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The Prevailing Role of Hotspots in Plasmon-Enhanced Sum-Frequency Generation Spectroscopy

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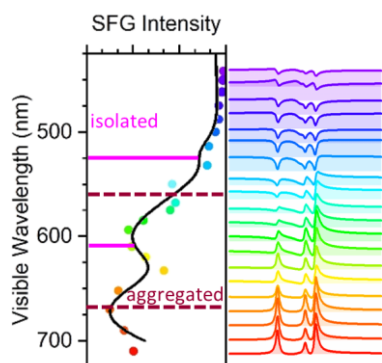
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ABSTRACT

The plasmonic amplification of non-linear vibrational sum frequency spectroscopy (SFG) at the surfaces of gold nanoparticles is systematically investigated by tuning the incident visible wavelength. The SFG spectra of dodecanethiol-coated gold nanoparticles chemically deposited on silicon are recorded for twenty visible wavelengths. The vibrational intensities of thiol methyl stretches extracted from the experimental measurements vary with the visible color of the SFG process and show amplification by coupling to plasmon excitation. Since the enhancement is maximal in the orange-red region rather than in the green, as expected from the dipolar model for surface plasmon resonances, it is attributed mostly to hotspots created in particle multimers, in spite of their low surface densities. A simple model accounting for the longitudinal surface plasmons of multimers allows to recover the experimental spectral dispersion.

TOC



Surface-Enhanced Raman Spectroscopy (SERS),¹ benefitting from local electromagnetic field enhancements in the visible through plasmon excitation, is a widely used optical tool giving access to vibrational fingerprints of molecules at surfaces. With the same assets as SERS as for chemical sensitivity and wavelengths ranges, infrared-visible Sum-Frequency Generation (SFG) spectroscopy is in addition intrinsically surface specific as a consequence of its symmetry properties. It has indeed proved its ability to extract static,^{2,3} dynamic,^{4,5} structural,^{6,7} and orientational information^{8–10} through vibrational excitations of molecules adsorbed on planar surfaces, as well as from a wide range of systems like air-water,^{6,11–16} solid-liquid or buried interfaces.^{11,17–25} For nanostructured materials, it should also become a useful tool to monitor the chemistry taking place at the surfaces of nano-objects,²⁶ essential for the comprehensive design of nanosensors²⁷ and nanocatalysts.²⁸

Despite the apparent discrepancy between the spherical symmetry of nanoparticles and SFG selection rules (a small spherical particle fully covered with molecules produces no measurable signal), the vibrational SFG response of molecules decorating nanospheres grafted on a substrate has been calculated and shows enhancements in the visible range (as in SERS) due to the local excitation of surface plasmon resonances.²⁹ This is also true for the molecules constituting the grafting monolayer sandwiched between the particles and the substrate.²⁹ Amplification of SFG spectroscopic signals has been shown on long deposited gold cylinders,³⁰ for which the inversion symmetry is greatly broken. In the case of spheres, no direct evidence of such enhancement has been provided and, for gold particles, the amplification factors are expected to be rather small. Consequently, SERS amplification has never been measured, to our knowledge, for isolated small gold spheres (even if the contrast part of the enhancement factors deduced from tip-enhanced Raman spectroscopy measurements relies on local field amplification between the half-sphere tip and the substrate³¹), which makes the challenge even more interesting. Several authors have shown the possibility to monitor by SFG molecules at

the surfaces of plasmonic spherical particles,^{32–41} and to make the difference between thiols adsorbed on the particles and silanes used to graft them on silicon surfaces.³⁶ Showing vibrational enhancement in the small (i.e. for diameters up to a few tens of nanometers) particle case will prove that SFG is a promising tool for a local spectroscopic analysis of all nanostructured materials, with a high sensitivity to species located in the very local field around the nanostructures.

In this letter, we provide experimental evidence of a plasmonic enhancement of SFG vibrational signatures of terminal methyl moieties of dodecanethiol (DDT) grafted on gold nanoparticles. The evolution of the vibrational intensities as a function of the visible wavelength shows a direct effect of the optical properties of the particles. It does not primarily relate to the surface plasmon resonances of the isolated particles but, despite their low surface density, to the plasmonic properties of the hotspots between nearby particles.

The SFG intensity radiated by a surface is given by^{42,43}

$$I(\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}) = \frac{8\pi^3 (\omega_{\text{SFG}})^2}{c^3 \cos^2 \theta_{\text{SFG}}} |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{vis}}) I(\omega_{\text{IR}}) \quad (1)$$

where θ_{SFG} is the emission angle of the SFG reflected beam and $I(\omega)$ stands for the beam intensity at frequency ω (refractive index of air is unity). The SFG signal experimentally measured is proportional to its total radiated intensity and, after taking into account the wavelength-dependent efficiency of the detection setup,⁴⁴ provides the dispersion of $|\chi_{\text{eff}}^{(2)}|^2$, $\chi_{\text{eff}}^{(2)}$ being the effective second order non-linear susceptibility⁴² (Fresnel factors on silicon show a smooth and rather small dispersion in the visible range, Fresnel-weighted $\chi_{\text{eff}}^{(2)}$ values will be used in the following for experimental points and simulations). The complex third rank order tensor $\chi_{\text{eff}}^{(2)}$ sums up one Lorentzian term per molecular vibration ($\chi_{\text{eff,mol}}^{(2)}$) and one

contribution ($\chi_{\text{eff,NR}}^{(2)}$) from the inorganic components, essentially the silicon substrate, labelled non-resonant (NR) with respect to the IR wavelength but varying in amplitude and phase with the visible wavelength. Interferences between these two contributions arise because of the summation of the $\chi_{\text{eff}}^{(2)}$ amplitudes, whereas only the total intensity is experimentally measured:

$$I(\omega_{\text{SFG}}) \propto \left| \chi_{\text{eff,mol}}^{(2)} + \chi_{\text{eff,NR}}^{(2)} \right|^2 \quad (2)$$

with

$$\chi_{\text{eff,mol}}^{(2)} = \sum_{\text{vibrations}} \frac{A_i}{\omega_{\text{IR}} - \omega_i + i\Gamma_i} \quad (3)$$

For the analysis of the coupling between plasmon excitation and non-linear optics, in line with our previous study on DDT adsorbed on gold,^{43,45,46} twenty vibrational spectra were recorded on DDT-coated gold nanoparticles deposited on silicon while tuning the visible color between 442 and 710 nm (see Experimental Section). Gold particles (diameter 13.5 nm) were grafted on silicon through an alkoxysilane layer (APTES) modified with mercaptoundecanoic acid (MUA). Such particles have a cuboctahedral shape,⁴⁷ and thiols form small self-assembled layers on the facets.^{48,49} As on planar gold, long alkanethiol chains favor lateral interactions and lead to long range molecular order.⁴⁹ We have checked by SFG that DDT led to a better organization than shorter alkanethiols (see Supplementary Information for sample preparation and characterizations). The corresponding $|\chi_{\text{eff}}^{(2)}|^2$ are shown in Figure 1. As is clearly seen in the red visible spectral range, they exhibit three vibrations corresponding to the stretching modes of DDT methyl endgroups at 2888 cm⁻¹ (symmetric stretch, *ss*), 2951 cm⁻¹ (Fermi resonance, *FR*) and 2974 cm⁻¹ (antisymmetric stretch, *as*). It is known that incomplete silanization reaction of alkoxysilanes on silicon may lead to poisoning from residual CH₂ and CH₃ modes from the grafting layer.^{36,50,51} The presence of CH₂ vibration modes is therefore

possible, their amplitudes showing the degree of disorder inside both the grafting and functionalization layers. We have checked that the sample was mostly free from these effects (see SI for details).

The spectra can be classified into three regions as a function of the visible wavelength: in the orange-red zone, high intensity CH_3 modes distinctly appear above a very small non-resonant background. At the blue side of the visible spectrum, the resonant amplitudes decrease whereas the non-resonant grows, as the SFG photons may excite electronic transitions inside silicon, producing spectra where Lorentzian-shaped peaks strongly interfere with a high level of background. In the intermediate zone (green region), the amplitudes of the resonant and non-resonant signals are comparable, resulting in pronounced interference with profiles evolving from peaks to dips through derivative shapes.

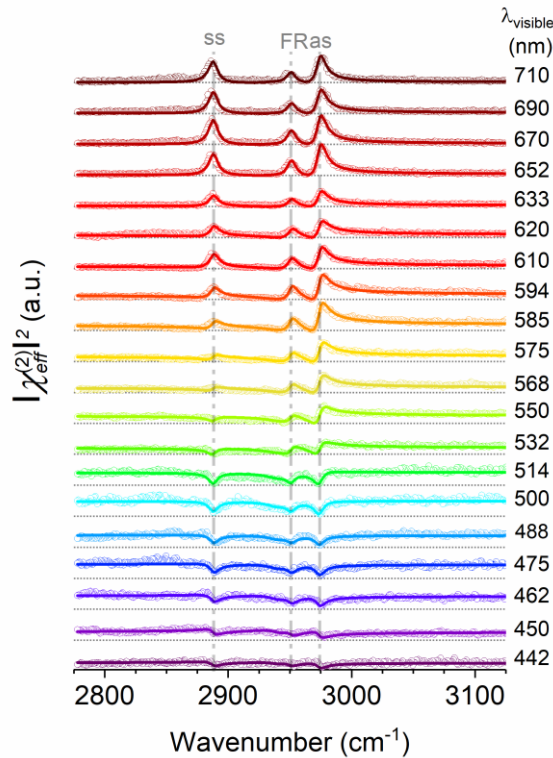


Figure 1. Series of SFG spectra of the Si/AuNP/DDT interface for twenty visible wavelengths (open circles). Lines are fits according to equations 2 and 3 (see text for details). All spectra share a common scale.

Determining the effects of plasmon excitation on the molecular vibrational amplitudes A_i requires extracting them from the experimental spectra. On planar gold,^{43,46} the complex amplitudes of vibrations do not depend on the visible color (for molecules without electronic resonances in the visible), and can be used as an internal reference for the gold signals in amplitude and in phase. The goal here is oppositely to measure their variations when the visible color is tuned, in order to quantify the influence of plasmon resonances on the molecular non-linear susceptibility. The presence of a non-resonant background, varying in amplitude and phase from blue to red, makes it necessary to fit the spectra according to Equations 2 and 3.^{42,43} Consistently fitting twenty spectra with three resonances, sharing a common width Γ , and a non-resonant with unknown amplitude and phase has been shown challenging in the past.^{43,52} Details are provided in the SI.

In Figure 2A, we show the evolutions of the vibrational intensities of the three CH_3 modes as a function of the visible wavelength. The coherent lineshapes for the three resonances show the reliability of the fits, as we expect similar evolutions for symmetric and antisymmetric stretches.²⁹ The intensities show a regular increase from blue to green, followed by two broad maxima in the low energy region around 580 and 660 nm. This fact proves that plasmon influences indeed the molecular SFG response in the vicinity of the nanoparticles and produces a net enhancement of the SFG intensities.

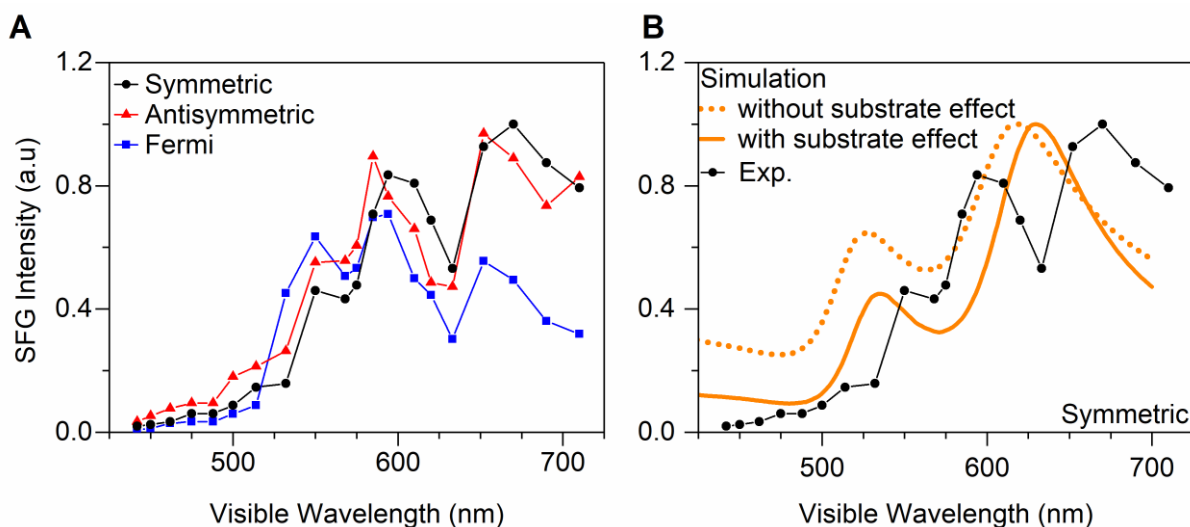


Figure 2. Intensities of the methyl vibrations versus the visible wavelength: (A) Experimental values extracted from the spectra of Figure 1. (B) Simulations of the experimental dispersion for symmetric stretch, with (solid line) and without (dotted line) inclusion of the substrate effects ($\epsilon_m=1.44$, $\alpha=35^\circ$) compared to the experimental points (black). Curves are scaled as indicated to ease comparison.

The observed trend however differs from the predictions of a straight plasmonic model for gold nanospheres, for which plasmon excitation by the visible beam lies around 510 nm (see Figure S1D for the visible absorption spectrum of the sample), and 620 nm for the SFG beam. We compare the experimental results with the predictions of the dipolar model developed in a previous paper²⁹ and summarized in the SI. In the calculations, we have set all the parameters to their experimental values (surface density of particles and particle diameter, see SI for details). The DDT layer thickness and CH₃ hyperpolarizability properties have been discussed before.²⁹ The free parameters of the model are essentially the refractive index n_m of the DDT layer (dielectric function $\epsilon_m = n_m^2$) around the particles, whose increase leads to a redshift of the plasmon peaks, and the half-aperture of the cone (α) describing the surface of the spheres covered with DDT, as thiol functionalization is performed after grafting the particles on the surface (Figure S6). We recall here that a spherical nanoparticle fully covered with molecules produces no measurable signal, only the symmetry breaking induced by the coverage cone making SFG production possible. Including the influence of the silicon substrate also induces an additional redshift. In Figure 2B, we compare the experimental intensities for the symmetric

stretch to the simulations with the reference values of $n_m = 1.2$ and $\alpha = 35^\circ$ (theoretical limit value for DDT in contact with the grafting layer²⁹, Figure S6) , with and without influence of the substrate. The comparison illustrates that these models do not account for the experimental results as they do not reproduce the positions of the peaks, their relative intensities and the decrease towards the blue side. This discrepancy may arise from the incorrect account of the influence of the silicon substrate on the electric fields, which is stronger below the particle than above it, creating an up-down asymmetry. We also considered hybrid particles, for which this asymmetry is recovered (see SI for details), but could not reproduce the experimental behavior either (Figure S7B). Finally, taking into account the distribution of sphere radii and local environments (through ϵ_m) only marginally modifies the calculated dispersion and does not change the conclusions.

The obvious experimental fact is that the experimental enhancement is redshifted with respect to the plasmonic model in the dipolar approximation for isolated spheres. Conversely, it is well-known that longitudinal plasmonic coupling between two (or more) nanoparticles creates hotspots, characterized by a redshift of the plasmon resonance⁵³ and a great increase of the local electric fields between the particles.⁵⁴ Depending on the conditions, in particular the distance between the particles, local field amplification of two orders of magnitude may be expected at the longitudinal plasmon wavelength for interparticle distances below one nanometer.^{54–56} As both the visible and SFG wavelengths may lie in its vicinity, we may expect enhancements up to four magnitude orders as compared to isolated spheres. In addition, the distribution of the electric field in a nanoparticle dimer strongly breaks the spherical symmetry of the ensemble, thus contributing proportionally more to SFG production than an isolated sphere. Finally, we note that the positions of the experimental SFG maxima are coherent with the plasmonic response of multimers as measured by absorbance spectroscopy (~600 nm) when many aggregates are present at the surfaces, as illustrated on Figure S2. Experimental evidences thus

suggest that hotspots created by particle multimers greatly contribute to SFG production, even if their surface density is low (but not vanishing). Considering their expected high electric field enhancement factors, those may compensate the small number of aggregates on the surface (which accounts for their absence in absorbance measurements). The same effect has been observed in SERS, where a very small fraction of sites showing giant enhancement factors has been proved to contribute more to the total experimental signals than the majority of low enhancement sites⁵⁷. As longitudinal coupling of plasmon resonances between nearby particles essentially takes place when the electric fields of light are polarized parallel to the surface, it would be interesting to perform the same kind of studies on a substrate favoring them through the *ssp*-polarization combination (glass, for example).

It is in principle possible to model the electric field distribution around a particle multimer using Mie theory.⁵⁸ However, this goes beyond the dipolar approximation used so far and, more important, it requires adjusting unknown parameters to reproduce the experimental conditions, namely the multimer geometries (interparticle separation, which may fluctuate a lot with great consequences on the plasmon resonance,^{59,60} number of aggregated particles and relative positions) and their surface densities (the small number of aggregates would require a big amount of large microscopy images for a statistically relevant experimental measurement²⁷). Here, we propose to account for the experimental behavior in a phenomenological way. We take advantage of the similarity of plasmon excitation properties between longitudinally coupled spheres and isolated spheres surrounded by a high dielectric function host (Figure 3A). In both cases, the surface plasmon resonance experiences a redshift, while keeping a reproducible shape as a function of the wavelength of light. Of course, the origins of both redshifts are different, but as far as electronic resonance is concerned, they share a common behavior. In a qualitative approach, we take into account the existence of dimers and multimers

by adding to the dipolar contribution of isolated spheres a second contribution described by a strongly redshifted dipolar distribution with high values of the dielectric function ϵ_m .

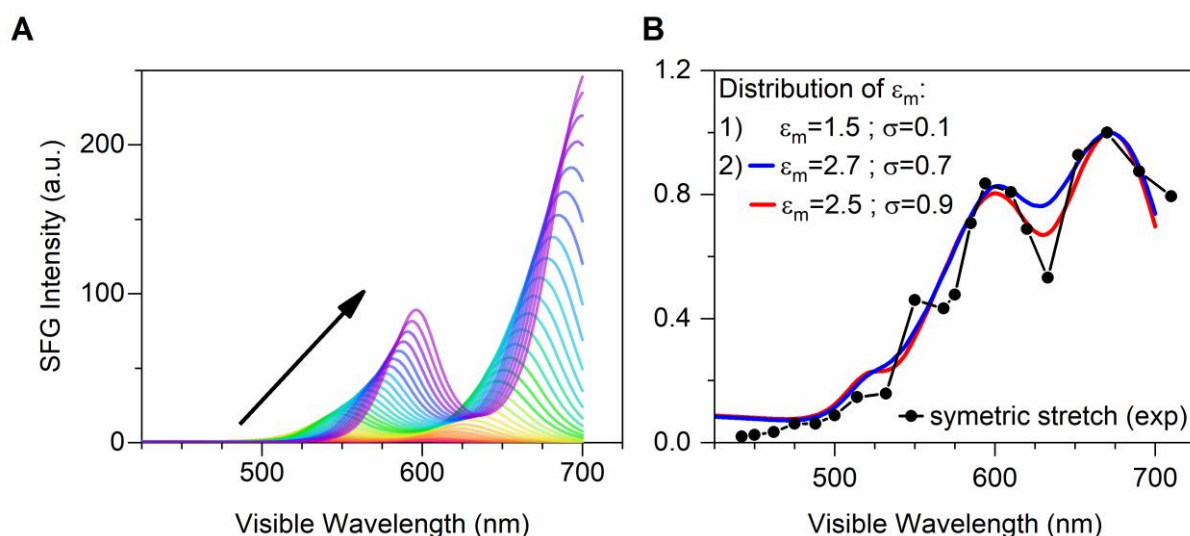


Figure 3. Evolution of the SFG response versus the visible wavelength: (A) As a function of ϵ_m . The graph displays the SFG intensities for thirty values of ϵ_m , varying from 1.0 to 4.0 along the arrow. (B) Simulations of the experimental dispersion for symmetric methyl stretch using two distributions in ϵ_m as described in the text.

We therefore optimized the fit of the experimental intensities using a sum of two Gaussian distributions of hybrid spheres: a narrow one centered at low values of ϵ_m represents the isolated spheres surrounded by the DDT layer, whereas a wider one centered at higher values of ϵ_m accounts for the diversity of couplings in the multimers due to the varieties of geometries and interparticle distances. The best fits are shown on Figure 3B, with the first Gaussian centered at $\epsilon_m = 1.5$ with a width (standard deviation) of 0.1, the second one at either 2.5 (width 0.9) or 2.7 (width 0.7), and $\alpha = 30^\circ$, close to the limit value. These values are consistent with the usual refractive index for organic monolayers as determined by SFG spectroscopy ($n_m \approx 1.2$) and with the peak positions for the redshifted resonances. The overall plasmonic amplification over the visible range is recovered in this way. Its shape comes from an overlap between plasmonic resonances at the visible and SFG wavelengths, both from isolated and interacting particles, the

latter being broadened by a large distribution of interaction geometries, mostly interparticle distances.

SFG spectroscopy of molecules adsorbed at the surfaces of grafted nanoparticles is strongly influenced by plasmon excitation. By probing the visible spectral range through the measurement of a series of vibrational SFG spectra, we have evidenced that the intensities of the molecular vibrational resonances depend on the visible wavelength. The molecular SFG signal may be resonantly amplified, even in the unfavorable case of small gold spherical nanoparticles for which the optical enhancement remains weak. The plasmon excitation enhancement cannot be accounted for by isolated gold particles alone. Despite the low surface density of multimers and aggregates, the observed redshift proves that these predominantly contribute to plasmonic coupling in the SFG process, as a consequence of the high local electric fields and symmetry breaking associated to hotspots between nearby particles. This hotspot effect is well-known for other enhanced spectroscopies, but is shown here for the first time in the case of sum-frequency generation spectroscopy, extending the field of non-linear plasmon excitation to molecular vibrational spectroscopy.

EXPERIMENTAL SECTION

The two-colour SFG set-up is analogous to the one described before.^{43,61} Briefly, a ~10-ps vanadate laser source is used to independently generate, after temporal shaping and amplification, tunable IR and visible beams through two dedicated optical parametric oscillators (OPO) based on LiNbO₃ and BBO nonlinear crystals, respectively. The presence of a tunable visible beam (in the range 440-710 nm) makes it possible to measure the SFG response in the visible spectral range. SFG signals are produced in a reflection geometry at the surface of the sample for *ppp*-polarization combination, with incidence angles of 55° and 65° for the visible and IR beams, respectively. SFG photons are filtered from reflected and scattered visible

light in a double grating monochromator and measured with a photomultiplier. At each step, vibrational SFG spectra are recorded as a function of the IR wavenumber in the 2800-3100 cm^{-1} region for a fixed visible color. In this spectral range, CH stretching vibration modes are detected and, for symmetry reasons, CH_3 modes from the methyl endgroups of alkanethiols are the dominant source of vibration resonances.

Associated Content

Supporting Information

Sample preparation and characterization, details on the data analysis and curve fitting, summary of the theoretical model, influence of the substrate on the plasmonic properties.

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Author contributions

L.D. and B.B. designed the research project. L.D. and C.H. performed the SFG experiments.

L.D. and B.B. analyzed the SFG data. L.D. performed the UV-Visible measurements, M. BH.

and S.B. prepared the samples and performed the TEM characterizations, G.B. performed the SEM characterization. All the authors discussed the results and wrote the manuscript.

Notes

The authors declare that they have no competing interest.

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