Optical properties of disordered metallic clusters

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Metallic particles of sub-wavelength dimensions separated by distances smaller than their size support strong optical resonances. Intense fields at the separating gaps characterize these resonances, which are thus of interest for SERS spectroscopy. Cucurbiturils[1] are molecular linkers that result in a very good control of the inter-particle distance providing reproducible optical properties. We study both theoretically and experimentally the optical response of clusters of gold particles separated by Cucurbiturils. The position of each particle depends on random processes, therefore we consider the effect of disorder on the optical properties[2].

We are able to experimentally monitor the behavior of gold spherical clusters as they grow in size[3]. Notably, the lower energy extinction peak considerably redshifts up to a saturation value, and the Raman Signal can strongly increase as dimers or longer chains are formed. We perform simulations using both BEM[4] and Open-Max [5] to better understand the experimental results.

We first consider the response of the clusters to be dominated by linear chains of an average length that increases with the size of the cluster. Straight linear chains of increasing length present a low energy peak that redshifts up to a saturation value[6]. This behavior helps to understand the redshift observed in the experiments. Since the chains are not perfectly straight, we consider next chains with different degree of disorder (Figure 1). Even substantial disorder affects weakly the position of the low energy peak, and only moderately its strength. The spectra of the disordered chains already reproduce much of the observed spectral behavior of the experimental clusters.

To further approach the experimental system, we consider branching clusters composed by several tens of spheres. Similarly to the measurements and chain simulations, a clear low-energy extinction peak appears at a wavelength considerably redshifted with respect to the resonance of the single sphere.

The extinction cross-section is a property of the whole cluster and it is not straightforward to extract much information about the local behavior at a particular position. To obtain this local information, we are presently looking at the near-field spectrum obtained at the gap between the particles. This near fields also allow to estimate the expected SERS signal. Initial results indicate a good correspondence between simulated and measured results. Simulations of complex clusters with well defined gap distances are thus of interest for a complete understanding of optical networks.

References

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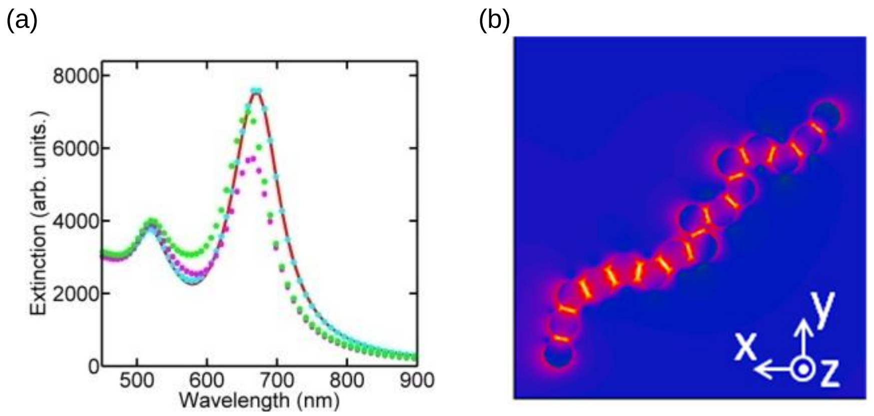
Figure 1



(a) Extinction spectra for chains composed by 16 gold spheres and different degrees of disorder. The values for a straight chain oriented along -1x+1y are plotted with a red line, while the green symbols correspond to the situation in (b). Other traces correspond to intermediate values of disorder. The sphere radius is 10nm and the separation is 0.9nm. Both the propagation vector and the E field are contained in the xz plane, making a 45 degree angle with the z axis.