On the significance of Shalaev’s ‘hot spots’ in ensemble and single-molecule SERS by adsorbates on metallic films at the percolation threshold

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Recent models of plasmon localization and local electromagnetic (EM) field distribution in silver-on-glass films at the percolation threshold (Shalaev and collaborators) have successfully modelled the scanning near-field optical microscopy (SNOM) pictures. The clearly visible so-called hot spots are believed to contribute heavily to the Raman enhancement for adsorbates at the hot spots exceeding $10^{11}$. However, when the theorem of optical reciprocity is properly taken into account, the ensemble EM enhancement factor contributing to surface-enhanced Raman scattering (SERS) in silver island films at the percolation threshold is calculated here as about $3 \times 10^5$, an order of magnitude lower than the overall SERS enhancement measured by Shalaev and collaborators. Given the experimental probability of 0.003 in finding a single dye molecule that is embedded within a Langmuir–Blodgett (LB) film coating a silver island film at a hot spot (observations of Aroca and collaborators), and assuming that these hot spots are of ‘Shalaev-type’, the corresponding EM enhancement does not exceed $10^6$ to $10^7$. In addition, this is in good agreement with the experiment. This enhancement is sufficient to observe the SERS from single dye molecules.

Earlier enhancement numbers produced by the rule of thumb, that the enhancement is given by the fourth power of the local field enhancement, are misleading by several orders of magnitude for Stokes shifts exceeding approximately 300 cm$^{-1}$. Copyright © 2006 John Wiley & Sons, Ltd.

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INTRODUCTION

An important contribution to the physics of condensed matter during the last one to two decades has been the theory of the optical properties of metallic aggregates (see for instance Refs 1–7).

Examples of the metallic aggregates are silver colloid aggregates (Fig. 18(b) in Ref. 3) that are assigned as fractals. Fractal means an approximate self-similarity at all scales above the scale of the monomer, which is the single nanoparticle. The aggregates in general have a linear extension of about 3 orders with respect to the monomer, but that will not render useless its assignment as a fractal.

This theory (henceforth addressed as Shalaev’s theory) has become important in single-molecule surface-enhanced Raman scattering (SM-SERS). Shalaev-type hot spots of enormously enhanced local field intensity (for example, Ref. 8) dominate the discussion on SERS of single molecules in aggregates of silver or gold nano particles in electrolytes, as used in the pioneering work of Kneipp et al.9,10 However, since the detection of SM-SERS of Rh6G on ‘single colloidal particles’11 was revealed as the Rh6G located at narrow junction sites between two colloidal particles,12 there exists a second theory of EM hot sites in junctions,13 not withstanding an additional electronic enhancement in SM-SERS at junction sites.14,15

This paper is devoted to the quantitative comparison of Shalaev’s theory of hot spots with SERS experiments. The theory first addressed fractal metallic structures and later silver and gold films at the percolation threshold. In both cases, the linear local field enhancement was the central issue, but its application to SERS was the more spectacular side attracting much interest.

This article starts with a short review of the application of Shalaev’s theory to fractal structures and the main part of this paper deals with the theory applied to island films.

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APPLICATION OF THE THEORY OF OPTICAL PROPERTIES OF FRACTALS TO SERS

The successful theory of the local optical intensity distribution has been applied to ‘multi-molecule’ or ensemble SERS in the gminating publication by Stockman et al. It is still used for the explanation of SERS (see Ref. 3).

The two-dimensional fractal is considered as a system of N polarizable monomers at sites \( l = 1, \ldots, N \), characterized by dipoles \( d_{ij} \) with dipole–dipole interactions \( \langle \alpha|W|\beta \rangle \). The letters \( \alpha \) and \( \beta \) denote two mutually perpendicular directions. The matrix elements are proportional to \( (r_{ij})^{-3} \), where \( r_{ij} \) is the distance between the dipoles \( i \) and \( j \). It is assumed that each monomer \( i \) of the cluster possesses, apart from the linear polarizability \( \chi(\omega) \), also Raman polarizability \( \kappa_{i} \), assumed for reasons of simplicity as scalar. The Raman polarizability \( \kappa \) may be either the polarizability of a monomer itself or that of the adsorbed molecules bound to the monomer. It is correctly assumed that the \( \kappa_{i} \) of the different monomers contain uncorrelated random phases, expressed as \( \langle \kappa_{i}^{*}\kappa_{j} \rangle = |\kappa_{i}|^{2}\delta_{ij} \). So there is no interference between the Stokes waves generated by the different monomers. So far, so good. However, several molecules on a monomer \( i \) (at monolayer coverage of a sphere of 5 nm radius with about 30 to 50 molecules) driven by the same field will on average lead to \( d_{ij}(\omega_{0}) \approx 0 \). The reasons are, (1) the vibrations of the molecules have, in the first order of approximation, individual, uncorrelated phases and, (2) because the Raman scattering from a single molecule is a coherent process, therefore the contribution of the Raman scattered field is locked to the vibrational phase of the individual adsorbate. Note that, of course, there is Raman scattering from the monomer \( i \) because \( \langle |d_{ij}(\omega_{0})|^{2} \rangle \neq 0 \) or, in other words, all molecules emit Raman intensity individually.

The decisive Eqns Nr. (2) and (16) in Ref. 16 are, in slightly changed nomenclature for the interaction of the dipoles at the laser frequency \( \omega_{L} \) and the Stokes frequency \( \omega_{S} \), as follow:

\[
d_{ij}(\omega_{L}) = \chi(\omega_{L})E_{iL}^{(0)}(\omega_{L}) - \chi(\omega_{S}) \sum_{j}(i\alpha|W|j\beta)d_{ij}(\omega_{S}) \tag{1}
\]

Here \( E_{iL}^{(0)}(\omega_{L}) \) is the external field. It is the same at every dipole because the area of the \( N \) monomers is assumed much smaller than \( \lambda_{L} \times \lambda_{L} \) in the calculation. All the dipoles \( d_{ij} \) vibrate in phase. The molecular coverage of the monomers may affect slightly the value of \( \chi(\omega_{L}) \), but this is neglected.

The interaction at \( \omega_{S} \) looks the same,

\[
d_{ij}(\omega_{S}) = \chi(\omega_{S})E_{iL}^{\text{norm}}(\omega_{S}) - \chi(\omega_{S}) \sum_{j}(i\alpha|W|j\beta)d_{ij}(\omega_{S});
\]

\[
E_{iL}^{\text{norm}}(\omega_{S}) = \frac{\kappa_{i}}{\chi(\omega_{S})}E_{iL}(\omega_{S}) \tag{2}
\]

but in reality it is completely different because, firstly, the field \( E_{iL}^{\text{norm}}(\omega_{S}) \) is not acting at the site \( j \) because there the corresponding field is \( E_{ij}^{\text{norm}}(\omega_{S}) \) and, secondly, the dipoles \( d_{ij} \) have random phases, notwithstanding that \( d_{ij}(\omega_{S}) \approx 0 \).

Nevertheless, Eqn (2) also has been formally processed like Eqn (1) in Ref. 16. Whereas, Eqn (1) yields finally the average enhancement \( G \)

\[
G(\omega_{L}) = \left( \frac{\langle |E_{\text{local}}(\omega_{L})|^{2} \rangle}{\langle |E_{iL}^{(0)}(\omega_{L})|^{2} \rangle} \right) \tag{3}
\]

where the averaging is over the fields at the \( N \) sites of the monomers, Eqn (3) is the successful basis of the theory of local intensity fluctuations described in the introduction. However, the according Eqn (4)

\[
G(\omega_{S}) = \left( \frac{\langle |E_{\text{local}}(\omega_{S})|^{2} \rangle}{\langle |E_{iL}^{(0)}(\omega_{S})|^{2} \rangle} \right) \tag{4}
\]

cannot be derived from Eqn (2) without the theorem of optical reciprocity, which unfortunately has not been quoted in Refs 3 and 16.

Therefore, the theorem of optical reciprocity is treated in the next section and will be also important in further sections.

OPTICAL RECIPROCITY

The principle of optical reciprocity is attributed to Helmholtz and was first stated in 1874. A good derivation may be found in Ref. 18. If there are two dipoles \( P_{i}(X_{i}), (i = 1, 2) \) with electric vectors \( E_{i}(X_{i}) \) in the far field oscillating with frequency \( \omega_{L} \), the theorem states that

\[
P_{1}(X_{1})E_{1}(X_{1}) = P_{2}(X_{2})E_{2}(X_{2}) \tag{5}
\]

Its use in Raman spectroscopy is given in Fig. 1.

The Raman polarizability (called \( \kappa \), given earlier) is \( \alpha \left( \omega_{1}, \omega_{2} \right) \). From this follows:

Intensity at detector

\[
= |E_{\text{adsorbate}}(X_{\text{detector}}, \omega_{S}) \times P_{\text{detector}}|^{2}
\]

\[
= |E_{\text{active}}(X_{\text{adsorbate}}, \omega_{S}) \times \alpha(\omega_{L}, \omega_{S})]
\times E_{\text{Laser}}(X_{\text{adsorbate}}, \omega_{L})|^{2}
\]

\[
= |\alpha(\omega_{L}, \omega_{S})|^{2}|E_{\text{active}}(X_{\text{adsorbate}}, \omega_{S})|^{2}
\times |E_{\text{Laser}}(X_{\text{adsorbate}}, \omega_{L})|^{2} \tag{6}
\]

The Raman intensity of a molecule in free space is given by

Intensity at detector, free molecule

\[
= |E_{\text{free molecule}}(X_{\text{detector}}, \omega_{S}) \times P_{\text{detector}}|^{2}
\]

\[
= |\alpha(\omega_{L}, \omega_{S})|^{2}|E_{\text{active}}(X_{\text{free molecule}}, \omega_{S})|^{2}
\times |E_{\text{Laser}}(X_{\text{free molecule}}, \omega_{L})|^{2} \tag{7}
\]

For the enhancement \( G \) of the Raman intensity of the adsorbed molecule with respect to the same molecule in free space, the equation is as follows:

\[
G(X_{\text{adsorbate}}) = \frac{|E_{\text{active}}(X_{\text{adsorbate}}, \omega_{S})|^{2}}{|E_{\text{active}}(X_{\text{free molecule}}, \omega_{S})|^{2}} \times \frac{|E_{\text{Laser}}(X_{\text{adsorbate}}, \omega_{L})|^{2}}{|E_{\text{Laser}}(X_{\text{free molecule}}, \omega_{L})|^{2}} \tag{8}
\]
With an obvious change of nomenclature, the theorem of optical reciprocity yields for molecules with a Raman tensor \( \alpha_{ij} \) the exact result of SERS by local field enhancement at site \( r \) (the \( \Omega \)'s are the directions and polarizations of incident Laser light and emitted Stokes light).

\[
G(r, \omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}, \Omega_{\text{Stokes}}) = \frac{|\langle \mathbf{E}(r, \omega_{\text{Laser}}) \rangle|^2}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Laser}}, \Omega_{\text{Laser}})|^2} \times \frac{|\langle \mathbf{E}(r, \omega_{\text{Stokes}}) \rangle|^2}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Stokes}}, -\Omega_{\text{Stokes}})|^2}
\]

The \( \Omega \)'s in the denominators shall remind that the local fields at \( r \) depend on the polarizations and directions of the incoming beams.

Averaging over \( r \) is denoted by \( \langle \rangle \) and yields as

\[
\langle G(r, \omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}, \Omega_{\text{Stokes}}) \rangle = \langle \frac{|\langle \mathbf{E}(r, \omega_{\text{Laser}}) \rangle|^2}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Laser}}, \Omega_{\text{Laser}})|^2} \rangle \times \langle \frac{|\langle \mathbf{E}(r, \omega_{\text{Stokes}}) \rangle|^2}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Stokes}}, -\Omega_{\text{Stokes}})|^2} \rangle
\]

This agrees with Shalaev’s Eqn (22) in Ref. 19. Shalaev argues that for a Stokes shift that is small with respect to the ‘halfwidth of the plasmon’ (probably meaning the frequency half width of the dipolar Mie resonance in small single particles), ‘so that the fundamental and Stokes fields are correlated in space’, then

\[
\langle G(r, \omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}, \Omega_{\text{Stokes}}) \rangle \approx \left( \frac{|\langle \mathbf{E}(r, \omega_{\text{Laser}}) \rangle|^4}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Laser}}, \Omega_{\text{Laser}})|^4} \right)
\]

This approximation is reasonable for the field enhancement of the Raman scattering of the breathing vibration of pyridine on small single silver spheroids, calculated by Kerker et al.\(^{20}\) Equation (10a) is the basis of the argument in Ref. 21 cited in the next section. This will show, on the basis of experiment and modelling, that for metal films at the percolation threshold and for Stokes shifts above 300 cm\(^{-1}\), the ‘decoupling’ by

\[
\langle G(r, \omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}, \Omega_{\text{Stokes}}) \rangle = \left( \frac{|\langle \mathbf{E}(r, \omega_{\text{Laser}}) \rangle|^4}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Laser}}, \Omega_{\text{Laser}})|^4} \right) \times \left( \frac{|\langle \mathbf{E}(r, \omega_{\text{Stokes}}) \rangle|^4}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Stokes}}, -\Omega_{\text{Stokes}})|^4} \right)
\]

is the far better approximation.

**ON THE QUANTITATIVE ASPECT OF SHALAEV’S THEORY USED IN SM-SERS IN FRACTALS**

It has become a custom in this field to neglect the Stokes shift and argue with Eqn (10a) for the ensemble-averaged SERS. Without doubt there are hot spots at some positions at and near \( r_{\text{hot spot}} \) with local fields at the laser frequency \( \omega_{\text{Laser}} \) given by

\[
G(r_{\text{hot spot}}, \omega_{\text{Laser}}, \Omega_{\text{Laser}}) = \left( \frac{|\langle \mathbf{E}(r_{\text{hot spot}}, \omega_{\text{Laser}}) \rangle|^4}{|\mathbf{E}_{\text{incident}}(\omega_{\text{Laser}}, \Omega_{\text{Laser}})|^4} \right)
\]

The SM-SERS is explained by the presence of a single molecule at such a hot site. The usual way of arguing has been very well described by Moskovits et al.\(^{21}\) ‘localization of the EM fields due to particle–particle interactions in an aggregate results in SERS enhancement (at hot spots) of the order of 10\(^{11}\); the remaining enhancement arises from resonance Raman excitation and the so-called chemical
effects,’ and ‘Raman is an incoherent, phase-independent process in which the enhancement is defined by the one-point correlation: $\langle |E|^{4}\rangle$. The very intense fields that exist at hot spots would dominate this average (V. M. Shalaev, personal communication to M. Moskovits’). These statements agree with Eqn 7.32 in Ref. 3, see also Refs 22 and 23.

The statement ‘localization of the EM fields due to particle–particle interactions in an aggregate results in SERS enhancement of the order of $10^{11}$’ in connection with single molecules makes sense only when the single molecule adsorbs at the hottest spot. However, where this molecule settles down depends on where it first touches a surface and to which site it can diffuse. This is decided by the detailed structure and surface of the composite, but not by the local field distribution of the incoming light. (Should there exist an extremely hot site, it will be highly localized, and electromotive forces on the molecule will only be active if the molecule has freely diffused to this site.) A further complication is that such highly localized resonances may be dark, meaning that the local field resonance cannot be excited by the laser beam.$^5$

Unfortunately, I have not found any quantitative comparison of Moskovit’s statement on hot spots with the experiment, which would require, for instance, the probability or density of hot spots classified according to the enhancement within the hot spot. Since there are competing theoretical concepts (see above) one cannot argue that an enhancement of $10^{11}$ at small Stokes shifts, as indeed verified by several research groups, is necessarily a proof of this way of interpretation of Shalaev’s theory.

Fortunately, the required comparison between theory and experiment can be done much better for island films. This article will for the first time discuss and compare the results of the theory of Shalaev et al. in a quantitative way with the experimental EM enhanced Raman scattering from adsorbates on silver island films in ultrahigh vacuum (UHV) at the percolation threshold, and for Raman scattering by single dye molecules in Langmuir–Blodgett (LB) films on silver island films.$^{24}$ This study demonstrates the high quality of Shalaev’s theory when it is properly applied.

**HOT SPOTS IN SEMI-CONTINUOUS METAL DIELECTRIC FILMS**

Recent studies combine scanning near field optical microscopy (SNOM), structure determination by atomic force microscopy, transmission and scanning electron microscopy and EM theory in nano-structured random media.$^{25,26}$ Figure 2 shows gold films on glass at the percolation threshold$^{25}$ where the first extended path for a d.c.-current appears. An example of the comparison of a ‘SNOM landscape’ and a ‘theory landscape’ is given in Fig. 3. In the example in Fig. 3, SNOM has monitored$^{27}$ the local field intensity at a height of about 10 nm above a gold film on glass with a filling factor $p$ that is about equal to the critical factor $p_c$ at the percolation threshold (hot junction sites cannot as yet be monitored by SNOM, as tips or fibres are too big with respect to the hot spots dimensions in junction sites). There are considerable intensity fluctuations (Fig. 3(a) and (d)). SNOM has a spatial resolution brought approximately by the diameter of the fibre tip of 100 nm, whereas the resolution of the theoretical model is about 100 × 100 pixels. The tip averages over approximately 10–15 pixels. The theoretical intensity fluctuates between 0 and approximately $3 \times 10^4$ (Fig. 3(c) and (f)). The narrow intensity maxima are called hot spots. By smoothing the theoretical spectrum by averaging over the resolution of the fibre tip, the averaged distributions in Fig. 3(b) and (e) have been obtained. The distribution of the fluctuations is well modelled by the theory.$^{27}$

The experimental and theoretical near field spectra$^{25}$ in Fig. 4 show that the local field enhancement at a given...
site varies very much at small changes of wavelength and wavenumber (the wavenumber difference between 700 and 770 nm is 1298 cm\(^{-1}\)). This range is small with respect to the half width of approximately 3000 cm\(^{-1}\) of the dipolar resonance of unaggregated silver colloids (see for instance Ref. 28) and even smaller with respect to the half width of the absorption band of silver island films. However, in this range of 1298 cm\(^{-1}\) the local field intensities are ‘decoupled’ according to Fig. 4 at a wavenumber of about 300 cm\(^{-1}\) and at sites 50 nm apart, the latter difference reflecting the spatial resolution of SNOM. An experimental ‘hot spot’ is extremely volatile in space when changing the wavelength (and also the angle of incidence and the polarization of the incoming light). This volatile behaviour at the SNOM resolution reflects the volatility of the intensity at the many underlying pixels of the theoretical calculation. It is just impossible that the intensity of ‘hot pixels’ under the SNOM tip remains constant, but SNOM registers highly variable intensities as a function of wavelength. Without exemption the interest in single dye molecule SERS concentrates on the vibrational modes in the range of 300–1800 cm\(^{-1}\), see Fig. 5. In the lowest part of Fig. 5, the experimental intensity spectrum in Fig. 4 at \(x = 0\) nm has been converted from a wavelength to a wavenumber scale (the corresponding wavelength limits of 700 and 770 nm are indicated). Within the range of the Stokes shifts of the experimental spectra the intensity at wavenumbers above 300 cm\(^{-1}\) is uncorrelated to the intensity at zero wavenumber. In the spectral range

**Figure 3.** Experimental, averaged theoretical, and raw theoretical optical intensity images over a 4 \(\times\) 4 \(\mu\text{m}^2\) area at \(p \approx p_0\). Images in the column on the left ((a), (b), and (c)) are at an illumination wavelength of \(\lambda = 543\) nm, and those in the column on the right ((d), (e), and (f)) are at an illumination wavelength of \(\lambda = 633\) nm. The first row ((a) and (d)) displays experimental SNOM data. The second row ((b) and (e)) shows theoretical data after the averaging process. The third row ((c) and (f)) show raw theoretical data. From Ref. 27.
of the experimental spectra in Fig. 5, the Stokes channel is completely decoupled from the laser channel. When a single molecule happens to reside at a hot spot in the laser channel, this site is most probably not hot in the Stokes channel. Therefore, the local intensities in Eqn (10) for wavenumbers above 300 cm\(^{-1}\) are completely decoupled and Eqn (10b) is a much better approximation than Eqn (10a) for wavenumbers above approximately 300 cm\(^{-1}\).

A useful short form of Eqn (10b) is

\[
G(\omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}, \Omega_{\text{Stokes}}) \\
\approx G(\omega_{\text{Laser}}, \Omega_{\text{Laser}}) \times G(\omega_{\text{Stokes}}, \Omega_{\text{Stokes}})
\]

(10d)

If one uses a 180° scattering geometry, where the same optics are used for focusing the excitation light and for collecting the Raman scattered light (for instance in Ref. 30), one may characterize the focusing by

\[-\Omega_{\text{detector}} = \Omega_{\text{Laser}}\]

This implies that the Raman spectrometer is only sensitive in the polarization direction of the incident laser light. I will come back to this point later.

This yields

\[
G_{\text{retro}}(\omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}) \approx \frac{|E(\omega_{\text{incident}})|^2}{|E(\omega_{\text{Laser}})|^2} \\
\times \frac{|E(\omega_{\text{Stokes}})|^2}{|E(\omega_{\text{incident}})|^2}
\]

(10e)

or in short form

\[
G_{\text{retro}}(\omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega_{\text{Laser}}) = G(\omega_{\text{Laser}}, \Omega_{\text{Laser}}) \\
\times G(\omega_{\text{Stokes}}, \Omega_{\text{Stokes}})
\]

(10f)

Equation (10f) will be used in the next chapter at the percolation threshold of semi-continuous metal dielectric films (gold\(^{25}\) or silver\(^{27}\) films on glass).

**ENSEMBLE AVERAGED SURFACE RAMAN ENHANCEMENT**

The results of Seal *et al.*\(^{27}\) and Genov *et al.*\(^{31,32}\) allow us to obtain the quantitative enhancement values for ensemble SERS.

**Figure 5.** Comparison of the single Raman spectra of Rh6G from Ref. 29 (laser wavelength 532 nm) and of salPTCD from Ref. 24 (laser wavelength 514 nm) with the observed intensity fluctuations in Fig. 4(a) at \(x = 0\) nm, (assuming Laser wavelength of 700 nm, wavelength differences up to 770 nm converted to wavenumbers.
In Ref. 32, a very efficient numerical method for calculating local field distributions is used. A random 2D metal dielectric film is modelled by a square conducting network. The four connections per knot point in x and y directions to the nearest neighbour, knot points are characterized by the optical conductivities $\sigma_{bond}$. The area of the network is taken much smaller than $\lambda^2$, it is continued by cyclic boundary conditions. Retardation is neglected, the electric vector is chosen in x or y direction. The optical conductivities are given by

$$\sigma_{bond} = -i\omega\sigma_{bond}/4\pi$$

metal: $\sigma_{bond} = \sigma_m = \sigma_b - (\omega_p/\omega)^2/(1 + i\omega_\tau/\omega)$ probability $p$
dielectric: $\sigma_{bond} = \sigma_d$ probability $(1 - p)$

(11a)

$\omega_\tau$ is the relaxation time.

The probabilities of having a metal or dielectric bond is given by the filling factor $p$ or $(1 - p)$ respectively. The filling factor at the percolation threshold is called $p_c$. It makes no sense to take the distance between the knots smaller and smaller in the sense of a fractal structure. The bonds characterize plasmonic resonances in the semi-continuous film, and only above a supra atomic monomer scale do these resonances exist. Given this method, the local field properties of random metal dielectric films were investigated in a wide spectral range and for a variety of metal concentrations $p$. An example is given in Fig. 6. The probability $P(I)$ of the local field intensity $I$ along a bond was sampled in terms of log $I$,

$$\frac{dP(I)}{d\log I} = \frac{1}{\Delta \sqrt{2\pi}} \exp \left[-\frac{[\log I - \langle \log I \rangle]^2}{2\Delta^2}\right]$$

with

$$\int_{-\infty}^{+\infty} \frac{dP(I)}{d\log I} d\log I = 1$$

(11b)

Given all the above points and Eqn (11b), one can now discuss the ensemble Raman enhancement of a single molecule at an unspecified adsorption site at $r$ within the composite structure.

As only the sites with $([I(r, \omega_{laser})]^2)/(\omega_{incident}(\omega_{laser}, \Omega_{laser})^2) \gg 1$ are of interest, we can replace the first right hand side factor in Eqn (9) by $I(r)$. This value is unknown, but given the local field distribution in Fig. 7 and Eqn (11b) one can calculate the average local field intensity at the laser frequency by

$$\langle I(\omega_{laser}) \rangle = \int_{-\infty}^{+\infty} \frac{dP(I)}{d\log I} d\log I$$

$$= 10^{\log 10 \frac{300}{2}}$$

(12)

As the local field fluctuations $I(r)$ are uncorrelated for differences between laser and Stokes wavenumbers exceeding 300 cm$^{-1}$, the probability $P(I(r, \omega_{Stokes})$ at $r$ does not depend on $I(r, \omega_{laser})$. Therefore the average contribution $\langle I(\omega_{Stokes}) \rangle$ of the second right hand factor in Eqn (9) can also be obtained as an analogue to Eqn (12).

Figure 6. The spatial distributions for the normalized local intensity $I(x,y)$ and for $I^2(x,y)$. The distributions are calculated for three different wavelengths: $\lambda = 0.370 \mu m (a),(b)$, $\lambda = 1 \mu m (c),(d)$, $\lambda = 5 \mu m (e),(f)$. The metal filling factor is chosen as $p = p_c$, for all cases.

Figure 7. Local field distributions $dP(I)/d\log I$ (called $P(I)$ here) for silver-glass films for $\lambda = 370 \text{ nm}$ and $\lambda = 1 \mu \text{m}$ at filling factor $p = p_c$ (percolation threshold).
The final result for the average enhancement for a single molecule in silver films at the percolation threshold is given by

\[
\langle G_{\text{retro}}(\omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega) \rangle = 10^{\langle \log(\omega_{\text{Laser}}) \rangle + \langle \log(\omega_{\text{Stokes}}) \rangle} \times 10^{\frac{\ln 10}{2} \left( \left| A_{\text{Laser}} \right|^2 + \left| A_{\text{Stokes}} \right|^2 \right)}
\]

(13)

One may read out of Fig. 7 \((\log(I)) \approx 1.6\), and at the wavelengths of 0.37 µm and 1 µm \(\Delta \approx 0.57\) and 0.94, respectively. The choice of the intermediate value of \(\Delta \approx 0.70\) at 0.5145 µm yields \(\langle \log(I) \rangle \approx 142\), and if we use this value both for the Laser and the Stokes frequency, \(\langle G_{\text{retro}}(\omega_{\text{Laser}}, \omega_{\text{Stokes}}, \Omega) \rangle \approx 2.04 \times 10^4\). If we allow for the outgoing Stokes radiation also the polarization direction perpendicular to the polarization direction of the laser, we should add a factor of 2. The role of the intensity fluctuations is contained in the factor \(10^{\frac{\ln 10}{2} \left( \left| A_{\text{Laser}} \right|^2 + \left| A_{\text{Stokes}} \right|^2 \right)}\), which is about a factor of 13.4 only. Nevertheless, in the sense of the citation in ‘On the Quantitative Aspect of Shalaev’s Theory used in SM-SERS in Fractals’ this factor may be described as spots “hotter” than the average dominating the ensemble average.

It is interesting to calculate also \(\langle |E(r)|^4 \rangle\), which yields

\[
\langle |E(r)|^4 \rangle = \langle |I(\omega, \lambda)|^2 \rangle = \int \frac{dP(I)}{d\log I} d\log I = 10^2 \langle \log(I) \rangle 10^2 \ln 10 \lambda^2
\]

(14)

With the data at the wavelength of 0.5145 µm one obtains 2.85 \(\times\) 10^3, which is about 5 orders less than the value of 10^11 given in Ref. 21. The value of 2.85 \(\times\) 10^3 is in approximate agreement with measurements by Shalaev and collaborators,\(^35\) who estimated for silver island films deposited at room temperature an ensemble enhancement of about 3 \(\times\) 10^6 at the excitation wavelength of 647.1 nm and 568.2 nm.

Genov et al.,\(^31\) Drachev et al.,\(^33\) and Kerker\(^20\) in his famous calculation of the SERS from spherical silver particles used, like many others, the optical constants of Johnson and Christy\(^34\) with the relaxation frequency \(\omega_r = 0.021\) eV. However, Kerker already points out that the relaxation is higher in small colloidal silver particles. The absolute part of the electric vector in resonances will scale with \(\omega_r^{-1}\), and of the enhancement according to Eqn (14) with \(\omega_r^{-4}\).

The ensemble EM enhancement was also measured on Ag island films deposited in UHV on sapphire (with average film thicknesses ranging between 3.0 and 7.7 nm, this includes the percolation threshold) after the electronic enhancement was suppressed by a small oxygen exposure.\(^35\) The experimental value was about 300. Considering the factor of 2 for the two polarization directions one can reach an agreement between the calculations given above and the experimental value by the assumption that the relaxation frequency in the island films produced in UHV at the percolation threshold is a factor of 3.4 higher than measured with the continuous films evaporated at 4 \(\times\) 10^-6 torr by Johnson and Christy.\(^34\) According to infrared transmission of silver islands produced in UHV just above the percolation threshold, the damping may be increased up to tenfold (A. Pucci, private communication). The analogue case for Fe films is well documented.\(^36,37\) In summary, the experimental result of the ensemble EM enhancement on silver island films in UHV produced at low substrate temperatures\(^35\) also lies within the range of the quantitative theoretical results, given the range of experimentally observed relaxations.

ON THE CONTRIBUTION OF ELECTROMAGNETIC ENHANCEMENT AT ‘SHALAEV-TYPE’ HOT SPOTS TO SINGLE-MOLECULE SERS OF DYE MOLECULES IN LANGMUIR–BLODGETT FILMS AND SILVER ISLAND FILMS

The theoretical results on the probability distribution of hot intensity spots at 1 µm wavelength and low relaxation frequency are given in Fig. 7. I can safely assume that curve 7 will not be much different choosing the laser wavelength somewhat below and the Stokes wavelength accordingly above 1 µm. According to the Section ‘Hot Spots in Semi-continuous Metal Dielectric Films’, for wavenumbers above 300 cm^-1, the laser and the Stokes channel are completely decoupled. In other words, at a given site \(r\) the probability of having a special intensity at the laser channel is not correlated with the probability of finding another intensity at the Stokes channel. Therefore, if one chooses for instance a spot that has the probability of 10^-3 both at the laser and the Stokes channel, one may read from Fig. 7 the enhancement of the local intensities both at the laser and Stokes channel of 10^4 at this spot.\(^4\) This leads immediately to a Raman enhancement \(G = 6.3 \times 10^6\) at the spots that can be expected with a probability of 10^-6. If one chooses unequal partitions of the overall probability of 10^-6 at a given spot to laser and Stokes intensity, \(G\) will be less according to Fig. 7. Is this relevant, are these the hot spots that ‘dominate’ (see Section ‘On the Quantitative Aspect of Shalaev’s Theory used in SM-SERS in Fractals) the single-molecule Raman scattering? In this case, the intensity distribution as function of the Stokes wavenumber should vary stochastically by several orders of magnitude because the absorption site of the molecule will be a ‘super-hot’ spot only at a special narrow Stokes wavenumber range. To my best knowledge nobody has observed this, the well-known single-molecule ‘blinking’ probably has a different origin.

A more fruitful approach is the discussion of good experimental results\(^24\) with the help of the theory outlined above. Aroca and collaborators\(^24\) mapped the spatial distribution of surface-enhanced resonance Raman scattering (SERRS) intensities of mixed dye–fatty acid LB monolayers...
deposited on nano-structured Ag island films. According to these authors, the dye molecules in the LB film are fixed within this film and cannot escape it to ‘fall’ into a narrow junction site between metal islands. Also, an electronic contact of the dye molecules to the metal may be negligible. Therefore, the only promising theory for comparison with the experiment is that of Shalaev.

The ensemble average spectra of a single LB layer consisting of arachidic acid (AA) and \( n \)-pentyl-5-salicyl-imido-perylene (salPTCD) with ratio10:1 on glass and on a silver island film is given in Fig. 8. At this concentration level, the average enhancement factor for resonance Raman scattering is \( \sim 10^3 \). By high dilutions of the dye, the transition of the ensemble averaging to single dye molecule SERS could be observed. At the average distribution of one dye molecule per \( 1 \mu m^2 \), the chance to observe a single dye molecule (Fig. 9) was about 0.3%, with a rather large variance (R. Aroca, private communication). In the sense of the discussion, above this number is the probability of finding a hot spot of Raman intensity among all available spots. One should note that this ratio does not depend on the area of the spots or the density of knots discussed above. When one assumes that the Raman hot spots are of Shalaev-type, then \( P_{\text{SM}}(I_{\text{Laser}}) \times P_{\text{SM}}(I_{\text{Stokes}}) \approx 0.003 \). Given this condition and the log normal distribution in Fig. 7, the highest \( G_{\text{SM}} = I_{\text{Laser}} \times I_{\text{Stokes}} \) is obtained at \( P(I_{\text{Laser}}) \times P(I_{\text{Stokes}}) \approx (0.003)^{1/2} \).

At laser wavelengths of 0.37 \( \mu m \) and 1 \( \mu m \) and with the relaxation of 0.021 eV\(^{34} \) this yields, according to Fig. 7, \( G_{\text{SM}} \approx 10^6 \) and \( G_{\text{SM}} \approx 10^7 \), respectively. At the wavelength of 1 \( \mu m \) the ensemble enhancement is \( G \approx 1.7 \times 10^5 \). The hot spots of surface concentration 0.003 and enhancement \( G_{\text{SM}} \approx 10^7 \) contribute about 18\% to the ensemble \( G \).

Therefore, in the case discussed here, Shalaev’s ‘realistic’ hot Raman spots (enhancement of \( \sim 10^6 \)) with probability 0.003) would have about the right enhancement to make single salPTCD molecules observable, as shown by the following simple arguments.

1. One arachidic acid molecule occupies about 25 \( \text{Å}^2 \) within the monolayer. In Fig. 8, each micron squared should contain approximately \( 4 \times 10^6 \) molecules. Of these, about \( 3.64 \times 10^6 \) will be arachidic acid molecules and about \( 3.64 \times 10^5 \) will be salPTCD molecules (R. Aroca, private communication)

2. Hence \( 3.64 \times 10^5 \) salPTCD molecules deliver the resonant Raman signal in Fig. 8.

3. A Raman spectrum from a single molecule of salPTCD was observed (Fig. 9).

Figure 8. (a) Resonance Raman spectrum of a single 10:1 AA-salPTCD monolayer deposited on glass. (b) Surface-enhanced resonant Raman scattering spectrum of a single 10:1 AA-salPTCD monolayer deposited on evaporated 6 nm Ag nanoparticle film, from Ref. 24.

However, Shalaev’s ‘realistic’ hot Raman spots (enhancement of \( \sim 10^6 \)) with probability 0.003) would have about the right enhancement to make single salPTCD molecules observable, as shown by the following simple arguments.
CONCLUSIONS

With the help of calculations of Shalaev and collaborators it is clearly demonstrated for the first time that, for Stokes wavenumbers exceeding 300 cm\(^{-1}\), the incident intensity enhancement at the laser frequency and the emitted intensity enhancement at the Stokes wavenumber are completely decoupled at any site of a fractal structure or a semi-continuous metal film. Using Shalaev’s theory in this way yields good agreement with measurements by Shalaev and collaborators\(^3\) who estimated for silver island films deposited at room temperature an ensemble enhancement of about 3 \(\times 10^7\) at the excitation wavelength of 647.1 nm and 568.2 nm.

Using realistic values of the damping in cold-deposited Ag films, ensemble Raman enhancement of single molecules in silver films at the percolation threshold in UHV derived by the proper use of Shalaev’s theory are in the order of 10\(^2\) to 10\(^3\), in agreement with experiment. The contribution of the fluctuating intensity is about 10\(^2\). If the hot spots observed within LB films by the group of Aroca\(^2\) are of ‘Shalaev-type’,\(^2\) the enhancement is at best only 10\(^6\)–10\(^7\). This enhancement is sufficient to explain single-molecule resonant Raman scattering observed by Aroca and collaborators.\(^4\) To the best of my knowledge, this is the first quantitative discussion of ‘Shalaev-type’ hot spots in the field of single-molecule SERS.

In summary, one should no more use the rule of thumb of setting the SERS enhancement in fractal and extended metal aggregates equal to the fourth power of the local field enhancement. This yields spectacular values of the predicted SERS enhancement, out of range with experimental reality. Shalaev’s theory is a very good theory, when used properly.

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REFERENCES