

Prediction and Optimization of Surface-Enhanced Raman Scattering Geometries

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Introduction

Raman Scattering is an inelastic scattering process between a photon and a molecule. The scattered photon is shifted in frequency by the energy of the molecule's characteristic molecular vibrations. The spectral information of the Raman scattered light enables identification of the scattering molecules.

Therefore Raman spectroscopy is a commonly used tool in bio-diagnostics and sensor technology. However, the Raman scattering cross section is very small (typically $\sigma=10^{-30}\text{cm}^2/\text{molecule}$) which yields low signal strength. Therefore, much effort is made in the field of Surface-Enhanced Raman Scattering (SERS) to increase signal strength and measurement sensitivity.

It is believed that three major mechanisms are responsible for SERS [1]:

- *electromagnetic enhancement* arising from high local electromagnetic fields in the proximity of metallic nanostructures induced by plasmon resonance,
 - *chemical enhancement* due to binding of the Raman molecules to the substrate resulting in an increased scattering cross section and
 - *geometrical enhancement* in consequence of an increased surface area.
- While the chemical enhancement factors are of the order of 100, the electromagnetic enhancement can exceed values of 10^6-10^{12} and is therefore the major contributing mechanism for SERS.

To account for high electromagnetic enhancement the SERS-surfaces should

- consist of *metallic* structures, preferably gold or silver because of their plasmon resonance in the visible range and their biocompatibility,
- reveal *sharp features* and strong curvature regions which give increased enhancement because of the lightning rod effect and
- consist of *closely spaced* interacting particles which provide extra field enhancement in their interstices.

In order to gain a deeper understanding of the electromagnetic enhancement effect, COMSOL Multiphysics is used to simulate the electromagnetic fields at nanostructured metallic surfaces and to calculate the Raman enhancement factors.

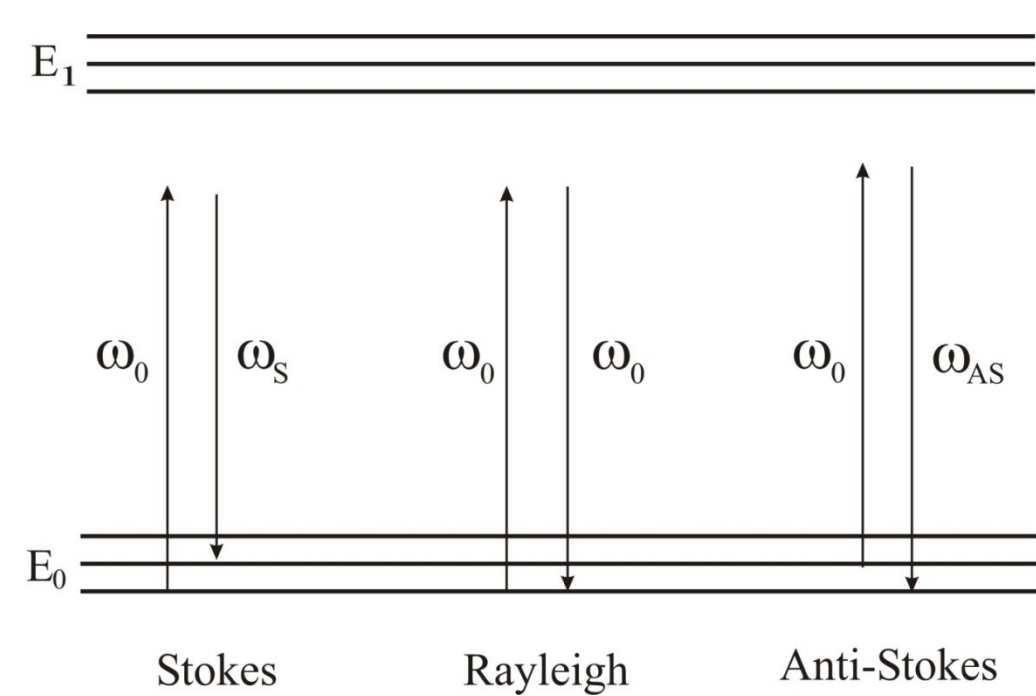


Figure 1: Schematic of Raman and Rayleigh Scattering

Model

The model is set up in the Scattered Harmonic Propagation Application Mode with periodic boundary conditions (Floquet periodicity) to simulate a unit cell of a periodically structured surface. An incident wave is introduced propagating perpendicular to the surface.

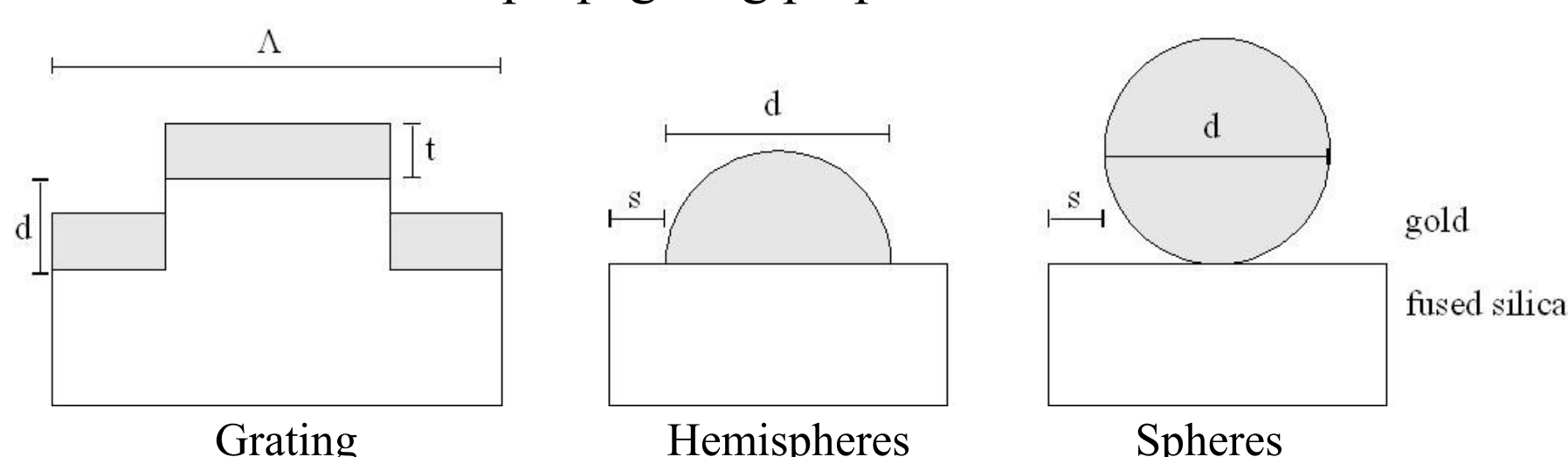


Figure 2: Models for the unit cells of the different SERS geometries

As the simulated structures are periodic in one direction, periodic boundary conditions are introduced in x-direction. Perfectly Matched Layers (PML) are used to terminate the computational domain in z-direction.

For calculation of an enhancement factor G^{SERS} , taking into account the electromagnetic and geometric enhancement, the fourth power of the E-field amplitude is integrated across the surface and normalized by the area A_0 of a corresponding unstructured surface.

$$G^{\text{SERS}} = \frac{1}{A_0} \int \frac{E_0^4}{E_{\text{loc}}^4} dA$$

This is an averaged enhancement factor assuming that the scattering molecules are distributed homogeneously across the substrate surface which is the case in many sensor applications.

Results - Gratings

The enhancement factors (figure 3) strongly depend on the incident wavelength. This is due to the *dispersion properties* of plasmons which depend on size and shape of the metal nanostructures. For wavelengths smaller than the plasmon resonance wavelength of 510nm plasmons cannot be excited and the enhancement is small. However, for wavelengths beyond 510nm the enhancements reach up to 4 orders of magnitude.

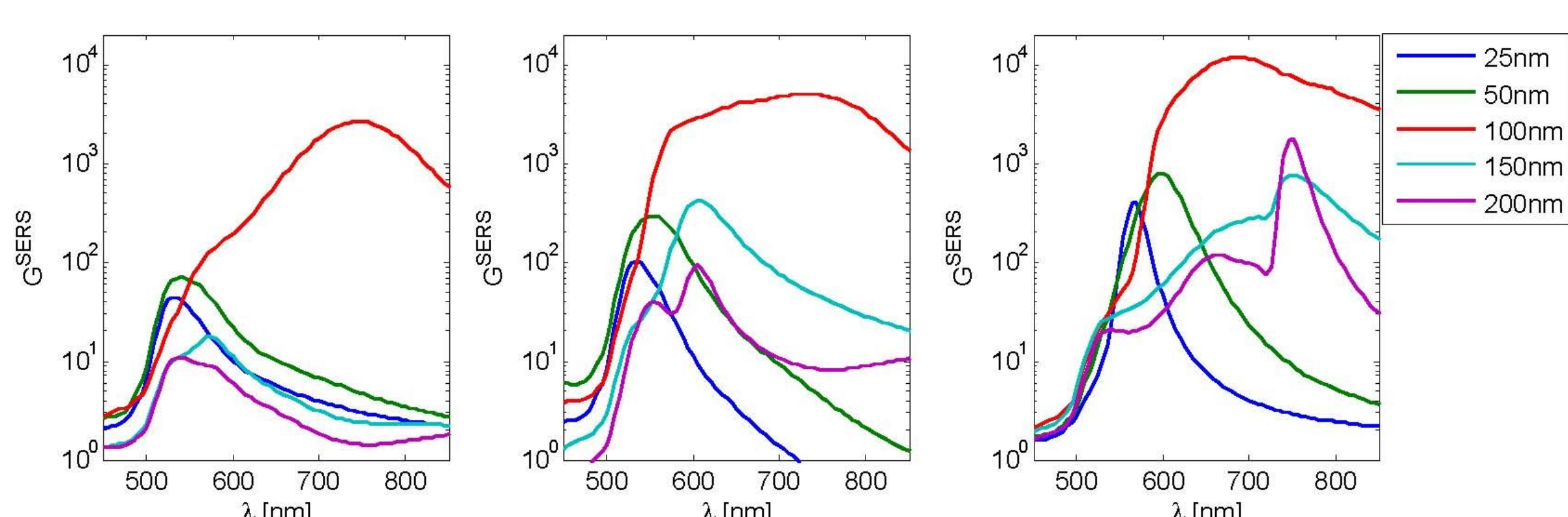


Figure 3: Modelled spectral Raman enhancement for a rectangular grating with gold layer thickness $t=100\text{nm}$, period $A=100\text{nm}$ (left), $A=300\text{nm}$ (center), $A=500\text{nm}$ (right) and varying depth between 25-200nm

The largest enhancements are achieved for a grating depth of 100nm which corresponds to the gold layer thickness. A comparison of the enhancement factors for different grating periods of constant depth shows that the *wavelength of the maximum enhancement is redshifted* with increasing period. This is consistent with the plasmon resonance redshift of single metal nanoparticles.

Spheres

Figure 4 shows a logarithmic plot of the local Raman enhancement for spheres of diameter 500nm and separation 1nm. The enhancement depends on the incident wavelength: At a wavelength of 450nm no plasmon resonance can be excited, thus enhancement is small, while for a wavelength of 670nm high near fields and large enhancement is achieved.

The averaged enhancement factors for spheres are about 4-5 orders of magnitude. Figure 5 shows the spectral Raman enhancement for different particle sizes and separations. The *wavelength of maximum enhancement is blueshifted with increasing particle separation*. The largest particles with a diameter of 500nm show multiple local maxima according to *multipole resonances* of higher orders which can be excited in large particles.

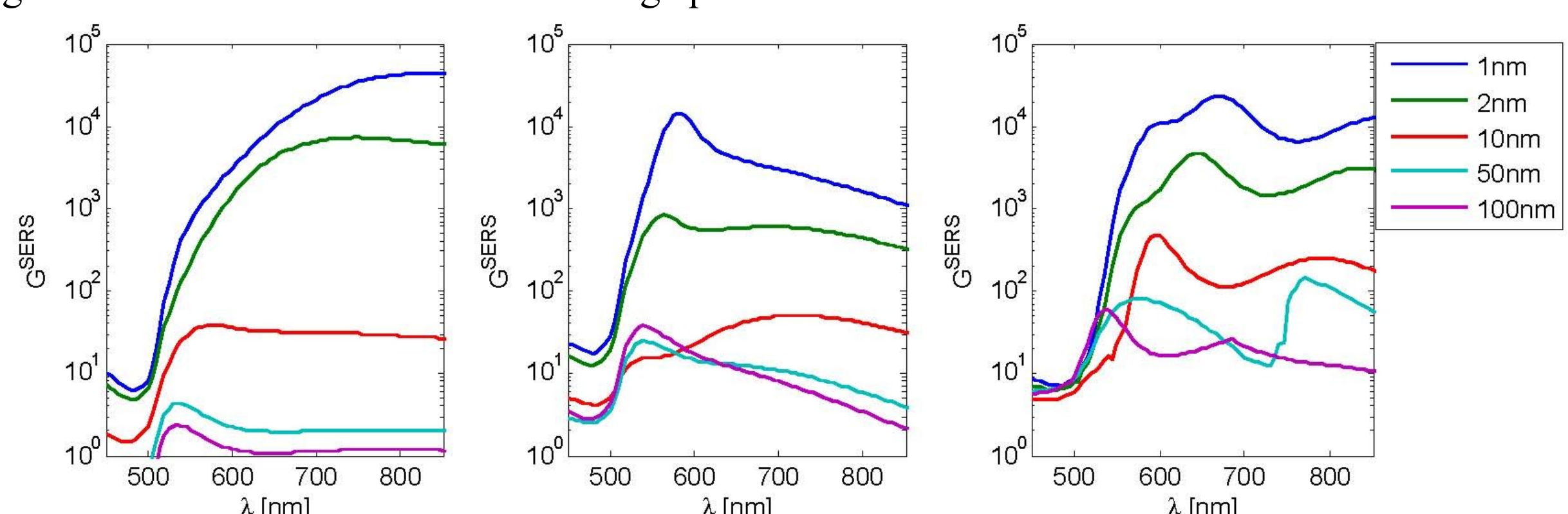


Figure 4: Logarithmic plot of the Raman enhancement for spheres with $d=500\text{nm}$ and $s=1\text{nm}$ at an incident wavelength of $\lambda=450\text{nm}$ (left) and $\lambda=670\text{nm}$ (right)

Hemispheres

Figure 7 shows the spectral dependence of the Raman enhancement for different particle sizes and separations. In general, the enhancements observed are 1-2 orders of magnitude higher than those for the spherical particles especially for larger particle sizes.

A general trend is the *strong dependence* of the predicted Raman enhancement on *feature separation*. This is illustrated in figure 6. For the hemispherical particles with a diameter of $d=25\text{nm}$ the difference between the enhancement for a separation of 1nm and 100nm is as large as 3-4 orders of magnitude.

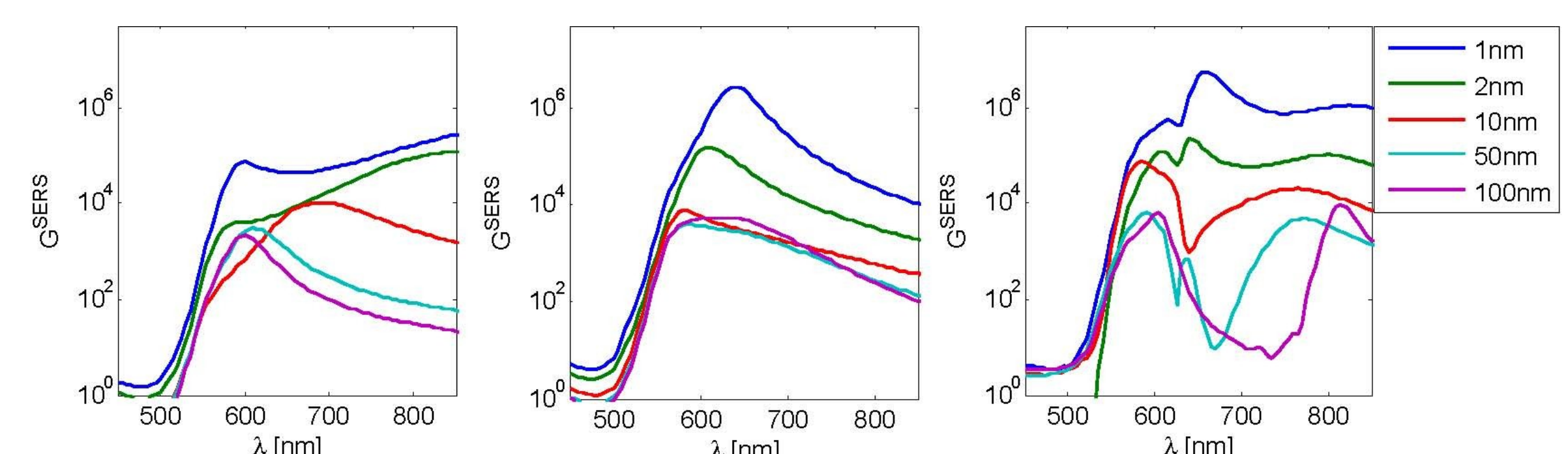


Figure 6: Relationship between Raman enhancement for spheres at an incident wavelength of $\lambda=785\text{nm}$ and feature separation for different particle diameters $d=25-500\text{nm}$

Summary

- There is a **strong dependence on wavelength** of the enhancement factors for a given geometry. This is due to the dispersion properties of plasmons which strongly depend on size and shape of the nanostructures. For wavelength below 500nm the enhancement is generally low because no plasmons are excited.
- **Small structures** do not necessarily provide the largest enhancement. The grating with the largest period results in larger enhancement factors than the other gratings, especially for wavelengths beyond 600nm.
- For spherical and hemispherical particles a **small feature separation** is crucial for high enhancements. The difference between Raman enhancements at a feature separation of 1nm and 100nm is as large as 3-4 orders of magnitude and independent on particle size.
- **Hemispheres** provide the largest averaged Raman enhancement of all geometries analyzed here.

Conclusion

The electromagnetic Raman enhancement from different metallic nanostructures - including gold coated gratings, spherical and hemispherical particles - is calculated by using the Finite-Element Method. The largest calculated enhancement is about *seven orders of magnitude*. Although many influencing factors such as the exact position of the molecules at the surface and the influence of the chemical enhancement are not known in detail, Raman enhancement from metal nanoparticles on a fused silica substrate obtained experimentally agree with the simulations within one order of magnitude.

The future aim will be to reliably predict SERS factors from a given substrate geometry and to be able to optimize the geometry of substrates with respect to their SERS enhancement.