Nanopillars as Plasmonic Platform to Enhance Nonlinear Vibrational Sum-Frequency Generation Spectroscopy

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Abstract.

Metallic nanostructures such as nanopillars and nanoantennas are able to confine the energy of an incident radiation into volumes much smaller than the wavelength of incoming waves through localized surface plasmon resonance (LSPR).[1] This electromagnetic-field enhancement, attributed to the collective motion of free electrons, has been extensively used for surface-enhanced Raman scattering (SERS) and other surface-enhanced spectroscopic processes. This has driven metal nanostructures to become a powerful tool for chemical and biological optical sensing experiments.[2]

In this work, we coupled such localized electromagnetic-field enhancement effect to a nonlinear second-order optical spectroscopy to obtain high molecular signal intensity and sensitivity. The technique is based on a three waves mixing process in which one infrared (ω_1) and one visible (ω_2) photon interact together with matter to generate a new coherent photon at the sum frequency ($\omega_{sfg} = \omega_1 + \omega_2$). The whole process relying on the second order nonlinear susceptibility $\chi^{(2)}$, the sum frequency generation (SFG) signal can be emitted only where the centrosymmetry is broken, that is at surfaces and interfaces separating two bulk media.[3,4] In fine, SFG spectroscopy is a background free vibrational surface-sensitive spectroscopy able to retrieve accurate information on molecular thin films properties, such as conformation, orientation, dynamics, bio-recognition processes, phase transitions.

Here, we report a strong enhancement of the vibrational SFG signal from molecules adsorbed on metallic nanopillars when those latter are excited at their localized plasmon resonance frequencies. In detail, gold nanopillars, sizing around 100 nm in height and 60 nm in diameter, stand vertically on a substrate of gold or platinum. The nanopillars exhibit two plasmon modes that can be selectively excited by the incident visible laser beam or by the generated SFG beam itself. Until now, for a density of 10^9 nanopillars/cm^2, the molecular SFG signal obtained on such nanostructured surfaces is more than 100 times larger that what can be achieved on unstructured flat surfaces. Besides, because of the directional profile of the two plasmon modes, an adequate choice of the beams polarizations and frequencies leads to a spatial selectivity of the SFG emission. It is indeed likely possible to selectively probe the molecules adsorbed onto the nanopillar side wall, the nanopillar top part (as shown on Figure 1), or the flat region of the substrate in-between the pillars. This gives promising issues to set up label free vibrational bio-recognition platforms with “multi-zone” enhanced sensitivity.

References

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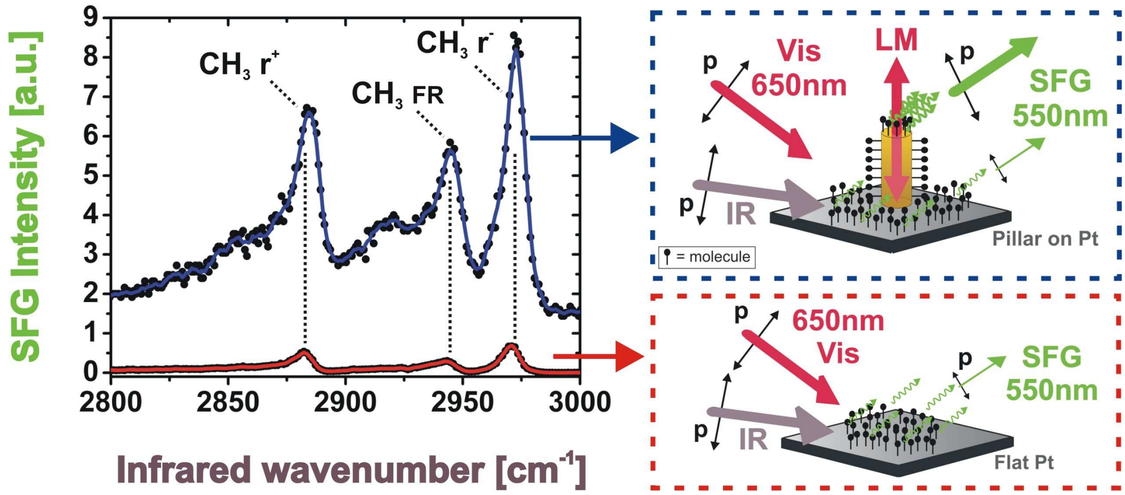

Figure 1: The left figure shows SFG spectra in *ppp* polarization (in the order SFG, Vis and IR beam) of a dodecanethiol (DDT) molecular film adsorbed over the sample surfaces. The red curve corresponds to the spectra of the DDT layer adsorbed over a flat platinum surface, while the blue curve is the spectra recorded on the gold nanopillar region when those latter have their longitudinal LSPR mode excited at 650 nm by the visible laser beam. A schematic representation of the the experimental conditions is shown in the right figure. An important SFG intensity increase (blue curve) is observed thanks to the excitation of the LSPR mode of the nanopillar.