Organization of Metal Nanoparticles for Surface Enhanced Spectroscopy: A Difference in Size Matters

Reshmi Thomas, and R. S. Swathi*

School of Chemistry, Indian Institute of Science Education and Research-Thiruvananthapuram, Kerala, India - 695016

E-mail: swathi@iisertvm.ac.in

*To whom correspondence should be addressed

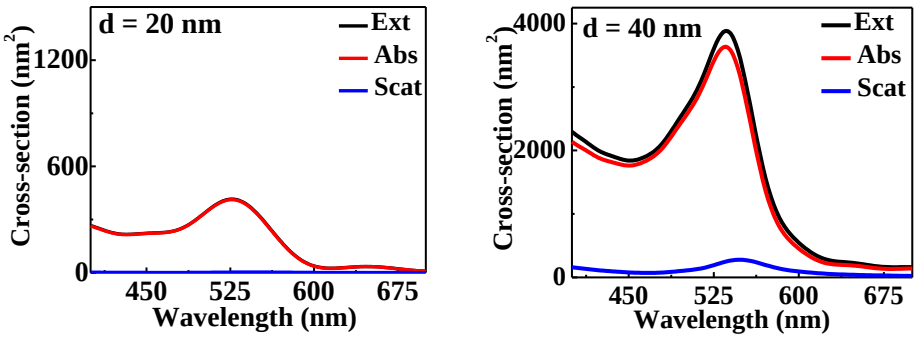

Figure S1: Simulated extinction spectra for the monomeric $d = 20\ nm$ and $d = 40\ nm$ Au NPs. Relative contributions of the absorption and the scattering to the extinction are also shown.

Table S1: SERS EFs evaluated at λ_{max} and at 633 nm for a typical probe in the vicinity of the monomeric Au NPs.

d (nm)	$\lambda_{max}(nm)$	$I(\lambda_{max})$	$I(633\ nm)$	$EF(\lambda_{max})$	$EF(633\ nm)$
20	527	23.5	13.7	5.5×10^2	1.9×10^2
40	535	36.7	19.5	1.3×10^3	3.8×10^2

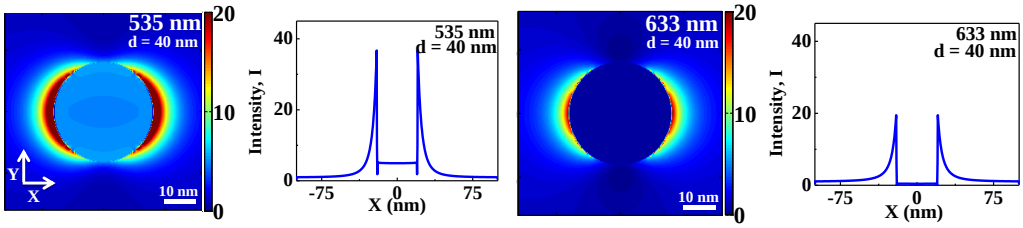

Figure S2: The electric field intensity profiles in the vicinity of the monomeric $d = 40\ nm$ Au NP at its λ_{max} and at 633 *nm*.

Table S2: SERS EFs evaluated at λ_{max} and at 633 *nm* for a typical probe in the vicinity of Au NP dimers for various gap sizes for the $\perp$ polarization of the incident light.

s (nm)	$\lambda_{max}(nm)$	$I(\lambda_{max})$	$I(633\ nm)$	$EF(\lambda_{max})$	$EF(633\ nm)$
3	524	20.3	13.1	4.1×10^2	1.7×10^2
6	525	20.6	13.5	4.2×10^2	1.8×10^2
9	527	21.8	13.8	4.8×10^2	1.9×10^2
12	527	22.1	14.0	4.9×10^2	1.9×10^2
15	527	22.3	14.2	4.9×10^2	2.0×10^2
40	529	24.1	14.9	5.8×10^2	2.2×10^2

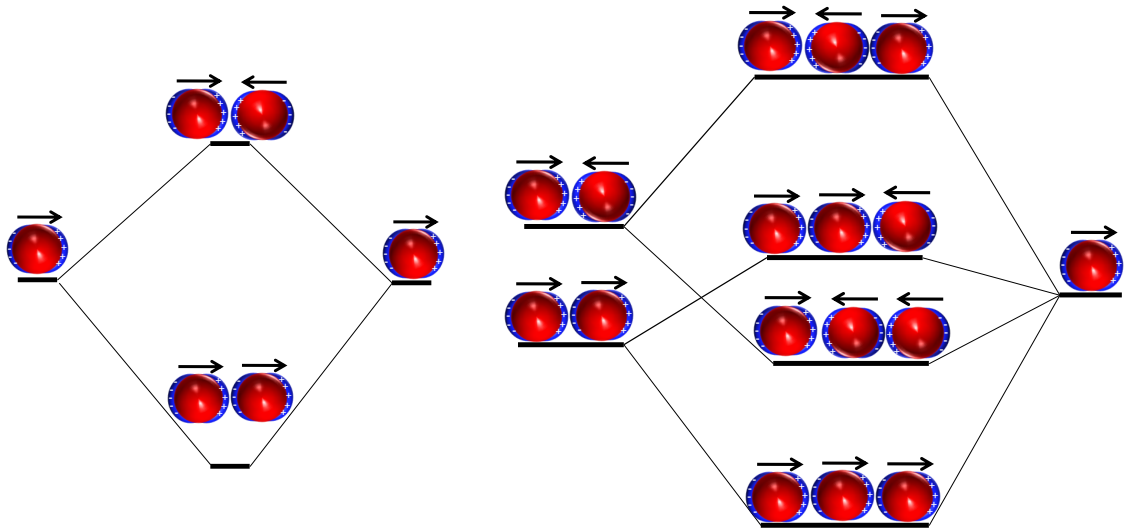

Figure S3: A schematic of the plasmon coupling in homodimers and homotrimers of metallic nanoparticles for the || polarization of the incident light.

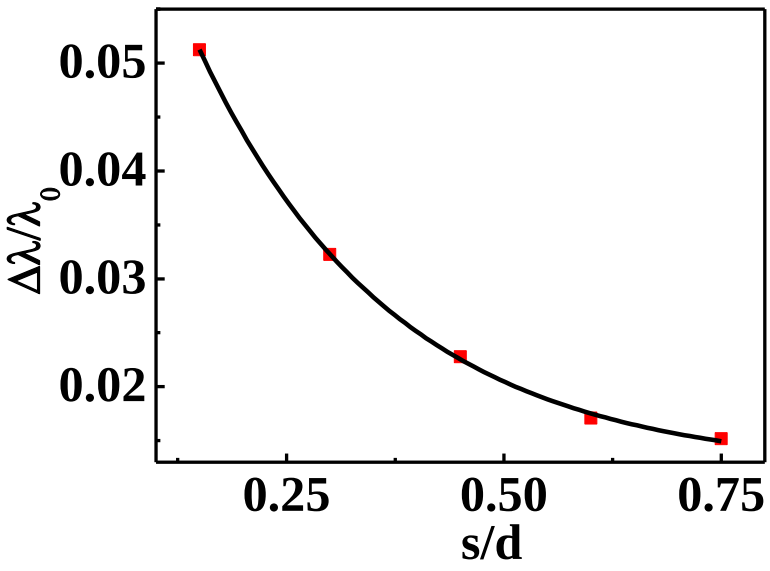

Figure S4: The fit of the extinction data of the homodimers for the || polarization of the incident light to the plasmon ruler equation.

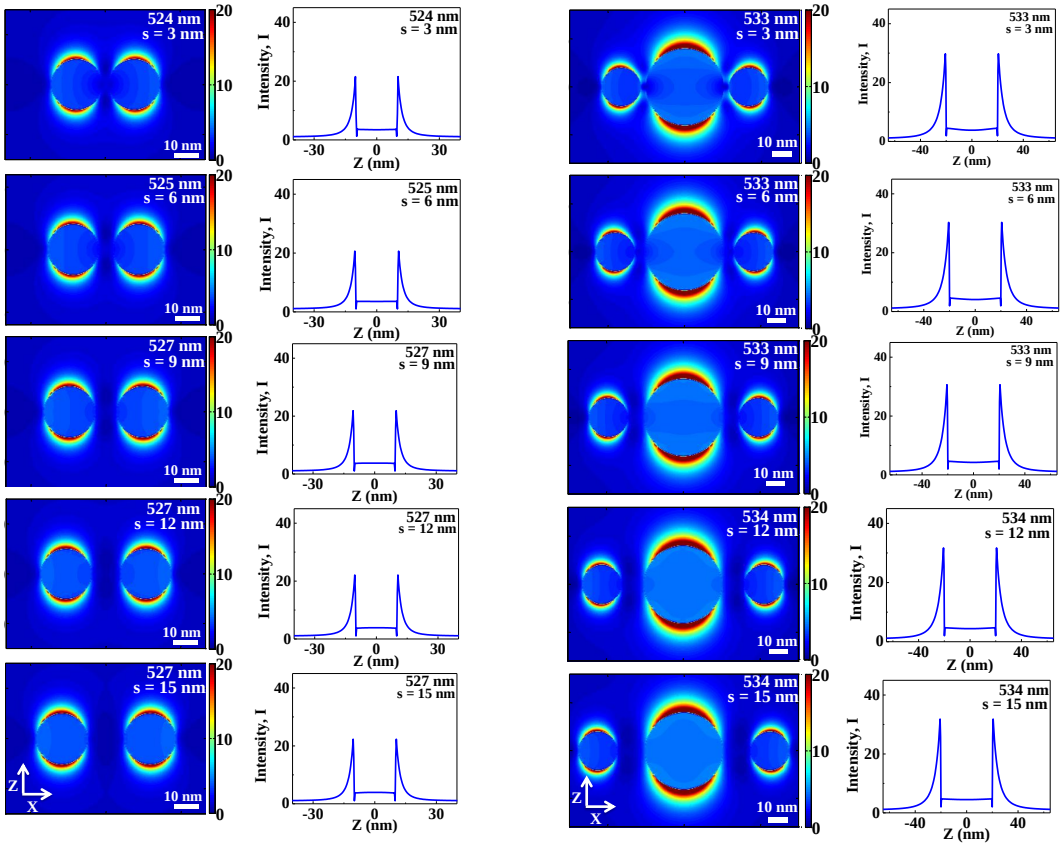

Figure S5: The electric field intensity profiles in the vicinity of the Au NP dimers and symmetric trimers at their λ_{max} as a function of the gap size for the $\perp$ polarization of the incident light. The plots of I vs Z show the cuts from the contours taken through the centers of the $d = 20\ nm$ and $d = 40\ nm$ NPs for the homodimers and the symmetric trimers respectively.

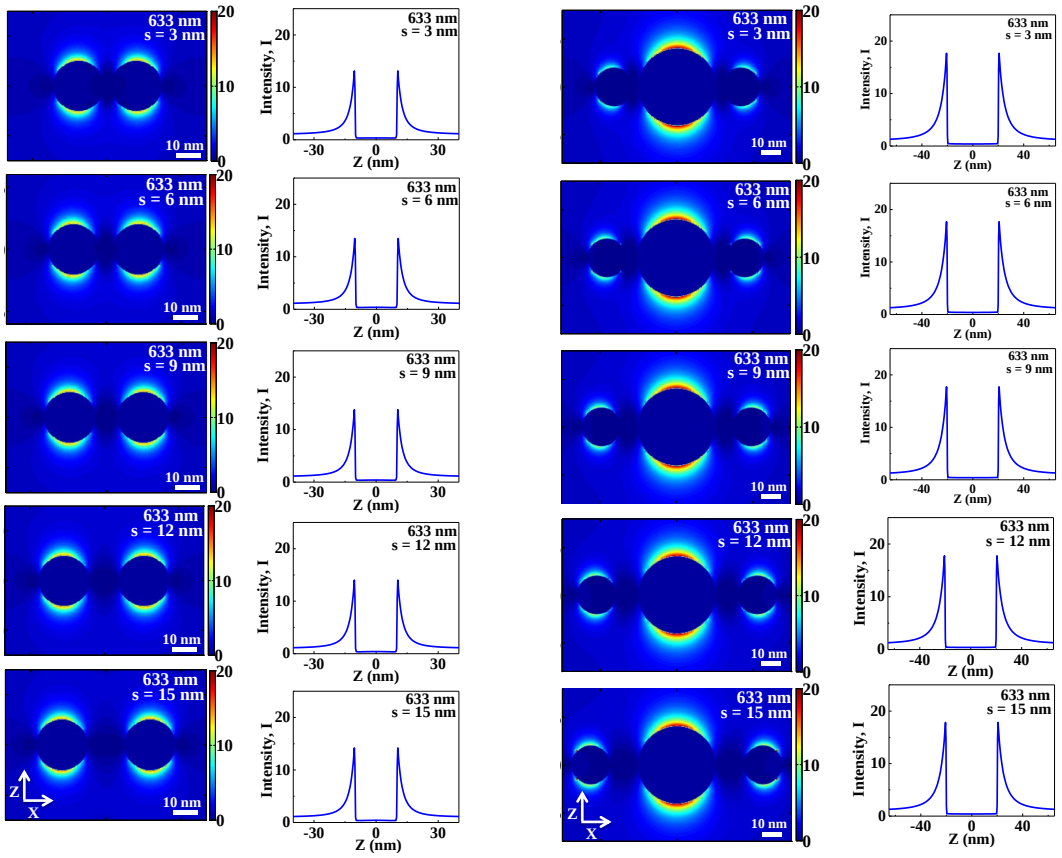

Figure S6: The electric field intensity profiles in the vicinity of the Au NP dimers and symmetric trimers at 633 *nm* as a function of the gap size for the $\perp$ polarization of the incident light. The plots of I vs Z show the cuts from the contours taken through the centers of the $d = 20$ *nm* and $d = 40$ *nm* NPs for the homodimers and the symmetric trimers respectively.

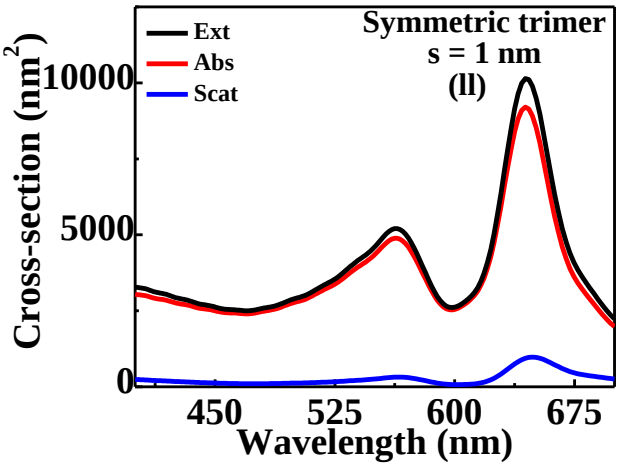

Figure S7: Simulated extinction spectrum of symmetric trimers for a gap size of $s = 1$ *nm* for the $\parallel$ polarization of the incident light. Relative contributions of the absorption and the scattering to the extinction are also shown.

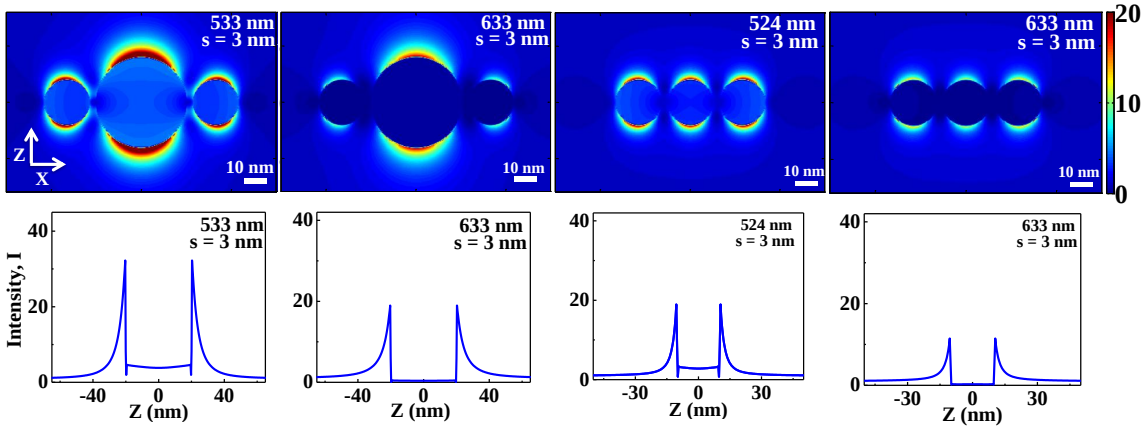

Figure S8: The electric field intensity profiles in the vicinity of the Au NP symmetric trimers and homotrimers with $s = 3$ *nm* at their λ_{max} as well as at 633 *nm* for the $\perp$ polarization of the incident light. The plots of I vs Z show the cuts from the contours taken through the centers of the $d = 40$ *nm* and $d = 20$ *nm* NPs for the symmetric trimers and the homotrimers respectively.

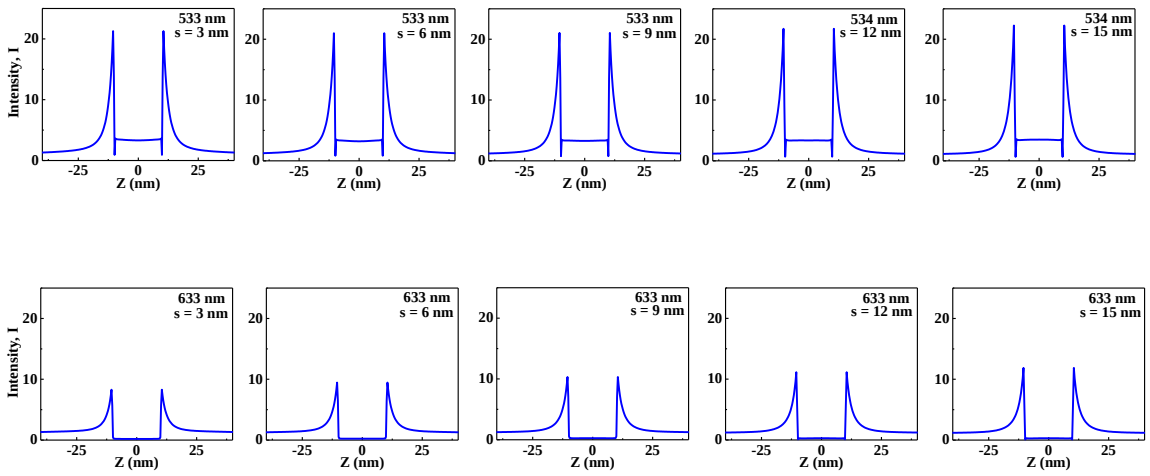

Figure S9: The electric field intensity profiles in the vicinity of the Au NP symmetric trimers for various gap sizes for the $\perp$ polarization of the incident light. The plots show the cuts from the contours shown in Figure S5 and Figure S6 taken through the centers of the $d = 20\ nm$ NPs.

Table S3: SERS EFs evaluated at λ_{max} and at $633\ nm$ for a typical probe in the vicinity of Au NP symmetric trimers for various gap sizes for the $\perp$ polarization of the incident light. Note that the intensities and the EFs are evaluated at two different locations of the symmetric trimers, namely the hottest spots and the hot spots. '*' refers to the intensities and the EFs evaluated at the hottest spots.

s (nm)	$\lambda_{max}(nm)$	$I^*(\lambda_{max})$	$I^*(633\ nm)$	$EF^*(\lambda_{max})$	$EF^*(633\ nm)$
3	533	29.8	17.7	8.9×10^2	3.1×10^2
6	533	30.3	17.7	9.2×10^2	3.1×10^2
9	533	30.6	17.7	9.4×10^2	3.1×10^2
12	534	31.7	17.7	1.0×10^3	3.1×10^2
15	534	31.8	17.8	1.0×10^3	3.2×10^2
40	536	34.1	18.1	1.2×10^3	3.3×10^2
s (nm)	$\lambda_{max}(nm)$	$I(\lambda_{max})$	$I(633\ nm)$	$EF(\lambda_{max})$	$EF(633\ nm)$
3	533	21.3	8.3	4.5×10^2	6.9×10^1
6	533	21.2	9.4	4.5×10^2	8.8×10^1
9	533	21.3	10.3	4.5×10^2	1.1×10^2
12	534	21.7	11.1	4.7×10^2	1.2×10^2
15	534	22.2	11.9	4.9×10^2	1.4×10^2
40	536	25.1	13.7	6.3×10^2	1.9×10^2

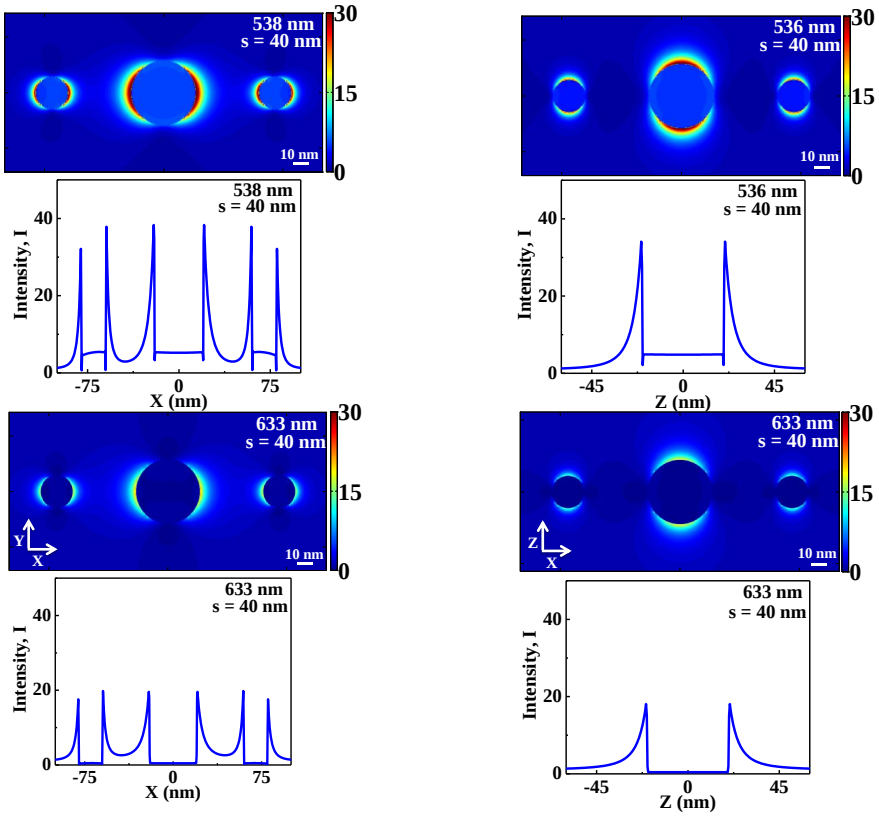

Figure S10: The electric field intensity profiles in the vicinity of the Au NP symmetric trimers for $s = 40\ nm$ at their λ_{max} and at 633 *nm* for the $\parallel$ as well as the $\perp$ polarizations of the incident light. The plots of I vs Z show the cuts from the contours taken through the centers of the $d = 40\ nm$ NPs.