Silver nanowires as infrared-active materials for surface-enhanced Raman scattering†

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Surface-enhanced Raman scattering (SERS) is increasing in significance as a bioanalytical tool. Novel nanosized metal substrates are required to improve performances and versatility of SERS spectroscopy. In particular, as biological tissues are relatively transparent in the infrared wavelength range, SERS-active materials suitable for infrared laser excitation are needed. Nanowires appear interesting in this respect as they show a very broad localized surface plasmon resonance band, ranging from near UV to near infrared wavelengths. The SERS activity of silver nanowires has been tested at three wavelengths and a fair enhancement at 1064 and 514 nm has been observed, whereas a very weak enhancement was present when exciting close to the nanowire extinction maximum. These experimentally measured optical properties have been contrasted with finite element method simulations. Furthermore, laser-induced optoacoustic spectroscopy measurements have shown that the extinction at 1064 nm is completely due to scattering. This result has an important implication that no heating occurs when silver nanowires are utilized as SERS-active substrates, thereby preventing possible thermal damage.

Introduction

Surface-enhanced Raman scattering (SERS) is a steadily growing research field. Its development is supported both by novel nanofabrication methods1–13 and by the availability of new experimental and interpretative tools.14–20 SERS spectroscopy is commonly performed in the visible range, whereas infrared-excited SERS spectroscopy is by far less usual in spite of its great potential in biological applications. Infrared radiation, in fact, can penetrate biological tissues to a much larger extent than visible light, especially between 700 and 900 nm (near-infrared I region), and between 1000 and 1400 nm (near-infrared II region).21–23 Therefore, developing new SERS-active materials is required to explore the opportunities to exploit SERS in these spectral regions. Presently, the choice is limited to aggregated metal nanoparticles24 or specially designed nano-structures,25,26 which can display a localized surface plasmon resonance (LSPR) band in the near infrared.

Silver nanowires (AgNWs) appear to be a natural choice because of their extremely broad LSPR extinction band, which covers the UV, visible, and infrared regions. They offer the additional advantage of a relatively high enhancement factor (EF), due to the optical properties of silver.27 Nevertheless, SERS spectroscopy with AgNWs has only been performed with excitation wavelengths shorter than 800 nm.28–35

In this work, we have tested the SERS activity of these systems with 1064 nm excitation and then compared the relative enhancement obtained by shorter-wavelength excitation. The optical properties of AgNWs have been further studied using a photothermal method, namely, laser-induced optoacoustic spectroscopy (LIOAS), with excitation wavelengths similar to those employed for SERS. Calibrated LIOAS measurements of plasmonic systems can selectively lead to a determination of the absorption contribution to extinction.36 The separation of this contribution is necessary, as both absorption and resonant Mie scattering contribute to the LSPR band,37–39 and it is relevant for two aspects. Firstly, it allows a comparison between the far-field properties and near-field enhancement (giving rise to SERS), which is presently unexplored for AgNWs. Secondly, it is a measurement of the photothermal conversion efficiency, which is an important property of metal nanoparticles as functional materials.40–43
Experimental methods

Materials

Ethylene glycol, polyvinylpyrrolidone (PVP), and benzenethiol were purchased from Sigma-Aldrich, and glycerol and pyridine were purchased from Merck. All reagents were used without further purification. Isopropanol (from Merck) was distilled before use. High-purity AgNO₃ was produced by Cabro. Water solutions were prepared with deionized (Milli-Q) water.

AgNW synthesis

AgNWs were obtained according to a polyl synthesis method using PVP as a capping agent and NaCl as a catalyst. 44–46 25 ml of 0.01 M NaCl and 35 g PVP were added to 500 ml of ethylene glycol at 60 °C under stirring to obtain a clear solution. 10 g AgNO₃ were diluted in 300 ml ethylene glycol in the dark with the help of an ultrasonic bath until a homogeneous pale yellow solution was obtained. This solution was poured into PVP at a [NaCl]/[AgNO₃] ratio close to 0.07. 47 The resulting solution became reddish. The temperature was kept at 80 °C for 20 min and then increased to 100 °C until the NOₓ red gases completely evaporated and the solution became grey. AgNWs were precipitated with acetone and dried, then redispersed with isopropanol.

AgNW purification and characterization

The as-synthesized material had to be further treated in order to remove residual PVP and to reduce the fraction of small-sized Ag nanoparticles. To this aim, AgNW samples were purified by continuous density gradient centrifugation. 48 Five glycerol/water solutions (30/70, 35/65, 40/60, 45/55 and 50/50 v/v) were prepared and 2 ml of each solution were stratified carefully in a 15 ml Falcon tube, starting with the 30/70 solution at the bottom. The tube was kept horizontally for about 15 minutes, and then centrifuged at 3000 rpm for 5 minutes. Right after, 200 μl of the AgNW isopropanol dispersion were added on the top of the glycerol solution and centrifuged at 3000 rpm until a precipitate was formed at the very bottom of the tube. Most of the samples stayed as a brown layer at the top of the tube. These two fractions were separated using a Pasteur pipette, and centrifuged for 10 minutes at 8000 rpm. The precipitates were resuspended in water and this procedure was repeated twice for each fraction. The samples for SERS and LIOAS measurements were prepared by diluting the top fraction in deionized water. The concentration range was 0.02–0.8% (metal mass/volume). Extinction spectra were recorded with a Cary 60 spectrophotometer (Agilent Technologies).

Scanning electron microscopy (SEM) instrumentation and methods

The instrument used for the secondary electron images was a Zeiss-EVO MA15 scanning electron microscope coupled with an Oxford INCA250 energy-dispersive spectrometer, operated at 25 kV accelerating voltage and working distance 7.5 mm. Water-dispersed AgNWs were dried in a convection oven at 80 °C for some hours. Immediately prior to SEM measurement, a gold thin film of about 10 nm was sputter-deposited over the sample.

SERS instrumentation and methods

SERS spectra at 407 and 514.5 nm excitation wavelengths were obtained with a dispersive spectrometer. The laser sources were a Kr⁺ laser (Coherent, Innova) and an Ar⁺ laser (Coherent, Innova 90-5) respectively. The incident light was focussed with a 25 cm focal length spherical lens onto quartz NMR tubes containing 0.2 ml aqueous dispersions of the samples. The back-scattered light was dispersed with a triple monochromator (consisting of two Acton Research SpectraPro 2300i working in the subtractive mode, and a SpectraPro 2500i in the final stage with 1800 grooves per mm grating), and detected with a liquid-nitrogen cooled CCD detector. The power at the sample was 5 mW, the spectral resolution <4 cm⁻¹ and spectral dispersion >1.2 cm⁻¹ per pixel. The accumulation time was 10 min. The spectra were calibrated with indene as a standard to an accuracy of 1 cm⁻¹. SERS spectra at 1064 nm were measured in a backscattering configuration with a Bruker MultiRAM FT-Raman system, equipped with a Nd:YAG laser. 0.2 ml aqueous dispersions of the samples were kept in a quartz cuvette with a 1 cm optical path. The power supplied to the sample was 200 mW and the spectral resolution was 4 cm⁻¹. 400 scans were averaged.

Samples for wavelength-dependent SERS measurements were prepared by adding a 10⁻² M benzenethiol aqueous solution to AgNWs to reach a final 10⁻⁴ M benzenethiol concentration. Pure isopropanol was added to a final 5% (v/v) concentration as an internal intensity standard to evaluate the SERS intensity when the excitation wavelength is changed. The presence of an internal standard is required, as the absorption of the incident and scattered light by the sample strongly depends on the wavelength.

Concentration-dependent measurements at 514.5 nm excitation wavelength yielded an estimate for the limit of detection (LOD) of benzenethiol (10⁻⁶ M < LOD < 10⁻⁵ M) and pyridine (10⁻⁴ M < LOD < 5 × 10⁻⁴ M). The SERS spectra are reported in the ESI, Fig. S1-S3.†

LIOAS instrumentation and methods

LIOAS signals are generated by thermal relaxation following light absorption, which produces a temperature rise in the environment surrounding the absorbing molecules 49 or particles. 50,51 The subsequent expansion acts as the source of a mechanical (acoustic) wave that is detected by means of a piezoelectric transducer. Light scattering does not contribute to the generated acoustic wave, at least in diluted solutions. 52 The amplitude $H$ of the photoacoustic signal is given by the following equation for diluted solutions:

$$H = kn_a$$  \hspace{1cm} (1)

where $k$ is an instrumental constant, $n_a$ is the number of incident photons at the excitation wavelength $\lambda$, and $a$ is the absorption factor of the solution

$$a = 1 - 10^{-A_\lambda} = 1 - T_\lambda$$  \hspace{1cm} (2)
where $A_\lambda$ and $T_\lambda$ are the decadic absorbance and the transmittance, respectively.

In contrast, in the case of a dispersion of scattering nanoparticles, absorption is only one of the contributions to extinction

$$E_\lambda = A_\lambda + S_\lambda$$  \hspace{1cm} (3)

where $S_\lambda$ is the scattering contribution.$^{53,54}$ Absorption can be isolated by calibrated LIOAS measurements, in which the signal of the sample and that of a calorimetric reference are recorded under strictly identical experimental conditions. A calorimetric reference is a substance which (i) attenuates the incident light without losses due to scattering, (ii) instantaneously releases all the absorbed energy as heat, and (iii) does not give rise to intrinsic volume changes upon photo-excitation.$^{55}$ It can be reasonably assumed that conditions (ii) and (iii) are also true for our AgNW sample, therefore, an observed sample signal decrease must be related to scattering losses.

The signals were detected with a 1 MHz resonant frequency piezoelectric transducer (Panametrics V103-RM) clamped to a spectrophotometry quartz cuvette with a 1 cm optical path. We averaged its output, once processed using a Panametrics 5660 B amplifier, with a Tektronix TDS-3054B digitizing oscilloscope. The minimum number of signals was 512 for each averaging cycle. The laser source was the output of a Quanta System Nd:YAG laser at 1064, 532 and 355 nm. The pulse duration was $\sim$10 ns and the repetition rate was 10 Hz. The incident laser energy ($<100 \, \mu J$) was measured behind the empty sample cuvette using a pyroelectric head energy meter, before and after each LIOAS measurement. The incident laser beam was shaped by a rectangular slit with $1 \times 10 \, \text{mm}$ size without focusing on the sample. Noticeably, the irradiance ($<1 \, \text{mW} \, \mu \text{m}^{-2}$) was below the threshold for the formation of bubbles according to the recent calculations in ref. $^{50}$. The laser energy at the sample was adjusted by means of neutral density filters. The LIOAS signal amplitude was considered as the peak to valley value of the waveform observed on the oscilloscope.

The calorimetric references for the calibration were KMnO$_4$ or CuSO$_4$ solutions. Extinction spectra were recorded before and after each measurement to check the integrity of the sample and reference solutions. In particular, extinction changes, which could point at AgNW reshaping effects, were not detected.

**Finite element method (FEM) simulations**

A 3D simulation on a single nanoparticle was performed to investigate the spectral behaviour of AgNWs at the near and far field, using commercial FEM based software Comsol Multiphysics®. The nanowire was modelled as a prism (length $= 4 \, \mu \text{m}$), with a pentagonal cross section (diameter $= 90 \, \text{nm}$) and rounded ends, in water ($\eta = 1.33$). The Ag dielectric constant was taken from ref. $^{56}$. The nanoparticle was excited by a plane wave polarized along the nanowire axis and with the wavevector direction perpendicular to it, which corresponds to the longitudinal excitation. As a result of such simulation, the absorption, scattering and extinction cross sections were achieved from 600 to 1100 nm. At the same time the near-field enhancement at 1064 nm was obtained. This is defined as the ratio of the local to incident electric field.

**Results and discussion**

**AgNW characterization**

SEM was used to study nanometer-scale features such as the morphology, length and diameter of our material. Fig. 1 displays randomly piled up AgNWs, with lengths between 1 and $4 \, \mu \text{m}$ and an average thickness of $90 \pm 10 \, \text{nm}$. The cross section of the nanowires appears rather prismatic than circular. A minority fraction of smaller nanoparticles with very different shapes and sizes was also observed. Additional SEM images are shown in ESI, Fig. S4.$^\dagger$

The extinction spectra of AgNWs are characterized by an extremely broad LSPR band, extending from the near UV to

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**Fig. 1** Representative SEM images of AgNWs at 30 000x and 110 000x magnification.
the infrared range. The as-synthesized material displayed a shoulder at 352 nm and a maximum at 386 nm, together with a shoulder at 411 nm (Fig. 2A). After purification, the main component gave rise to a spectrum with a maximum at 387 nm without the shoulder at a longer wavelength (Fig. 2B), whereas the residual fraction yielded a spectrum with a prominent shoulder at 432 nm (Fig. 2C). The latter fraction possibly corresponds to the smaller nanoparticle population observed by SEM. These results were in line with those obtained by a previously described purification procedure.

In particular, the extinction spectrum of purified AgNWs was very similar to the previous one, which was interpreted as originating from AgNWs with a pentagonal cross section on the basis of electronic microscopy images and previous theoretical work. The shoulder at 352 nm can therefore be assigned to the transverse quadrupole resonance, the latter fraction possibly corresponds to the smaller nanoparticle population observed by SEM. These results were in line with those obtained by a previously described purification procedure.

Extinction spectra of the AgNW aqueous dispersion before purification (A), and of the top (B, solid line) and bottom (C, dashed line) fractions (see Experimental methods). The three spectra have been normalized to unity. Representative SEM images of fractions A and B are shown.

SERS excitation wavelength dependence

The exceptionally large width of the LSPR band suggests that SERS spectra can be obtained from AgNWs with the laser excitation wavelength, \( \lambda_{ex} \), in a very broad range. To test this opportunity, we performed SERS with excitation at 407 nm, i.e., close to the extinction maximum; at 514 nm, on the red edge of the LSPR band and at 1064 nm, where the extinction reaches a plateau. The experimental conditions were specifically adjusted to obtain a reliable comparison of the SERS intensities at different wavelengths. We chose benzenethiol as a SERS probe because this molecule does not display electronic resonances in this wavelength range. AgNWs were used as aqueous dispersions where we added isopropanol as an internal standard which does not interact with the metal surface. We tested three different benzenethiol concentrations, namely, \( 10^{-4} \) M, \( 10^{-5} \) M, and \( 10^{-6} \) M (see Fig. S1 and S2 in the ESI†). Then, the intensity ratio between the Raman bands of \( 10^{-4} \) M benzenethiol and those of isopropanol at different values of \( \lambda_{ex} \) was evaluated. This ratio yielded the wavelength dependence of the EF, even if we did not perform a determination of the absolute EF, which had been previously shown to be \( 5.8 \times 10^3 \) (at 514 nm \( \lambda_{ex} \)) for similar AgNWs.

Fig. 3 (upper panel) shows the extinction spectrum of AgNWs after the addition of \( 10^{-4} \) M benzenethiol. The only effect of the analyte addition was a slight red shift of the LSPR band maximum. Fig. 3 (lower panel) shows the SERS spectra of benzenethiol adsorbed on AgNWs at the three selected \( \lambda_{ex} \). The spectra matched the published SERS spectra of benzenethiol on Ag surfaces. In particular, the intensity of the strong band at 1000 cm\(^{-1}\) – which can be assigned to the ring breathing mode – was similar to the intensity of the bands at 1073 cm\(^{-1}\) and 1575 cm\(^{-1}\). This feature is typical of benzenethiol adsorbed onto Ag surfaces, and contrasts with the spectrum of pure liquid benzenethiol, where the band at 1000 cm\(^{-1}\) is by far the strongest one. The spectra were most intense for 514 nm excitation. At 1064 nm excitation, the relative intensity of the bands of benzenethiol was weaker. For example, the band at 1000 cm\(^{-1}\) was weakened by a factor of 1.5. The bands of benzenethiol could be hardly detected at 407 nm excitation (see Table S1 in the ESI†). The relative intensities at the three \( \lambda_{ex} \) values are plotted in the upper panel of Fig. 3.

The SERS excitation wavelength dependence of AgNWs can be put into the frame of existing observations and theoretical predictions. As a first approximation, \( \lambda_{ex} \) is expected to lie within the extinction band in order to observe plasmonic enhancement. In fact, the EF for SERS is related to the same resonances that give rise to extinction.\(^{38}\) The relationship between \( \lambda_{ex} \) and extinction, though, is more complex because of several reasons:

(i) the EF for SERS is related to the electric field amplitude \( E \) at the metal surface at both \( \lambda_{ex} \) and \( \lambda_s \), the wavelength of the Raman-scattered light:

\[
\text{EF} (\lambda) \propto |E(\lambda_{ex})|^2 |E(\lambda_s)|^2.
\]
Therefore, the EF is maximum when λ_{max}, the LSPR band maximum, lies between λ_{ex} and λ_{s} \cite{64}. This would lead to a blue shift of the SERS dependence on λ_{ex} compared to the LSPR extinction maximum. However, this blue shift has been observed in a limited number of cases \cite{65-67}.

(ii) Early SERS substrates, which consisted of aqueous dispersions of salt-aggregated Ag nanoparticles, displayed intense EFs in the 500–1000 nm wavelength range, although the LSPR extinction maximum was around 400 nm \cite{68}. The reason was the presence of small amounts of extended nanoparticle aggregates, displaying especially high EFs at long wavelengths: therefore, the extinction spectrum was dominated by the contribution of monomeric Ag nanoparticles, whereas the dependence of EF on λ_{ex} was given by the nanoparticle dimers, trimers, etc \cite{69}.

(iii) Many analytes, e.g., heterocyclic aromatic molecules, can form charge-transfer complexes with the metal surface \cite{70}. This leads to the appearance of new electronic transitions, often lying at wavelengths longer than the LSPR band. This situation, originally indicated as a “chemical effect”, gives a more complicated SERS wavelength dependence than that expected solely on the basis of plasmonic resonances.

(iv) An additional factor must be specifically taken into account in the case of anisotropic nanoparticles, namely, the presence of diverse LSPRs, which can contribute to extinction and SERS EF to a strongly different extent \cite{71,72}. For instance, nanorods \cite{73,74} and nanosphere dimers \cite{75,76} are characterized by a relatively weak resonance at shorter wavelengths and a stronger one at longer wavelengths, giving rise to distinct near-field and far-field spectral distributions. Extinction—which is a far-field property—displays both resonances. The wavelength dependence of the electric field intensity at the metal surface—giving rise to near-field enhancement and therefore to SERS—follows the shape of the extinction spectrum. However the near-field enhancement is increased by several orders of magnitude for the longer wavelength resonance, whereas extinction changes to a much lesser extent. Therefore, SERS on anisotropic nanoparticles is most effective for λ_{ex} in the red/near infrared region \cite{38}.

The data in Fig. 3 are a clear example of the non-coincidence of extinction and EF. We cannot exclude that reasons (ii) and (iii) contribute to the SERS wavelength dependence. However, our interpretation is that the last point—AgNW anisotropy—is the determinant, i.e., the SERS enhancement at longer wavelengths originates from resonance with a longitudinal mode. The FEM simulations shown in Fig. 4 confirm this possible explanation.

**Laser-induced optoacoustic measurements**

Besides the usual comparison between SERS EF and extinction, some relationships between far-field scattering and near-field enhancement in plasmonic materials have been observed in a number of cases, i.e., especially high SERS EFs are often related to enhanced far-field scattering \cite{78-80}. Then, the question arises whether those excitation wavelengths which are most SERS-effective (514.5 and 1064 nm in the present case) lie in an extinction region where scattering is the main component of extinction \cite{81-83}. We have previously addressed this issue in the case of Au/silica nanoshells \cite{84}. For this material, we separated the absorption and scattering contributions to extinction through LIOAS, and we measured the SERS EF wavelength dependence. The main results were that (i) the spectral distribution of absorption and scattering does not coincide, the latter being shifted to longer wavelengths, and (ii) the spec-
central distribution of the EF for SERS is shifted to even longer wavelengths.

We performed calibrated LIOAS measurements at three wavelengths which were sufficiently close to $\lambda_{\text{ex}}$ for SERS, namely, 355, 532 and 1064 nm. For each $\lambda_{\text{ex}}$, we prepared at least three AgNW samples with increasing extinction at that wavelength, $E_{\lambda}$, and three calorimetric reference solutions (see Experimental methods). For each sample, we measured the signal amplitude at increasing laser intensity (data are shown in Fig. S5 in the ESI†). The slope of the signal vs. the laser intensity plot for each sample is the ordinate value indicated as the optoacoustic signal amplitude in Fig. 5. Finally, we linearly fitted the signal vs. $(1 - 10^{-E_{\lambda}})$ plots and compared the slopes for the calorimetric reference and the nanoparticle sample, $H_{\text{ref}}$ and $H_{\text{sam}}$. The ratio of these slopes allows the determination of the photothermal conversion efficiency: if the slopes were the same, this would indicate that extinction is completely due to absorption, and scattering losses are absent. When the ratio is less than unity, it yields the fractional absorption contribution to extinction:

$$\frac{H_{\text{sam}}}{H_{\text{ref}}} = \frac{A_{\lambda}}{E_{\lambda}}. \quad (5)$$

The fractional scattering contribution $S_{\lambda} / E_{\lambda}$ can then be obtained by the difference $S_{\lambda} = E_{\lambda} - A_{\lambda}$. This kind of determination is a microscopic one and can be fruitfully compared with macroscopic methods that rely on temperature rise measurements. An alternative approach consists of a direct, accurately calibrated measurement of scattering.

When LIOAS measurements were performed at 1064 nm excitation in aqueous solutions, the absorption of water also
contributed to the signal. For this reason, the signal amplitude for pure water is plotted in Fig. 5. Remarkably, the signal of AgNWs had the same amplitude as that of pure water at all the concentrations we tested. This implies that AgNW extinction at this wavelength is completely due to Mie scattering. At shorter excitation wavelengths, the signal amplitude of AgNWs significantly increased. The $H_{\text{sam}}/H_{\text{ref}}$ ratio was 0.122 at 532 nm (see Table 1), implying that scattering is still overwhelming at this $\lambda_{\text{ex}}$ and reached 0.29 at 355 nm. The values in Table 1 are plotted as $A_{\lambda}/E_{\lambda}$ ratios in Fig. 6 in order to compare them with the extinction spectrum of AgNWs. The $S_{\lambda}/E_{\lambda}$ ratios at the three wavelengths, obtained by difference, are also plotted. This set of LIOAS measurements is experimental evidence that the broad LSPR band of AgNWs is dominated by scattering, especially in the long-wavelength side. This is in agreement with numerical calculations performed for similar AgNWs, showing that the longitudinal excitation gives rise to a broad near-infrared extinction band, which mainly consists of scattering. Our FEM simulations in Fig. 4 yield a similar result.

An interesting comparison can be made with the case of Au nanowires, which have been especially investigated in the context of surface-enhanced infrared spectroscopy. It has been demonstrated, for example, that an increase of the transverse size enhances the scattering contribution to the infrared extinction progressively, until all extinction is due to scattering.

The optoacoustic results add important information to the SERS results. First of all, they suggest that an increased EF of AgNWs is obtained when the $\lambda_{\text{ex}}$ for SERS is tuned away from absorption – not from extinction. We found a similar result in our previous investigation on Au nanoshells, where SERS spectra had a very low intensity for relatively short $\lambda_{\text{ex}}$ values. In addition, LIOAS results indicate that the absorption at 1064 nm is negligible. This has important consequences in the field of AgNW applications. It has been recently reported that highly absorbing SERS substrates display a rapid decrease of the SERS signal under laser irradiation, because of high temperatures around the nanoparticle surface. The importance of the absence of heat losses has been highlighted by simulations performed for metallic and dielectric potential SERS substrates. In contrast, AgNWs can act as SERS substrates without heating and therefore may be advantageous when compared to other plasmonic systems.

## Conclusions

The combination of SERS and photoacoustic spectroscopy has allowed us to roughly decompose the apparently featureless, broad plasmonic band of AgNWs in three different regions, and to discriminate the far-field and near-field properties. When the excitation wavelength was close to the extinction maximum, we could only detect very weak SERS activity. Moving to the red edge of the plasmonic band, we observed an increase in both far-field scattering and SERS intensities. Finally, a noticeable situation was encountered for near-infrared (1064 nm) excitation. Here, AgNWs were still SERS-active and absorption did not significantly contribute to extinction. The importance of SERS enhancement without heating due to absorption by the plasmonic substrate adds interest to AgNWs as SERS-active materials. The effect is outstanding at 1064 nm, nevertheless, low heating and high SERS efficiency are maintained at shorter wavelengths (514.5 nm for SERS, 532 nm for LIOAS). This adds versatility to AgNWs as SERS substrates.

## Conflicts of interest

There are no conflicts to declare.

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Table 1: Slopes of the linear fitting curves in Fig. 5, $H_{\text{sam}}$, and $H_{\text{ref}}$, at the three excitation wavelengths. The errors are the standard deviation of the fitting curves from the data points. For the $H_{\text{sam}}/H_{\text{ref}}$ ratio, the propagation of the errors was considered.

<table>
<thead>
<tr>
<th>$\lambda_{\text{ex}}$ (nm)</th>
<th>$H_{\text{sam}}$</th>
<th>$H_{\text{ref}}$</th>
<th>$H_{\text{sam}}/H_{\text{ref}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>0.103 ± 0.014</td>
<td>0.353 ± 0.007</td>
<td>0.293 ± 0.040</td>
</tr>
<tr>
<td>532</td>
<td>0.021 ± 0.000</td>
<td>0.172 ± 0.010</td>
<td>0.122 ± 0.007</td>
</tr>
<tr>
<td>1064</td>
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<td>0.125 ± 0.006</td>
<td>−0.099 ± 0.065</td>
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</tbody>
</table>

![Fig. 6](image-url) $A_{\lambda}/E_{\lambda}$ and $S_{\lambda}/E_{\lambda}$ ratios, obtained by LIOAS measurements as described in the text. In this figure (at variance with Fig. 2 and 3) the water absorption band at ~980 nm has not been subtracted from the spectrum.
CSIC, Madrid, Spain) are acknowledged for their collaboration in refining the experimental conditions for SERS.

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