Red-Shift Effects in Surface Enhanced Raman Spectroscopy: Spectral or Intensity Dependence of the Near-Field?

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Abstract :

Optimum amplification in Surface Enhanced Raman Scattering (SERS) from individual nanoantennas is expected when the excitation is slightly blue-shifted with respect to the Localized Surface Plasmon Resonance (LSPR), so that the LSPR peak falls in the middle between the laser and the Stokes Raman emission. Recent experiments have shown when moving the excitation from the visible to the near-infrared that this rule of thumb is no more valid. The excitation has to be red-shifted with respect to the LSPR peak, up to 80nm, to obtain highest SERS. Such discrepancy is usually attributed to a Near-Field (NF) to Far-Field (FF) spectral shift. Here we critically discuss this hypothesis for the case of gold nanocylinders. By combining multi-wavelength excitation SERS experiments with numerical calculations, we show that the red-shift of the excitation energy does not originate from a spectral shift between the extinction (FF) and the near-field distribution (NF), which is found to be not larger than 10nm. Rather, it can be accounted for by looking at the peculiar spectral dependence of the near-field intensity on the cylinders diameter, characterized by an initial increase, up to 180nm diameter, followed by a decrease and a pronounced skewness.

Introduction:

Surface Enhanced Raman Scattering (SERS) is a powerful technique to detect and characterize chemical¹⁻⁷ or biological⁸⁻¹² species. Due to the high enhancement factor that can be reached in SERS, it has already been demonstrated that molecules can be detected at very low concentrations paving the way to the single molecule sensitivity¹³⁻¹⁹. SERS exploits the optical properties of metallic nanostructures and their resonant interaction with light. It is mainly based on two mechanisms: (i) a chemical^{20, 21} and (ii) an electromagnetic^{22, 23} effect. The former results from substrate-adsorbate-photon interactions²⁴. The enhancement factor from chemical effect is estimated to be of the order of 100^{25,26}. The second effect is due to the high enhancement of the electromagnetic field at the vicinity of the nanostructure surface. This Near-Field (NF) enhancement is directly related to the excitation of the Localized Surface Plasmon Resonance (LSPR), which is associated to the collective oscillation of the free electron cloud inside the nanostructure. The LSPR is associated to a high electromagnetic field close to the nanostructure. The electromagnetic enhancement can reach up to 10⁸ and is then considered as the predominant contribution^{27, 28}. Such a giant amplification factor comes from a two-step process in which both the excitation and the Raman scattered light are enhanced^{29,32}.

The SERS intensity can be written³²:

$$I_{\text{SERS}} = \mu_{\text{S}} G M(\lambda_{\text{LASER}}) M(\lambda_{\text{Raman}}) \frac{\partial \sigma_{\text{RS}}}{\partial \Omega} \Delta \Omega_{\text{Det}} S_{\text{inc}} \quad (1)$$

where μ_{S} is the surface density of the molecules on the substrate, G a geometrical factor (See supplementary information), $M(\lambda)$ the local field enhancement averaged over the substrate surface at the wavelength λ , $\frac{\partial \sigma_{\text{RS}}}{\partial \Omega}$ the differential Raman scattering cross-section, $\Delta \Omega_{\text{Det}}$ the solid angle for detection and S_{inc} the incident irradiance in the plane of the substrate.

The close relation between the LSPR and the SERS intensity then depends strongly on the spectral features of the enhancement factor $M(\lambda)^{33-39}$. It has been shown that it is necessary to finely tune the optical properties of the nanostructures in order to reach the highest enhancement factor. Optimization requires maximizing the product of the NF at the excitation and at the Raman band wavelengths (equation 1), which depend strongly on the nanoparticle shape^{30, 35} and on the excitation wavelength^{30, 37}.

Several studies claimed that the best enhancement factor is reached for a LSPR position at the midway between the λ_{LASER} and λ_{Raman} ^{29, 34, 36, 37}.

$$\lambda_{\text{LSPR}}^{\text{Opt}} = \frac{\lambda_{\text{LASER}} + \lambda_{\text{Raman}}}{2} \quad (2)$$

In former studies^{38, 40}, it has been suggested that the deviation between the position of the LSPR given by equation 2 and the experimental results are due to spectral shift between the far-field (FF) resonance, i.e. the energy at which maximum extinction occurs, and a more subtle near-field (NF) resonance, i.e. the energy at which the enhanced field experienced by the molecules in the NF of the nanoantennas is maximum. In other words, does the LSPR peak measured in the FF correspond to the maximum of the NF? Many papers have debated on this subject theoretically and experimentally⁴⁰⁻⁴⁸. It has been shown that the NF is generally redshifted compare to the FF⁴⁰⁻⁴⁶ and this spectral shift increases with the particle volume^{44,45}. However, the cause of this redshift is still being investigated. Recent papers aimed to find phenomenological explanation. Zuloaga and co-workers⁴⁶ demonstrated that this effect comes from the losses by the nanoparticles in analogy with driven damped harmonic oscillator and then demonstrated the universality of this rule. This work was completed by Kats and co-worker⁴⁷. Recently Moreno *et al.* confirmed the universality of this NF to FF redshift in the case of small particles with a strong dipolar contribution⁴⁸.

In this paper, we investigate the origin of the wavelength dependence of the SERS enhancement of gold nanocylinders (NCs) by combining extinction spectroscopy, SERS measurement of a probe molecule with multi-wavelength excitation and numerical simulation.

Experimental and Theoretical Methods

This study was performed with gold NCs produced by electron-beam lithography and lift-off techniques³⁶ on a microscope glass slide. Their diameters range from 70 nm to 200 nm with a 10 nm step. The distance between the NC is fixed at 200 nm in both directions. The gold height is 50 nm with a chromium adhesion layer of 2 nm.

The samples were cleaned by UV-Ozone process during 30 min, plunged into an ethanol solution and then dried prior to the extinction measurements. The extinction spectra were acquired on a LabRam Xplora spectrometer (Horiba Scientific). The extinction measurements were recorded in transmission configuration with a 10X objective (NA=0.25) on an area of 100 μ m diameter selected by the confocal hole. The sample was illuminated in normal incidence with collimated white light.

The probe molecule was deposited on the nanostructures by immersion in a 10^{-3} M solution of trans-1,2-bis(4-pyridyl)ethylene (BPE) during 1 h and dried with nitrogen gas flow. The SERS spectra were acquired on three different spectrometers from Horiba Scientific: a LabRam 300 at 633 nm, an Xplora at 660 nm and 785 nm and a LabRam HR800 at 691 nm. The signals were collected using a 100x objective with a numerical aperture of 0.9. Acquisition time for one spectrum was 60s with 200 μ W power. For each diameter, measurements were done nine times on different points to analyze the reproducibility of the signal. SERS signals were then averaged and a standard deviation was calculated and represented as the error bars.

The FF and NF calculation was carried out using DDSCAT 7.3^{49, 50}. Single gold NC and array of gold NCs was considered on top of a layer of N-BK7 glass, a chromium film of 2 nm-thickness in between. The refractive index of gold was taken from Johnson and Chrity⁵¹, the chromium one from Sopra database and the refractive index of the glass substrate was taken from the Schott database. The NC top angle was rounded with a radius of curvature of 10 nm to take into account the imperfection of nanoparticles fabrication process. The interdipole length was set to 2 nm (see supplementary data). The height of the NC was 50 nm and the diameters were 100 nm, 130 nm, 150 nm, 180 nm, 200 nm, 230 nm, 260 nm, 280 nm and 300 nm. The calculations were performed at wavelength from 500 to 1000 nm with 50 nm steps far from the resonance and with 25nm step close to the resonance. They were performed with the high performance computing facilities of Pôle de Calcul Intensif pour la Mer⁵². The substrate was incorporated in the object as a slide of glass of 100nm. This choice is described and motivated in the supplementary data.

The NF enhancement was calculated by averaging the electric field in a volume of 2 nm-thickness around the nanoparticles. The mean SERS enhancement was assessed by the product of the NF enhancement at the laser wavelength and at the vibrational mode wavelength (Supplementary informations). The uncertainties on the position of the FF and NF plasmon bands as well as on the FWHM were assessed from interpolation errors.

Figure 1: Experimental (a) and theoretical (b) extinction spectra of the NCs. The inset of the curve of figure 1.a) shows a Scanning electron microscopy (SEM) image of the 200 nm–diameter NC array (the white scale bare is 1 μm). Positions (c) and FWHM (d) of the measured (blue curve) and calculated (red curve) extinction bands.

Results and Discussion

The experimental and theoretical extinction spectra are plotted in figure 1a and 1b respectively. The positions of the extinction bands red shift when the particle diameter increases as previously demonstrated by Zorić *et al*⁵³. The position of the expected LSPR peaks (figure 1c, blue symbols) show a linear growth similar to the experimental data (figure 1c, blue symbols), although the values are slightly underestimated. This discrepancy is consistent with the

geometrical uncertainties of the nanostructures geometry and a surface roughness of few nm⁵⁴. The Full-Width at Half Maximum (FWHM) of the extinction bands are plotted on figure 1d. They appeared constant over the range of particle diameter experimentally studied, meaning a constant damping of the nanoparticle resonance³¹. The Full Width at Half Maximum (FWHM) of the LSPR peaks in experiments are between 7 to 23% broader than those in simulations. First, the SEM images of the nanostructures showed that the sizes of the nanocylinders are very reproducible from one NC to the other (Fig. 1.a). The diameter distribution is then very sharp. Second, the FWHM of the LSPR peaks is related to the imaginary part of the relative permittivity, which can show some significant changes from one deposit to the other⁵⁵. The overestimation of the FWHM can then be attributed to the gold relative permittivity change.

The U-shape of the theoretical FWHM curve is similar to that reported by Shen *et al*⁵⁶. The gold absorption is minimal in the 600-700 nm range⁵¹, which lead to a resonance sharper in this domain. In addition, as the volume of the NC increases the radiation damping rises and then the resonance peak widens. These two effects contribute to this typical U-shape.

To determine the SERS signal, a probe molecule: the trans-1,2-Bis(4-pyridyl)Ethylen (BPE) was deposited on the NCs. This compound has been extensively used for probing electromagnetic enhancement as the chemical contribution was proven negligible⁵⁷.

Figure 2: Spectrum of BPE on the 160 nm diameter NCs excited by the laser at 660 nm.

Figure 2 shows the SERS spectrum of BPE on 160 nm diameter NCs. The four main peaks at 1007, 1200, 1606 and 1636 cm^{-1} are easily observed. They are in agreement with the bands previously reported^{57, 58}. They can be attributed to the ring-breathing mode of pyridine, the C = C stretching mode, the aromatic ring stretching mode and the in-plane ring mode, respectively^{58,59}.

Figure 3: Measured Raman bands intensity at 1007 cm^{-1} , 1200 cm^{-1} and 1622 cm^{-1} with regards to the LSPR positions for four excitation wavelengths: 633 nm (a), 660 nm (b), 691 nm (c) and 785 nm (d)

Multiwavelength-excitation SERS experiments have been carried out with four different laser wavelengths (633, 660, 691 and 785 nm). The results are plotted in figure 3. For each laser line the SERS intensity of the different Raman modes was plotted as a function of the LSPR wavelength of the NCs. The 1622 cm^{-1} wavenumber corresponds to the average of the two peaks at 1606 and 1636 cm^{-1} . The SERS intensity of each peak was normalized to its maximum value. The intensity profiles are fitted with lorentzians⁵⁶ to determine the LSPR of the NCs that provide optimal SERS intensity, noted $\lambda_{\text{LSPR}}^{\text{Opt}}$ hereafter. As expected from equation 2, the larger the

excitation wavelength, the larger the LSPR wavelength of the nanostructures providing the optimal SERS enhancement (Figure 4)

Figure 4: Position of the optimal LSPR wavelengths measured (solid symbols) and expected from eq. 2 (lines) with regards to the excitation wavelength. Data are plotted for all the three Raman bands considered (black for the 1007 cm^{-1} , red for the 1200 cm^{-1} and green for the 1622 cm^{-1} doublet. Data for the 785nm laser comes from ref 38.

Tableau 1: Deviation of the expected optimum from Eq. 2 to experimental results for the 1200 cm^{-1} band.

$\lambda_{\text{LASER}}\text{ (nm)}$	$\Delta\lambda_{1200}\text{ (nm)}$
633	1
660	12
691	25
785	80

At 633 nm, the experimental and expected optimal LSPR positions are very similar whereas for larger laser wavelength, the experimental value found for $\lambda_{\text{LSPR}}^{\text{Opt}}$ is gradually blue shifted

compare to the expected one (Figure 4 and Table 1). In the case of a 785 nm excitation, we could not reach the maximum of the SERS intensity. However, Guillot et al.³⁸ demonstrated that the maximum SERS intensity was achieved at 750 nm with similar experiment but larger NCs. At this excitation wavelength, the discrepancy of the theoretical to experimental values then goes even up to 80 nm.

The fact that maximum SERS is observed on NCs with a LSPR blue shifted with respect to the expectations has been attributed to a not-well-understood red shift phenomenon between NF and FF as previously debated^{38,41-48}. Recently, Zuloaga et al.⁴⁶ proposed an explanation based on the harmonic oscillator model. The electron cloud of the nanoparticle is described as a damped harmonic oscillator (HO) driven by the electric field of the incoming light. In such a system, two resonances exist: a first one is related to the position of the electron cloud while the second one is related to its speed. Zuloaga et al. assimilate the NF resonance to the former while the FF to the latter. They then demonstrate that the pulsations of the NF and the FF resonances, respectively noted ω_{NF} and ω_{FF} , are related by:

$$\omega_{\text{NF}} = \omega_{\text{FF}} \sqrt{1 - \frac{\gamma^2}{2\omega_{\text{FF}}^2}} \quad (\text{Eq.3})$$

where γ is the damping parameter of the HO.

For low damping, $\gamma \ll \omega_{\text{FF}}$, the relative shift between the wavelength of the NF and FF resonances is expected to be

$$\omega_{\text{FF}} - \omega_{\text{NF}} \propto \gamma^2 \lambda_{\text{FF}} \quad (\text{Eq. 4})$$

where $\lambda_{\text{FF}} = 2\pi c/\omega_{\text{FF}}$ that can be measured in far field and corresponds to the λ_{LSPR} and c is the speed of light.

Several things can be noticed: first, the NF resonance occurs at higher wavelengths with respect to the FF one, i.e. a red-shift is expected in the NF; second, at constant damping, the higher the FF resonance, the higher the expected red-shift; finally, the NF to FF red shift increases with the plasmon damping. The first two predictions from the HO model seem in qualitative agreement with our experimental findings.

Figure 5 a) Extinction efficiency of arrays of NCs whose diameters vary from 100 to 300 nm calculated by DDA. b) Mean square electric field around the NCs. c) NF to FF spectral shift

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3 calculated by the HO model from experimental (blue square) and calculated (green circle)
4 extinction bands and from near-field calculation (red diamond).
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9 To investigate quantitatively the origin of the red-shift, the spectral dependence of the near-
10 field distribution for each cylinder diameter was calculated by DDA as the square of the electric
11 field averaged in a 2 nm thick layer around the nanoparticle. The results are plotted on figure 5b.
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13 The NF to FF shift is shown on figure 5c (red diamonds). For comparison, the expected NF to FF
14 shift was calculated using the HO model. The γ term of eq. 3 was estimated from the FWHM of
15 the measured and calculated extinction bands. The results are shown on figure 5c. In the range of
16 the experimental measurement, the NF to FF shift calculated by DDA and HO model are similar
17 and remains lower than 10 nm. For lower resonance wavelengths, NF to FF shift shows an
18 increase while remaining lower than 20 nm. This change is consistent with an increase of the
19 absorption of gold and then of the red shift according to the HO description. For larger resonance
20 wavelengths, the HO model predicts shifts larger than the DDA calculations, but still smaller than
21 30nm. Indeed, the model proposed by Zuloaga and co-workers is dedicated to isolated particles
22 small compared to the wavelength and then cannot be applied to larger NCs.
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39 The shift between the optimal positions of the extinction band to the maximum SERS
40 enhancement can reach 80 nm for larger particles and an excitation wavelength of 785 nm
41 (Figure 4). Then, we believe that the discrepancy of the experimental data to the equation 2 does
42 not come from a NF to FF spectral shift.
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49 To get more insight on the origin of the discrepancy between the optimal LSPR and the values
50 predicted by equation 2 let's compare the NF of the different NCs (figure 5b). We firstly observe
51 that the NF plasmon bands have some asymmetric profile and positive skewness⁶¹. Furthermore,
52 the NF intensity increases for diameters from 100 to 180 nm and then decreases for higher
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diameter, whereas the FF extinction efficiency maximum keeps increasing in this range of particle sizes. The NF intensity gets maximum for an LSPR position around 650-700 nm. In this spectral range, the FWHM of the extinction bands are minimum (figure 1b). The quality factors of the corresponding resonators are then maximum, which lead to the highest near-field^{56, 60}.

Figure 6: Normalized SERS signal of the 1200cm^{-1} band with regards to the extinction band position of the array of NCs measured (on the left hand side y-axis) and the mean SERS enhancement calculated by DDA (on the right hand side y-axis) for the four laser wavelengths: 633 nm (a), 660 nm (b), 691 nm (c) and 785 nm (d).

The theoretical SERS intensity was calculated from equation 1 (supplementary data) for the four excitation wavelength. The results are plotted on figure 6 and superimposed to the experimental data. The theoretical points were fitted by a lorentzian as Shen and co-workers⁵⁶.

Theoretical and experimental fit very well for the first three laser line meaning that the enhanced NF calculated by DDA gives an accurate description of the spectral feature of NF as well as the relative intensity. For the 785 nm laser, the missing experimental points for diameter higher than 200 nm make the comparison more difficult even if the experimental points are close to the DDA calculations.

Figure 7: Optimal LSPR position with regards to the excitation wavelength measured (plain markers) and calculated by DDA (shallow markers) and calculated from equation 2 (plain line).

Figure 7 represents $\lambda_{\text{LSPR}}^{\text{Opt}}$ for the 1200cm^{-1} Raman shift with regards to the laser wavelengths. The experimental results are enriched by values of previous work done at 785 nm^{38} . Two sets of data are shown: the experimental measurement and the theoretical value calculated from NF DDA simulation. The experimental and theoretical results are very consistent and within the error tolerance except for the 785 nm laser. Indeed, at this wavelength the theoretical $\lambda_{\text{LSPR}}^{\text{opt}}$ is overestimated by 30 nm with regards to the experimental one, which is above the error tolerance. This is attributed to the experimental dissimilarities between our study and ref 38.

Figure 8: Mean Electric field square around the NC.

Based on this good agreement between the simulation and the experimental data, we propose an explanation for the discrepancy between the optimal extinction band positions measured and calculated with equation 2. Actually, a careful attention has to be paid to the NF intensity and not only to the position of its maximum. For the case of NCs, DDA calculations tell us that the NF intensity gets maximum for an LSPR position around 650-700 nm (figure 6b), corresponding to diameters between 150 and 180nm. Then, as the NC diameter further increases, the intensity of the maximum of the NF intensity decreases. Moreover, the NF curves widen and become asymmetric with a positive skewness increasing with the diameter of the NC. It can be seen on figure 6 that for a laser wavelength of 785 nm, the highest SERS enhancement is then reached if the laser line is close to the maximum of the NF enhancement. This becomes clear when looking at figure 8: the best enhancement is achieved when the intersections of the two dotted lines (the laser of 785 nm and the Raman shift of 1200cm^{-1} wavelength) with the NF plasmon band are the highest. This occurs for the NC of 230 nm diameter whose plasmon band is maximum at about 780 nm.

The blue shift experimentally observed does not come from a spectral shift of the NF compare to the FF but from the spectral shape of the NF that is quite different compared to the extinction band (more asymmetric).

Conclusions:

This work characterized the FF and NF properties of gold NCs of diameters from 100 to 300 nm fabricated by electron-beam lithography. The FF properties were investigated by extinction spectroscopy while the NF by SERS measurements of a probe molecule adsorbed on the nanoparticles. DDA simulations were then performed to provide some phenomenological description.

This study aims to provide some explanations on the position of the optimal LSPR for SERS with regard to the laser line. A rule of thumb states that the best SERS enhancement is achieved when the LSPR is located at the midway between the laser and the Raman lines. However, this does not apply to all the samples, in particular for large laser wavelength. This discrepancy was often assumed to come from a NF to FF spectral shift.

This work clearly demonstrated that there is no significant spectral shift between the NF and the FF with arrays of far-field coupled NCs. The discrepancy between the optimal LSPR for SERS measured and expected from the aforementioned rule cannot be attributed to any NF red-shift. The explanation lay in the intensity of the NF plasmon band. The NF enhancement is maximum for LSPR about 670 nm and then decreases with the LSPR position. A higher SERS signal is then achieved with a LSPR close to this value. The optimal position is then a compromise between the position of the Raman and the laser lines compared to the LSPR and the intensity of the NF band.

ASSOCIATED CONTENT

Supporting Information:

- Modeling parameters and assessment of the results
- Relation between the near-field and the measured SERS intensity

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

NF, Near-field; FF, Far-Field; BPE, trans-1,2-Bis(4-pyridyl)Ethylen; EBL, Electron Beam Lithography, SEM, Scanning electron microscopy; DDA, Discrete Dipole Approximation; NC, Nanocylinder; FWHM, Full-Width at Half Maximum; SERS, Surface Enhanced Raman

Scattering, LSPR, Localized Surface Plasmon Resonance, FDTD, Finite Difference Time Domain; HO, Harmonic Oscillator.

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Table of Content Graphic

Table of content image

Experimental (a) and theoretical (b) extinction spectra of the NCs. The inset of the curve of figure 1.a) shows a Scanning electron microscopy (SEM) image of the 200 nm– diameter NC array (the white scale bare is 1 μm). Positions (c) and FWHM (d) of the measured (blue curve) and calculated (red curve) extinction bands.

177x124mm (300 x 300 DPI)

Spectrum of BPE on the 160 nm diameter NCs excited by the HeNe laser.
88x62mm (300 x 300 DPI)

Measured Raman bands intensity at 1007 cm^{-1} , 1200 cm^{-1} and 1622 cm^{-1} with regards to the LSPR positions for four excitation wavelengths: 633 nm (a), 660 nm (b), 691 nm (c) and 785 nm (d)
88x63mm (300 x 300 DPI)

Position of the optimal LSPR wavelengths measured (solid symbols) and expected from eq. 2 (lines) with regards to the excitation wavelength. Data are plotted for all the three Raman bands considered (black for the 1007 cm^{-1} , red for the 1200 cm^{-1} and green for the 1622 cm^{-1} doublet. Data for the 785nm laser comes from ref 38.

88x62mm (300 x 300 DPI)

a) Extinction efficiency of arrays of NCs whose diameters vary from 100 to 300 nm calculated by DDA. b) Mean square electric field around the NCs. c) NF to FF spectral shift calculated by the HO model from experimental (blue square) and calculated (green circle) extinction bands and from near-field calculation (red diamond).

88x200mm (300 x 300 DPI)

Normalized SERS signal of the 1200cm⁻¹ band with regards to the extinction band position of the array of NCs measured (on the left hand side y-axis) and the mean SERS enhancement calculated by DDA (on the right hand side y-axis) for the four laser wavelengths: 633 nm (a), 660 nm (b), 691 nm (c) and 785 nm (d).

177x124mm (300 x 300 DPI)

Optimal LSPR position with regards to the excitation wavelength measured (plain markers) and calculated by DDA (shallow markers) and calculated from equation 2 (plain line).
88x61mm (300 x 300 DPI)

Mean Electric field square around the NC
88x62mm (300 x 300 DPI)

Table of Contents Image
177x126mm (300 x 300 DPI)