

Plasmonic enhancement of hyper Raman scattering by gold nanostructures

F. Madzharova, Z. Heiner and J. Kneipp

Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

Hyper Raman scattering (HRS) is the two-photon excited Raman process, where the signal gives the entire vibrational spectrum of the sample shifted relative to the second harmonic of the excitation wavelength. In the local optical fields of plasmonic nanostructures, HRS can benefit from strong surface enhancement, similar to spontaneous Raman scattering in surface enhanced Raman scattering (SERS). Surface enhanced hyper Raman scattering (SEHRS) is therefore complementary to SERS, and provides additional spectroscopic information due to the different selection rules [1]. In addition to advantages that come with near-infrared excitation, SEHRS is more sensitive than SERS with respect to local environmental changes and molecule-surface orientation [1, 2]. Nevertheless, vibrational probing by means of SEHRS strongly relies on understanding the enhancement from plasmonic nanostructures that are required to overcome the low HRS cross sections.

Here, we focus on the plasmonic enhancement of HRS generated by gold nanostructures. We investigated spherical nanoparticles with different sizes and nanorods, which can provide plasmonic properties specifically suited for enhancement in SEHRS [3]. By comparing SEHRS spectra of crystal violet at 1064 nm excitation (Fig. 1) with normal HRS spectra of the dye, enhancement factors for the different nanostructures are determined, and discussed along with FDTD simulations of the local electromagnetic fields (Fig. 2). Our results demonstrate that gold nanostructures provide efficient enhancement of HRS, which would allow using biocompatible gold nanosensors in future bioanalytical applications of SEHRS.

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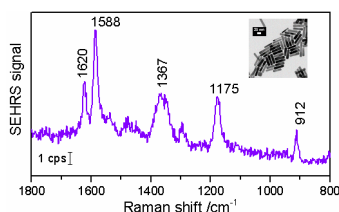


Fig. 1: SEHRS spectrum of crystal violet with gold nanorods.

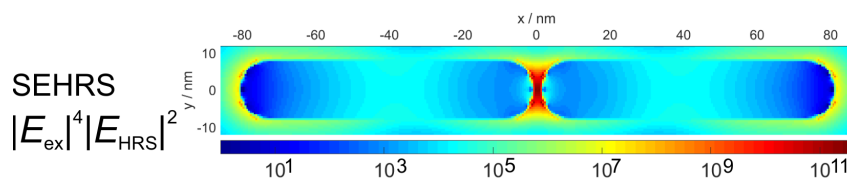


Fig. 2: Spatial distribution of the SEHRS intensity for two gold nanorods (obtained from FDTD simulations).

[1] Madzharova F, Heiner Z, Kneipp J, *Chem. Soc. Rev.* 2017, **46**: 3980.

[2] Madzharova F, Heiner Z, Kneipp J, *J. Phys. Chem. C* 2017, **121**: 1235.

[3] Madzharova F, Heiner Z, Selve S, Simke J, Kneipp J, *J. Phys. Chem. C* 2018, **122**: 2931.