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Theory of Surface Enhanced Raman Scattering from a molecule adsorbed on a cluster of metallic nanoparticles and nanoshells

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Abstract

The Raman scattering cross-section of a molecule is believed to be enhanced by more than 10 orders of magnitude when it is adsorbed on a cluster of silver nanoparticles. These large enhancements are attributed to the resonant excitation of the surface plasmon modes of the cluster.

The electric field of these plasmon modes of the metal particle cluster formed from nanospheres and nanoshells are very sensitive to the geometry. Using multiple Mie scattering in wave-vector space, we have calculated the resonant position of the enhanced electric field, for clusters of any geometry. We find the maximum enhancement in the Raman scattering cross-section can reach up to 10 orders of magnitude for silver particle clusters.

Very sharp resonant features are predicted for a linear chain of three or more particles, and is extremely sensitive to the polarization of the incident photon. These features will be helpful in identifying and fabricating SERS substrate geometries necessary for ultrasensitive detection of trace chemicals and biological cells.

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Motivation

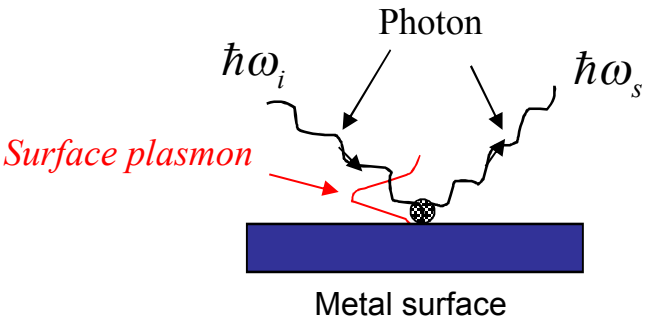
Raman spectra, rich in molecular information, enable increased molecular specificity for diagnostic applications. However, scattering cross sections are low, typically 10^{-30} cm^2.

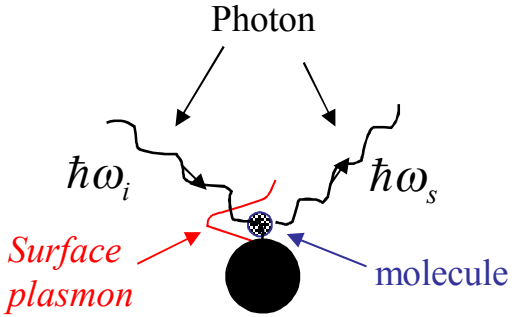
Surfaced Enhanced Raman Spectroscopy (SERS) cross sections can be as high as those of fluorescence, 10^{-16} cm^2, enabling the detection of a single molecule or cell.

The development of a mathematical model to understand and predict the optimum SERS substrate geometry will guide the direction of future fabrication of SERS based ultrasensitive chemical and cellular detectors.

Surface Enhanced Raman Scattering (1977)

The normal Raman cross-section from a molecule is enhanced by ~ 5 – 6 orders of magnitude when the molecule is adsorbed on a spherical metal (Ag, Au) nanoparticle or on a rough metal surface





This enhancement is due to the resonant excitation of the localized surface plasmon modes of the metal surface.

If the molecule lies close to the surface it experiences a large EM interaction.

Why Raman Spectroscopy and SERS?

Raman spectroscopy is a powerful tool to analyze molecular structure.

$$\sigma^{Raman} \propto \left| \frac{< g,1 \left| \vec{r}.\vec{E}(\omega_s) \right| m,1 >< m,1 \left| H_{el-vib} \right| m,0 >< m,0 \left| \vec{r}.\vec{E}(\omega_i) \right| g, v=0 >}{\left(E_m - E_g - \hbar\omega_s\right)\left(E_m - E_g - \hbar\omega_i\right)} \right|^2$$

$$\sigma^{free\ mole} \approx 10^{-30}\, cm^2 / molecule, \Rightarrow bulk\ \ sample \sim 10^{23}\, molecules / cm^3,$$

$$\sigma^{SERS} / \sigma^{free\ mole} \approx 10^6 \Rightarrow monolayer \sim 10^{15}\, molecules / cm^2,$$

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Recent SERS experiments from R6G

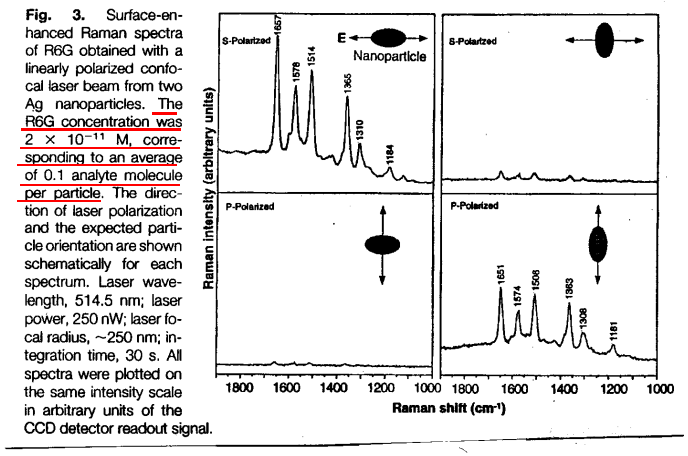

Fig. 3. Surface-enhanced Raman spectra of R6G obtained with a linearly polarized confocal laser beam from two Ag nanoparticles. The R6G concentration was 2×10^{-11} M, corresponding to an average of 0.1 analyte molecule per particle. The direction of laser polarization and the expected particle orientation are shown schematically for each spectrum. Laser wavelength, 514.5 nm; laser power, 250 nW; laser focal radius, ~250 nm; integration time, 30 s. All spectra were plotted on the same intensity scale in arbitrary units of the CCD detector readout signal.

Hot Particles

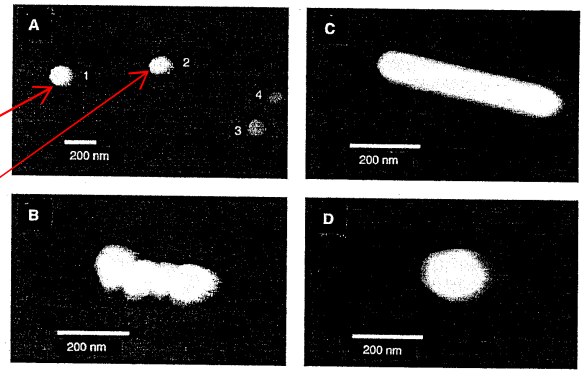

Fig. 2. Tapping-mode AFM images of screened Ag nanoparticles. (**A**) Large area survey image showing four single nanoparticles. Particles 1 and 2 were highly efficient for Raman enhancement, but particles 3 and 4 (smaller in size) were not. (**B**) Close-up image of a hot aggregate containing four linearly arranged particles. (**C**) Close-up image of a rod-shaped hot particle. (**D**) Close-up image of a faceted hot particle.

S. Nie and S.R. Emory, Science 275, 1102 (1997)
K. Kneipp et al, Chem. Rev. 99, 2957 (1999)
H. Lin et al., J. Phys. Chem. B 108, 11654 (2004)

Raman cross section becomes comparable to that of Fluorescence

$$\sigma \approx 10^{-16} cm^2 / molecule$$

and can be used for single molecule detection

$$\frac{\sigma^{SERS}}{\sigma^{free}} \approx 10^{12} - 10^{14}$$

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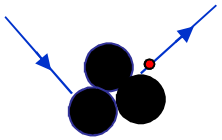
Enhanced Electric Field near a spherical nanoparticle cluster using Multiple Scattering Approach

(K. Arya, PhysRevB (74) 195438 (Nov 2006)

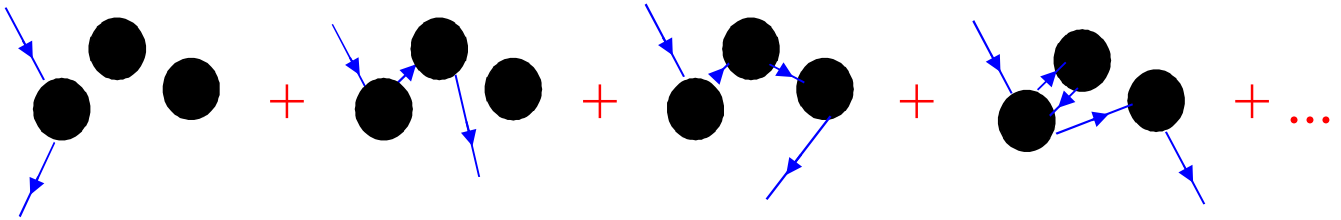
$$\vec{E}(\vec{r},\omega) = \vec{E}_{inc}(\vec{r},\omega) + \int d^3r' d^3r'' \vec{\vec{d}}^{\,0}(\vec{r},\vec{r}',\omega).\vec{\vec{T}}(\vec{r}',\vec{r}'',\omega).\vec{E}_{inc}(\vec{r}'',\omega)$$



E_{scat}

Vacuum Green function

Scattering T-matrix



$$\vec{\vec{T}} = \sum_{\alpha} t_\alpha + \sum_{\alpha,\beta} \vec{\vec{t}}_\alpha.\vec{\vec{d}}^{\,0}.\vec{\vec{t}}_\beta g(\alpha|\beta) + \sum_{\alpha,\gamma,\beta} \vec{\vec{t}}_\alpha.\vec{\vec{d}}^{\,0}.\vec{\vec{t}}_\gamma.g(\alpha|\gamma)\vec{\vec{d}}^{\,0}.\vec{\vec{t}}_\beta g(\gamma|\beta) + \ldots.$$

Single sphere scattering matrix

$$\begin{cases} = 0, \alpha = \gamma \\ = 1, \text{otherwise} \end{cases}$$

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Multiple T Matrix Scattering Theory

$$\vec{\vec{T}} = \sum_{\alpha,\beta} \vec{\vec{T}}_{\alpha\beta} \qquad \vec{\vec{T}}_{\alpha\beta} = \vec{\vec{t}}_{\alpha}\delta_{\alpha\beta} + \sum_{\gamma} \vec{\vec{t}}_{\alpha}\,\vec{\vec{d}}^{\,0}\,g(\alpha\,|\,\gamma)\vec{\vec{T}}_{\gamma\beta}$$ Tensor Integral equation

$$\vec{\vec{t}}(\vec{k},\vec{k}',\omega) = \frac{4\pi i}{k}\sum_{lm\sigma} \vec{Y}_{lm\sigma}(\Omega_k)\,c_{kl\sigma}\,\vec{Y}^{*}_{lm\sigma}(\Omega_{k'})$$ Vector spherical harmonics

Mie scattering coefficients

$$\vec{\vec{T}}_{\alpha\beta}(\vec{k},\vec{k}',\omega) = \frac{4\pi i}{k}\sum_{lm\sigma,l'm'\sigma'} i^{l'-l}(-1)^{\sigma'-\sigma}\,\vec{Y}_{lm\sigma}(\Omega_k)\,c_{kl\sigma}\,Q(lm\sigma\alpha\,|\,l'm'\sigma'\beta)\,Y^{*}_{l'm'\sigma'}(\Omega_{k'})$$

$$Q(lm\sigma\alpha\,|\,l'm'\sigma'\beta) = \delta_{ll'}\delta_{mm'}\delta_{\sigma\sigma'}\delta_{\alpha\beta} + \sum_{l_1m_1\sigma_1\gamma} B(lm\sigma R_\alpha\,|\,l_1m_1\sigma_1R_\gamma)\,c_{kl_1\sigma_1}\,Q(l_1m_1\sigma_1\gamma\,|\,l'm'\sigma'\beta)$$ Scalar matrix equation

$$B(lm\sigma R_\alpha\,|\,l'm'\sigma'R_\gamma) = i^{l-l'}(-1)^{\sigma-\sigma'}\int d\Omega_k\,\vec{Y}^{*}_{lm\sigma}(\Omega_k)\,\vec{Y}_{l'm'\sigma'}(\Omega_k)\,e^{-i\vec{k}\cdot(\vec{R}_\gamma-\vec{R}_\alpha)}\,g(\alpha\,|\,\gamma)$$

Coupling matrix

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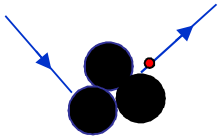
The large SERS enhancement is due to 3 factors



$$Q = \left[I - BC \right]^{-1}$$

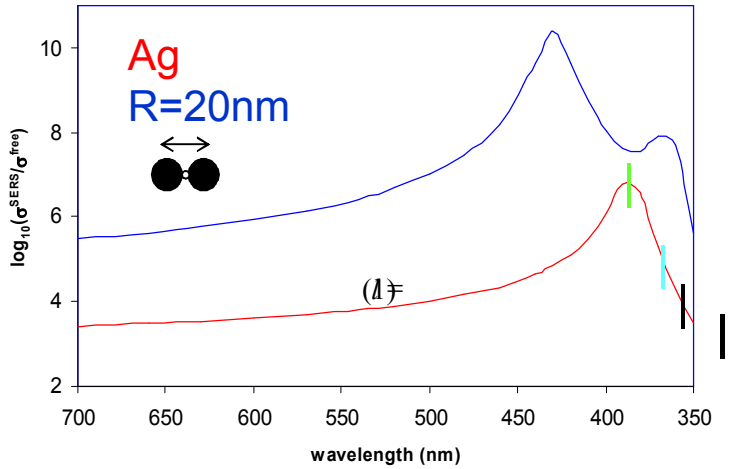
$$\vec{E}(\vec{r},\omega) = \vec{E}_{inc}(\vec{r},\omega) + \sum_{lm\sigma} \vec{A}_{klm\sigma}(\vec{r}) \sum_{l_1 m_1 \sigma_1 l'm'\sigma'\alpha\beta} B(lm\sigma 0 \left| l_1 m_1 \sigma_1 R_\alpha \right.) c_{kl_1\sigma_1} Q(l_1 m_1 \sigma_1 \alpha \left| l'm'\sigma'\beta \right.) a^{inc}_{l'm'\sigma'}(\vec{k}) e^{i\vec{k}.\vec{R}_\beta}$$

The resonant excitation of the localized surface modes of the cluster. The resonant position of these modes is given by the poles of the scattering T-matrix or poles of Q matrix and depends on the shape and size of the cluster

The probability of the excitation of these modes by the incident photon that depends on the polarization and the wavelength of the photon

The spatial distribution of the near field amplitude of these modes across the cluster

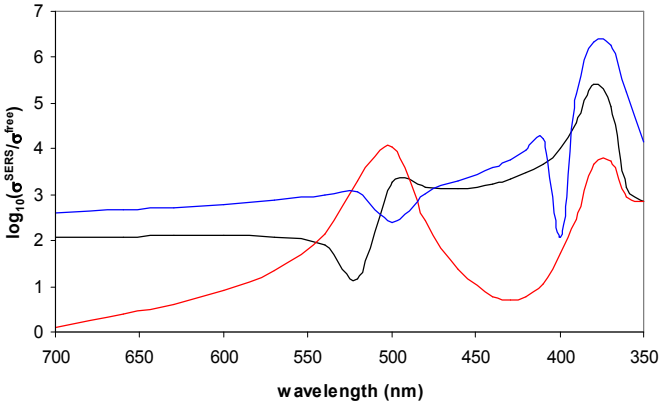
2 Particle cluster (dimer)

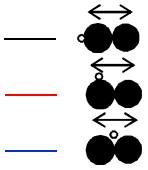


Dipole approx. (6 modes)

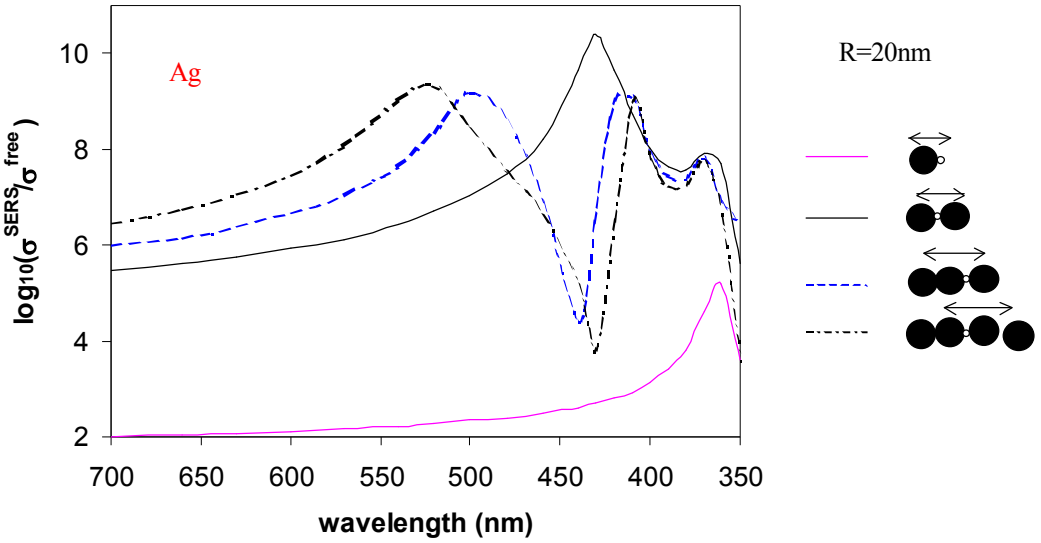
2 longitudinal

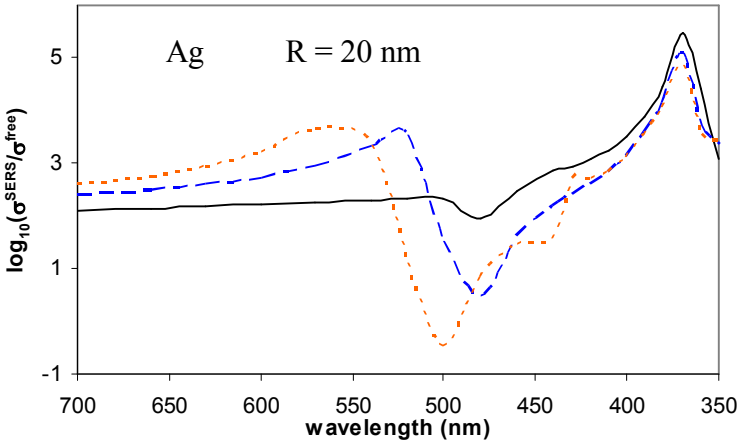
4 transverse

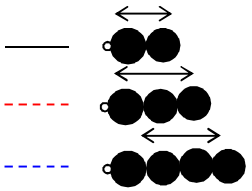




Linear chain clusters







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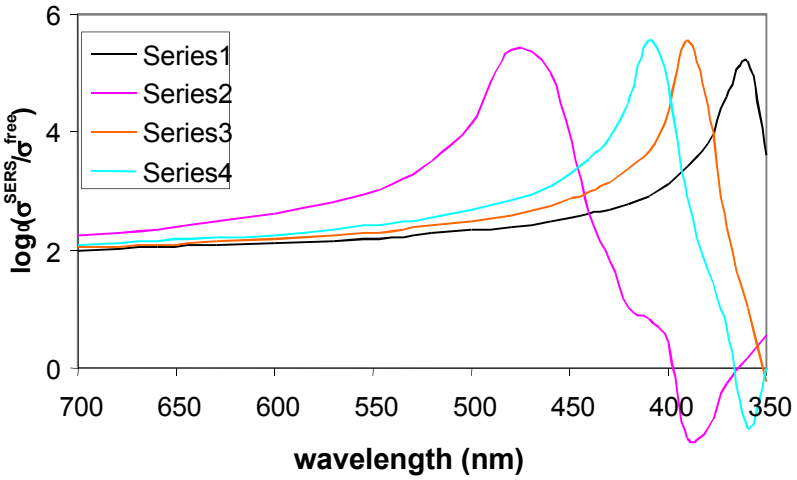
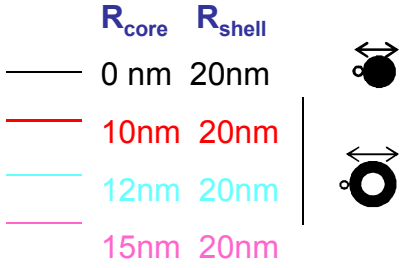
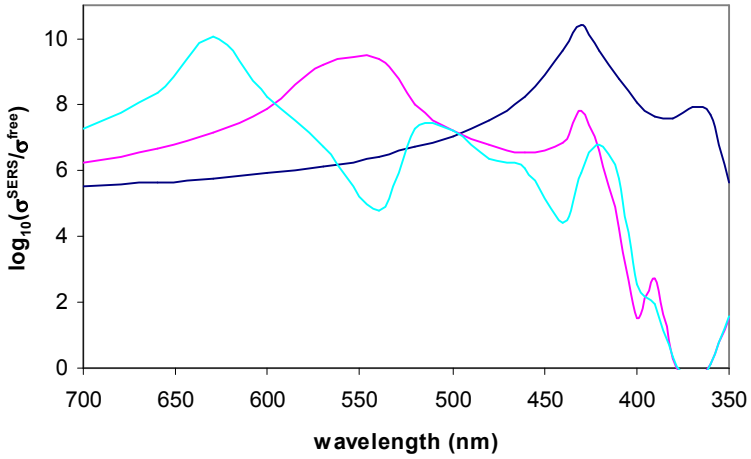
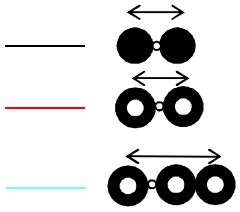
Nanoshell clusters









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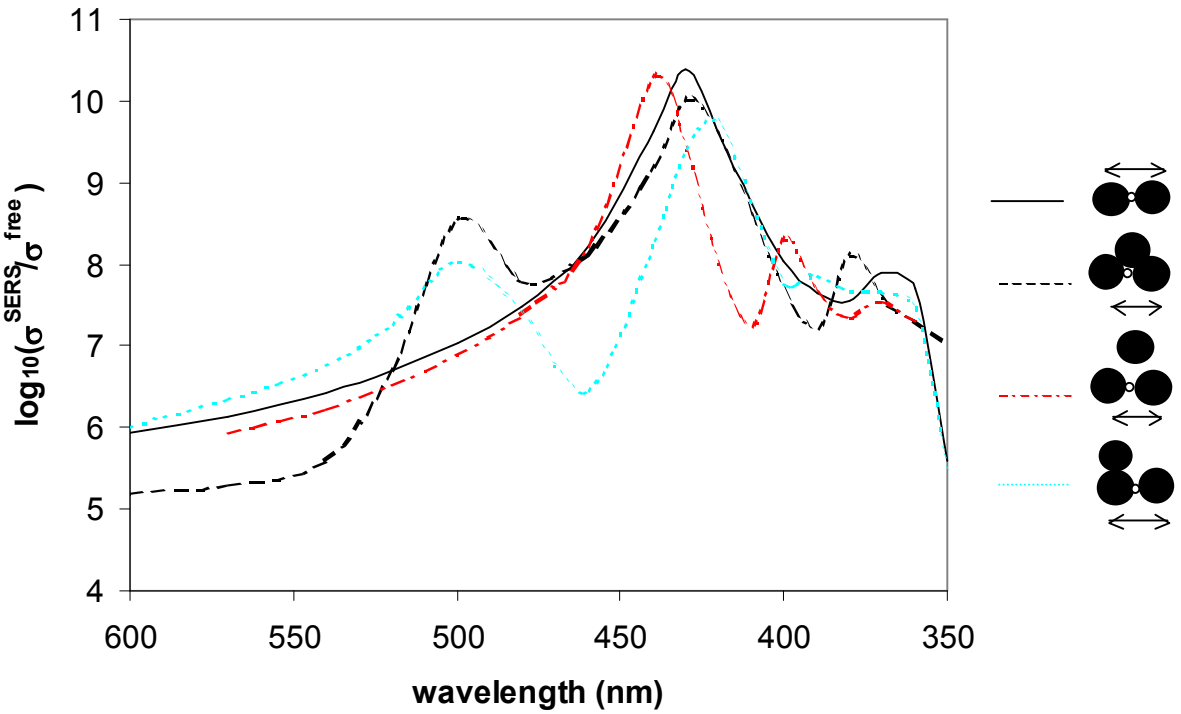
Triangular shape clusters



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Conclusions

We have developed an exact theory to calculate the localized surface plasmon modes of a single metal particle cluster and the enhanced near field using a multiple scattering approach.

This theory can be applied to any shape or size of cluster containing particles of different radii.

The maximum enhancement in Raman cross section is found to be ~ 10 orders of magnitude for a Ag nanoparticle cluster and exhibits a broad frequency range of excitation.

Future Work

Characterize SERS substrates using holographic techniques to prepare controlled particle geometries.

Apply NIR excitation and gold colloids for highly fluorescent biological and chemical samples.

Integrate Attenuated Total Reflection and SERS (ATR/SERS) to study, in real time, the growth of Self Assembled Monolayers (SAMs) on both silver and gold films.

References

1. K. Arya, Phys Rev B, 78 (2006)
2. Jackson, Classical Electrodynamics, 3rd Edition
3. S. Nie and S.R. Emory, Science 275, 1102 (1997)
4. K. Kneipp et al, Chem. Rev. 99, 2957 (1999)
5. H. Lin et al., J. Phys. Chem. B 108, 11654 (2004)

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