Polarization-dependent effects in surface-enhanced Raman scattering (SERS)

P. G. Etchegoin, C. Galloway and E. C. Le Ru

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A few key examples of polarization effects in surface-enhanced Raman scattering (SERS) are highlighted and discussed. It is argued that the polarization of the local field, which is felt by an analyte molecule in a location of high electromagnetic field enhancement (hot-spot), can be very different from that of the incident exciting beam. The polarization dependence of the SERS signal is, therefore, mostly dictated by the coupling of the laser to the plasmons rather than by the symmetry of the Raman tensor of the analyte. This sets serious restrictions for the interpretation of both single-molecule SERS polarization studies and for the use of circularly polarized light in techniques like surface-enhanced Raman optical activity.

1. Introduction

Surface-enhanced Raman scattering (SERS)[1,2] is based on the amplification of Raman signals by interaction with surface plasmon resonances. Besides a small amplification called "chemical"[3,4]† most of the boost in the signal can be accounted for by the electromagnetic enhancement.[1] An obvious degree of freedom in spectroscopy is polarization. Polarization selection rules in molecular spectroscopy (and Raman spectroscopy in particular) are standard textbook material.[5,6] It is desirable then to try to understand whether we can gain some new insights into the SERS phenomenon by using the degree of freedom provided by polarization studies. These types of experiments are slowly coming of age in SERS.[7]

The question is interesting for several reasons. Firstly, SERS signals can be boosted to a level where single molecule detection is possible.[8,9,10] A natural question is, accordingly, to see if we can combine polarization studies with single molecule detection to understand very basic aspects of the interaction of the molecule with the surface like, for example, its orientation or chemical interaction with the metal.[11,12,13] This could eventually provide not only a much better insight into the SERS phenomenon itself but also become an invaluable tool for surface science. In addition to this, the understanding of polarization studies in SERS[14] could, in principle, be used to extend the application of the technique to areas of polarization modulated Raman scattering; of great importance for biological molecules among others. An example of the latter is the possibility of SERS optical activity, which has been proposed recently but only briefly studied in the literature.[15]

In this paper, we explore the difficulties and highlight several important principles of the interpretation of polarization-dependent SERS phenomena. We argue that the difference between incoming and local field polarizations—produced by surface plasmon resonances—needs to be taken into account in order to interpret correctly the experimental results. We show that many claims in the literature can be explained easily with very general properties of plasmon resonances and, therefore, do not reveal as a rule anything about the orientation of the molecules except, possibly, in exceptional circumstances. The considerations also set stringent limits to the applicability of SERS optical activity.

2. General properties of hot-spots

Let us divert the discussion momentarily to a few general properties of electromagnetic hot-spots in dimers formed by metallic colloidal particles. We take a specific case for the sake of definiteness, but the properties we discuss are completely general and easily extended to other situations, as we shall argue later in this section (*vide infra*).

Consider a dimer formed by two metallic colloids. We take the radii of the particles to be $a = 25$ nm (a typical value for sodium citrate reduced Ag colloids), separated by a gap of 2 nm and we use the best parametrization of the dielectric function of Ag from ref. 16–18. The dimer, together with its relative orientation with respect to a fixed laboratory reference frame, is explicitly shown in Fig. 1(a). We study the electromagnetic response of this dimer for light impinging at different angles with respect to the equatorial plane (Fig. 1(a)), with different wavelengths (λ) and for two different polarizations $\vec{E}_p$ or $\vec{E}_s$ (mutually perpendicular to each other) forming a triad with the propagation direction $\vec{k}$. From the latter, any arbitrary state of incident polarization (including circular polarization) can be built by taking linear combinations (with complex coefficients) of $\vec{E}_p$ and $\vec{E}_s$.

In order to avoid any problems with approximations, we solve the electromagnetic problem using generalized Mie theory after ref. 7 and 19. Fig. 1(b) shows the local-field

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The MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand

† The chemical enhancement in SERS comes from the modification of the Raman polarizability by direct electronic interaction with the metal (by itself or through a surface complex involving an ion). It can be thought as a change in the intrinsic "identity" of the adsorbate produced by this interaction.[1]

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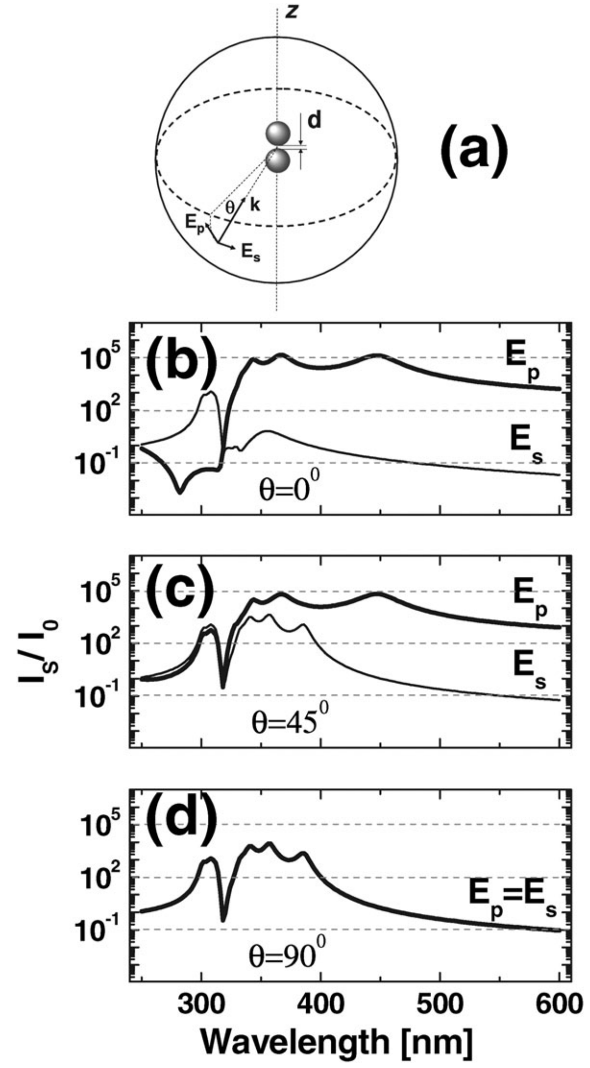

Fig. 1 (a) A dimer formed by two Ag colloids with radii $a = 25$ nm separated by a gap of $d = 2$ nm. The best analytic parametrization available for Ag[16–18] is used as dielectric function for the colloids. Light impinges on the dimer with a wavevector $\vec{k}$ at an angle θ with respect to the equatorial plane and with either $\vec{E}_p$ or $\vec{E}_s$ polarization. Any arbitrary state of polarization can be built from a linear superposition (with complex coefficients) of $\vec{E}_p$ and $\vec{E}_s$. Calculations are performed for the particles immersed in air. The same conclusions hold for water immersion, except that the resonances are red-shifted with respect to the values shown here. Variations in θ in the range $0 \leq \theta \leq 90°$ for both $\vec{E}_p$ and $\vec{E}_s$ cover all the possibilities by symmetry. The local field enhancement factors (I_s/I_0), immediately at the surface of the top colloid in the gap, for the incoming wave with either $\vec{E}_p$ (thick line) or $\vec{E}_s$ (thin line) and three different incident angles are shown in (b) ($\theta = 0°$), (c) ($\theta = 45°$) and (d) ($\theta = 90°$). In (d) both curves are coincident ($\vec{E}_p \equiv \vec{E}_s$) due to the symmetry along the axis. Note the logarithmic scale for the intensities.

intensity enhancements in the gap, at the surface of the top colloid on the z axis, for different polarizations and incident angles. Note that SERS enhancement is given, in a first approximation, by the square of the local field intensity. Let us summarize very briefly the basic phenomenology of the results. We concentrate on the response in the visible range due to the fact that the overwhelming majority of SERS experiments are done in this region (for example 514 nm as shown in Fig. 1(b)–(d), which is a typical laser line used in many experiments). The result in Fig. 1(b)–(d) can be summarized as follows: (i) For $\theta = 0°$ there is a $\sim 10^4$–10^5 difference in intensity (depending on the exact wavelength) between $\vec{E}_p$ and $\vec{E}_s$ polarizations. (ii) The difference is still between 3 and 4 orders of magnitude at $\theta = 45°$. (iii) Only at $\theta = 90°$ the response between $\vec{E}_p$ and $\vec{E}_s$ is the same (as expected by symmetry) but then the overall enhancement for the two can be 6 or 7 orders of magnitude smaller compared to the one of $\vec{E}_p$ for $\theta = 0°$ and, in fact, the enhancement can be smaller than one (quenching) in the red and near infrared regions. This depends, of course, on the exact separation between the two colloids and their size, but a rule of thumb is that the higher the enhancement the wider the contrast will be between the responses for $\vec{E}_p$ and $\vec{E}_s$. All these facts are explicitly shown in Fig. 1(b)–(d). This conclusion is very robust and fairly insensitive to wavelength, as demonstrated also in ref. 7.

So far in Fig. 1 we were only concerned with the intensity of the local field for different incident angles and polarizations of the incoming beam. But, the polarization of the local field is also an important parameter of the discussion and it cannot be inferred directly from the incident polarization. This complementary aspect is explicitly shown in Fig. 2, where the main result is that the local field polarization in the visible is always along the dimer axis, for as long as there is a small component of the incident field along that direction; its intensity is dictated by the projection of the incident field along z (with a $\cos^2\theta$ dependence, that can be obtained from a detailed angular study not shown here). We append these results to a whole series of facts that are not shown explicitly in Fig. 1 or 2 but form part of the well-established phenomenology of plasmon resonances and have been studied in detail elsewhere,[7,21,22] to wit: (i) The maximum intensity in the visible/near infrared range always happens at the gap (on the surface) and is due to a localized coupled plasmon resonance between the two particles. (ii) A red-shifted plasmon-resonance (with respect to the intrinsic resonance of a single colloid) develops *via* the interaction and it shifts further to longer wavelengths for smaller separations. For the example in Fig. 1(b)–(d) this resonance peaks at $\sim$450 nm and it behaves essentially like a dipole along z in its coupling to the external electromagnetic field.[21] This can be seen, for example, by its complete disappearance at $\theta = 90°$ in Fig. 1(d). (iii) The calculations in Fig. 1 are performed for the particles in air. If the particles are immersed in water the resonances will be red-shifted in view of the different dielectric constant of the medium. As a guide, resonances at 360 and 450 nm in air correspond to resonances at 410 and 550 nm in water ($\varepsilon = 1.77$).

An interesting question at this stage is: How general are these enumerated properties for more complicated clusters of many particles and with both distributions of sizes and separations among them? It is easy to show through many different examples that the answer to this question is that: Quantitatively the situation will change according to the specific case, but the qualitative picture remains, in particular

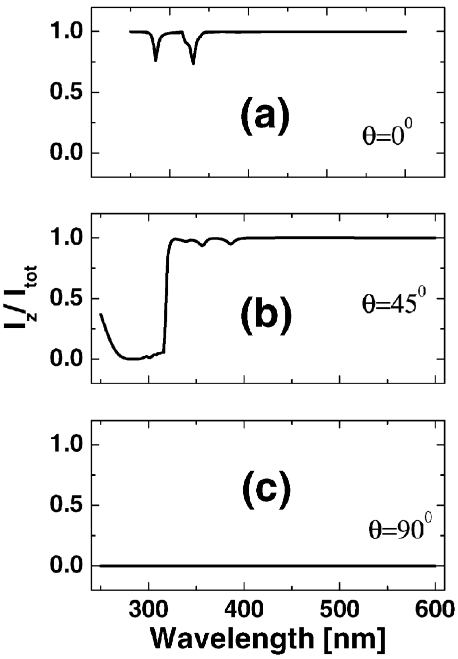

Fig. 2 The function I_z/I_{tot}, where $I_z = |E_z|^2$ and $I_{\text{tot}} = |E_x|^2 + |E_y|^2 + |E_z|^2$, represents the total intensity that is polarized along z evaluated at the same position of Fig. 1 (on the surface of the top colloid in the gap). The different plots are for $\vec{E}_p$-polarization and for the same incidence angles seen in Fig. 1, namely: (a) $\theta = 0°$, (b) $\theta = 45°$ and (c) $\theta = 90°$. In (c) all the light is polarized perpendicular to $\hat{z}$ and that is the reason for having $I_z/I_{\text{tot}} = 0$ (this is also the case for $\vec{E}_s$-polarization). The other two cases show that, for most of the visible range, the polarization at the hot-spot on the surface in the gap is predominantly linearly polarized along z. The case $\theta = 45°$ exemplifies the point we are rasing, namely that the polarization of the local field is not directly connected to the polarization of the incoming beam.

in terms of the physics and characteristics of hot-spots. Arguably, the example of the dimer contains the essence of all the physics of the highest enhancements in SERS. Simulations with generalized Mie theory for multiple particles have been reported in the literature.[22] It is easy to convince oneself that as far as hot-spots are concerned, more complicated geometries behave simply like "collections of adaptable dimers" with more possibilities to achieve high resonance conditions in different places due to their more complicated geometry. But the dominant part of the enhancement through hot-spots always comes from gaps between two interacting objects that behave in essence like dimers, albeit with slight modifications according to the environment and specific geometry. Accordingly, the considerations given above will hold in general. This simple and general phenomenology of plasmon resonances and hot-spots in SERS has already wide-ranging consequences for some of the experimental results and techniques proposed in the literature, as we shall discuss in the next section.

3. Experimental studies with polarization in SERS

In this section we review a few key aspects of experimental results reported in the literature in the light of the considerations in the previous section. Consider first the case of SERS optical activity (SEROA). It is obvious that in order to profit from SERS we would like to be able to both: (i) reach the probe with circular polarization and (ii) preserve the high enhancement of SERS. However, it is not enough to fix the external polarization as circular to ensure that this is actually the polarization felt by the analyte molecule, because *what matters is the polarization of the local field felt by the probe.* Incident circular polarization can be studied by taking the incident polarization to be $\vec{E}_{\pm} = 1/\sqrt{2}(\vec{E}_p \pm i\vec{E}_s)$. Fig. 1(b)–(d) and 2 show immediately that *high enhancements in hot-spots in the visible are incompatible with circular polarization* due to the huge difference in response for $\vec{E}_p$ and $\vec{E}_s$. If we want the probe to be exposed to true circular polarization, we can only use a narrow range of incidence angles around $\theta \approx 90°$ in Fig. 1(a). However, as can be seen from Fig. 1(d) this can imply working with enhancements that can be $\sim 10^2$ times smaller than normal SERS enhancements in the visible and in a situation where only a small fraction of the hot-spots (dimers with the axis approximately aligned with the incoming wave-vector $\vec{k}$) will contribute to a difference between $\vec{E}_+$ and $\vec{E}_-$. Moreover, ROA signals are intrinsically much weaker that Raman itself. All these facts imply the need in SEROA to distinguish a very small difference on top of a very large background signal which is insensitive to polarization modulation.

So far we concentrated on what happens at the gap in the dimer, but the real situation is in fact much more complex. If we look at different positions on the surface of the colloids, the following can happen: (i) The local field can be circularly polarized for an incoming linearly polarized beam; and (ii) the local field polarization for left and right incoming circularly polarized light can be different at some specific points on the surface. This can give a ROA signal even for molecules that do not normally show Raman optical activity. All these theoretical considerations show that SEROA may not be possible, except in very specific and carefully controlled situations. The effect of surface roughness on a nanometer size scale in a real system will add further complexity to the interpretation of results in terms of the polarization of the local field.

Additional experimental problems need to be resolved for SEROA. A real experimental confirmation of a very weak polarization-dependent effect can only be obtained by polarization modulation techniques with an elasto-optic modulator. This is typically incompatible with CCD-detection in modern Raman systems due to the fact that CCDs are not prepared for lock-in modulation and have strong limitations with readout times. Polarization modulation with a photomultiplier and mono-channel spectral acquisition is required if credible evidence for SEROA is to be produced. This casts some doubts on the evidence available so far for SEROA[15] which was obtained in the visible and by simple subtraction of signals. The stability and reproducibility of the signal would have to be better than one part in several millions (to account for the difference in the intrinsic cross section of the effect and the much weaker enhancement and unfavorable angular averaging) to be able to extract this information by simple subtraction. Even if a signal is observed, the considerations presented here show that its interpretation might not be

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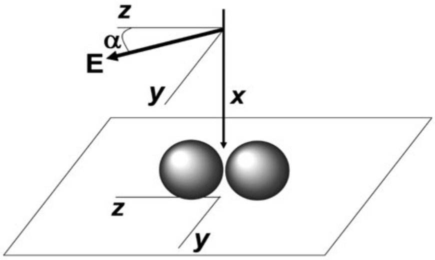

Fig. 3 A standard dimer configuration on a surface where polarization studies can be carried out. This configuration is achievable in many experimental situations[7,12,13,20] and SERS polarization studies have been carried out by several authors[7,12,13]. An incident beam coming along x and linearly polarized in the y–z plane is used and the scattered polarization is analyzed in the backscattered direction ($-x$). In the visible, the coupling to the gap is completely dominated by the response along z; *i.e.* only the projection of the electric field $\vec{E}$ along z couples effectively to a molecule in the gap. For the same reason, scattered radiation only happens along z (*via* the coupling with the same localized plasmon resonance). If the backscattered radiation along x is analyzed for polarization $\parallel$ or $\perp$ to $\vec{E}$, this produces automatically a $I_{\parallel} \propto \cos^4\alpha$ and $I_{\perp} \propto \cos^2\alpha\sin^2\alpha$ dependence (see the text). The depolarization ratio defined as $\rho \equiv (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$ is then $\rho = \cos 2\alpha$, which is exactly what is observed experimentally. This depolarization ratio is related to the coupling of the incoming beam to the plasmon resonances and does not reveal anything about the orientation of the molecule by itself.

straightforward and could be more linked to the local fields of the plasmon resonances than to an intrinsic property of the probes.

Another simple consequence of the phenomenology of hot-spots presented above relates to the polarization dependence of Raman signals in the single molecule limit. Single molecule signals can only come from hot-spots (*i.e.* from regions with the highest enhancements). Let us consider the situation in Fig. 3 (which has been studied experimentally[7,11–13]) and consider the ideal situation of a single molecule in the gap in between the two colloids, as has been proposed in the literature.[12,13] In the visible, the coupling of the hot-spot with the external electromagnetic wave is strongly dominated by the projection along z of the incident polarization in Fig. 4. This means that the local field intensity on the probe will be proportional to $\cos^2\alpha$. Moreover, the incident polarization on the probe will always be along z. By the same token, the Raman emission will be emitted along the same axis. For as long as the Raman tensor of the probe has a component along z, this will be the only fraction that will be emitted (and enhanced) in the far-field. Except for a small correction due to the Raman shift, it is essentially the same plasmon resonance that couples the incoming beam to the probe and the emitted Raman photon with the far-field detected signal.‡ Accordingly, the emitted radiation will also be polarized along z. If the signal is detected in the backscattering direction for polarization parallel ($\parallel$) and/or perpendicular ($\perp$) to $\vec{E}$, this produces automatically: $I_{\parallel} \propto \cos^4\alpha$ and $I_{\perp} \propto \cos^2\alpha \sin^2\alpha$. For this type of experiment the SERS depolarization ratio is often defined as $\rho = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, which gives then $\rho = \cos^2\alpha$, as indeed observed experimentally.[12,13] This result is therefore *not related to the orientation of the molecule but rather to the strong anisotropy in the coupling of the laser with the collective plasmon resonance producing the enhancement*. For as long as the Raman tensor of the probe has a non-zero projection along the z axis, *i.e.* the molecule is capable of emitting Raman photons along z, the SERS signal will always have the same symmetry $\rho = \cos^2\alpha$.

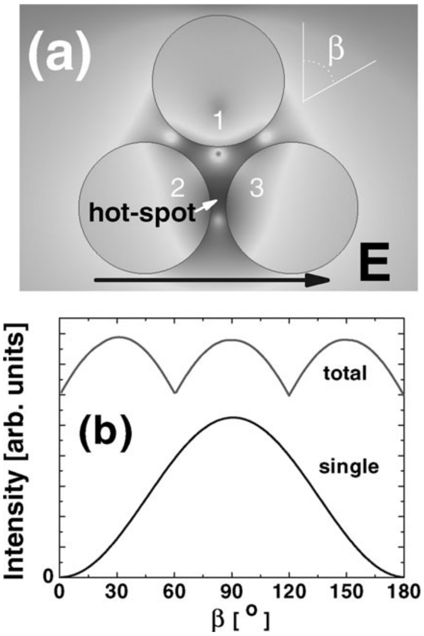

Fig. 4 A simple example of a cluster with quasi-isotropy. In this case we show the example of a 2D cluster formed by three cylinders (radii = 25 nm) with a small separation gap (d = 6.7 nm) among them. The problem is solved for the same dielectric function of Ag used in the calculations in Fig. 1, but in the electrostatic approximation[16] at λ = 357 nm. This is the wavelength at which the enhancement on the surface of the particles is the largest (as determined by a wavelength dependent study not shown here). The polarization is changed in the plane for different angles β as shown in (a) where the electromagnetic intensity (on a logarithmic grey-scale) is explicitly shown for the case $\beta = 90°$. A hot-spot in between cylinders 2 and 3 can be easily seen. If we look at the maximum enhancement at any point on the surface of the cluster, there will always be a place that profits the most from the particular orientation of the field and we obtain the curve labelled as "total" in (b). The three maxima in the latter are the three possible two-cylinder hot-spots in this cluster that achieve their highest value when the field is aligned along the axis joining any two of them. If the surfaces were uniformly covered with analyte, an almost isotropic response is obtained. The degree of isotropy increases with the complexity of the cluster. However, if the enhancement *at one specific point is monitored* (in this case the enhancement in the gap in between 2 and 3) we obtain the curve labelled as "single" in (b) which shows the full anisotropy of any single hot-spot. Claims of single molecule SERS anisotropy at one single point cannot ignore the high anisotropy of the local field in any analysis of the symmetry of the problem.

One could argue that more complicated clusters and geometries have an "isotropic" or "quasi-isotropic" response

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‡ This is the origin of the so-called $|E|^4$ approximation to the total enhancement.

from the highest enhancement places to the incident polarization,[7] but this implies a different type of phenomenon, as exemplified in Fig. 4. These phenomena are so general for coupled plasmons in clusters that the exact approximations and methods are most of the time irrelevant for the final conclusion. Fig. 4 shows the example of a two-dimensional (2D) "trimer" of cylinders solved in the electrostatic approximation[16] at $\lambda = 357$ nm for different polarization directions. The figure and the corresponding caption are self-explanatory; it suffices to say here that a cluster can have an overall "isotropy" or "quasi-isotropy" which is achieved by spatially moving the location of the most intense hot-spot to different places. It is in this sense that complicated clusters (like those studied in ref. 22) have more possibilities and are more adaptable to produce two-particle hot-spots for differing polarization directions. Under a relatively uniform surface coverage with analyte on the surface of the colloids, they will show a considerable degree of isotropy as a whole. However, in a single molecule experiment, we are interested in the local field at only *one* point and the field will have the full anisotropy seen in an isolated dimer. While this fact is recognized by many authors, it is possible to find interpretations based on the "isotropy" of the response of hot-spots.[11] While the presence of different angular dependencies for the SERS signals of different modes[11] is certainly challenging to understand, we believe that an analysis based on the wrong assumptions may produce the wrong conclusions. The existence of multiple (or hidden) hot-spots picking up signals from different molecules at different polarization directions is also an experimental difficulty which will have to be resolved and controlled if an in-depth understanding of polarization effects in single molecule SERS is sought.

4. Conclusions

In summary: As far as the polarization is concerned, the *local field* is the dominant effect fixing the type of polarization both felt by the probe and re-emitted as SERS signal. We cannot impose this by choosing different polarization states in the incoming wave. *The coupling to the plasmons is an inevitable part of the analysis*. The largest enhancements come from hot-spots and these are almost inevitably of a highly uniaxial character (dipolar-like) in their response to the electromagnetic field. Claims of single molecule anisotropy of the Raman tensors cannot ignore this fact. In like manner, the highly uniaxial nature of the coupling of hot-spots with lasers puts serious restrictions to the use of circular polarization modulation. The high uniaxial character of the local field makes the largest enhancements in SERS not compatible with circular polarization. Some sort of enhancement for circular polarization is still feasible, albeit coexisting with a much larger background signal coming from the contribution of other dimers in different orientations. The polarization of the local field cannot be ignored in any attempt to understand polarization modulation in SERS.

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