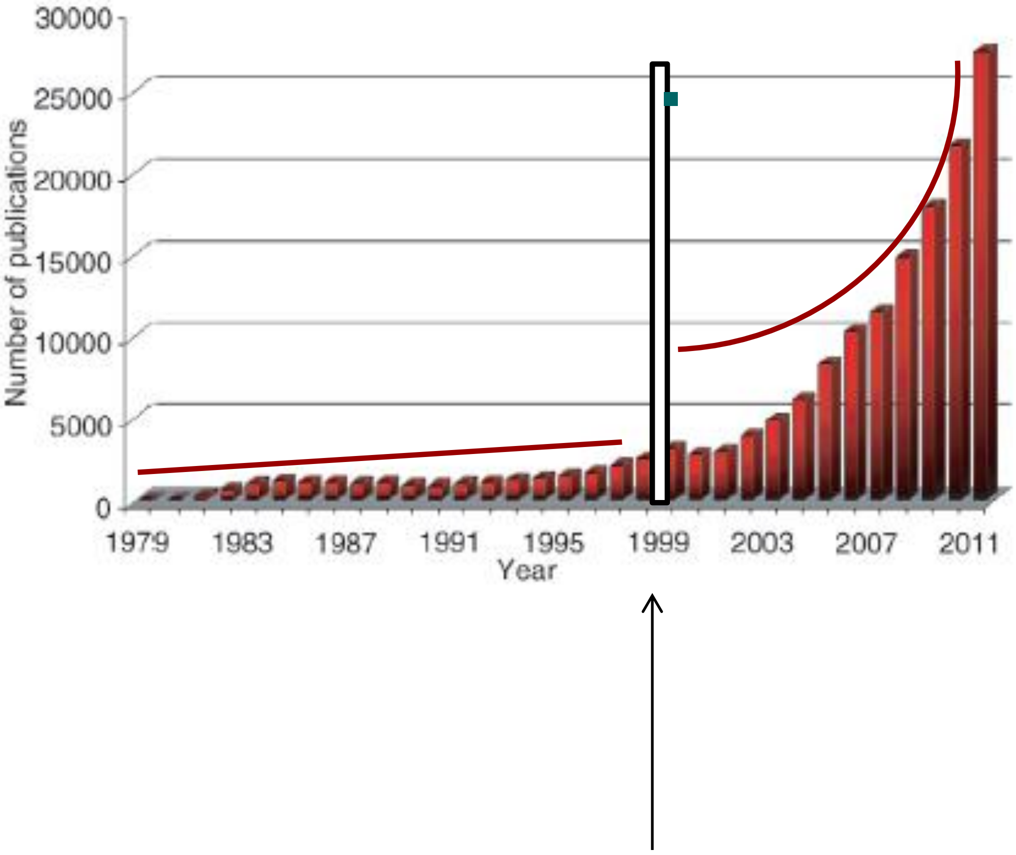




- **Détection de molécules uniques – SM SERS: Nie et Kneipp (1997), plus récemment E. Le Ru (2006)**

[Nie *et al*. <u>Science</u> 1997, Kneipp *et al.* <u>Phys. Rev. Lett.</u> 1997, Le Ru *et al.* <u>J. Phys. Chem .B</u> 2006]

Growing popularity of SERS. This plot shows citation data in Web of Science dor the term : « surface enhanced Raman » (Sept. 2011)



Single molecule detection in SERS

Effet SERS: principe

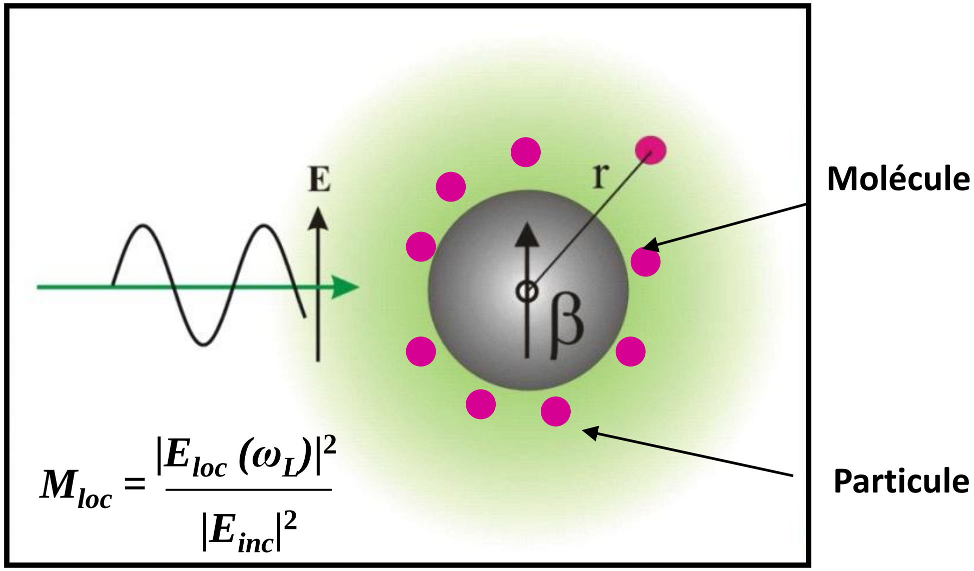
- **M: induced dipolar moment**
  - **Raman signature**

$$\boxed{\vec{M} = [\alpha] . \vec{E}}$$

Molecular origin
model of charge transfer

Electromagnetic field enhancement
due to localized surface plasmons resonance

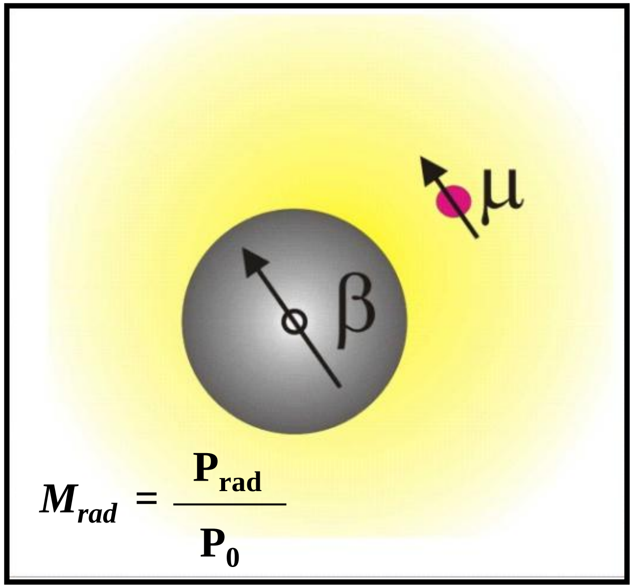
Exaltation à l'excitation $M_{loc}(\omega_L)$:



$$M_{loc} = \frac{|E_{loc}(\omega_L)|^2}{|E_{inc}|^2}$$

Champ électrique ressenti par la molécule à ω_L

Exaltation à l'émission $M_{rad}(\omega_R)$:



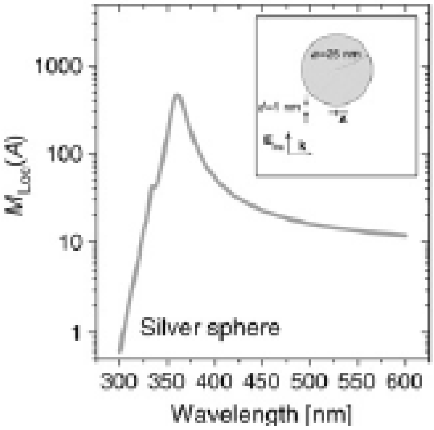
$$M_{rad} = \frac{P_{rad}}{P_0}$$

Emission du dipôle à la fréquence Raman à ω_R
(P: puissance totale rayonnée par le dipôle)

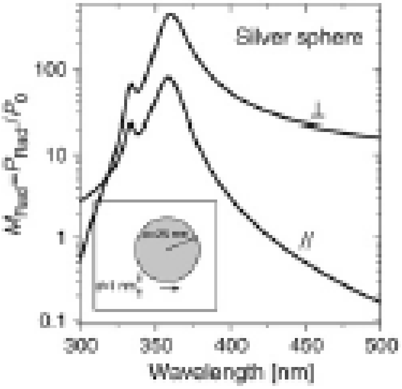
$$<G_{SERS}> = M_{loc}(\omega_L) . M_{rad}(\omega_R)$$

Approximation en $|E|^4$

$$<G> = M_{\mathrm{Loc}}(\omega_L) M_{\mathrm{Rad}}(\omega_R)$$



$$M_{\mathrm{Rad}}(\omega) \approx M_{\mathrm{Loc}}(\omega)$$



http://www.victoria.ac.nz/raman

$$\hbar\omega_\nu = \hbar\omega_L - \hbar\omega_S \sim 0\text{–}200\ \mathrm{meV}$$

$$M_{\mathrm{Loc}}(\omega_L) = M_{\mathrm{Loc}}(\omega_R)$$

Small compared to the typical frequency ranges where M shows substantial changes

$$<G> = M_{\mathrm{Loc}}(\omega_L) M_{\mathrm{Rad}}(\omega_R) \approx M_{\mathrm{Loc}}(\omega_L) M_{\mathrm{Loc}}(\omega_R)$$

$$\boxed{<G_{\mathrm{SERS}}> \sim M_{loc}^{2} \sim \frac{|E_{loc}(\omega_L)|^4}{|E_{inc}|^4}}$$

Localized surface plasmon *versus* SERS

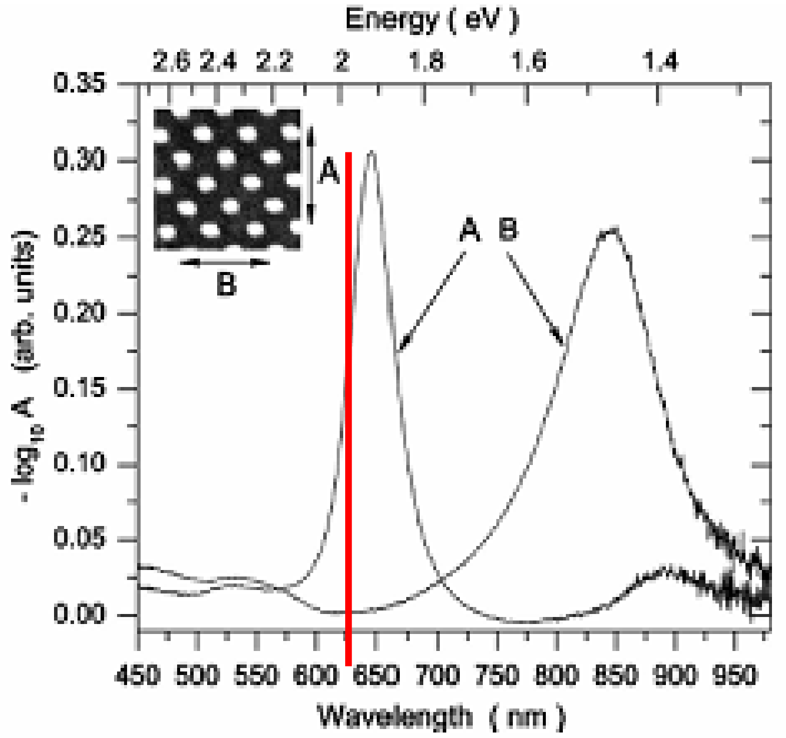
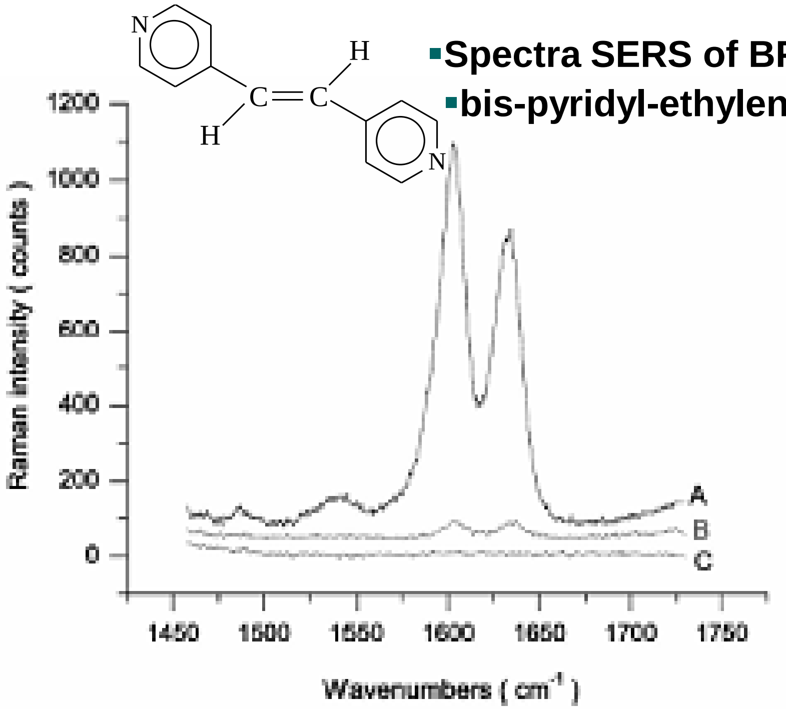


FIG. 1. Extinction spectrum of a regular array of gold elongated nanoparticles; major and medium axes of 175 and 126 nm, respectively, are parallel to the substrate (particle aspect ratio $r = 1.39$), particle height is 40 nm, and the spacing between particles is $\Lambda = 461$ nm. The spectrum is acquired by transmission under normal incidence in water; "A" denotes the transverse polarization and "B" the longitudinal one. Inset: scanning electronic image of the array (detail).



- **Spectra SERS of BPE**
- **bis-pyridyl-ethylene**

FIG. 2. SERS spectra of a 5×10^{-4} M BPE aqueous solution for the array shown in the inset of Fig. 1. Spectra A and B correspond to laser excitation along the transverse (A) and longitudinal (B) LSP resonances, respectively; spectrum C is recorded out of the array. Spectra A, B, and C were recorded under identical experimental conditions: laser excitation 647 nm; power 15 mW at the sample, slit width 300 μm; three accumulations of 180 s counting time each. The spectra are vertically shifted for clarity.

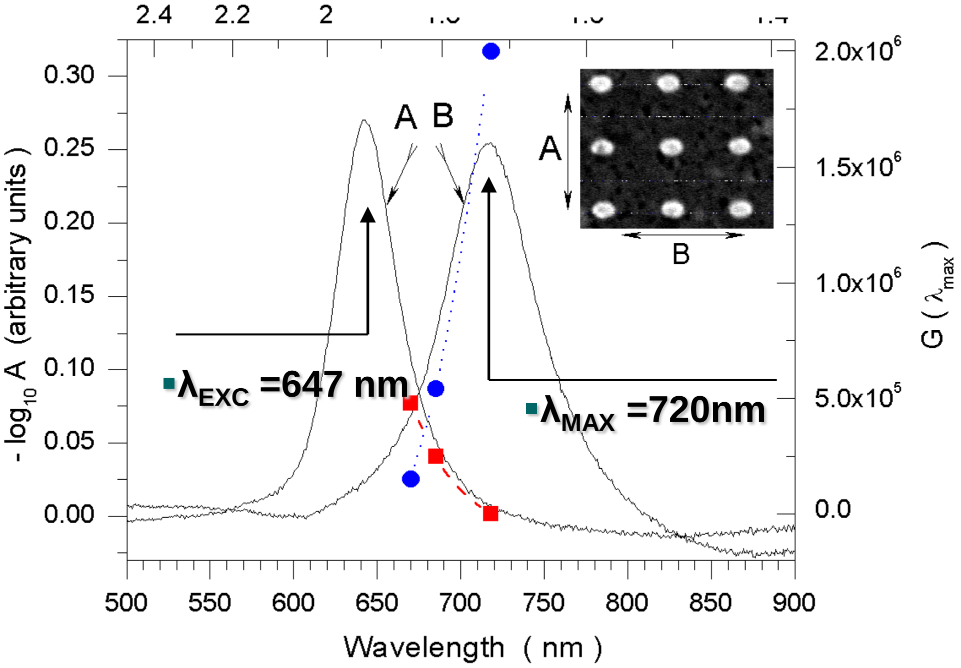
Appl. Phys. Lett., Vol. 82, No. 18, 5 May 2003

Effet SERS: optimisation du gain Raman

$$< G > = M_{\mathrm{Loc}}(\omega_L) M_{\mathrm{Rad}}(\omega_R) \approx M_{\mathrm{Loc}}(\omega_L) M_{\mathrm{Loc}}(\omega_R)$$

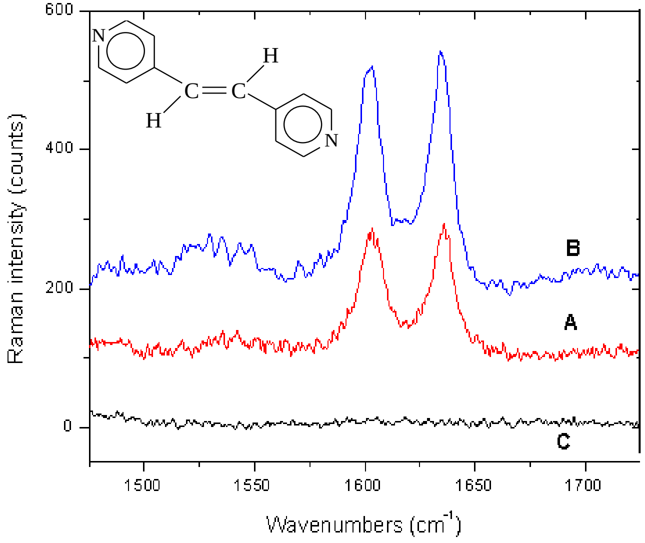
$$\lambda_{\mathrm{max}} = (\lambda_{\mathrm{exc}} + \lambda_{\mathrm{RS}})/2.$$

	λ_{RS} (nm)		λ_{max} (nm)	
λ_{exc} (nm)	1610 cm^{-1}	1640 cm^{-1}	1610 cm^{-1}	1640 cm^{-1}
633	704.6	706.1	668.7	669.5
647	722.2	723.8	684.6	685.5
676	758.6	760.3	717.3	718.2



Extinction : gold elongated particles on ITO

- **SERS of BPE : Excitation at 647 nm**
- **A : transverse polarization, B : longitudinal polarization**
- **C : out of the NP array**



N.Félidj et al., Appl. Phys.Lett. 82, 3095 (2003)

SERS: polarization effects...

- **Raman bands intensity follows the LSP band profile**

$$F(\mathbf{r}) \approx M_{\mathbf{Loc}}(\mathbf{r},\omega_L)M_{\mathbf{Loc}}(\mathbf{r},\omega_R)$$

$$= \left|\frac{\mathbf{E}_{\mathbf{Loc}}(\mathbf{r},\omega_L)}{E_{Inc}}\right|^2 \left|\frac{\mathbf{E}_{\mathbf{Loc}}(\mathbf{r},\omega_R)}{E_{Inc}}\right|^2$$

Spatial averaging:

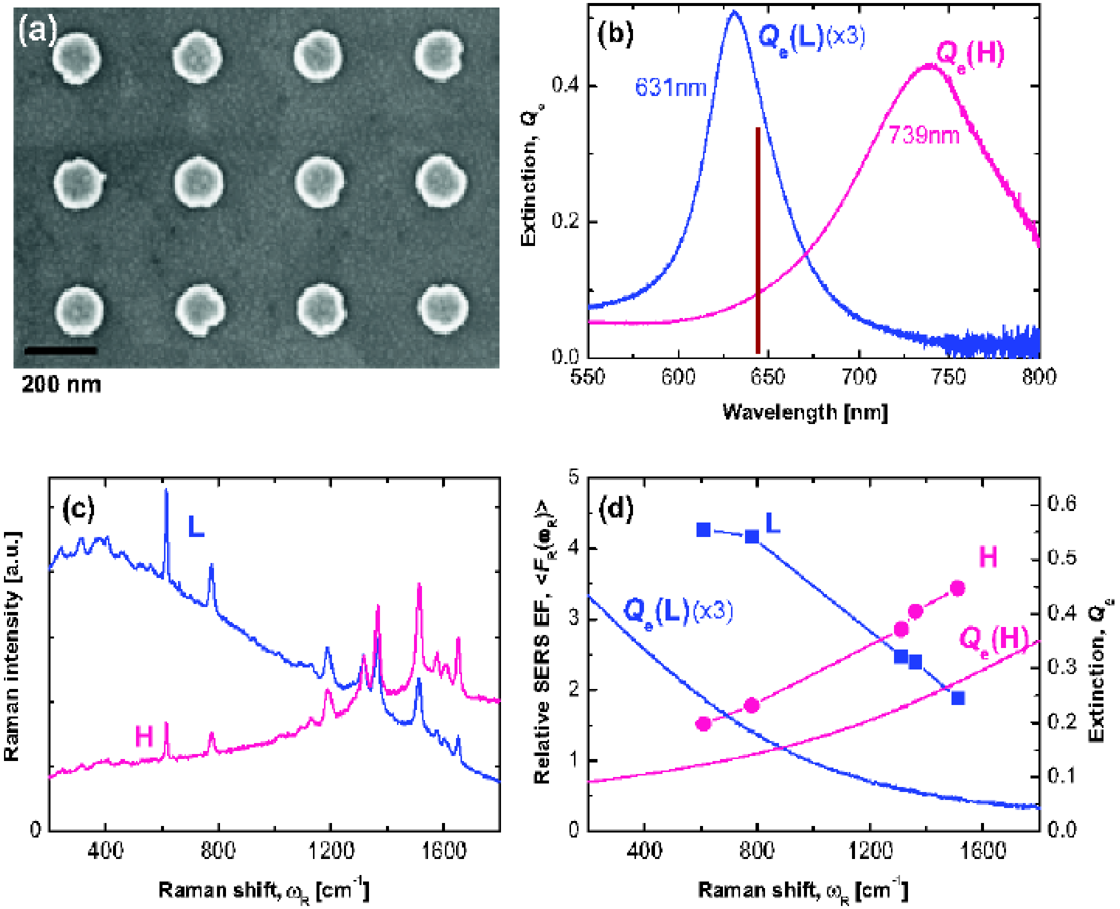
$$\langle F(\mathbf{r})\rangle \approx A(\omega_L)A(\omega_R)$$

$$A(\omega) \equiv \langle M_{\mathbf{Loc}}(\mathbf{r},\omega)\rangle$$

should have the spectral profile as

$$Q_{ext}(\omega)$$

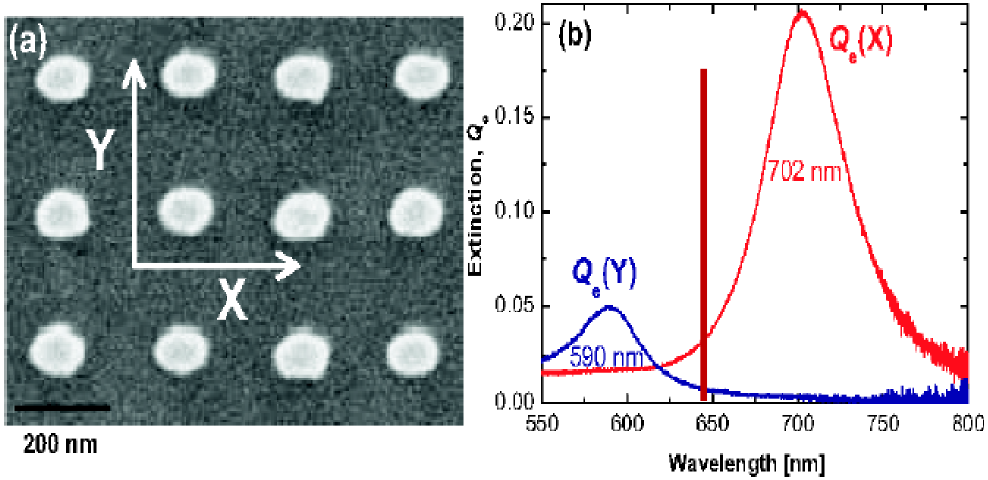
J. Phys. Chem. C 112, 8117 (2008)



(a) Representative SEM image of an array of gold oblate NPs. (b) Extinction spectrum for two arrays of oblate particles of height ~50 nm and diameter 100 nm (L) and 160 nm (H), respectively. (c) Corresponding SERS spectra at 633-nm excitation (with the ITO background subtracted) after dipping arrays L and H in a 10^{-5} M Rhodamine 6G solution. (d) Comparison between the relative EFs of the SERS peaks (symbols) and the extinction profile for each array (lines).

… beyond the $|\mathbf{E}|^4$ –approximation

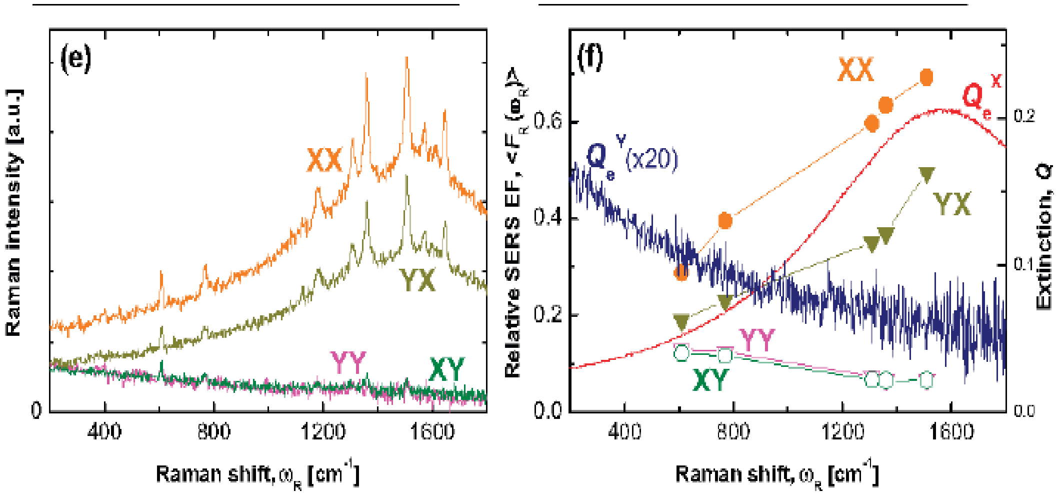
$$F^{ED}(\mathbf{r}) = \left| \frac{\mathbf{E}^{D}_{loc}(\mathbf{r},\omega_R)}{E_{Inc}} \bullet \hat{\alpha}_N \bullet \frac{\mathbf{E}^{E}_{loc}(\mathbf{r},\omega_L)}{E_{Inc}} \right|^2$$



D (*E*): detection (exciting) polarization

Spatial averaging:

$$\left\langle F^{ED}(\mathbf{r}) \right\rangle \approx A^{E}(\omega_L) A^{D}(\omega_R)$$



And again:

$$A(\omega) \propto Q_{ext}(\omega)$$

- **Depolarization factor**

Gain Raman: mesure expérimentale

Le gain est défini par rapport aux propriétés non-SERS

<u>Qu’est-ce qu’une bonne sonde moléculaire?</u>

En principe, toutes les molécules conviennent en SERS.

On préfèrera celles qui ont une forte section efficace de diffusion Raman (importante pour les colorants, en particulier quand l’excitatrice est proche de la bande d’absorption: <u>resonant Raman scattering: **SERRS**</u>

- **Nécessite de caractériser la molécule en non-SERS (connaître sa section efficace de diffusion Raman).**

Gain Raman moyenné (lié à un champ électrique local très inhomogène)

- Gain moyen pour un ensemble de molécules sur la surface
- Important pour toutes applications analytiques
- Valeurs typiques 10^4 (facile) – 10^6 (bien) – 10^8 (max)

$$\mathrm{EF} = \frac{I_{\mathrm{SERS}}/N_{\mathrm{Surf}}}{I_{\mathrm{RS}}/N_{\mathrm{Vol}}}$$

Gain Raman pour une molécule unique ?

- Gain pour une molécule unique SMEF:

$$\mathrm{SMEF} = \frac{\mathrm{d}\sigma_{\mathrm{SERS}}}{\mathrm{d}\Omega} \Big/ \frac{\mathrm{d}\sigma_{\mathrm{RS}}}{\mathrm{d}\Omega}$$

- Dépend de sa localisation : nécessité de se situer au voisinage d’un point chaud.
- Maximum SMEF $\approx 10^{10}$-10^{11} (points chauds)

Gain Raman pour une molécule

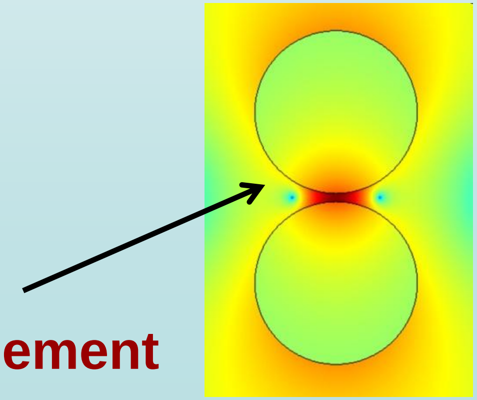
- Section efficace minimum détectable par un instrument Raman
  - Dépend des paramètres expérimentaux
  - Typiquement pour SM-SERS, 1-10 mW, objectif x100 large NA, τ = 0.1s

$$\Rightarrow \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{Min}} \approx 10^{-19}\ \mathrm{cm}^2/\mathrm{sr}$$

- Gain SERS minimum pour SM-SERS
  - Pour un section efficace non-SERS $\approx 10^{-27}$ cm^2/sr

$$\Rightarrow F_{\mathrm{Min}} \approx 10^8$$

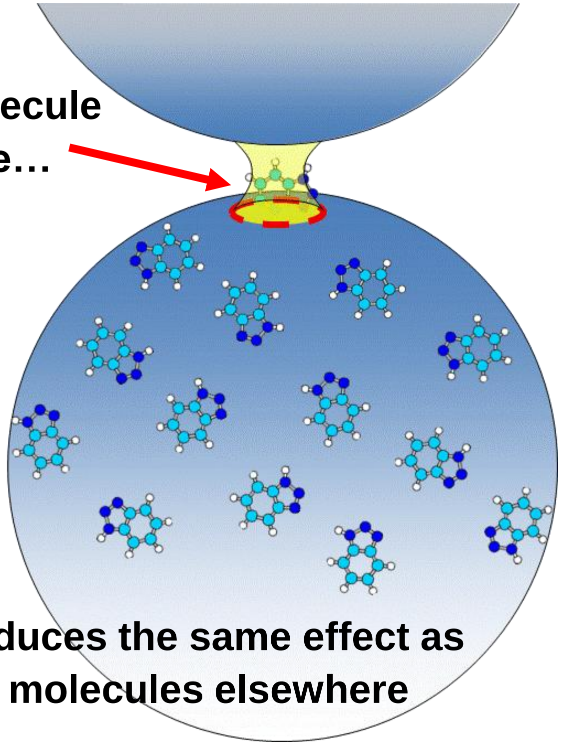
  - Molécule très résonante : $F_{\mathrm{Min}} \approx 10^5$
  - Molécule non- résonante : $F_{\mathrm{Min}} \approx 10^{10}$-$10^{11}$



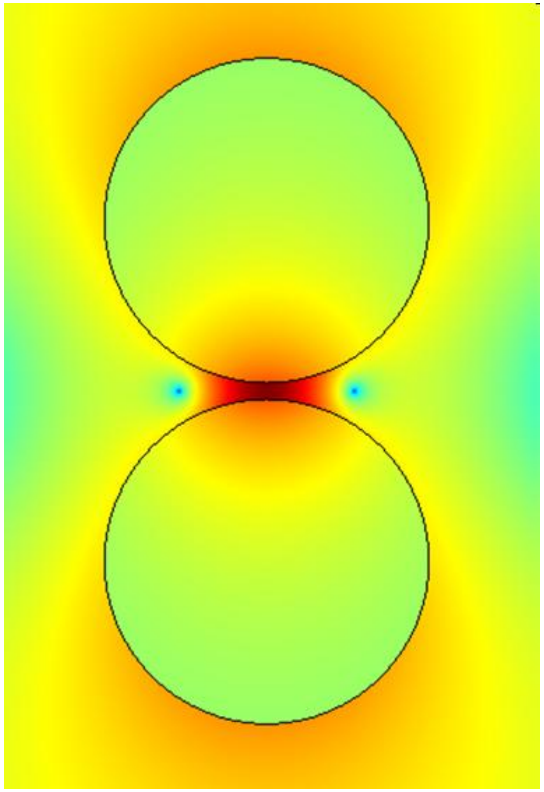
$\Rightarrow$ **SM-SERS détectable aux « points chauds » uniquement**

SERS: points chauds

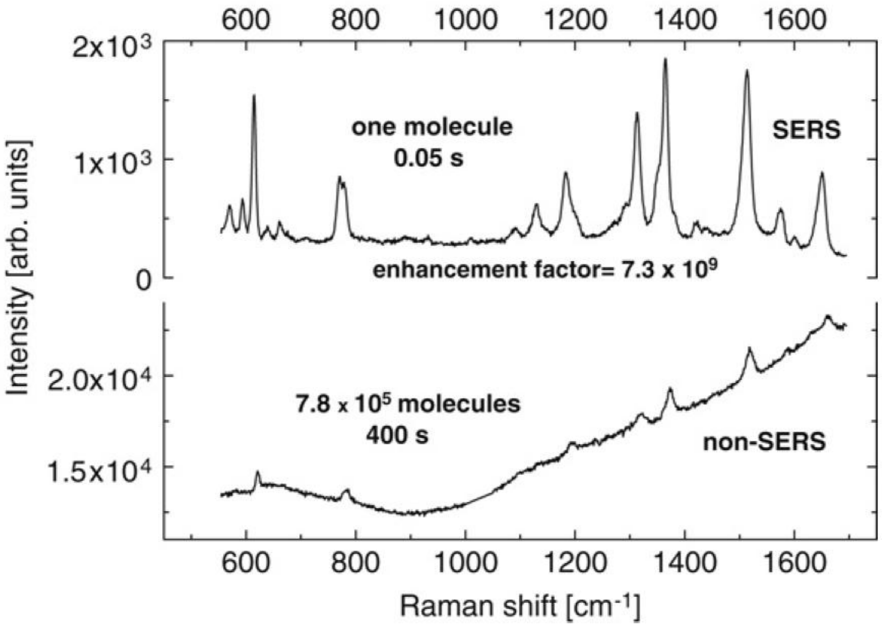
- $F_{Max} \approx 10^{10}$
- Mais $p\ (F > 10^8) \approx 1\%$
- $\langle F \rangle \approx 10^7\text{-}10^8$
- Une molécule au point chaud contribue 100-1000 fois plus qu’une molécule « moyenne »



- 1 molecule here…
- Produces the same effect as ~300 molecules elsewhere



SERS et molécules uniques



$$\mathrm{SMEF} = \frac{I_{\mathrm{SERS}}^{\mathrm{SM}}}{\langle I_{\mathrm{RS}}^{\mathrm{SM}} \rangle}$$

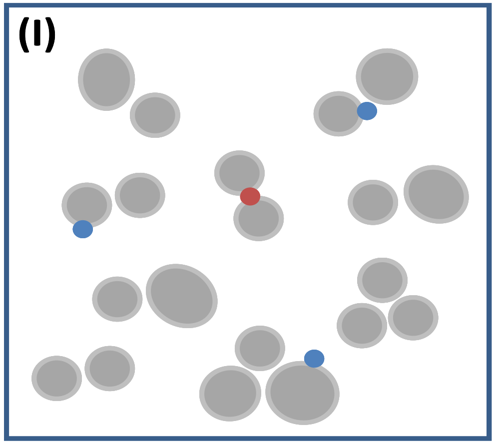
- **Raman EF: 7.3 x 10^9**

Raman (non-SERS) and SERS spectra at 633nm laser excitation (3mW) for rhodamine 6G molecules (RH6G). The (vertical) intensity axis is in arbitrary units but the same for both spectra.

Bottom spectrum: signal of 7,8 .10^5 RH6G molecules (100 microM solution in a 13 m^3 scattering volume, 100 immersion objective with 400 s integration time).

Top: signal from a single RH6G molecule (isolated by the two-analyte method) under the same experimental conditions but with 0.05 s integration time. In order to go from the spectrum at the bottom to the one at the top, an amplication of the Raman signal by an enhancement factor of 7,3. 10^9 is required.

Single Molecule SERS problematic : pioneer work



▪**Original work by**:

- Nie and Emory, Science 275, 1102 (1997)
- Kneipp *et al*., PRL 78, 1667 (1997)

▪**How?**

- Silver colloidal particles
- Ultra-low concentration of analytes (pM-fM)
- Every recorded spectra should *statistically* originate from a single molecule

▪**Drawbacks**:

- Ultra-low concentration: prone to error
- Inhomogeneous enhancement **x** ultra-low concentrations **=** extremely poor statistics of SM-SERS events
- No absolute proof of single-molecule detection

▪**Advantage of these pioneer studies**:

- Hint that SM-SERS is a real possibility

Détection de la molécule unique par SERS (SM-SERS): problématique

Trois problèmes du point de vue expérimental:

- **(I) Démonstration de la faisabilité du SM-SERS**

- **(II) Etude de la phénoménologie SM-SERS**
  - Etude des points chauds
  - Propriétés SERS de molécules uniques (orientation, etc…)
  - Nécessite un grand nombre de spectres SM-SERS

- **(III) Détection de *toutes* les molécules uniques**
  - Nécessite de positionner parfaitement la molécule au point chaud
  - Nécessite un bon contrôle du substrat SERS

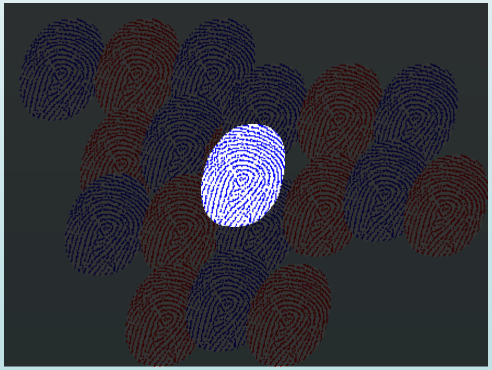
Bi-Analyte SERS

Principe

- Mélange de 2 types de molécule

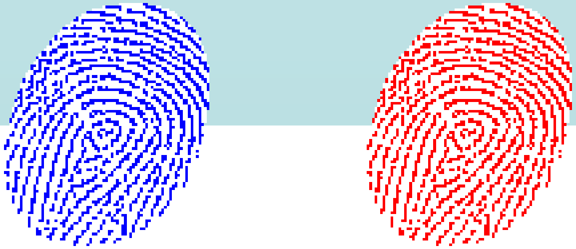
- 3 régimes possibles en fonction de la concentration:

- **Faible concentration:**
  - **Une molécule maximum au point chaud**



- **ou**

  - **Observation de spectres SERS « pure »**

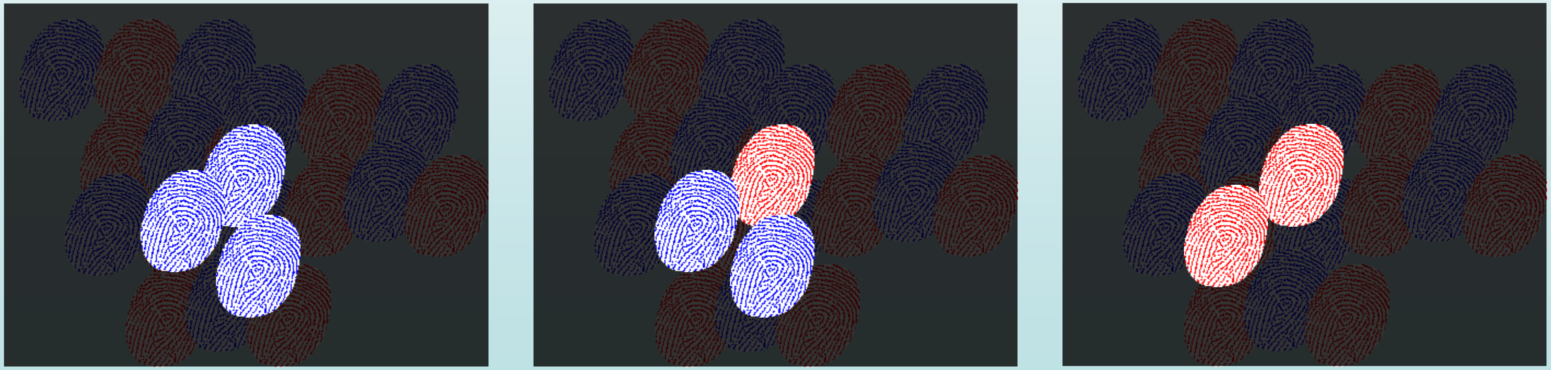


Bi-Analyte SERS

Principe

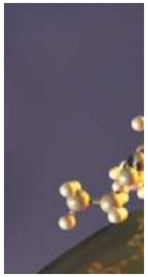
- Mélange de 2 types de molécule
- 3 régimes possibles en fonction de la concentration:

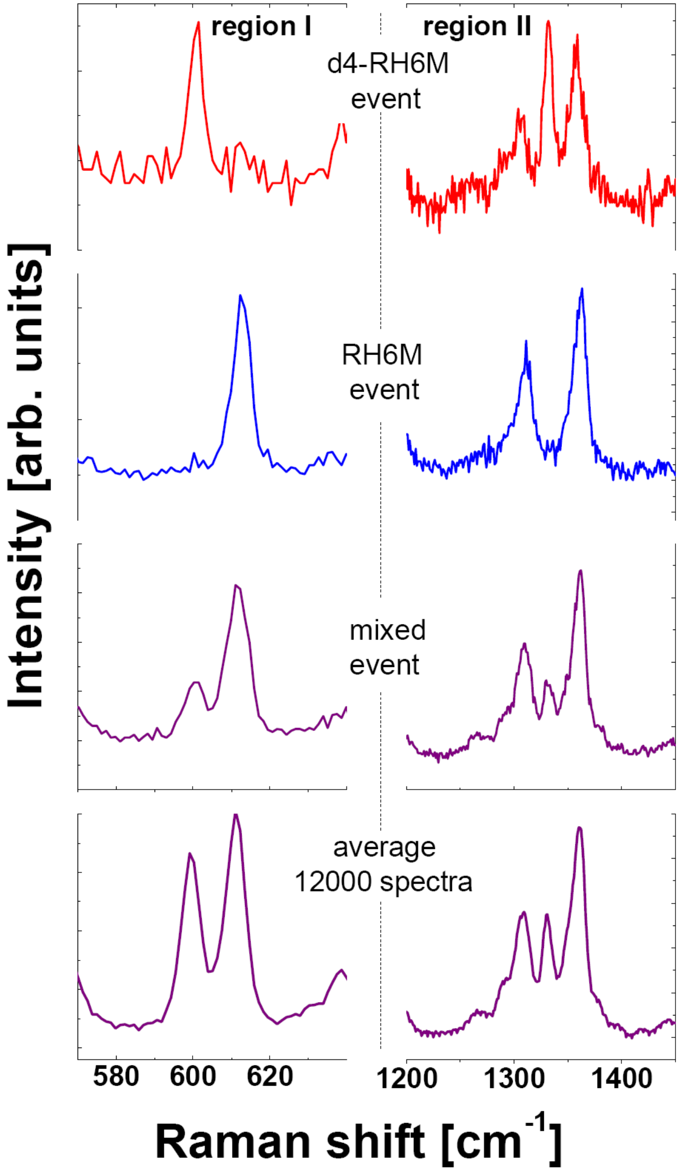
- **Concentration intermédiaire:**
  - **Quelques molécules maximum au point chaud**



  - **Observation de spectres SERS « pure » et « mixtes »**

Bi-Analyte SERS





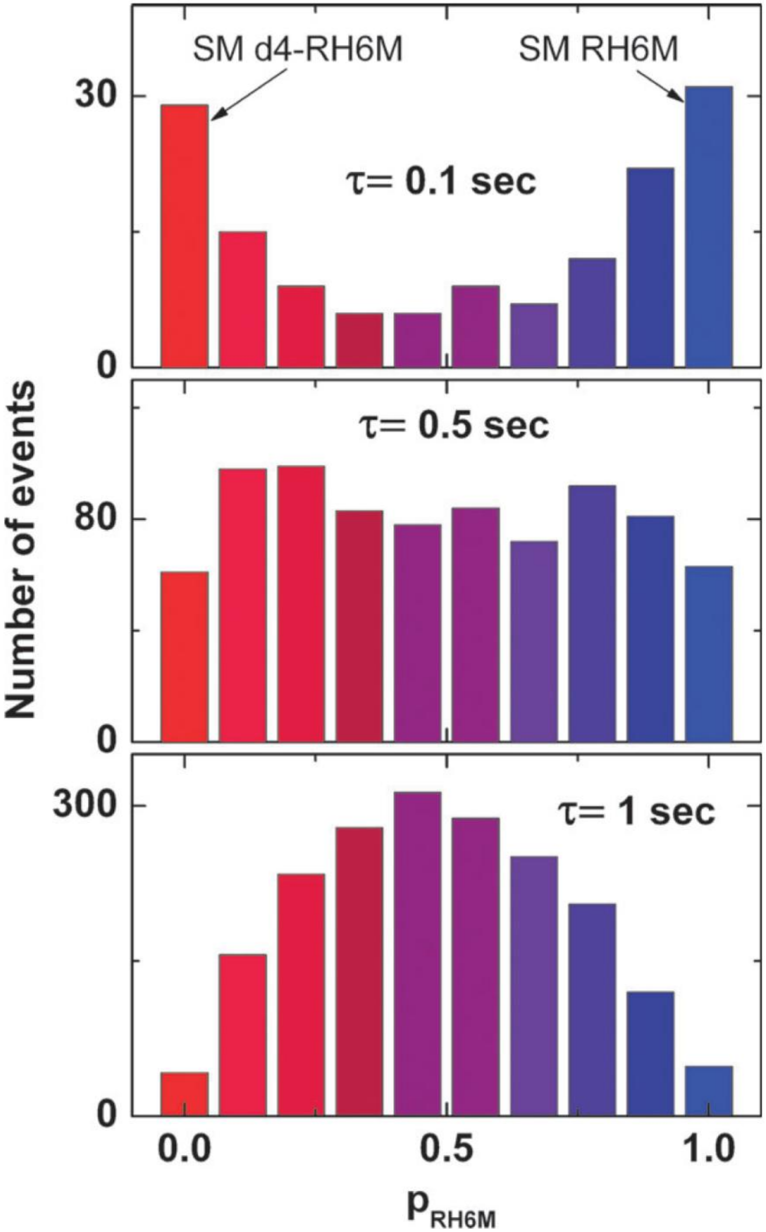


Figure of merit for SM-SERS efficiency

By comparing the **average** and the **maximum** (single molecule) SERS Enhancement Factors

$$\eta = \frac{AEF}{SMEF}$$

- **Analytical Enhancement Factor (Average EF)**

$$AEF = \frac{I_{SERS} / c_{SERS}}{I_{RS} / c_{RS}}$$

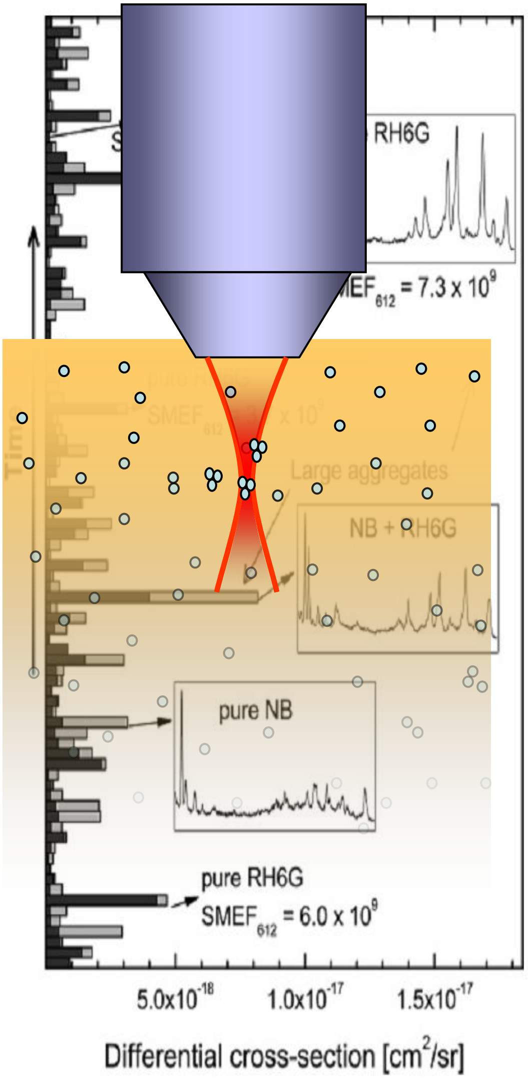
- **Single-Molecule Enhancement Factor**

$$SMEF = \frac{d\sigma_{SERS} / d\Omega}{d\sigma_{RS} / d\Omega}$$

- Ideal SERS substrate: $\eta = 1$
- => every analyte is located at a HS *i.e.* experience the same (maximum) EF

η for a typical SERS substrate?

- Typical SERS substrate for SM-SERS experiment: Ag colloids + KCl



- 1nM of RH6G + 1nM of Nile Blue

~ 12 molecules of each type per colloid

one hot-spot ≈ 1% total area available

- Brownian motion ensures sampling

- Max SMEF ≈ 10^{9} -10^{10} for RH6G
- AEF ≈ 10^{5}-10^{6} for RH6G

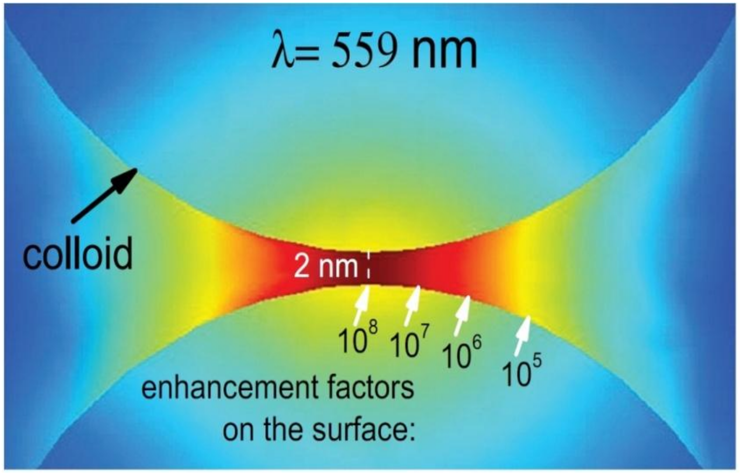
$$\Rightarrow \eta \approx 10^{-4}$$

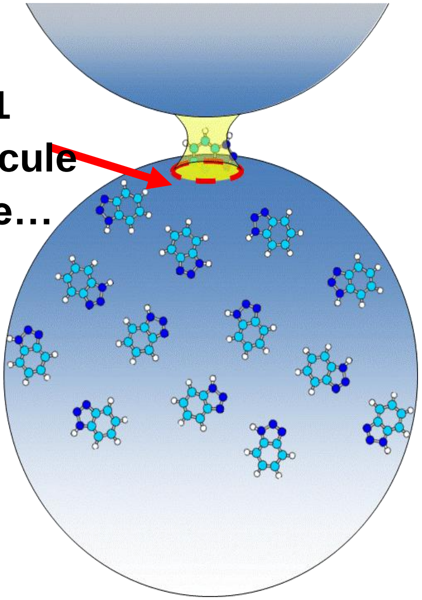
▪*E. Le Ru et al., J. Phys. Chem. C.**111**, 13794 (2007)*

Why is η so low?

- High non-uniformity of the EF distribution

- Large EFs occur only at hot-spots => this is precisely the EF measured by the SMEF !





- **1 molecule here…**

- **Produces the same effect as ~300 molecules elsewhere**

- Polydispersity of colloidal clusters and therefore of their resonance conditions

- *E. Le Ru et al., J. Chem. Phys.* ***125****, 204701 (2006).*

How to increase η ?

In other words:

How to force a single available molecule to go to the right position in order to observe its SERS signal?

- TERS?

$\Rightarrow$ fine control over the position and characteristics of a single hot-spot

But there remains the problem of having the molecule precisely at the hot-spot…

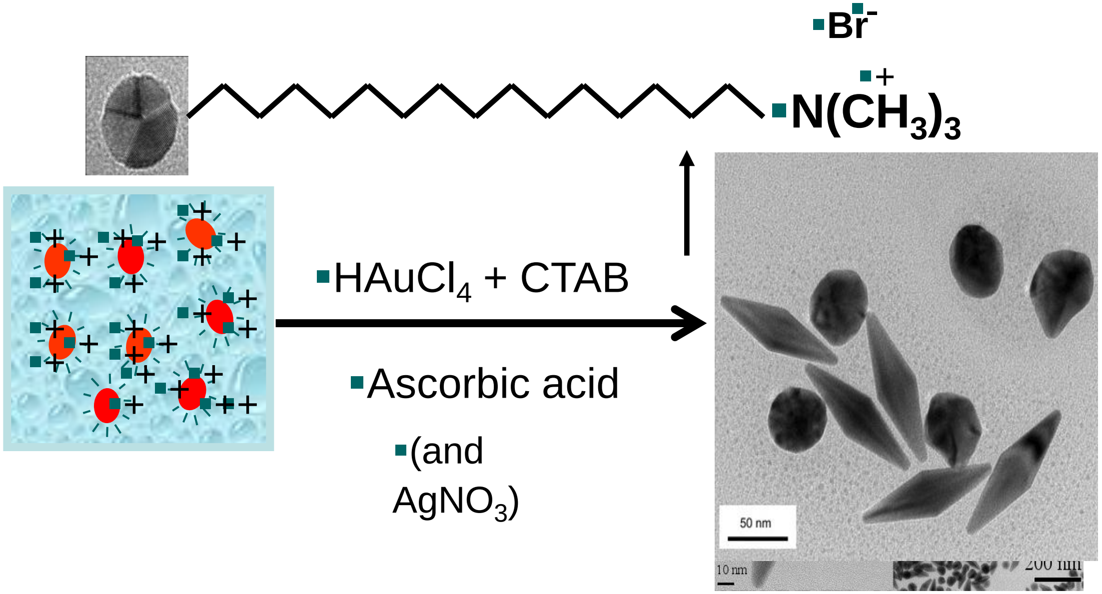
- What if…

$\Rightarrow$ **…** we can chemically block access of the analyte to the surface, ***except*** at the hot-spot?

$\Rightarrow$ let’s try this…

Colloidal Gold Bipyramids

- Two step synthesis (seed+growth):
  - 3nm gold particles serve as seed…
  - …for growth of Bipyramids in a slow, controlled reducing step



Br^-

$\overset{+}{N}(CH_3)_3$

$HAuCl_4$ + CTAB

Ascorbic acid

(and $AgNO_3$)

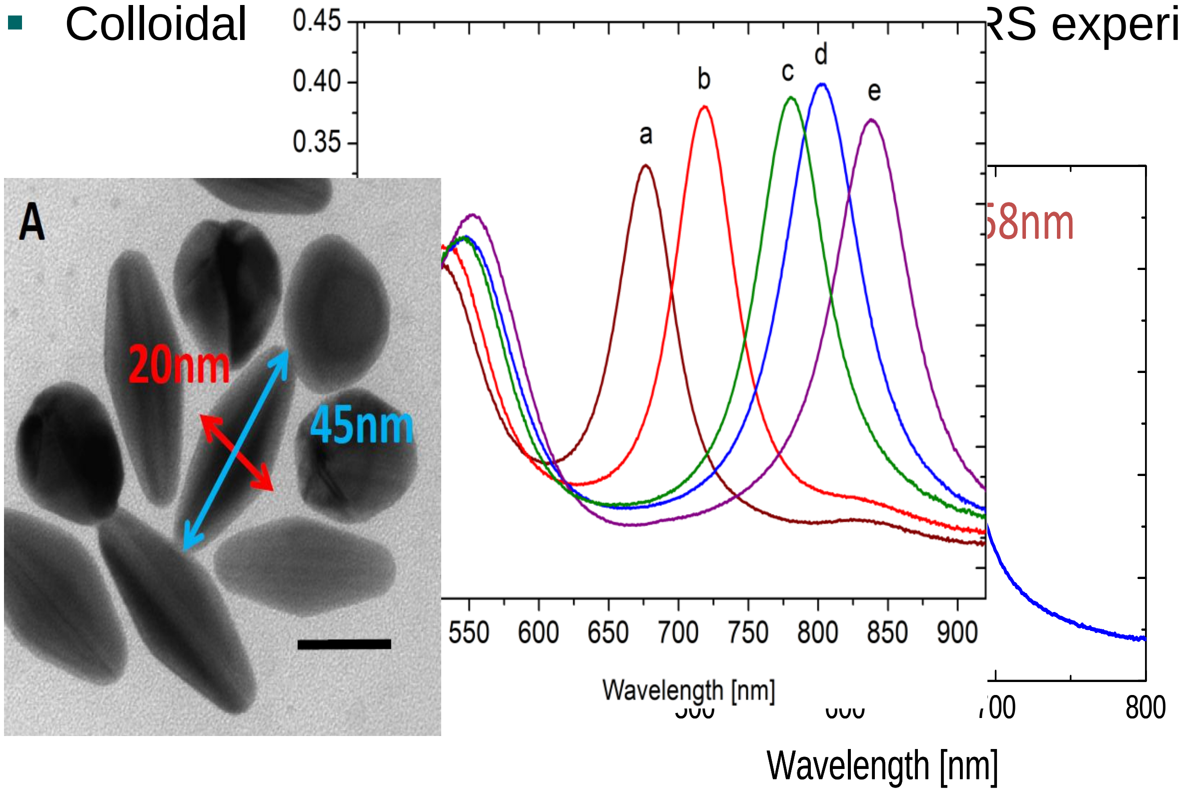
  - Mixture of gold spheres and Bipyramids (~ 2:1 ratio)
  - Good monodispersity

BiP Optical characterization

- The BiP growth is controlled by the amount of gold seed solution

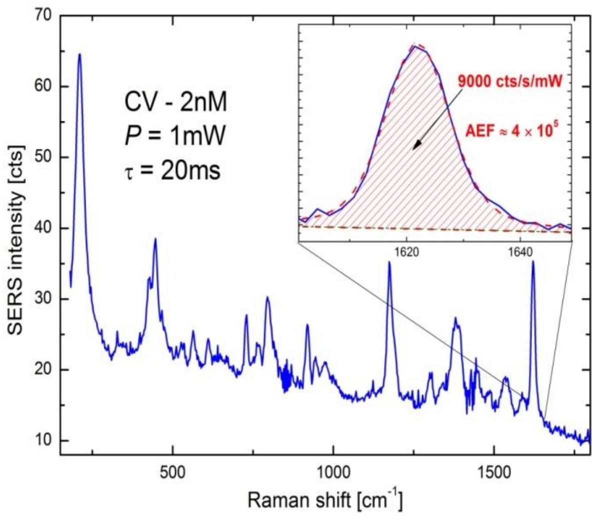
⇒ spectral tuning of the Localized Surface Plasmon Resonance is possible:

- Colloidal RS experiments:



SERS experiments with BiP

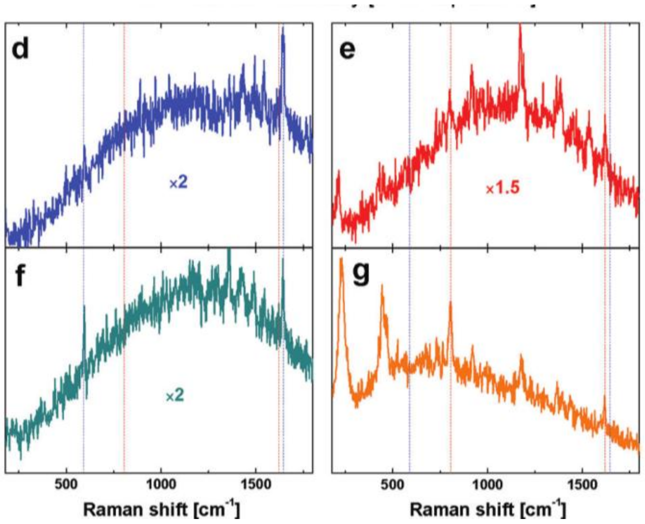
- Excitation @633nm
- SERS probe: Crystal Violet (CV)
    - pre-resonance condition
    - low fluorescence (i.e. $d\sigma_{RS}/d\Omega$ can be measured)
- [CV] = 2nM ≈ 30-60 molecules per particle, depending on whether it adsorbs on spheres or not
- Average SERS spectrum obtained from 1000 individual spectra:

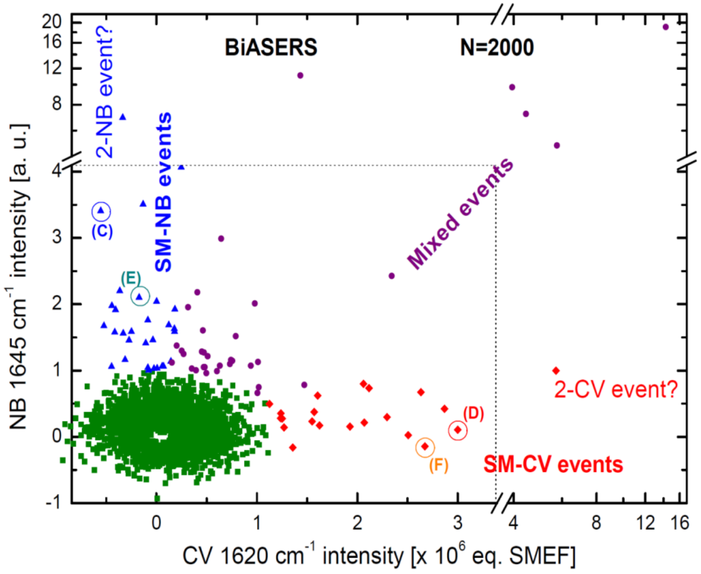


AEF ≈ 4.10^5 for the 1620 cm^{-1} band

SM-SERS Regime and SMEF estimation

- Bi-analyte experiments at increasingly reduced number of molecule per particle
- Bi-analyte partner to CV: Nile Blue (NB)





- **SM-SERS CV**
- SM-SERS **NB**
- **Mixed** spectra
- Below sensitivity

(d,f):NB, (e,g): CV

~ 1 molecule/HS

✓ SM-regime

✓ SMEF in the range 1.5-3x10^{6}

E. Le Ru et al., NanoLetters, 2011

η for these BiPyramids

- The figure of merit introduced earlier is then: $\eta = \frac{AEF}{SMEF} \approx 0.13$

- Which means: every CV molecule experiences a SERS EF very close in magnitude to the maximum value

- Then: if this maximum SERS EF is large enough *and* the detection sensitivity adequate, every CV molecule can be detected

- η is a factor of ~1000 better than the commonly used Ag colloids

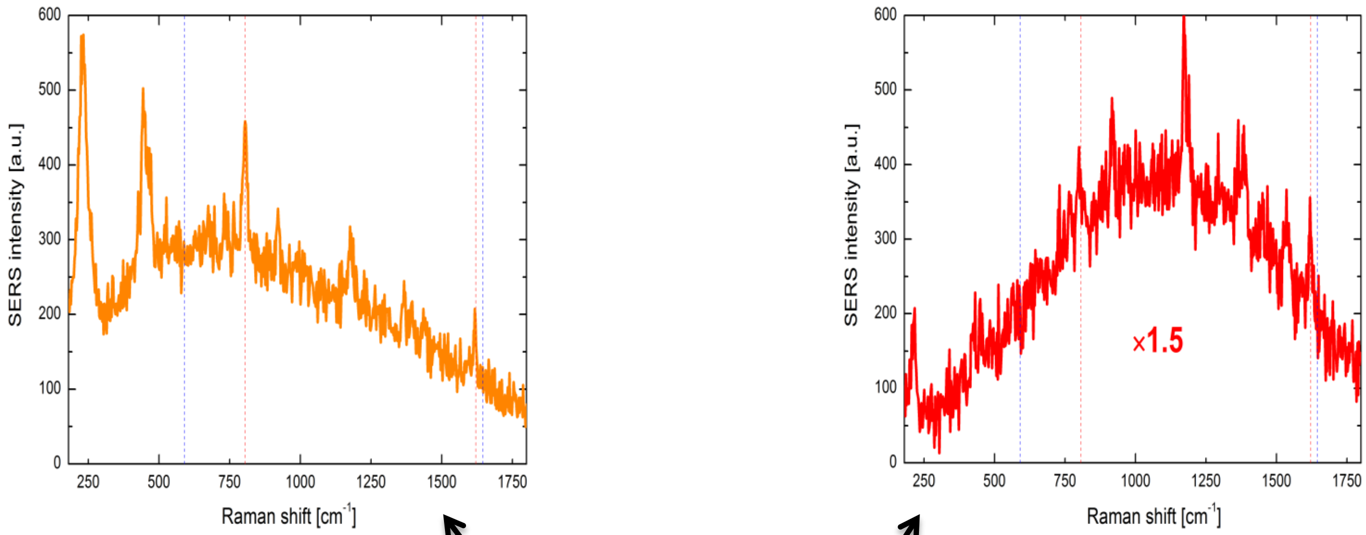
Improving η

- There is a remaining factor of 7-8 to reach $\eta = 1$

- Main factor to improve: polydispersity of the BiP solution...

- ...even if notably quite low compared to the common Lee & Meisel silver colloids

- Small changes in LSP resonance condition from one BiP to another are evidenced by the changes in the SM-spectra background:



- Two SM-SERS spectra of CV

SERS

Spectroscopie Raman

- Propriétés Raman des molécules
- Résonance Raman
- Calculs (DFT, etc…)

Chimie et physique des surfaces

- Adsorption
- Electrochimie
- Fonctionnalisation

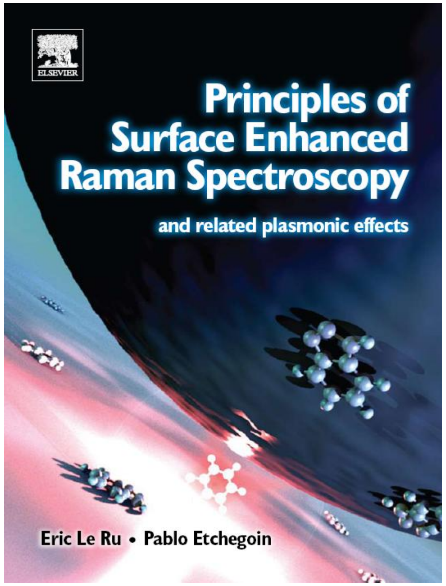
SERS

Plasmonique

- Propriétés optiques des métaux
- Etude des résonances plasmons
- Fabrication de nano-structures

⇒ *Electromagnetisme, nano-photonique, nano-technologies*

Références



http://www.victoria.ac.nz/raman

-**M. Moskovits, *Persistent misconceptions regarding SERS*, PCCP, 2013, 15, 5301**