Rigorous justification of the $|E|^4$ enhancement factor in Surface Enhanced Raman Spectroscopy ☆

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Abstract

We present and apply a general method to formally calculate Surface Enhanced Raman Scattering (SERS) enhancement factors, based on the optical reciprocity theorem. This approach emphasizes the fact that the widely used SERS enhancement factor proportional to the fourth power of the field ($|E|^4$) is an approximation. It can moreover be used to define the range of validity of the $|E|^4$ approximation and to provide a rigorous justification of a more general formula.
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Surface Enhanced Raman Scattering (SERS) has regained interest recently following the demonstration of single molecule detection [1–3], and possible applications in biology/analytical chemistry [4] and nano-plasmonics [5]. Large SERS enhancement factors of the order of 10^{10} and more have been estimated [1,2,6] and are believed to be mainly electromagnetic (EM) in origin [6,7]. Localized surface plasmon resonances give rise to places with large local field enhancements; so-called hot-spots. SERS signal are typically assumed [6,8,9] to be proportional to the 4th power of the factor $|E_{\text{Loc}}/E_0|$, i.e., a power of two accounting for the excitation part, and a power of two for the emission. This widely used assumption has, however, never been rigorously justified.

In this Letter, we apply the optical reciprocity theorem (ORT) [10] to show that SERS EM-enhancement factors are, in fact, given by a generalized version of the commonly used $|E|^4$ factor, which is shown to be an approximation with certain (generally overlooked) limitations. This approach emphasizes, in addition, the importance of the

Raman tensor of the probe and the scattering geometry. We also give an example where the $|E|^4$ approximation fails drastically in the calculation of SERS depolarization ratios.

SERS enhancements can be calculated within a classical EM approach, which we briefly summarize here [7,11–13]. The incident field on the molecule $\mathbf{E}_{\text{Loc}}$, with frequency ω_L induces a Raman dipole $\mathbf{d} = \alpha\mathbf{E}_{\text{Loc}}$, oscillating and radiating at the Raman frequency ω_R with a power $\propto |\mathbf{d}|^2$, which is detected in the far field. In SERS conditions, there are two main sources of EM enhancements:

- First, the field $\mathbf{E}_{\text{Loc}}$ at the scatterer is usually different to the incident field $\mathbf{E}_0$. In particular, close to metallic surfaces the amplitude of the local field can be much larger than $|\mathbf{E}_0|$, leading to a *local field enhancement factor* $M_{\text{Loc}}(\omega_L)$, which is present for all linear optical processes. For Raman scattering, it is related to the excitation of the Raman dipole and depends on the Raman tensor of the probe. We only consider here two common cases. For an isotropic Raman tensor we have simply $\mathbf{d} = \alpha\mathbf{E}_{\text{Loc}}$, and

$$M_{\text{Loc}} = |\mathbf{E}_{\text{Loc}}|^2/|E_0|^2. \tag{1}$$

For a uniaxial tensor (axis along $\mathbf{e}_d$), the induced dipole is $\mathbf{d} = \alpha(\mathbf{e}_d \cdot \mathbf{E}_{\text{Loc}})\mathbf{e}_d$, and

$$M_{Loc} = |\mathbf{e}_d \cdot \mathbf{E}_{Loc}|^2 / |E_0|^2. \tag{2}$$

- Second, similarly to modified spontaneous emission [14], the Raman dipole emission at ω_R is also affected, with two (interlinked) effects: (i) the total radiated power is modified and can be greatly enhanced under the right conditions [14] and (ii) the radiation pattern can also be altered. Overall, for a given detection direction, the radiated power $dP/d\Omega$ is modified by a factor $M_{Rad}(\omega_R)$.

We define the SERS enhancement factor as $EF = I_{SERS}/\langle I_{RS} \rangle$, where I_{SERS} is the SERS intensity and $\langle I_{RS} \rangle$ is the conventional Raman intensity under the same conditions, averaged over all possible orientations of the probe. This definition avoids problems when $\mathbf{e}_d$ is along the detection direction: a free-space dipole does not radiate along its axis and one would get an infinite enhancement without averaging. A similar problem can occur for M_{Rad}, which we therefore define as $M_{Rad} = (dP/d\Omega)/A(d)$ with $A(d) = (\omega^4 d^2)/(32\pi^2 \epsilon_0 c^3)$, i.e., power (per unit solid angle) emitted by a free-space dipole $\mathbf{d}$ perpendicularly to its axis. The choice of these definitions will be discussed elsewhere in more detail; they do not affect the discussion here except for constant factors of the order of ~ 1.

The SERS enhancement factor can therefore be expressed as

$$EF = \beta M_{Loc}(\omega_L) M_{Rad}(\omega_R), \tag{3}$$

where β is a constant of order ~ 1 depending on the Raman tensor and the scattering configuration. In backscattering, for example, $\beta = 1$ or 15/4 for an isotropic or uniaxial probe, respectively (note that M_{Loc} is also different in each case, which may compensate for the difference in β). We ignore this factor β in the following for simplicity. Eq. (3) seems in stark contrast with the standard $|E|^4$-approach. The difference stems mainly from the second (re-emission) term: $M_{Rad}(\omega_R)$, instead of $M_{Loc}(\omega_R)$. These two terms have a priori nothing in common, and the determination of M_{Rad} is in principle a very different problem to finding M_{Loc}. However, both have the same physical origin: coupling to surface plasmon resonances. One could therefore expect that they follow qualitatively the same resonances. Moreover, for simple cases like a single small sphere, analytical results were derived and a relation of the type $M_{Loc}(\omega_L)M_{Loc}(\omega_R)$ was obtained for the SERS enhancement [15,16]. Such an expression is used commonly in the literature for more complex structures.

A general approach to justify formally this approximation is to use the ORT, which states [10] that the field $\mathbf{E}$ created at a given point M by a dipole $\mathbf{d}$ (at point O) is related to the field $\mathbf{E}_2$ at O created by a dipole $\mathbf{d}_2$ at M according to $\mathbf{d} \cdot \mathbf{E}_2 = \mathbf{d}_2 \cdot \mathbf{E}$. This theorem is quite general as can be seen from its demonstration [10]. It is in particular valid in the presence of boundaries and absorbing media within a bounded region. We show the ORT enables one to derive the far-field properties of an emitter

in a given direction from the solution of two plane wave excitation (PWE) problems without any source singularities, which would otherwise be required to solve the EM problem.

We consider a dipole $\mathbf{d}$ at O as in the top-left inset of Fig. 1, and focus on its far-field emission at a distance R in direction $\mathbf{e}_r$ defined by angles (θ, ϕ). The radiation field is transverse and can be decomposed into E_θ and E_ϕ, along unit vectors $\mathbf{e}_\theta$ and $\mathbf{e}_\phi$. The Pointing vector is $\mathbf{S} = (\epsilon_0 c/2)|E|^2 \mathbf{e}_r$. To apply the ORT, we consider the problem of a dipole $\mathbf{d}_2 = d_0 \mathbf{e}_\theta$ situated at M. The ORT yields $d_0 \, E_\theta = \mathbf{d} \cdot \mathbf{E}_2$, where $\mathbf{E}_2$ is the field created by $\mathbf{d}_2$ at O. For large R, this field can be approximated by a plane wave propagating along $-\mathbf{e}_r$, polarized along $\mathbf{e}_\theta$, and with amplitude $E_P = k^2 d_0 \exp(ikR) /(4\pi\epsilon_0 R)$. We can now choose d_0 so that $E_P = E_0$. The problem then reduces to solving Maxwell's equation for excitation with a plane wave polarized along $\mathbf{e}_\theta$, propagating along $-\mathbf{e}_r$, and of amplitude E_0. We denote $\mathbf{E}^{PW-\theta}$ the field at O for this problem. The θ component of the radiation field of $\mathbf{d}$ at M is then

$$E_\theta = \frac{k^2 e^{ikR}}{4\pi\epsilon_0 R |E_0|} \mathbf{d} \cdot \mathbf{E}^{PW-\theta}. \tag{4}$$
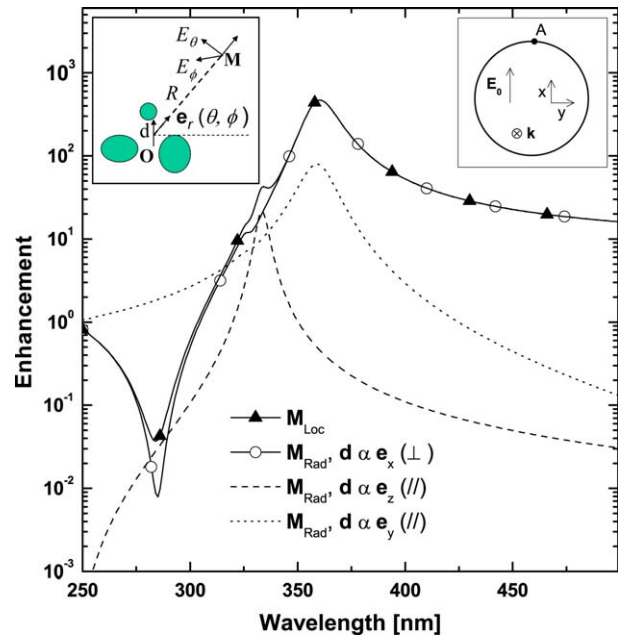

Fig. 1. Example of calculations using the ORT approach for a silver sphere of radius $a = 25$ nm and a dipole situated at $d = 1$ nm from the surface at point A (see schematic in right inset). The local field enhancement $|E|^2/|E_0|^2$ and the radiative enhancement M_{Rad}^{BS} in the BS direction (along $-\mathbf{k}$) for a dipole aligned along either $\mathbf{e}_x$ (perpendicular), or $\mathbf{e}_z$ or $\mathbf{e}_y$ (parallel), are shown for comparison. For the perpendicular dipole, M_{Rad}^{BS} is similar to M_{Loc}, but for other dipole orientations, it is clear that M_{Rad}^{BS} can be very different from M_{Loc}. Left inset shows a schematic representation of the EM problem of an emitter (dipole) in close proximity to a metallic environment.

A similar expression is obtained for E_ϕ, but note that this requires the solution of a *different PWE problem* with polarization along $\mathbf{e}_\phi$. The time-averaged power radiated per unit solid angle can then be calculated. Our convention leads to the simple expression

$$M_{\text{Rad}}(\theta, \phi) = \frac{|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^{\text{PW}-\theta}|^2}{|E_0|^2} + \frac{|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^{\text{PW}-\phi}|^2}{|E_0|^2}. \quad (5)$$

It is easy to verify that this is fully consistent with an isolated dipole in free-space. The important result here is that *the radiation in a given direction of a dipole in a complex environment is obtained by modelling two PWE problems, without a dipolar singularity*. Eq. (5) also shows that the far-field emission of a dipole in a given direction is in a way related to the local field enhancement factors of Eqs. (1) and (2) for PWE from this direction. This will be the basis for the generalization of the $|E|^4$ SERS enhancement factor.

We illustrate first the use of the ORT approach in Fig. 1 for a silver sphere. Mie theory [17,18] was used to obtain exact results. The radiative enhancement in direction $-\mathbf{e}_z$ is calculated for dipoles located at point A (see inset) with three different orientations. The results are compared to calculations of the local field enhancement factor $M_{\text{Loc}} = |E|^2/|E_0|^2$ for PWE along $\mathbf{e}_z$. Local field and radiative enhancements are nearly identical for the perpendicular dipole, but differ for other orientations. This highlights the difficulties of using purely a local field enhancement approach to the problem of radiative enhancement.

The two approaches can be reconciled by use of the ORT, which has in fact been used in the past [19] to study SERS enhancement factors in gratings. We apply it here using Eq. (5) to justify the use of the $|E|^4$-factor. In most experiments the signal is detected in the far field in only one direction $(\theta_{\text{d}}, \phi_{\text{d}})$, which depends on the specific scattering configuration (the signal is integrated over a small solid angle defined by the numerical aperture of the collecting optics). The SERS enhancement factor is then given by $\text{EF}(\theta_{\text{d}}, \phi_{\text{d}}) = M_{\text{Loc}}(\omega_{\text{L}})M_{\text{Rad}}(\theta_{\text{d}}, \phi_{\text{d}}, \omega_{\text{R}})$. For simplicity, we will focus on the backscattering (BS) configuration along (O_z), where the incident wave is polarized along (O_x). The use of the ORT then requires one to find the solution of two PWE problems with polarization along (O_x) and (O_y). We denote $\mathbf{E}^X$ and $\mathbf{E}^Y$ the electric fields at the scatterer position for these two problems. The BS radiative SERS enhancement factor is

$$\text{EF}_{\text{BS}} = M_{\text{Loc}}(\omega_{\text{L}}) \left[\frac{|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^X(\omega_{\text{R}})|^2}{|E_0|^2} + \frac{|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^Y(\omega_{\text{R}})|^2}{|E_0|^2} \right], \quad (6)$$

which has some similarities with the conventional $|E|^4$-factor. However, the latter (which would be here proportional to $|E^X(\omega_{\text{L}})|^2|E^X(\omega_{\text{R}})|^2$) requires the solution of only one PWE problem with polarization along (O_x). Since PWE problems along (O_x) and (O_y) are two independent

problems, one concludes that the $|E|^4$ approach is at best an approximation. In fact, the failure of the $|E|^4$ approximation (at least for a BS configuration) is related to the fact that the molecule (more specifically the induced Raman dipole) is not necessarily aligned parallel to the electric field of the pump beam. We would like to stress here that the alignment between pump beam polarization and Raman dipole is not common in SERS and happens only in specific conditions. There are two reasons for this: First, the local field polarization at the molecule position can be very different to that of the pump beam (as a result of interaction with the metallic SERS substrate). Take for example, the standard SERS model of a dimer with a molecule in its gap. The local field polarization in the gap is along the dimer axis for all incident beam polarization (except when it is exactly perpendicular to the dimer axis, situation in which the enhancement is small anyway). Second, for a molecule with a uniaxial Raman tensor (a common situation for dyes), the induced dipole alignment is dictated by the orientation of the molecule, and not by the local field polarization. For these reasons, the $|E|^4$-factor is almost always an approximation (except in a few exceptional cases), but it is in many cases a useful approximation (thanks to its simplicity) of the order of the enhancement factor.

The exact expression can be further simplified for specific Raman tensors. For an isotropic tensor, $\mathbf{d} = \alpha \mathbf{E}^X(\omega_{\text{L}})$, and

$$\text{EF}_{\text{BS}} = \frac{|\mathbf{E}^X(\omega_{\text{L}})|^2|\mathbf{E}^X(\omega_{\text{R}})|^2}{|E_0|^4} + \frac{|\mathbf{E}^X(\omega_{\text{L}}) \cdot \mathbf{E}^Y(\omega_{\text{R}})|^2}{|E_0|^4}. \quad (7)$$

For a uniaxial tensor, the Raman dipole is $\mathbf{d} = \alpha(\mathbf{E}^X \cdot \mathbf{e}_{\text{d}})\mathbf{e}_{\text{d}}$, and

$$\text{EF}_{\text{BS}} = \frac{|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^X(\omega_{\text{L}})|^2|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^X(\omega_{\text{R}})|^2}{|E_0|^4}$$
$$+ \frac{|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^X(\omega_{\text{L}})|^2|\mathbf{e}_{\text{d}} \cdot \mathbf{E}^Y(\omega_{\text{R}})|^2}{|E_0|^4}. \quad (8)$$

From the derivation of Eq. (5), we see that the first term in the above expressions corresponds to polarized detection along (O_x) ($\|$ to excitation), while the second is for $\perp$ (O_y) polarization. The first term is the conventional $|E|^4$-factor, which can therefore be exact, for example, if all the following conditions are met: (i) plane wave excitation, (ii) BS-configuration, (iii) polarized detection $\|$ to excitation, and (iv) isotropic or uniaxial Raman tensors. If condition (iii) is not met, for example, for non-polarized detection, the $|E|^4$-factor should still be in most cases a good order-of-magnitude approximation. However, for depolarization effects the standard $|E|^4$ factor is not adequate and the full treatment is necessary. Similarly, for other scattering configurations, for example, at 90°, the standard $|E|^4$-factor can lead to erroneous conclusions. This emphasizes one important conclusion of this study often overlooked in
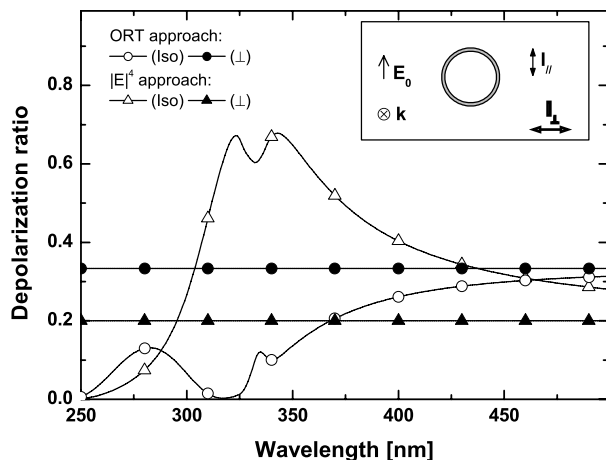
Fig. 2. Comparison of the predictions from the standard $|E|^4$ approach (triangles), with that of the ORT (circles). The SERS depolarization ratio $R = I_\perp/I_\parallel$ is shown (solid lines) as a function of wavelength for a continuous distribution of probe molecules on the surface of a silver sphere of radius $a = 25$ nm. Two Raman tensors are considered: isotropic (Iso – clear symbols), or uniaxial with the main axis perpendicular to the sphere surface ($\perp$ – filled symbols). Symbols are only used to identify the plots. This illustrates the failure of the $|E|^4$ approximation under certain conditions.

the past: accurate SERS enhancement calculations are only possible if the Raman tensor of the probe and the scattering configuration are clearly specified.

One clear illustration of the failure of the $|E|^4$-factor is in SERS depolarization ratios. This is shown in Fig. 2 for the simplest canonical example of a silver sphere covered with a continuous distribution of probe molecules. Two situations are considered: isotropic or uniaxial Raman tensors. In the latter case, the axis needs to be specified and we assume it fixed and $\perp$ to the surface of the sphere. Choosing the BS-geometry along (O_z), the excitation is polarized along (O_x) and detected with polarizers along (O_x) ($\parallel$) or (O_y) ($\perp$). Both intensities are evaluated by integrating on the sphere's surface for the contribution of all molecules. Accordingly, the depolarization ratio $R = I_\perp/I_\parallel$ for the isotropic case is

$$R^{\text{ORT}} = \frac{\int |\mathbf{E}^X(\omega_L) \cdot \mathbf{E}^Y(\omega_R)|^2 d\Omega}{\int |\mathbf{E}^X(\omega_L)|^2 |\mathbf{E}^X(\omega_R)|^2 d\Omega}. \qquad (9)$$

Using the conventional $|E|^4$-factor, combined with standard techniques of depolarization scattering, one would obtain:

$$R^{\text{E4}} = \frac{\int |\mathbf{E}^X(\omega_L)|^2 |\mathbf{e}_y \cdot \mathbf{E}^X(\omega_R)|^2 d\Omega}{\int |\mathbf{E}^X(\omega_L)|^2 |\mathbf{e}_x \cdot \mathbf{E}^X(\omega_R)|^2 d\Omega}. \qquad (10)$$

Similar expressions are obtained for the $\perp$ uniaxial case.

For simplicity, we also make the common assumption of a negligible Raman-shift: $\omega_L \approx \omega_R$. Despite the appar-

ent similarities between the ORT and $|E|^4$ expressions, they are actually very different, in particular in the numerators. In the first case, one needs to solve a second PWE problem with polarization along (O_y) to obtain $\mathbf{E}^Y$, while in the second, one PWE problem is sufficient and the solution is simply projected onto $\mathbf{e}_y$. This conceptual difference leads to drastically different predictions, as shown in Fig. 2, where the two models are plotted as a function of wavelength. In the uniaxial case, the $|E|^4$-approach predicts a constant (wavelength independent) ratio of 1/5, whereas a ratio of 1/3 is predicted from the ORT approach. For the isotropic tensor, the behavior at the surface plasmon resonance of the sphere is simply the opposite. The standard $|E|^4$-approach predicts a ratio increasing to ≈ 0.7, while the generalized approach predicts a decrease to ~ 0. Such discrepancies are also likely in more complex geometries; a subject which will be explored in further detail elsewhere.

In closing, we have presented a rigorous and general approach to the calculation of the SERS radiation enhancements based on the ORT, which highlights the shortcomings of the usual $|E|^4$-factor often assumed in the literature. It moreover defines clearly the range of validity of this approximation and provides a direct recipe for its exact calculation.

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