

Fano interference in Au nanorod clusters for localized surface plasmon resonance (LSPR) applications.

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Introdução

LSPR results from excitation of free electron collective modes on the surface of metals. Such resonances enable a vast range of applications from surface-enhanced spectroscopies, like SERS (surface-enhanced Raman scattering) to biomedicine, through the resonance sensitivity on small variations in the local dielectric constant and the possibility to use temperature increases for cancer therapy.¹ It has been shown that Fano resonances (interferences between bright and dark modes) may enhance such applications.² In this work we theoretically explore Fano (asymmetric lineshapes) resonances in Au nanorods (NRs).

Resultados e Discussão

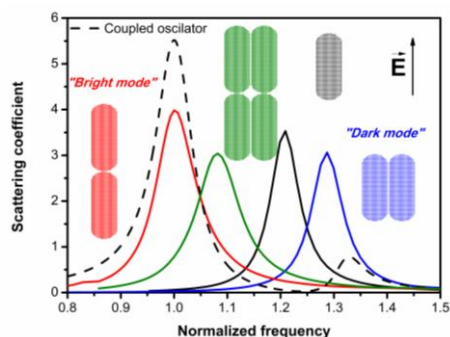


Figure 1. Scattering spectra for Au NR aggregates simulated by DDA. For 4 NRs the spectrum was divided by 4 to keep the same intensity scale.

Figure 1 shows discrete-dipole approximation (DDA) simulations for the scattering spectra of a single Au NR and aggregates with different geometries. All resonances can be described by symmetric lineshapes, indicating the absence of interactions between plasmonic bright and dark modes in such structures. An interesting fact on Au NRs is that the side-by-side (ss) aggregation leads to a decrease in the scattering efficiency due to strong charge repulsions.³ Therefore, Fano resonances can be realized from interactions between ss and end-to-end (ee) plasmon modes, differently from the common case of interference between dipolar and quadrupolar modes. This can be visualized by the coupled oscillator simulation presented in Figure 1 (dashed line), where it is clear the interference

effects on the lineshapes, specially close to the dark mode frequency. Therefore, we can expect to observe interferences in structures that contain both aggregation geometries, as it can be observed for the trimer presented in Figure 2.

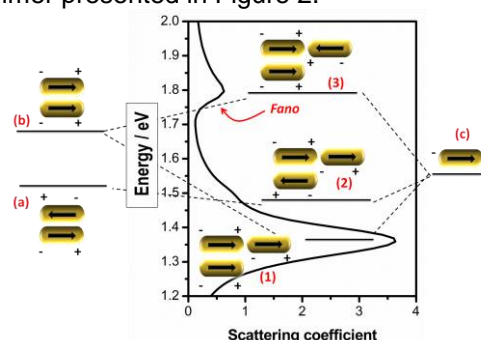


Figure 2. DDA Au NR trimer spectrum and a molecular orbital-like representation of the modes resultant from interaction between an ss dimer and a monomer.

Besides the symmetric (1) and Fano (3) lineshapes formed by interferences between (a)/(b) and (c), it is possible to observe a plasmon mode (2) resultant from the coupling between (a) and (c). In Figure 2 we also present the polarizations in each NR in the structure. As it will be shown in this presentation, the very different charge density distributions on the NRs for different modes affect the electric field distributions around the aggregate, condition that affects the local field properties for a given application, as the SERS performance.

Conclusões

In this work the mechanism of Fano interferences in the Au NRs trimer will be fully discussed, as well as its local field properties that result from dipolar bright and dark modes interferences, which may improve LSPR applications.

Agradecimentos

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¹ Ru, E. C. L.; Etchegoin, P. G. *Principles of Surface-Enhanced Raman Spectroscopy And Related Plasmonic Effects*; Elsevier, 2008.

² Baldwin, C. L.; Bigelow, N. W.; Masiello, D. J.; *J. Phys. Chem. Lett.* 2014, 5, 1347

³ Lee, A.; *et al.* Ahmed, A.; dos Santos, D. P.; Coombs, N.; Park, J. I.; Gordon, R.; Brolo, A. G.; Kumacheva, E.; *J. Phys. Chem. C* 2012, 116, 5538.