Surface-enhanced Raman scattering as a higher-order Raman process

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Surface-enhanced Raman scattering (SERS) is the giant increase in the Raman scattering cross section of a molecule coupled to a localized surface plasmon (LSP). We propose to understand SERS as a higher-order Raman process that contains the excitation of the LSP. To implement our idea, we adopt the microscopic theory of Raman scattering that is based on perturbation theory. SERS is described with fourth-order perturbation theory, as depicted by a Feynman diagram in Figure 1a. Our description of SERS differs fundamentally from the theory of electromagnetic (EM) enhancement, which treats the plasmonic excitation as a strongly increased light field that drives the Raman process (Figure 1b) [1].

We derive analytic expressions for all coupling matrix elements by employing a formalism that is based on the second quantization of the LSP [2]. This leads to a general expression for the SERS enhancement that can be applied to an arbitrary plasmonic nanostructure. We derive the plasmon eigenvectors of a gold nanosphere from Mie theory and of a gold nanosphere dimer within the quasi-static approximation. This enables us to calculate the enhancement of the Raman cross section of a molecule coupled to the dipole plasmon mode. The enhancement beside the gold nanosphere is found to be up to two orders of magnitude stronger than predicted by the theory of electromagnetic enhancement (Figure 2a). For a molecule in the hot spot of the gold nanodimer the enhancement can be up to three orders of magnitude stronger (Figure 2b). The difference in enhancement is most pronounced in vacuum and drops with increasing dielectric constant of the embedding medium. The predictions from our higher-order Raman description of SERS correlate with
observations in recent experiments in which measured enhancement was two to four orders of magnitude higher than calculated EM enhancement [4-6]. This highlights the dominance of plasmonic enhancement in SERS.

**Figure 2** Plasmonic enhancement from SERS as higher-order Raman scattering (HORa) and EM enhancement (EM) for a molecule (a) positioned 2 nm beside a gold nanosphere and (b) in the hot spot of a gold nanoparticle dimer. [Parameters for (a): vacuum, Raman shift 1000 cm\(^{-1}\), molecule \(\parallel\) light polarization, full lines correspond to enhancement from calculations based on Mie theory, dashed lines correspond to quasi-static approximation, diamonds mark enhancement from EM dipole radiation theory [3]; Parameters for (b) 30 nm sphere diameters, Raman shift 1000 cm\(^{-1}\), molecule \(\parallel\) dimer axis & light polarization]

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**REFERENCES**