

Research article

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Purcell factor and local intensity enhancement in surface-enhanced Raman scattering

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Abstract: We prove that, at any point of any reciprocal structure, the local field intensity enhancement, which is averaged over the incident wave polarizations and the incidence directions, exactly coincides with the radiative part of the Purcell factor, which is averaged over the orientations of the emitter. This result is important for gaining a better understanding of the electromagnetic Raman gain in the surface-enhanced Raman scattering and for the further development of this technique.

Keywords: Purcell factor; local intensity enhancement; surface-enhanced Raman scattering; Green's function; reciprocity.

1 Introduction

The commonly adopted theory of the electromagnetic Raman gain G_R in the surface-enhanced Raman scattering (SERS) claims that, in the case of non-coherent SERS, when the structure is electromagnetically linear, $G_R \approx L_E^4 = L_I^2$ (as indicated in papers [1–8] and books [9–13]). Here, $L_I = L_E^2$ is called the local field intensity enhancement, and L_E is called the local field enhancement (LFE). LFE is defined as the ratio of the local electric field amplitudes $|\mathbf{E}_{\text{ls}}|/|\mathbf{E}_{\text{io}}|$, where \mathbf{E}_{ls} is the field oscillating with the source frequency ω_1 and acting on the molecule in presence of the resonant structure, and \mathbf{E}_{io} is that acting on the molecule in free space. The Raman gain G_R is defined as the ratio of the power of the Raman signal $P_{\text{ms}}(\omega_R)$ radiated

in the presence of the resonant structure to the power $P_{\text{mo}}(\omega_R)$ radiated in its absence. Here, ω_R is either the Stokes ($\omega_R = \omega_1 - \Omega_R$) or anti-Stokes ($\omega_R = \omega_1 + \Omega_R$) Raman frequency (Ω_R is the Raman shift).

After an extensive study of the classical and modern literature reporting the electromagnetic mechanism of the Raman gain in SERS, we did not find a convincing justification of this critically important result when applied to structures that are more complex than spherical or spheroidal nanoparticles. The applicability bounds of this result remain unclear for many existing SERS schemes (see, e.g. discussions in Refs. [5, 6, 8, 14–16]). In a relatively recent review on the electromagnetic theories of SERS [17], it is concluded that an “... effort to apply plasmonic theory systematically to develop radically more efficient systems that are able to massively concentrate optical fields so as to exploit the chemical and physical capabilities of such systems has not yet been attempted”.

In the absolute majority of related works, the result $G_R \approx L_E^4$ is explained in terms of the dipole-dipole interaction between the Raman dipole $\mathbf{p}_R^{(s)}$ of a molecule (induced by the local field \mathbf{E}_{ls}) and the dipole \mathbf{p}_{NP} induced in the resonant nanoparticle by the molecule at the frequency ω_R . For a reference molecule shown in Figure 1 (where, as an example of the SERS substrate, an array of plasmonic nanopillars is schematically depicted), this approximation means that this molecule interacts only with the pillar near which it is located, whereas the electromagnetic response of this pillar is dipolar. Given that the Raman dipole moment $\mathbf{p}_R^{(s)}$ of the molecule in the presence of the resonant substrate and the Raman dipole moment $\mathbf{p}_R^{(0)}$ of the same molecule in free space are proportional to the local fields \mathbf{E}_{ls} and \mathbf{E}_{io} , respectively, we have the relation,

$$\mathbf{p}_R^{(s)} = \alpha_R \mathbf{E}_{\text{ls}} = L_E(\omega_1) \alpha_R \mathbf{E}_{\text{io}} = L_E(\omega_1) \mathbf{p}_R^{(0)}, \quad (1)$$

for the absolute values of these Raman dipole moments, where α_R is the molecule Raman polarizability (considered as a scalar value in the cited works). This dipole oscillating at the frequency ω_R induces the dipole moment \mathbf{p}_{NP} in the coupled resonant nanoparticle. Given that the structure is linear, we have $\mathbf{p}_{\text{NP}} = L_p(\omega_R) \mathbf{p}_R^{(s)}$. The coefficient $L_p(\omega_R)$, which relates the induced and the primary

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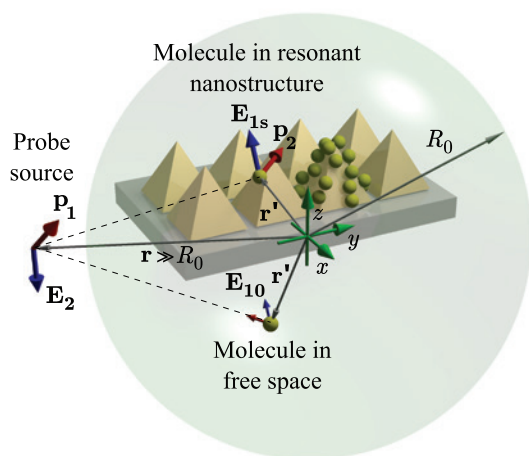


Figure 1: An illustration of the concept of the Raman gain: the molecule near a resonant nanopyramid array (top), at a large distance from the field source, the probe dipole \mathbf{p}_1 , and the same molecule in free space (bottom) at the same distance from the source.

dipoles oscillating at ω_R , can be found from the solution of the quasistatic dipole-dipole interaction problem. The quasistatic approximation is adopted in Refs. [1–7, 14] as an obvious implication of the dipole-dipole interaction approximation.

For the spheroidal plasmonic nanoparticles considered in the literature (e.g. Ref. [7]), in the approximation that the nanoparticle contribution dominates in the local and scattered fields, the coefficient L_p , which describes the dipole-dipole interaction, amazingly turns out to be exactly equal to L_E calculated at ω_R . Then, taking into account that, in practical SERS schemes, $L_I = L_E^2 \gg 1$, Equation (1) results in the following approximate relation for the Raman gain:

$$G_R \equiv \frac{P_{ms}(\omega_R)}{P_{m0}(\omega_R)} = \frac{|\mathbf{p}_R^{(s)} + \mathbf{p}_{NP}|^2}{(p_R^{(0)})^2} \approx \frac{p_{NP}^2 (p_R^{(s)})^2}{(p_R^{(s)})^2 (p_R^{(0)})^2} = L_I(\omega_R) L_I(\omega_1). \quad (2)$$

If the Raman shift is smaller than the bandwidth of the plasmon resonance centered at ω_1 , then, from (2), we have $L_I(\omega_R) \approx L_I(\omega_1)$ and $G_R \approx L_I(\omega_1)^2 = L_E(\omega_1)^4$.

There is nothing surprising in the fact that $L_p \gg 1$ and the electromagnetic Raman gain is very high. For example, in the Uda-Yagi antenna, a small active dipole enhanced by a resonant passive dipole (or an array of such passive dipoles) is not the main radiator. Basically, it is an element that efficiently couples the resonant passive system to the power source. Most of the antenna radiation is created by the indirectly excited passive elements. The

role of the plasmonic nanoparticle in SERS is quite similar to that of the passive part of the Uda-Yagi antenna. First, the nanoparticle enhances the coupling of the molecule to the source field, allowing it to take more energy from it. Second, this energy (converted by the molecule into that of its vibrations) is collected by the nanoparticle from the molecule in a non-radiative way and, finally, radiated into the free space by the nanoparticle. This two-fold action of the nanoparticle (first, at the frequency ω_1 , and, second, at ω_R) explains the tremendous values of G_R for specific locations of the molecule (e.g. the location at the nanopyramid tip in Figure 1, Ref. [15]). It also explains the high Raman gain after averaging over all possible positions of the molecule on a textured substrate [18].

However, this model evokes a few critical questions. First, what is the physics behind the equality $L_p(\omega) = L_E(\omega)$? Second, in which geometries and under which approximations does Equation (2) hold? The problem of direct calculation of L_p allows an analytical solution only for a spheroidal nanoparticle excited by a point dipole [1–7, 14]. Thus, analytical theories explain the result (2) only for a nanoparticle shaped as a sphere, tablet (oblate spheroid) or rod (prolate spheroid). What about a pyramid as in Figure 1 or any other shape? In some works, such as Ref. [4], it is suspected that the equality $L_p(\omega) = L_E(\omega)$ is a general property of any SERS substrate and follows from the reciprocity. However, this claim is not proven and it remains unclear how the problem of L_p (the quasistatic dipole-dipole coupling) is linked to the problem of LFE (the local field produced by a distant source, when the molecular dipole is not involved at all).

In fact, some works have used the optical reciprocity theorem to refute the generality of Equation (2). In particular, in Ref. [19] the authors show that, when scattering in a particular direction is considered (e.g. back scattering), Equation (2) is at best an approximation. They conclude that the failure of this approximation is related to the fact that the induced Raman dipole is not necessarily aligned parallel to the electric field of the pump beam. In Ref. [13], Stockman calculates the electromagnetic Raman gain for a molecule in an arbitrary reciprocal plasmonic environment by involving the semi-classical model of the Raman radiation and the apparatus of the dyadic Green's functions. Stockman obtains a result expressed by his formula (45) which, after some approximations, is reduced to another formula (46). His formula (46) is analogous to our Equation (2). This result is obtained by Stockman for a linearly polarized plane wave incoming from a given direction. Unfortunately, in his theory, it is again an *approximate* result. Nevertheless, the majority of publications on SERS in plasmonic structures use the result (2) without any serious justification.

Such a blind belief in the equality $L_p(\omega) = L_e(\omega)$ tells nothing about the applicability of (2) for advanced SERS structures where the molecule is coupled to the resonant clusters of nanoparticles (as in Refs. [20–22]), to open resonators (as in Ref. [23]), or to regular arrays of nanoantennas (as in Ref. [18]). In many such works, the Raman gain, G_R and LFE L_e , are numerically calculated and (or) measured and averaged over all possible positions of the molecule on the substrate (as is depicted in Figure 1, e.g. the second pyramid from the right). In all these works, after the averaging, one obtains the Raman gain and the LFE related as $G_R \approx L_e^2(\omega_i) L_e^2(\omega_R)$. However, is the relation (2) a general property of SERS or is it a feature of those specific SERS schemes?

2 Results and discussion

In this section, we will show that, with a proper definition for the *average* SERS enhancement factors, the result (2) can be *strictly* proven for the reciprocal structures of the arbitrary geometry, based on the symmetry properties of the dyadic Green's function.

In order to do this, we represent the *integral* Raman gain as a product of two factors, which are the local intensity enhancement and the Purcell factor. Note that SERS is explained through the Purcell enhancement, also in Refs. [24, 25]. First, let us multiply and divide the definition of G_R by the power P_m , radiated by the molecule located in free space and having the dipole moment enhanced L_e times. This power is proportional to $(p_R^{(s)})^2$ (which is responsible for a small part of P_{ms} , as we have seen above that P_{ms} is radiated mainly by the elements of the resonant environment). Thus, the definition of the Raman gain can be written as follows:

$$G_R \equiv \frac{P_{ms}(\omega_R)}{P_{m0}(\omega_R)} = \frac{P_{ms}(\omega_R)}{P_m(\omega_R)} \frac{P_m(\omega_R)}{P_{m0}(\omega_R)} = \frac{P_{ms}(\omega_R) (p_R^{(s)})^2}{P_m(\omega_R) (p_R^{(0)})^2}. \quad (3)$$

In the right-hand side of (3), the second factor equals the source field intensity enhancement $L_f(\omega_i)$, whereas the first factor is the radiative Purcell factor F_p taken at the frequency ω_R . Indeed, the radiative Purcell factor is defined as the power radiated by an active dipole, which is coupled to the resonant structure divided by the power radiated by the *same* active dipole (in SERS it is $\mathbf{p}_R^{(s)}$) located in free space [26–28]. Understanding the Purcell factor through the enhancement of radiation from an arbitrary electric dipole (with a fixed dipole moment) by a resonant environment

was recently introduced in Refs. [26–28], where the equivalence of this definition of the Purcell factor to the classical definition (through the enhancement of the spontaneous emission decay rate) was proven.

From Equation (3), a formula for the Raman gain follows, which represents G_R as an implication of two effects: The local intensity enhancement, e.g. resulting from a plasmon resonance of the textured substrate, and the Purcell effect granted by the same substrate [a similar result appears also in Ref. [24], Equation (12)], which is presented as follows:

$$G_R = F_p(\omega_R) L_f(\omega_i). \quad (4)$$

The relevance of (4) for SERS becomes clear after reading Ref. [23], where two commonly known components of the Purcell factor – the effective mode volume and the effective resonator quality – are separately identified from the Raman gain for a plasmonic crevice resonator. However, being mixed with the components of the LFE, this finding did not allow the authors of Ref. [23] to represent their result in the form (4).

Let us now prove that, when properly averaged over orientations of the molecule and the incidence directions, $F_p = L_f$, i.e. the relation (2) *strictly holds in whatever reciprocal structure* under these conditions. In our proof, we consider that (1) the incident wave can be arbitrarily polarized, (2) that the molecule polarizability is anisotropic and that (3) the Raman radiation can be as well arbitrarily polarized due to the random orientation of the molecule. Correspondingly, we average the Purcell factor over all possible directions of the molecule dipole moment, and the local intensity enhancement is averaged over all possible directions and polarizations of the source radiation. We call these two averaged factors *the mean factors of SERS*.

Note that the averaging over the directions of the Raman dipole moment and the wave polarization is very common in SERS models as this accounts for the inevitable randomness in molecule placement and orientation in the real experiments. The averaging over the incidence directions is required when also the orientation of the nanoscatterer (e.g. a plasmonic dimer) is random, which is typical in colloids. Finally, the averaging over all radiation directions means that we essentially deal with the integral Raman scattering.

Let a molecule located in a nonmagnetic environment (e.g. coupled to a plasmonic resonant structure, as is shown in Figure 1) be excited by a remote probe source \mathbf{p}_i . In general, such environment can be characterized by a non-uniform complex dyadic permittivity $\bar{\epsilon}_r(\omega, \mathbf{r}')$, such that $\bar{\epsilon}_r(\omega, \mathbf{r}')^T = \bar{\epsilon}_r(\omega, \mathbf{r}')$. Assume that, at large distances R from the molecule, the environment transitions into free

space, as is shown in Figure 1 [i.e. $\bar{\varepsilon}_r(\omega, \mathbf{r}') = \bar{1}$, where $\bar{1}$ is the identity dyadic, if $R > R_0$].

In SERS, a molecule located in the vicinity of the plasmonic structure radiates as an elementary electric dipole $\mathbf{p}_2(\omega) = \mathbf{p}_R^{(s)}$. The electric field of this radiation at an arbitrary point \mathbf{r} can be expressed through the dyadic Green's function for the electric field \bar{G}_e given by

$$\mathbf{E}_2(\omega, \mathbf{r}, \mathbf{r}') = \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}') \cdot \mathbf{p}_2(\omega). \quad (5)$$

Similarly, the field of the probe source \mathbf{p}_1 calculated at \mathbf{r}' is given by the same formula with \mathbf{r} and \mathbf{r}' permuted and the pair $\mathbf{p}_2, \mathbf{E}_2$ replaced by $\mathbf{p}_1, \mathbf{E}_{1s}$. Here, $\bar{G}_e(\omega, \mathbf{r}, \mathbf{r}')$ is the solution of the dyadic equation given by

$$\nabla \times \nabla \times \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}') - k^2 \bar{\varepsilon}_r(\omega, \mathbf{r}) \cdot \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}') = \varepsilon_0^{-1} k^2 \delta(\mathbf{r} - \mathbf{r}') \bar{1}, \quad (6)$$

where $\nabla \equiv \partial/\partial \mathbf{r}$, $k = \omega/c$ and ε_0 is the free space permittivity. In the reciprocal ambient, the dyadic Green's function satisfies $\bar{G}_e(\omega, \mathbf{r}', \mathbf{r}) = \bar{G}_e^T(\omega, \mathbf{r}, \mathbf{r}')$ (e.g. Ref. [13]). Below, we use the reciprocity of the Green's function when relating the local intensity factor L_l and the Purcell factor F_p .

We define the mean local intensity factor at the point \mathbf{r}' as follows:

$$L_l^{\text{mean}}(\omega, \mathbf{r}') = \lim_{R \rightarrow \infty} \frac{\sum_i \oint |\mathbf{E}_{1s}(\omega, \mathbf{r}', \mathbf{r})|^2 d\Omega}{\sum_i \oint |\mathbf{E}_{10}(\omega, \mathbf{r}', \mathbf{r})|^2 d\Omega}, \quad (7)$$

where $\mathbf{r} = (R \sin \theta \cos \varphi, R \sin \theta \sin \varphi, R \cos \theta)$ and the integrations are taken in the spherical coordinates over the angles θ and φ with $d\Omega = \sin \theta d\theta d\varphi$. The summations are performed over the index $i = 1, 2, 3$ enumerated through a triplet of mutually orthogonal source dipoles $\mathbf{p}_i(\omega) = p_0(\omega) \mathbf{e}_i$, with the unit vectors \mathbf{e}_i of an orthogonal coordinate system (e.g. $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 = \hat{\mathbf{r}}, \hat{\boldsymbol{\varphi}}, \hat{\boldsymbol{\theta}}$ or $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$). In the denominator of Equation (7), the electric field $\mathbf{E}_{10}(\omega, \mathbf{r}', \mathbf{r})$ is the field of the same probe source in absence of the resonant structure, which can be expressed through the following free space Green's function \bar{G}_{e0} :

$$\mathbf{E}_{10}(\omega, \mathbf{r}', \mathbf{r}) = \bar{G}_{e0}(\omega, \mathbf{r}', \mathbf{r}) \cdot \mathbf{p}_1(\omega). \quad (8)$$

With (8), Equation (7) can be equivalently rewritten as follows:

$$\begin{aligned} L_l^{\text{mean}}(\omega, \mathbf{r}') &= \lim_{R \rightarrow \infty} \frac{\oint \sum_i (\mathbf{e}_i \cdot \bar{G}_e^+(\omega, \mathbf{r}', \mathbf{r}) \cdot \bar{G}_e(\omega, \mathbf{r}', \mathbf{r}) \cdot \mathbf{e}_i) d\Omega}{\oint \sum_i (\mathbf{e}_i \cdot \bar{G}_{e0}^+(\omega, \mathbf{r}', \mathbf{r}) \cdot \bar{G}_{e0}(\omega, \mathbf{r}', \mathbf{r}) \cdot \mathbf{e}_i) d\Omega} \\ &= \lim_{R \rightarrow \infty} \frac{\oint \text{Tr}[\bar{G}_e^+(\omega, \mathbf{r}', \mathbf{r}) \cdot \bar{G}_e(\omega, \mathbf{r}', \mathbf{r})] d\Omega}{\oint \text{Tr}[\bar{G}_{e0}^+(\omega, \mathbf{r}', \mathbf{r}) \cdot \bar{G}_{e0}(\omega, \mathbf{r}', \mathbf{r})] d\Omega}, \end{aligned} \quad (9)$$

where the symbol $^+$ denotes the conjugate-transpose (Hermitian conjugate) operation. Next, we define the mean radiative Purcell factor $F_p^{\text{mean}}(\omega, \mathbf{r}')$ as follows:

$$F_p^{\text{mean}}(\omega, \mathbf{r}') = \lim_{R \rightarrow \infty} \frac{\sum_i \oint \hat{\mathbf{r}} \cdot \mathbf{S}_2(\omega, \mathbf{r}, \mathbf{r}') d\Omega}{\sum_i \oint \hat{\mathbf{r}} \cdot \mathbf{S}_{20}(\omega, \mathbf{r}, \mathbf{r}') d\Omega}, \quad (10)$$

where $\hat{\mathbf{r}} \equiv \mathbf{r}/R$, and the radius vector \mathbf{r} and the integration in $d\Omega$ are defined in the same way as in Equation (7). The difference is that, now, the point \mathbf{r} corresponds to an observation point on the sphere with large radius $R \gg R_0$, whereas the emitting dipole $\mathbf{p}_2 = p_0 \mathbf{e}_i$ (see Figure 1) is located inside the sphere with the radius R_0 . Respectively, in Equation (10), $\mathbf{S}_2(\omega, \mathbf{r}, \mathbf{r}')$ is the Poynting vector at the point \mathbf{r} , which is produced by the probe dipole $\mathbf{p}_2(\omega)$ placed in the considered environment at the point \mathbf{r}' , and $\mathbf{S}_{20}(\omega, \mathbf{r}, \mathbf{r}')$ has the same meaning as $\mathbf{S}_2(\omega, \mathbf{r}, \mathbf{r}')$, but for the free space environment.

At large radial distances $R \gg R_0$ [note that $R \rightarrow \infty$ in Equation (10)], the radiated field is transverse. Therefore, the only meaningful (radial) component of the Poynting vector is equal to $\hat{\mathbf{r}} \cdot \mathbf{S}_2(\omega, \mathbf{r}, \mathbf{r}') = (\eta_0^{-1}/2) |\mathbf{E}_2(\omega, \mathbf{r}, \mathbf{r}')|^2 = (\eta_0^{-1}/2) |p_0(\omega)|^2 \mathbf{e}_i \cdot \bar{G}_e^+(\omega, \mathbf{r}, \mathbf{r}') \cdot \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}') \cdot \mathbf{e}_i$, where η_0 is the free space impedance. Therefore, analogous to L_l , Equation (10) can be rewritten as follows:

$$\begin{aligned} F_p^{\text{mean}}(\omega, \mathbf{r}') &= \lim_{R \rightarrow \infty} \frac{\oint \text{Tr}[\bar{G}_e^+(\omega, \mathbf{r}, \mathbf{r}') \cdot \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}')] d\Omega}{\oint \text{Tr}[\bar{G}_{e0}^+(\omega, \mathbf{r}, \mathbf{r}') \cdot \bar{G}_{e0}(\omega, \mathbf{r}, \mathbf{r}')] d\Omega}. \end{aligned} \quad (11)$$

The general properties of the trace operator and the reciprocity of the Green's function allow us to rewrite the integrands in Equation (11) as follows (we show all intermediate steps for clarity):

$$\begin{aligned} &\text{Tr}[\bar{G}_e^+(\omega, \mathbf{r}, \mathbf{r}') \cdot \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}')] \\ &= \text{Tr}[\bar{G}_e^+(\omega, \mathbf{r}, \mathbf{r}') \cdot \bar{G}_e(\omega, \mathbf{r}, \mathbf{r}')^T] \\ &= \text{Tr}[\bar{G}_e^T(\omega, \mathbf{r}, \mathbf{r}') \cdot \bar{G}_e^*(\omega, \mathbf{r}, \mathbf{r}')] \\ &= \text{Tr}[\bar{G}_e(\omega, \mathbf{r}', \mathbf{r}) \cdot \bar{G}_e^+(\omega, \mathbf{r}', \mathbf{r})] \\ &= \text{Tr}[\bar{G}_e^+(\omega, \mathbf{r}', \mathbf{r}) \cdot \bar{G}_e(\omega, \mathbf{r}', \mathbf{r})]. \end{aligned} \quad (12)$$

With this result, Equations (9) and (11) become equivalent, and we have the following for a molecule located at \mathbf{r}' :

$$F_p^{\text{mean}}(\omega, \mathbf{r}') = L_l^{\text{mean}}(\omega, \mathbf{r}'). \quad (13)$$

Definitely, a similar result was considered in Ref. [13], but only as an approximation, because the averaging over the angles and polarizations had not been performed.

3 Conclusion

In this brief article, we have proven that, in the reciprocal environments that transition at some distance into free space, the *mean* locality factor at every frequency *exactly* coincides with the *mean* radiative Purcell factor. Hence, this result not only theoretically explains the tremendous values (10^{12} – 10^{14}) of the Raman gain in the advanced SERS schemes, where the LFE for specific locations of the molecule attains thousands [8, 11, 12, 15, 16, 18, 20–23], it is highly important for the future development of SERS as well. Indeed, it clarifies the notion that, in any reciprocal SERS scheme, only two parameters need to be optimized: the LFE and the bandwidth of the plasmon resonance. The optimization of the resonant band is needed in order to keep $L_f(\omega_R) \approx L_f(\omega_i)$. One of the possible ways to combine these two targets was pointed out in Ref. [29].

Moreover, aside from SERS, the proven identity is important for other applications, in which both the LFE and the Purcell effect take place. Such applications exist, for example, in the related areas of microlasers and Dicke superradiance. In accordance with the seminal works [30, 31], the Purcell effect is of key importance for the emission from microcavities. In Ref. [32], one may find discussions of the Purcell effect for such emission, where the local field enhancement for the pumping radiation is pointed out as well. We believe that our result is also relevant for the metal-enhanced fluorescence, which is a very promising technique for biosensing applications [33].

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