Influence of tip geometry on the spatial resolution of tip enhanced Raman mapping*

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In 2013, a breakthrough experiment pushed the Raman mapping of molecules via the tip-enhanced Raman scattering (TERS) technique to a sub-nanometer spatial resolution, going into the single-molecule level. This surprising result was well explained by accounting for the critical role of elastic molecule Rayleigh scattering within a plasmonic nanogap in enhancing both the localization and the intensity level of the Raman scattering signal. In this paper, we theoretically explore the influence of various geometric factors of the TERS system on the spatial resolution of Raman mapping, such as the tip curvature radius, tip conical angle, tip–substrate distance, and tip–molecule vertical distance. This investigation can help to find out the most critical geometric factor influencing the spatial resolution of TERS and march along in the right direction for further improving the performance of the TERS system.

Keywords: tip-enhanced Raman scattering, Rayleigh scattering, surface plasmon resonance

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1. Introduction

Raman spectroscopy offers a powerful means to observe vibrational, rotational, and other low-frequency modes in molecules, and thus has become a popular and useful technology for molecular identification. As the cross section of Raman scattering is extremely low under usual conditions of laser excitation, many methods have been explored to advance the power of Raman spectroscopy to the fundamental single-molecule limit. Among them, surface-enhanced Raman scattering (SERS)[1] is an important spectroscopic tool with which the Raman signals from molecules adsorbed on the surface of noble metal (Au, Ag, etc.) nanoparticles and nanostructures can be significantly enhanced. Many schemes have been investigated to build high-performance SERS substrates, including nanoparticles with sharp corners and tips[2–8] and Ag nanoparticle dimers[9,10] or aggregates[11,12] that involve nanogaps.

An important goal of Raman spectroscopic science and technology is to probe the Raman signal with ultrahigh spectroscopic sensitivity down to the single-molecule detection level[11,12] and ultrahigh spatial resolution down to the single-molecule size scale. This would allow people to identify, monitor, and manipulate single molecules in both temporal and spatial domains. When Raman spectroscopy works together with various mature scanning probe microscopy technologies under the scheme of tip-enhanced Raman spectroscopy (TERS),[13–21] the spatial resolution of Raman probing and monitoring can be greatly upgraded and essentially reach the single-molecule level.[19,21] The metal tip in either atomic force microscopy (AFM) or scanning tunneling microscopy (STM) can induce a highly concentrated electric field focus spot far below the diffraction-limit scale (about half of the laser wavelength, usually several hundred nanometers) with greatly enhanced field intensity in the vicinity of the tip apex due to the surface plasmon resonance (SPR) effect. It is generally believed that the spatial resolution of TERS is nearly the same as the focus spot size of the metallic AFM or STM tip, which strongly depends on many factors, such as the molecule–tip vertical distance, the curvature radius of the tip, the excitation wavelength, and the substrate composition, but at best is on the order of 10 nm. However, in 2013, a seminal experimental work[19] pushed the TERS into the sub-nm spatial resolution regime, which allows for probing and mapping the chemical infrastructure of molecules, and stimulated intensive investigations and discussions on the inner new physical origin.[22,23]

Recently, we have proposed a brand-new physical picture and a systematic theoretical formalism to understand single-molecule Raman mapping via TERS.[24] In this theory, the elastic Rayleigh scattering always accompanies the inelastic Raman scattering when the incident light shines on molecules, and the Rayleigh scattering can play a much more pronounced role than it is generally assumed in the conventional Raman physics. In fact, the role of Rayleigh scattering is completely omitted in the classical Raman scattering theory. By introducing the near-field interaction of the molecule with the plas-

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monic nanogap formed between the metallic tip and the substrate of the TERS system, the local field and its interaction with the inelastic scattering of the molecule (Stokes and anti-Stokes light radiated by the vibrational molecule) are strongly modified by the multiple elastic scattering not only from the nanostructure (Mie scattering) but also from the molecule itself (Rayleigh scattering). Applying our theory to the TERS system, we have succeeded in clarifying the surprising experimental discovery of sub-nanometer resolution in TERS. Although there are many works[13–21] about how the geometry factors of TERS influence the spatial resolution in the framework of the traditional SERS theory, our new theory would reveal some different results. Furthermore, it would yield useful suggestions for improving the resolution because the near-field interaction strongly depends on many geometry factors, such as the molecule–tip vertical distance and the curvature radius of the tip. Therefore, in this paper we proceed to investigate in detail how the TERS scanning resolution is influenced by various geometric factors of TERS considering the molecule Rayleigh scattering. This systematical investigation would help to uncover the critical factor determining the spatial resolution of TERS and point to the right direction to improve the resolution.

2. Model and method

For completeness, we first briefly summarize the major physics in the new Raman theory. In the form of dipole approximation, the Stokes (or anti-Stokes) light radiated by the vibration molecule could be expressed as the radiation from the induced dipole

$$\boldsymbol{\mu}(\boldsymbol{r}_0,\omega_{\mathrm{R}}) = \overleftrightarrow{\boldsymbol{\alpha}}(\omega_{\mathrm{R}},\omega)\boldsymbol{E}(\boldsymbol{r}_0,\omega), \tag{1}$$

where $\boldsymbol{E}$ is the local electric field, ω is the frequency of the excitation radiation, ω_{R} is the Stokes (or anti-Stokes) frequency of the Raman signal, and $\boldsymbol{r}_0$ is the molecule position. $\overleftrightarrow{\boldsymbol{\alpha}}(\omega_{\mathrm{R}},\omega)$ is the polarizability (called Raman tensor in general) that describes the transition intensity of the Raman frequency shift process connecting the excitation frequency and the vibration shift frequency, and it is closely related with the molecular quantum states involved with the Raman process. In the conventional theory of SERS and TERS, the optically enhanced Raman signal is described by a factor

$$G_{\mathrm{S}}(r_0) = G_{\mathrm{E}}(\omega)G_{\mathrm{R}}(\omega_{\mathrm{R}}) \approx \left|\boldsymbol{E}(\boldsymbol{r}_0,\omega)\right|^4/\left|\boldsymbol{E}_0(\boldsymbol{r}_0,\omega)\right|^4, \tag{2}$$

where $G_{\mathrm{E}}(\omega)$ and $G_{\mathrm{R}}(\omega_{\mathrm{R}})$ are the enhancement factors (EFs) for the excitation process and the radiation process, respectively, and $\boldsymbol{E}(\boldsymbol{r}_0,\omega) = \boldsymbol{E}_0(\boldsymbol{r}_0,\omega) + \boldsymbol{E}_{\mathrm{s}}(\boldsymbol{r}_0,\omega)$ is the local field in the nanogap, which consists of the incident field $\boldsymbol{E}_0(\boldsymbol{r}_0,\omega)$ and the greatly enhanced scattering field from the plasmonic nanogap $\boldsymbol{E}_{\mathrm{s}}(\boldsymbol{r}_0,\omega)$.

In contrast, in our theory,[24] when considering the molecule self-interaction in the nanogap, the local electric field is expressed as

$$\boldsymbol{E}_{\mathrm{N}}(\boldsymbol{r}_0,\omega) = \boldsymbol{E}_0(\boldsymbol{r}_0,\omega) + \boldsymbol{E}_{\mathrm{s}}(\boldsymbol{r}_0,\omega) + \boldsymbol{E}_{\mathrm{m,s}}(\boldsymbol{r}_0,\omega). \tag{3}$$

The local field $\boldsymbol{E}_{\mathrm{N}}(\boldsymbol{r}_0,\omega)$ now involves a new term, the correctional part $\boldsymbol{E}_{\mathrm{m,s}}(\boldsymbol{r}_0,\omega)$ due to the multiple Rayleigh scattering of molecule. $\boldsymbol{E}_{\mathrm{m,s}}(\boldsymbol{r}_0,\omega)$ is proportional to the local field $\boldsymbol{E}(\boldsymbol{r}_0,\omega)$ and the elastic scattering capability of the adsorbed molecule, which could be described as molecular polarizability $\overleftrightarrow{\boldsymbol{\beta}}(\omega)$. Similarly, the molecule self-interaction has an equally prominent effect on the Raman radiation process. Overall, the true Raman enhancement factor when considering the important molecule Rayleigh scattering induced self-interaction is given by the following formula:

$$\begin{aligned} G_{\mathrm{S}}(\boldsymbol{r}_0) &= G_{\mathrm{E}}(\omega)G_{\mathrm{E,S}}(\boldsymbol{r}_0,\omega)G_{\mathrm{R}}(\omega_{\mathrm{R}})G_{\mathrm{R,S}}(\boldsymbol{r}_0,\omega_{\mathrm{R}}) \\ &\approx \left|\boldsymbol{E}_{\mathrm{N}}(\boldsymbol{r}_0,\omega)\right|^4/\left|\boldsymbol{E}_0(\boldsymbol{r}_0,\omega)\right|^4 \\ &\approx g^4(\boldsymbol{r}_0,\omega)\left|\boldsymbol{E}(\boldsymbol{r}_0,\omega)\right|^4/\left|\boldsymbol{E}_0(r_0,\omega)\right|^4, \end{aligned} \tag{4}$$

where $G_{\mathrm{E,S}}(\omega)$ and $G_{\mathrm{R,S}}(\omega_{\mathrm{R}})$ are the correctional EFs for the Raman excitation and radiation processes due to the molecule self-interaction, and $g(\boldsymbol{r}_0,\omega)$ is the local field correctional factor, which is defined as $g(\boldsymbol{r}_0,\omega) \approx |\boldsymbol{E}_{\mathrm{N}}(\boldsymbol{r}_0,\omega)|/|\boldsymbol{E}(\boldsymbol{r}_0,\omega)|$. This factor has been found to play a key role in advancing the sub-nm spatial resolution in TERS.[24] We have established two methods to calculate the quantitative values of the correctional factor due to the molecule self-interaction. The first one is to utilize the image-dipole approximation. The second one is to use numerical simulations to directly calculate the total Raman enhancement factor, e.g., using the three-dimensional finite-difference time-domain (3D-FDTD) method by modeling the adsorbed molecule as a small particle with an effective molecular polarizability.

3. Results and discussion

Figure 1 presents the scheme of the normal TERS configuration. Here we assume that the tip apex and the substrate are both composed of silver and the tip is a smooth tapering conical tip. The radius of the tip apex is R and the conical angle is θ. The distance between the tip apex and the substrate is d. The excitation light has a wavelength of 532 nm, p-polarization, and an incident direction of 60° with respect to the vertical z axis. The molecule with scalar polarizability β is localized at $\boldsymbol{r}$. Following the physical picture and theoretical formalism presented in Section 2, the spatial resolution is essentially determined by how small the hot spot (or super-hot spot) size sensed by the molecule is. Therefore, how the resolution depends on the geometry of the tip can be generally understood from two aspects. One is that the field profile, in particular, the size of the plasmon hot spot formed in

the nanogap should depend on the geometry of the tip. Second, the self-interaction of the molecule with the nanogap is more sensitive to the overall geometric configuration of the tip–molecule correlated system.

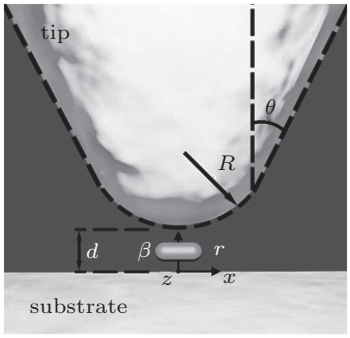


Fig. 1. The schema for the TERS configuration, where R is the radius of the tip apex, θ is the conical angle, $\boldsymbol{r}$ (r_x, r_z) is the site of the molecule with scalar polarizability β, and d is the tip–substrate distance. The excitation wavelength is 532 nm, the excitation light is p-polarized, and the incident direction is 60° with the z axis.

First, we consider the influence of the conical angle to the local field. We use the 3D-FDTD method to simulate the local field of the nanostructure, where the tip is set as $R = 25$ nm, $d = 2$ nm, and θ varies from 0° to 50°. Our calculation demonstrates that the shape and profile of the local field, in particular the hot spot size, is not sensitive to the conical angle. This means that the local field is mainly determined by the geometry of the local nanostructure (such as the curvature radius of the tip apex and the tip–substrate distance). Figure 2 shows that the full width at half maximum (FWHM) of the local field intensity of the hot spot at different conical angles is 10.4 nm and 4.2 nm for the conventional and the modified theories, which denote the conventional Raman theory omitting the molecule self-interaction and the new Raman theory considering the molecule self-interaction, respectively. In the calculation, we use a dielectric sphere in the nanogap to model the molecule, where the radius of the sphere is 1 nm and the permittivity is 3. Then we find that the molecule polarizability is about $\beta = 4.5\beta_0$, where $\beta_0 = 0.1 \times 10^{-37}$ C·m^2/V. However, we can still find some useful modifications to the local field of the hot spot by changing the conical angle. As illustrated in Fig. 2, the local field enhancement factors calculated by the conventional and the modified theories are both maximum at $\theta = 30°$. Thus through modifying the conical angle, we could control the coupling intensity of the nanogap mode.

Then we consider the influence of the geometry of the local nanostructure like the radius of the tip apex. Figure 3(a) shows the dependence of the resolution on the tip apex radius R. When R varies from 10 nm to 40 nm, the scanning resolution has a nearly linear relation with the tip apex radius under the conventional or modified theory. In the conventional theory, the resolution is about 5–8.5 nm for $R = 10$–40 nm, which is not refined enough for single molecule Raman mapping. Considering the molecular self-interaction, the resolution for $R = 10$ nm could be improved to about 1–2 nm for large molecular Rayleigh scattering. For further understanding the mystery of the super resolution considering the molecular self-interaction, we analyze the local field intensity profiles. Figure 4 shows the local field profiles for the nanogap mode under the conventional and the modified theories. Here we assume the molecule with polarizability $\beta = 5\beta_0$ is localized at the middle of the gap ($r_z = 1$ nm, $r_x = 0$ nm). We call the mode in the right panels "super hot spot" which is more spatially confined and stronger compared with the conventional "hot spot" in the left panels. In the conventional theory, the local field is independent of the molecule, and the scanning resolution just depends on the FWHM of the local field. However, that physical picture is not so correct for our theory. According to the above depiction, the local field is strongly correlated with the molecule, and a small displacement of the molecular site would induce a large local field modification. Figure 5 illustrates this strong correlation, in which one can clearly find that the super hot spot is moving along with the moving molecule ($r_x = 1$, 3 nm). Therefore, the scanning resolution in our theory depends on the variation rate of the local field during the molecule moving. As illustrated in Figs. 3(a) and 5, the intensity of the local field changes fastest at $R = 10$ nm, which leads to the best scanning resolution when the radius varies from 10 nm to 40 nm. An intuitive interpretation is that a smaller radius could lead to a larger gap distance variation when the molecule has a horizontal displacement. Due to the special characteristics of the super hot spot, the super resolution in TERS could be reasonably understood and clarified.

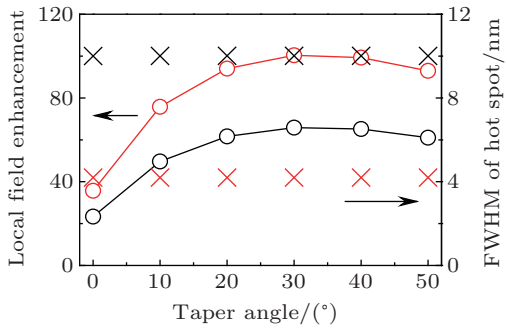


Fig. 2. (color online) The local field enhancement (circle) and the full width half maximum of the local field intensity (cross) calculated by the conventional (black) and the modified (red) theories for various taper angles θ, where $R = 25$ nm, $d = 2$ nm, the wavelength is 532 nm.

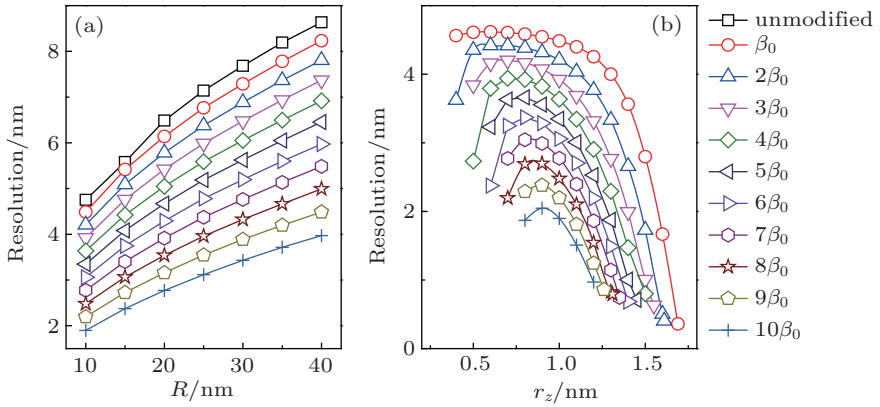


Fig. 3. (color online) The dependence of the scanning resolution on the tip apex radius and the molecule height considering the molecule self-interaction, where the molecular polarizability $\beta = 1$–$10\ \beta_0$. (a) The molecule locates at height $r_z = 1$ nm. (b) The tip apex radius is 10 nm.

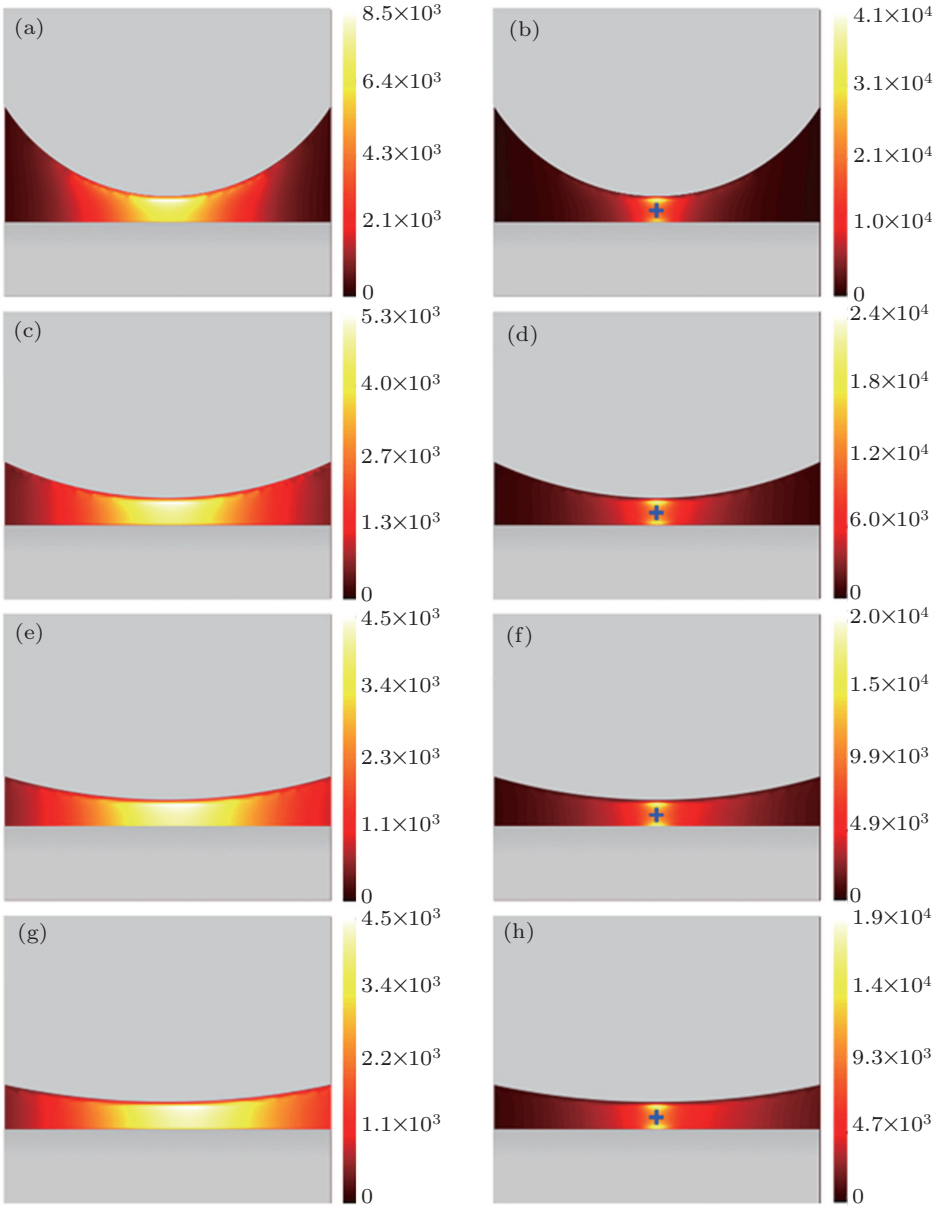


Fig. 4. (color online) The local field intensities for different tip apex radii obtained under the conventional theory ((a), (c), (e), (g) for $R = 10$ nm, 20 nm, 30 nm, 40 nm) and the modified theory considering the molecular self-interaction ((b), (d), (f), (h) for $R = 10$ nm, 20 nm, 30 nm, 40 nm). The molecule (polarizability $\beta = 5\beta_0$) locates at $r_z = 1$ nm, $r_x = 0$ nm (blue mark) and the tip–substrate distance is $d = 2$ nm.

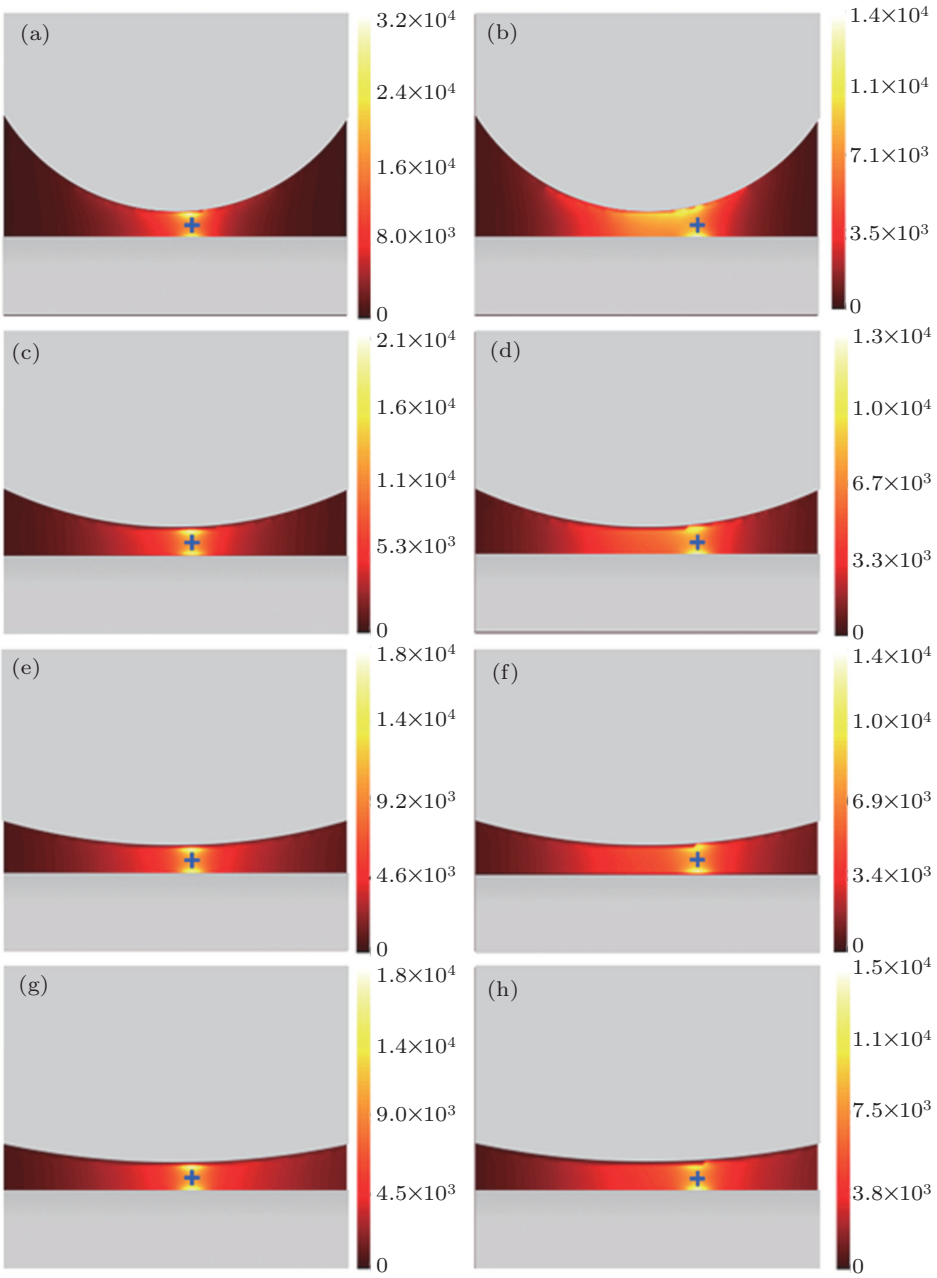


Fig. 5. (color online) The local field intensities for different tip apex radii considering the molecular self-interaction. The molecule (polarizability $\beta = 5\beta_0$) locates at $r_z = 1$ nm and $r_x = 1$ nm ((a), (c), (e), (g) for $R = 10$ nm, 20 nm, 30 nm, 40 nm), 3 nm ((b), (d), (f), (h) for $R = 10$ nm, 20 nm, 30 nm, 40 nm). The tip–substrate distance is $d = 2$ nm.

After acknowledgement of the connection between the super hot spot and the super resolution of TERS in our theory, some tentative designs could be proposed to improve the resolution. An easy attempt is changing the height of the molecule. Figure 3(b) shows the calculated scanning resolutions for various molecular heights. It is obviously found that when the molecule is near the tip apex, the resolution could be improved to 0.5 nm. Similarly, we can understand the mechanism of this observation through the mode profile of the nanogap mode for various molecular vertical distances. As shown in Fig. 6, the super hot spot seemingly follows the vertical movement of the molecule. When the molecule is closer to the substrate, the local field is more concentrated at the substrate and the super hot spot would vary slowly with the horizontal displacement. It would lead to a low scanning resolution. Inversely, when the molecule is closer to the tip apex, the local field is more concentrated at the tip apex. Because the local field is more concentrated at the tip apex with a large gradient, the horizontal displacement of the molecule would lead to a more obvious change of the super-hot spot and consequently a better scanning resolution.

From the above comprehensive analyses, the super resolution of TERS directly originates from the special characteristics of the super hot spot. Moreover, a larger gradient in the nanostructure and the nearby local field would benefit the

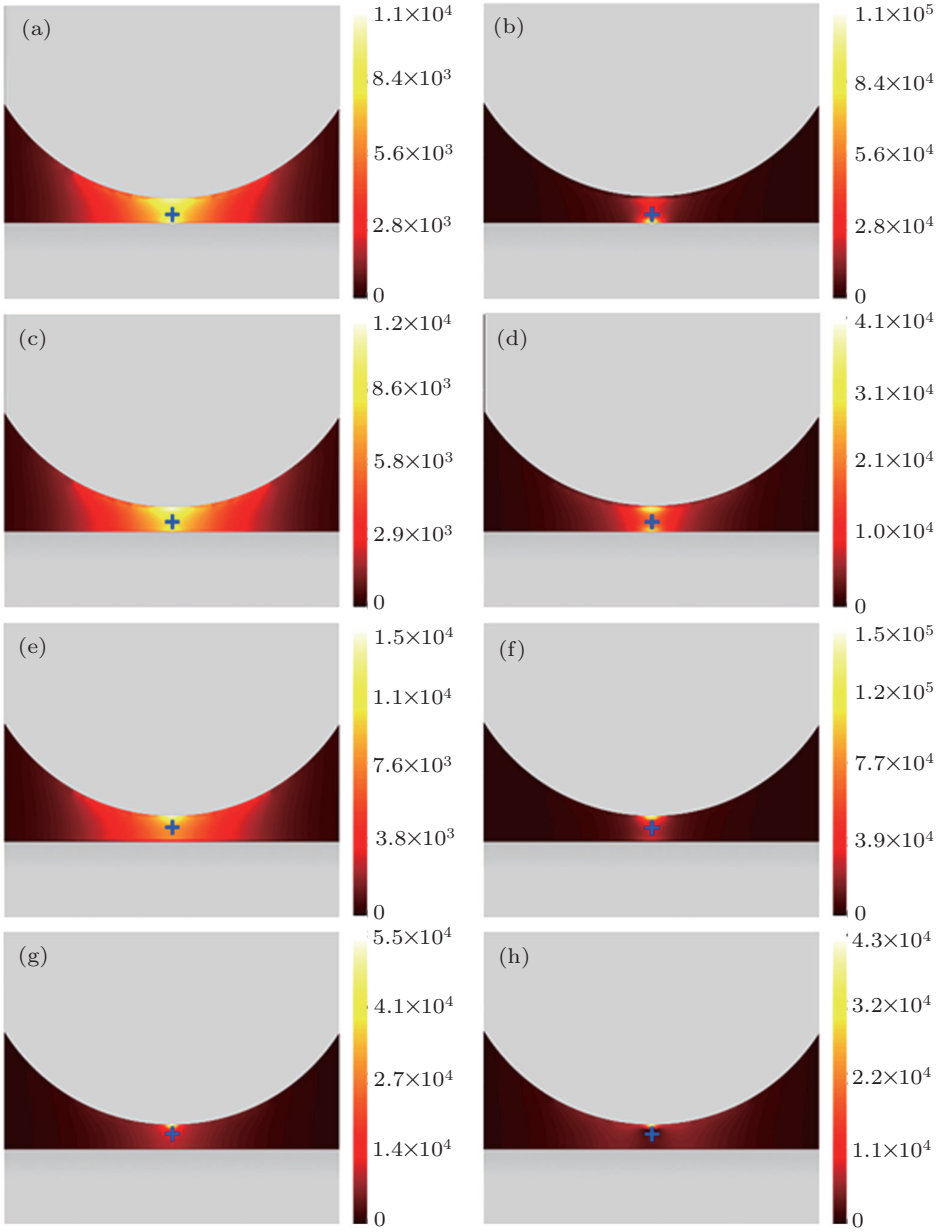


Fig. 6. (color online) The local field intensities for different molecular locations considering the molecular self-interaction: $\beta = 1$, (a), (c), (e), (g) for $r_z = 0.7$ nm, 1 nm, 1.3 nm, 1.6 nm; $\beta = 5\beta_0$, (b), (d), (f), (h) for $r_z = 0.7$ nm, 1 nm, 1.3 nm, 1.6 nm. The radius of the tip apex is $R = 10$nm and the tip–substrate distance is $d = 2$ nm.

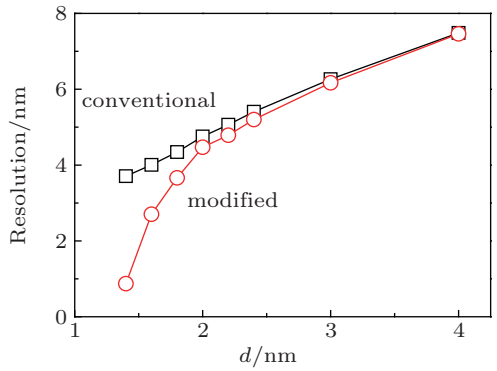


Fig. 7. (color online) The dependence of the scanning resolution on the tip height considering the molecule self-interaction, where the molecular polarizability $\beta = 1.5\beta_0$ and the tip apex radius is 10 nm. The molecular dipole is set at $r_z = 1.0$ nm.

scanning resolution. Following this conception, some suggestions could be made to improve the performance of TERS. One is to manufacture a sharp tip. Although the head radius of the tip fabricated by the electrochemistry method is limited to tens of nanometers, one can still try to do some tip apex modification to improve the gradient, such as adsorbing a small molecule or cluster on the tip apex. Another useful suggestion is to decrease the relative distance between the molecule and the tip, which could construct a nanogap mode more concentrated at the larger gradient nanostructures. A simple method is reducing the height of the tip relative to the molecule or raising the molecule vertical position relative to the tip apex. Figure 7 shows the dependence of the scanning resolution on the tip height. Our theory predicts an exponential decay of the scanning resolution upon the tip height. It expects a much

better resolution promotion compared with the linear decay of the conventional theory. This analysis is further justified in Fig. 8, which shows the local field intensities in the conventional theory and the modified theory considering the molecular self-interaction. One can find a faster decay of the FWHM considering the molecular self-interaction.

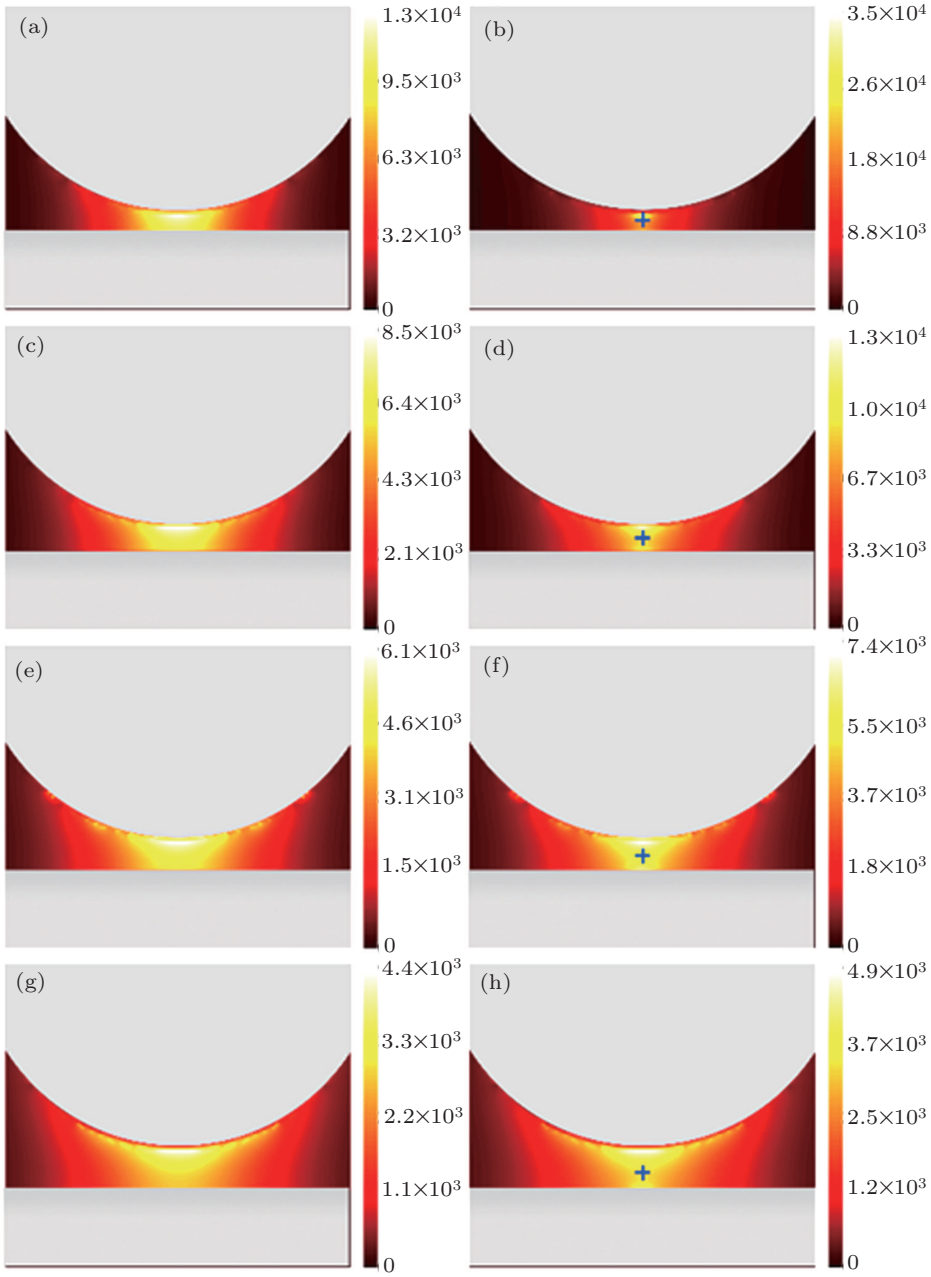


Fig. 8. (color online) The local field intensities for different tip heights obtained by the conventional theory ((a), (c), (e), (g) for $d = 1.6$ nm, 2.0 nm, 2.4 nm, 3.0 nm) and the modified theory considering the molecular self-interaction (polarizability $\beta = 1.5\beta_0$, (b), (d), (f), (h) for $d = 1.6$ nm, 2.0 nm, 2.4 nm, 3.0 nm)). The radius of the tip apex is $R = 10$ nm and the molecular locates at $r_z = 1.0$ nm.

4. Summary

We have considered the influence of various geometry factors to the scanning resolution of TERS when considering the molecule self-interaction effect that originates from the multiple Rayleigh scattering of molecule upon the local field. According to the analysis of the movement of the "upper hot spot", we have illustrated some recipes for designing the tip–molecule nanostructure to have a better performance for TERS. With the new theory, we have gained some deeper understanding of TERS, which is helpful for the further development of this technology.

It is well known that Rayleigh scattering is much stronger than Raman scattering for molecules. However, the old wisdom is that these two processes are mutually independent, or in other words, Rayleigh scattering has no contribution to Raman scattering. Although this is right for Raman experiments

involving molecules in air and other usual homogeneous media, at the nanoscale where many SERS and TERS experiments are involved, Rayleigh scattering can play a critical role in shaping Raman scattering. These two physical processes are strongly intercorrelated via the nanoscale environment, e.g., a plasmonic nanogap, surrounding the molecule. Because of this strong correlation, many geometric factors can strongly and sensitively influence the performance of the TERS system used for Raman mapping against molecules. From these observations, one can find the most critical factor that determines the scanning resolution of TERS. More importantly, these analyses allow one to march along the right direction toward an even better spatial resolution of Raman mapping, e.g., against a small molecule like O_2, CO_2, and so on.

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