A Kretschmann setup at acoustic frequencies for studying molecular vibration

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Abstract

In this study, simultaneous measurement of surface plasmon resonance (SPR) and surface enhanced Raman scattering (SERS) on flat metallic surfaces was demonstrated in a setup based on the Kretschmann configuration at acoustic frequency. This asset facilitates matching the photon and the surface plasmon polaritons wavevectors by tunneling the photon in the total internal reflection geometry and we demonstrate the compensation for the absence of hotspots typical on rough surfaces. The optomechanical asset allows detecting the two signals and prevents their interference. Experimental and numerical analyses were done for characterizing the two signals. The results emphasize the enhancement of the electromagnetic field at the surface, which provides high sensitivity for detecting the signals coming from the Raman probe molecules such as Congo red and thiols such as cysteamine. The combination of simultaneous SPR–SERS microspectroscopy at low frequencies opens up interesting prospects that facilitate experimental conditions using standard SPR setups, with a dramatic reduction in sensor cost.

1. Introduction

The simultaneous detection of surface plasmon resonance (SPR) and surface enhanced Raman scattering (SERS) represented an interesting possibility to be explored and several optomechanical assets have been proposed [1–3]. In particular, combining the advantages of the two techniques seemed important for fostering analytical investigations [4–8].

In 1979, the first observations of Raman scattering from flat surfaces were reported; but, the signal from the flat metallic surface, the most used plasmonic substrate, was minuscule for allowing molecular testing [9].

The modes of photon–phonon coupling became the focus of explorations. Indeed, the solution came from the fundamentals of plasmonics [10–13], relying on excitation of the conduction electrons, which absorb photon energy then transfer it to phonons. At the metal/dielectric interface, the surface plasmon polaritons (SPPs) (quasi-particles existing due to strong coupling between the two oscillators i.e. the photon and the plasmonic cloud) are excited and propagate [14–16]. The photon and SPP wavevectors match upon photon tunneling in the total internal reflection geometry, and this configuration compensates for the absence of hotspots, typical of a nanostructured surface [17]. To excite a surface plasmon polariton by p-polarized light incident on a planar metal surface from the adjacent dielectric medium, the incident light and the SPPs must have the following conditions: identical frequency and the wavevector of the incident light parallel to the surface must equal the wavenumber of the SPP [18]. While the first condition can be easily achieved, the last condition is more complicated, unless the photon and SPP wavevectors match after photon tunneling in the total internal reflection geometry [19, 20]. Indeed, in this configuration, there is an...
Strong coupling is a fundamental premise of the following measurements, and is a crucial condition for deterring hot electrons from propagating to thicknesses deeper than the optical absorption depth and generating detectable waves. Quantum confinement and inter-band transition positively contribute to coupling enhancement [21, 22]. In particular, the positive contribution of inter-band transition occurs when the photon energy overcomes the inter-band transition energy (e.g. 2.4 eV for Au and 4 eV for Ag) [16]. The valence electrons on the 5d band are excited to above the Fermi level and become free electrons. This leaves electronic holes behind and reduces the screening effect between free electrons and ionic cores to enhance coupling.

The question arising here is related to the possibility of designing a setup that provides a clean and neat signal of both SPR and SERS using an utterly flat metallic layer and simultaneously enabling a signal strong enough for allowing the molecular analysis.

Optomechanical assets combining SPR and SERS analysis have already been designed and investigated [23–26], based on the forward [27] or backward [11] readout of Raman scattering. They facilitate measuring the refraction index and the thickness and chemical content of the layer. However, analysis of the molecular readout has rarely been achieved.

In this paper, we propose a fresh approach to this problem by combining the two sensing techniques in a Kretschmann configuration at acoustic frequencies [28–30]; besides, we intend to show the significance of the resultant molecular analysis. We intend to demonstrate enhancement of the electromagnetic field occurring on a flat Au film, which is optimized for SPR measurements. Moreover, plasmon–exciton coupling have been shown to be coupled states with the dye denoted Congo red and a thiol (cysteamine) has been used for testing the sensitivity of the apparatus.

We observed that the plasmon–exciton state could be investigated by a combination of SERS and SPR in a Kretschmann configuration, collecting the signal from flat Au substrates in an opportune range of frequencies. This was achieved using an arrangement that has no limitations on the relative aperture and is suitable for simultaneous functioning as part of the SPR sensor.

There are several advantages related to the optomechanical asset we propose here. It prevents the SPR from having any influence on the SERS measurements, because the two systems of detection lie on different sides of the prism. Combined measurements of the SERS and SPR signals can be simultaneously carried out, while time dependent experiments characterized by the addition of chemicals can benefit from the simple interchange of the samples for easily widening the existing database.

It is interesting to observe that triggering SERS signal on flat Au film simplifies the design of the sensors through cheaper and faster protocols of fabrication compared to those requested for the architectures of nanostructured substrates.

Finally, we believe that coupling flat Au substrates into a Kretschmann configuration and at low frequencies can foster interesting applications in nanophotonics and significantly simplify the design of the substrates.

2. Experimental

2.1. Description of the apparatus

The combined spectrometer consisted of two modules based on Kretschmann asset: SPR and SERS.

A schematic diagram of the system architecture is presented in Figure 1(a). The SPR system was housed on the back part of the prism [31, 32]. One of the two arms held the light source, which consisted of a 5 mm red-dot laser (Shenzhen Futhe Tech. Co. Ltd.). This had a peak emission at \( \lambda = 650 \text{ nm} \) wavelength [full-width-at-half-maximum (FWHM), FWHM = 20 nm], with light collimated by C1 (RC12FC-P01; Thorlabs Inc.). The polarizer P1, a double Glan–Taylor calcite polarizer (Thorlabs Inc.), provided the required polarization state at the correct orientation, and an optical iris K reduced the noise of the laser. The beam from the prism was collimated by C2 and filtered by P2 (Glan Thompson polarizer BBAR: 650–1050 nm, CA: 10.0 mm; Thorlabs Inc.) before being collected into a multimode optical fiber and sent to a high-resolution spectrometer (Ocean Optics HR4000, Custom). The laser beam was focused on the hypotenuse of a prism onto the sample layer, where the surface plasmon was excited. During the experiment, the samples were coupled to the surface of the prism (UV fused silica 25 mm right-angle prism, \( n = 1.466 \text{ RIU} \) at \( \lambda = 650 \text{ nm} \), Thorlabs Inc.), by an index matching fluid (refractive index \( n = 1.515 \text{ RIU} \), Shanghai Specimen and Model Factory, China).

The system was mounted on a two-arm goniometer, whereas the corner of the prism was aligned with the centerline of the table (figure 1(b)). The distance from the light source along the \( y \)-position could be moved by a micrometer position stage housed at the front side of the prism.
Figure 1. (a) Top: Optomechanical setup including the SPR and SERS modules. Bottom: Schematic of the optical configuration. L, laser; C, Condensator; P, Polarizer; K, Iris; D, Photodiode and capacitor. SPR and molecular detection conducted by the spectrometer and oscilloscope. (b) Housing of the prism on the table for alignment and centering. A, O, A: three corners of the prism. From A to O the rotation is $\vartheta = 90^\circ$. $\alpha, \alpha'$: the two faces of the prism where the laser enters and leaves, respectively. (c) Spot of the laser beam after alignment. The in and out angles are coincident.

The optomechanical mounting integrated standard and custom components. The prism and the photodiode support were designed to be integrated with the standard parts and were precisely fabricated (tolerance $\pm 0.01$ mm) in aluminum. The system could be considered as three subsystems: (i) the lighting arm, including the light source, collimator (C1), and polarizer (P); (ii) the prism support with vertical and lateral adjustments and the chip holder; and (iii) the receiving arm including the polarizer and the collimator. The two lighting and receiving arms were mechanically independent, such that their relative position could be changed as required, and the rotation angles were set using high precision rotation mounts (Standa, 5PPH50-1). This allowed control of the movement with a resolution of $0.001^\circ$.

The SERS system was housed in the front part of the prism [33]. The light was collected by a silicon photodiode (FDS 10 × 10 Thorlabs, $\lambda = 340–1100$ nm, peak $\lambda_0 = 960$ nm responsivity $R(\lambda_0) 0.62$ A/W), and the noise was reduced by a ceramic disk milli-capacitor. A cable carried the signal to the photo-oscilloscope (Pico Technology, Series 5000). The photodiode was integrated with the micrometer stage, which allowed a minimum distance of ($3 \pm 0.001$) mm to be reached between the prism and the diode. The holder of the photodiode allowed precise positioning of the prism in the center of the table, according to the scan angle.

2.2. Setting up the samples
The alignment of the optical components was achieved by coupling the Au sample prism to the hypotenuse of the prism, which was placed with the corner in correspondence to the centerline of the table (figure 1(c)). The two arms (labeled in the figure as side $\alpha$ and side $\alpha'$) of the SPR system were then fixed at $\vartheta = 45^\circ$ and the distance between prism and laser beam was tuned by the micrometer positioner. This was completed when a configuration with the same in and out angles was achieved and the center of the outlet beam was in the center of the filter. The positioning of the prism with the micromanipulator allowed simultaneous alignment of the photodiode for detection of the SERS signal.

2.3. Test method
The setup was tested to check its performances as a sensing platform. This was achieved by (a) measuring the coverage of a self-assembled monolayer (SAM) of Au affine molecules in contact with air as the external
medium \[34\], and (b) the coverage of selected Raman probe molecules. The experimental tests were carried out in air and the spectra were shown after subtraction of the laser background.

2.4. Au deposition

Efficient plasmonic transducers should be prepared to deposit an appropriate thickness of Au (typically between 40 and 70 nm) to observe a significant decay of the reflectance. The coverslips were first cleaned by ultrasonication in acetone and then in ethanol and were then dried under N\(_2\) stream.

The Au deposition was realized in an ultra-high vacuum chamber (base 10\(^{-9}\) Torr) using an electron gun. The deposited Au was 99.99% pure. The thickness of the Au film was controlled by a quartz micro-balance and two different thicknesses were deposited: 40 and 70 nm.

2.5. Thiol and Raman probes layer on Au film

The SAM of a selected thiol of a selected thiol, the cysteamine, was grown by dipping the Au substrates in a 1 mM solution of cysteamine hydrochloride dissolved in DI water for 2 h, at 4 \(\degree\)C. The samples were thoroughly rinsed with the fresh solvent to remove weakly adsorbed molecules. During incubation, the thiol group of the cysteamine formed a strong covalent bond with Au, producing a tightly packed carpet of molecules \[35–37\].

Congo red was selected as the Raman probe, because it can be deposited easily on metal surfaces at monolayer or sub-monolayer coverage by dipping/rinsing techniques in a 10\(^{-2}\) mM aqueous solution for 6 h at room temperature. After the samples were removed from the solution, they were gently rinsed once with fresh DI water to remove weakly adsorbed molecules from the surface and then dried overnight at room temperature.

The ultrapure water (>18.0 M\(\Omega\) cm\(^{-1}\)) used in all experiments and it was purified using a Millipore Milli-Q gradient system.

3. Results and discussion

The capability of measuring resonance was tested by detecting the Au (111) samples, which has been characterized elsewhere [31]. Briefly, from the crystallographic configuration of the 40 nm Au film sputtered on the top of the BK-7 cover glass (figure S1(a), supplementary data (https://stacks.iop.org/NJP/22/103035/mmedia)), the characteristic diffraction pattern at \(2\theta = 38.1\degree\) corresponding to the Miller index (111) lattice parameter was observed. The growth domains of the monocrystal Au exhibited molecular arrangements oriented along different directions with a height of 10.6 nm (figure S1(b), supplementary).

The resonance was measured on Au film (40 nm thick), and Au film (70 nm thick) was used to ascertain the dependence of the plasmon on the thickness of the noble metal layer. The angle-resolved far-field measurement of the substrate was performed under transverse magnetic TM polarization. Figure 2(a) depicts the evolution of the wavevector-resolved reflectance spectra obtained at \(\lambda = 650\) nm, as the incidence angle was scanned approaching and departing from the resonance angle in a range between 40\degree\ and 50\degree. For the naked Au, the reflectance had strong angle-dependence in the proximity of the resonance, which was measured at an angle of incidence \(\theta_{\text{inc}} = 46.076\degree\). Moreover, the geometrical configuration and the coupling with the prism allowed \(\epsilon \approx 7\%\) of the energy to reflect for the 40 nm thick sample and 40\% for the 70 nm sample. The spectra of the two thicknesses of Au fitted to a Lorentz function displayed identical linewidth for both samples: FWHM = \((1.16 \pm 0.48)\degree\).

It has been widely demonstrated that the SPP dispersion curve lies below the cone of the free space light in the dielectric, and apart from the origin, there is no point where the SPR curve and the light line intersect. Then, the normal light cannot simultaneously provide the correct wavevector and angular frequency to excite a surface plasmon, but the phase matching needs to be set, this allows that the momentum transfer takes place and the SPP are excited, condition which results not possible if only energy and momentum conservation are set (\(\omega_{\text{light}} = \omega_{\text{SPP}}\) and \(k_{\text{light}} = k_{\text{SPP}}\)).

The Kretschmann asset based on total internal reflection involves the coupling of the SPPs to the evanescent electromagnetic field of the light beam in an optically dense medium. Under this configuration, the layer of the metal is illuminated through the dielectric prism at an angle bigger than the total internal reflection (supplementary).

Metal-dielectric interfaces introduce the coupling between the SPPs of individual interfaces and slows down the appropriate resulting SPP-mode making accessible nm-sized field localization at any wavelength. A thin film of metal with thickness \(d\) in contact with a dielectric on both sides (like the condition occurring in Kretschmann configuration) is such that two identical SPP modes start overlapping with each other for small thicknesses of the metal film (figure 2(b)).
Figure 2. (a) Reflectivity of Au (111) 40 and 70 nm layers. Measurement in air at $\lambda = 650$ nm. Dashed lines represent the Lorentz model used for the fitting ($R^2 = 0.99$). (b) Surface plasmon polaritons at the interface Au/air. (c) Mode effective index (left) and propagation length (right) versus Au thickness according the explicit dispersion model. (d) Dispersion curves $\omega(k_y)$ of surface plasmons over a 40 nm Au–air interface and that of the photons in coupling (prism) materials. 1: dispersion of incident light from air; 2: dispersion of incident light from prism; 3: air curve; 4: dispersion of SP. Square: Couple point at the resonance. (e) Dispersion curves $\omega(k_y)$ of surface plasmons over a 100 nm Au–air interface and that of the photons in coupling (prism) materials.

Upon setting the boundary conditions to the equation of both the normal and tangential component of the electric field, the dispersion relation for SPPs can be stated as: \[ \tan\frac{\alpha}{2} = \frac{-\varepsilon_2}{\varepsilon_1} \], where $\alpha, \varepsilon_1 = (k_1^2 - \varepsilon_1 k_0^2)^{0.5}$ and $k_0 = \frac{2\pi}{\lambda}$ and it is useful to adopt the following simplification: $\left(k_1^2 - \varepsilon k_0^2\right)^{0.5} \approx k_0(\varepsilon_1 - \varepsilon)^{0.5}$ for deriving the explicit dispersion relation:

\[ k_{sp} = k_0 \sqrt{(\varepsilon_1 + \varepsilon_1 - \varepsilon_2) \left(\frac{\alpha}{2}\right)^2 \cdot \tanh^2(0.5k_0d(\varepsilon_1 - \varepsilon)^{0.5})}. \]

Applying this equation to a thin layer of gold surrounded by air at excitation wavelength of 650 nm, the effective mode index, $N_{\text{eff}} = \text{Re}(k_{sp})/k_0$, and propagation length, $L = [2 \text{ Im}(k_{sp})]^{-1}$, can be calculated for SPP. The solution of the explicit dispersion equation results in accurate values of the mode effective index and propagation lengths for in the whole range of film thicknesses, down to the thickness of 10 nm (figure 2(c)). It worth observing that only the symmetric mode has been calculated.

We also have reported the results of the dispersion relationship according to two different thicknesses of gold when the light is tunneled in a glass prism (figures 2(d) and (e)). The FDTD model has been implemented referring to the expression of the dispersion dispersion relation $k_{sp} = kn_1\sin\theta$, where $n_1$ is the refractive index of the prism. With the increase of the metal film thickness, the excitation of the SPP at the interface between the prism and metal becomes more difficult. The bigger thickness shifts the angle of
resonance until the couple point between the SP dispersion and the dispersion of incident light from prism becomes invisible, because the wavevector of SPP at this interface is greater than the photon wavevector in the prism unless to modify the angles of incidence and find the new condition of resonance.

Because of the better plasmonic behavior of the 40 nm samples, all following experiments were referred to this sample. The cysteamine capped on the 40 nm Au sample was tested. Figure 3(a) presents a comparison of the background-corrected reflectance of the Au before and after the coating with the cysteamine. A shift to a higher resonance angle was recorded after the capping ($\vartheta_{\text{inc}} = 46.60^\circ$) with a reflection of $\varepsilon \approx 15\%$ of the energy. The FWHM was also measured using the Lorentz fitting curve, and the measurements resulted in a wider than the naked Au linewidth, $\text{FWHM} = (1.31 \pm 0.24)^\circ$.

The position of minimum reflectivity corresponding to the functionalized sample exhibited an evident right shift with respect to the reference minimum. We theoretically evaluated the maximum shift of the angles with a multilayer model implemented in Winspall software [38]. To implement the model, we considered a prism (UV fused silica refractive index $n = 1.515$ RIU), an Au layer (dielectric constant $\varepsilon = -14.5 + 1.04i$), and air as the adjacent medium. With an approximate refractive index of $n_{\text{Cys}} = 1.22$ RIU [34] for the monolayer of the thiol, the numerical simulation provided a shift of resonance angles $\Delta \vartheta_{\text{max}} = 0.95^\circ$ and a good overlap between the theoretical prediction and experimental results.

The performance of a plasmonic sensor is described by several parameters, such as the resonance angle, depth of dip (namely the reflectance at the resonance angle), sensitivity, linewidth or FWHM, and figure of merit (FOM) [39].

In the angular interrogation mode, the resonance angle $\vartheta_{\text{res}}$ changes with the refractive index of the analyte $n$. Consequently, the sensitivity $S$ can be expressed as the ratio between the resonance angle variation $\Delta \vartheta_{\text{res}}$ and the variation of refractive index of the analyte $\Delta n$ as follows: $S = \frac{\Delta \vartheta_{\text{res}}}{\Delta n}$. The FOM then can be estimated as $\text{FOM} = \frac{S}{\text{FWHM}}$. Here, upon accounting the angles of resonance and the refractive ndices of the naked and cysteamine capped Au ($n_{\text{Au}} = 0.72$ RIU, $n_{\text{Cys}} = 1.22$ RIU), the sensitivity was estimated as $S = 1.58^\circ$/RIU, while the figure of merit was estimated as $\text{FOM} = 1.21$ RIU.

The Au coated by the Congo red was then used for testing the SPR system (figure 3(b)). The angle of the resonance shifted to $\vartheta_{\text{inc}} = \vartheta_{\text{res}} = 47.10^\circ$ (Congo red $n = 1.593$) [40] and the linewidth was measured as $\text{FWHM} = 5.8^\circ$. It worth noting that a wider linewidth of the Congo red and cysteamine shows a lower SPR sensitivity of those two samples in respect to the naked Au.

Above we have emphasized that the coupling necessary for the combined SPR/SERS readout is achieved in Krestchmann configuration. Indeed, because of the prism, (1) the light follows a well-defined optical path in incidence and emission, (2) the focal length and numerical aperture of the exciting/collecting optics influences the spread of incident angles and the range of collected angles. This signifies that the optomechanical coupling to SPPs in the Kretschmann configuration is crucial for the molecular vibration signal. Under our experimental conditions (40 nm Au film, 650 nm pump), we measured the coupling factor of our system as $g_{\text{e0}} = 0.12$ MHz, which seemed strong allowing for the discussed coupling [33] and the simultaneous SPR/SERS measurements.

Raman spectroscopy of which SERS is a special application invokes a combined enhancement caused by the plasmonic hotspot of the incoming electromagnetic field and the scattered field. Hotspots of high electromagnetic fields associated with localized plasmonic resonances enable an enhancement factor.
proportional to the fourth power of the field enhancement accounted for in the SERS gain equation:

$$EF = \left| \frac{E_{\text{loc}}(\lambda_{\text{ex}})}{E_0} \right|^2 \left| \frac{E_{\text{loc}}(\lambda_{\text{s}})}{E_0} \right|^2 \left| \frac{E_{\text{0}}}{E_{\text{0}}} \right|^2.$$ 

Here, the excitation field intensity $E_0$ and the local fields at the excitation $E_{\text{loc}}(\lambda_{\text{ex}})$ and Raman scattering $E_{\text{loc}}(\lambda_{\text{s}})$ wavelengths are included [41–43].

To prove the occurrence of an enlarged electronic field around the incident spot at resonance, we modelled and simulated the electric field distribution. A detailed description of the model is shown in figure S2, supplementary. Figures 4(a) and (b) shows the $E^2$ map according to the angle of incidence for the plain and red-coated Au at $\lambda = 650$ nm in air. The maps were calculated using the spatial average of $|E_{\text{loc}}|^2/|E_0|^2$ (or $|E_{\text{loc}}|^2$ considering the initial incident intensity as unitary, meaning the local electric field is normalized to the incident intensity and integrated over a line 1 nm away from the side surface of the Au ($E^2 = \int |E_{\text{loc}}|^2/|E_0|^2 \, dl$, where l is referred to as the molecules adsorbed on the surface).

This distribution allows extraction of the resonance angle where a maximum near-field enhancement is achieved, and further addresses the differences between plain and coated Au. Further, there is a well-identified angle of incidence (resonance), which corresponds to the maximal intensity of the field. This is indicated in more detail in figures 4(c) and (d) where the local field intensity enhancement factor (LFIEF) (according to the incident angles) resulted in a maximum at the surface where the dip of reflectivity takes place, recovering the accepted electromagnetic enhancement.

All of this would appear to be in contrast with the fact that low roughness of the flat and naked Au substrates must generate an irrelevant Raman scattering. Nevertheless, a preliminary analysis of the signal emitted to the front part of the prism holding the sample displayed the emittance of an elastically scattered Rayleigh light, which was visible to the naked eye.

This premise encouraged us to measure and analyze the transmittance. The Fourier transform of the time domain FFT spectra (on-resonance and out-of-resonance) were plotted for the plain Au and for the Congo red/Au samples. Figure 5(a) shows the SERS signal in air at $\lambda = 650$ nm at two different angles of incidence ($\theta_{\text{inc}} = \theta_{\text{res}}$, and $\theta_{\text{inc}} = 49^\circ$) under the condition of TM polarization.

The spectrum of the metallic layer was characterized by the elastic scattered Rayleigh peak attributable to the pump at a frequency of $\omega = 5$ MHz, and by the peaks in the anti-Stokes and Stokes regions, the elastic Brillouin peaks, at $(\omega - \Delta\omega)(=4.51$ MHz) and $(\omega + \Delta\omega)(=5.63$ MHz). Moreover, on-resonance
flat Au displayed a peak at $\omega = 8.50$ MHz, which was invisible under the out-of-resonance condition. Hence, following the trend of the spectra through different angles approaching and departing from resonance, it could be observed that the intensity of the peaks increased when approaching the resonant angle and decreased when departing. This was true for both the naked and coated Au (figure S3, supplementary).

This result indicated that coupling between the plasmonic cloud and molecular vibration can occur on-resonance. Figure 4(a) also shows that the spectrum of the Congo red had the same elastic scattered Rayleigh peak, in addition to Stokes and anti-Stokes.

The comparison of the Au and Congo red samples under the condition of resonance evidenced that the spectrum of the dye was characterized by two peaks ($\omega = 6.48$ MHz and $\omega = 6.85$ MHz), which were both invisible off-resonance (figure 5(b)) [44]. Moreover, the analysis and comparison between the plain and coated Au samples excluded the possibility that the last two oscillations emanated from the Au itself, because on-resonance Au only displayed a peak at $\omega = 8.50$ MHz.

To explain the differences between the spectra, the structural configuration of the molecule used as a dye was taken into consideration (figure 5(c)). Congo red has the phenyl group (C=C), which was associated with the peak of frequency $\omega = 6.48$ MHz, while amine (N=N) was associated with the frequency $\omega = 6.85$ MHz, as suggested by the pure Raman analysis of the red dye. This showed that the two characteristic peaks were close to each other (figure S4, supplementary) [31]. The relationship between the molecules and their spectra leads us to consider these results as the fingerprint of the molecules.

The intensity of the peak at a frequency of 6.81 MHz for several concentrations of Congo red solutions (figure S5 supplementary) was tested (figure 6(a)). The SERS signal was positively correlated ($R^2 = 0.975$) with the content of the red dye, with a limit of detection (LOD) measured at 3.567% (figure 6(b)).

Then, the cysteamine was analyzed. The cysteamine is a bifunctional thiol, wherein the S atom binds to the metal surface, and the amine group can be used to adsorb other molecules for biochemical analysis,
then it is of very common use [45, 46]. In our previous investigation, we observed the plasmonic singular behavior of cysteamine [32]. The sulfur capped Au exhibited a behavior influenced by the interface between the metal and S atoms, where the creation of an intermediate state was avoided. This enabled decay of a plasmon by directly exciting an electron from the metal to the strongly coupled acceptor. An explanation came from the NH$_3^+$ tail group, which has a withdrawing power conferring the behavior of the Au(0)–thiyl bonding to the metal and interferes with the plasmon.

Here, we coated the Au with the 5.5 wt% of cysteamine (figure S1(c), supplementary) and analyzed the molecular vibrational signal under resonance conditions (figure 7(a)). The spectrum of the thiol displayed peaks in the Stokes region, meaning there are no electrons emitting energy. This represents a worthwhile result, confirming the observation about the behavior of the electrons in the vicinity of the cysteamine molecules (as already observed using SPR). Moreover, the spectrum of the thiol exhibited characteristic peaks relative to the C-S vibration at $\omega = 6.35$ MHz (the taller) and at $\omega = 6.83$ MHz [47]. The lower frequency was attributable to the trans-configuration of the structure of the S–C–C chain of the adsorbed cysteamine molecule, and the higher to the gauche-configuration. The different intensity of the two peaks evidenced that the thiol preferred the trans-form during the capping mechanism and that the gauche-one was only partially reached.

It is worth noting that the coherent phonons are low frequency with wavevectors in the probe region, and that a very high-quality of the interface among the layers would also allow the detection of high-frequency coherent phonons.

The analysis of the cysteamine capped gold was concluded with an overview on the Raman linewidth of the peak (figure 7(b)). It was calculated using a Lorentzian peak fitting routine after subtraction of the background (figure S6, supplementary). The linewidth of two peaks resulted respectively in FWHM$_{6.35} = (0.414 \pm 0.001)$ MHz and FWHM$_{6.83} = (0.007 \pm 0.0007)$ MHz for the cysteamine, while the laser had a characteristic linewidth of $(0.001 46 \pm 0.00006)$ MHz (figure S6), significantly lower than the two of the cysteamine. From one perspective, this result provides evidence of the characterization of the typical peaks of the cysteamine. From another perspective, this confirms an important condition for the vibration of Raman signals to be consistent, which relies on the proof that the linewidths of the measured spectra are at least as wide as the excitation source. Then, the baseline of the obtained spectra achieves high signal-to-noise ratio SERS signals, and potentially allows the detection of a minute volume of samples.

From the analysis of the spectra, the shift of the Stokes peak of the Au capped by the cysteamine was also observed. This meant that the electrons absorbed a higher intensity of energy from the photon.

4. Conclusions

The results reported in this paper represent a proof-of-principle. When the two sophisticated sensing techniques (SPR and SERS) are combined using a setup based on the Kretschmann configuration, it becomes possible to implement Raman scattering with existing spectroscopic platforms easily. We ascribe the frequency shift to the resonant optical excitation of the plasmon, which enhances the Raman scattering from acoustic vibrations localized on the surface of the metal.
The strength of this combined technology relies upon its simplicity and predictability, because the surface-plasmon-polaritons are excited on flat metallic surfaces. We envisage several advances from this research, including increasing the sensitivity of our control further and performing a complete molecular scanning from plasmonic behavior to molecular vibrational analysis.

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