

# Stimulated Tip-Enhanced Raman Scattering on Single Molecule in Plasmonic Nanocavity

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In this work, the analysis of tip-enhanced Raman scattering (TERS) of light on a single organic molecule in the plasmonic nanocavity formed by the tip of a metal probe of a microscope and a gold substrate is carried out. The linear and nonlinear regimes of TERS are considered, and the conditions and reasons for the selective enhancement of Raman bands in the TERS spectrum are determined using anisotropic molecules of the free base porphyrin (FBP, H2P) dye as an example

Plasmonic nanocavities formed by a metal nanoparticle located close to a thin metal film or other nanoparticle are of great interest for nanophotonics. Their properties can be used for optical superresolution [1,2], optoelectronics [3,4], and the creation of new materials with increased non-linearity [2]. However, the interpretation of TERS spectra amplified by a nanoresonator is complicated by depolarization effects [5]. Another application of plasmonic nanoresonators is connected with Raman cooling [6].

The aim of this work is to study the effects of inhomogeneous amplification of the SERS spectra of single molecules in linear and nonlinear regimes. The inhomogeneous amplification of the lines is related to the type of symmetry of the molecular vibration. In the nonlinear regime, the induced dipole moment at the Stokes frequency  $\omega_\nu$  has the form:

$$\mathbf{p}_R(\omega_\nu) = \overset{\leftrightarrow}{\alpha}_\nu \mathbf{E}_{\text{local}}(\omega) + \overset{\leftrightarrow}{\alpha} \mathbf{E}_{\text{images}}(\omega_\nu) + \overset{\leftrightarrow}{\alpha}_\nu^{(3)} |\mathbf{E}_{\text{local}}(\omega)|^2 \mathbf{E}_{\text{images}}(\omega_\nu), \quad (1)$$

where  $\mathbf{E}_{\text{local}}$  is the local field at the incident frequency  $\omega$ ,  $\mathbf{E}_{\text{images}}$  is the local field of molecule images in the substrate and tip apex [7,8],  $\alpha$ ,  $\alpha_\nu$ ,  $\alpha_\nu^{(3)}$  are the electronic, Raman, and cubic polarizabilities, respectively, determined on the basis of calculations according to the density functional theory. The interaction is described by means of the formalism of the tensor Green's function [5], extended by the image method for a polarizable sphere [7].

In a plasmonic nanoresonator, three processes contribute to the enhancement of Raman scattering: localization of the electric field (1), interaction with molecular image fields (2), and dynamic back action of the Stokes wave (stimulated Raman scattering) (3). The last two depend on the spatial orientation of the molecule and significantly affect the depolarization of the near field (Fig. 1). Because of this, the observed vibrational symmetry of the molecule changes during spectroscopic measurements using TERS. We believe that our results are beneficial for the development of the tools to control vibrations of molecules at the nanoscale

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## References

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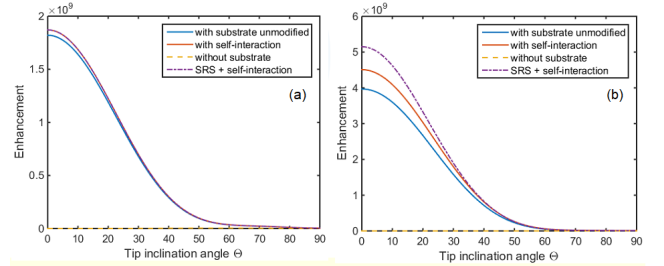


Figure 1: Dependence of the enhancement of the Raman band at  $1395 \text{ cm}^{-1}$  (type  $A_{1g}$ ) of the FBP on the tilt of the probe when FBP is oriented parallel (a) and perpendicular (b) to the substrate normal at an incident light intensity of  $I_0 = 3 \text{ MW/cm}^2$

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