# Linear chains as optical building blocks of complex metallic clusters

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Self-assembled clusters formed by metallic particles usually show clear plasmonic resonances, with hot-spots characterized by very intense local fields [1]. These aggregates are of particular interest for surface enhanced Raman spectroscopy (SERS), which relies on the strong increase in the Raman signal emitted by a molecule when placed in a hot-spot. Here we study gold clusters glued by cucurbiturils, a macrocyclic molecule that acts as a linker between particles in the aggregate, setting the gap-distance between contiguous particles to approximately 1nm [2]. In contrast with other self-assembled systems, the interparticle distance is not only very small but it also presents relatively little variability between different gaps. Furthermore, the cucurbiturils may also serve as a cage that captures a molecule under investigation at the positions between particles where the hot-spots are created. Such clusters show reliable and systematic optical properties and lead to clear Raman signals from gold particles of different sizes.

Clusters of metallic particles linked by cucurbiturils are thus a promising system for Raman spectroscopy of molecules. We focus our study on aggregates in solution presenting diffusion-limited growth and formed by gold spheres of fixed diameter, but other alternatives are possible. The diameter varies between clusters from 10 to 60 nm. We present experimental results of the optics of such clusters and interpret the phenomena observed using a simple model based on the optical activation of linear chains of particles within the cluster [3-6].

Notably, our experimental set-up allows for real time measurement of the extinction spectra and SERS signal, and thus for gaining information on the dynamics of the aggregation process and how it affects the plasmonic response. In general, we observe a redshift of the lowest energy extinction peak that eventually reaches saturation. The exact results, however, depend on the diameter considered. Smaller particles lead to significantly weaker redshifts. Further, the number of particles in the cluster that optimizes the SERS signal also depends on the diameter of the spheres.

Our simulations [3-5,7-8] help to interpret the optical measurements. We consider complex clusters of up to 100 spheres, and observe how they support various resonances at different wavelengths, preferentially affecting different subunits of the full structure: at larger frequencies dimers and short chains modes are excited at the periphery of the cluster, while at larger wavelengths long chains modes are present, often located in the interior of the structure[4]. The measured and calculated extinction spectra are similar, which gives confidence on the validity of the particular simulations of aggregates to model the experimental situation. It is possible to identify in the spectra measured two different contributions [3] that can be associated with the dimers and long chains modes observed in the simulations.

These results supports the validity to model the optical response of the aggregate as that of a composite of linear chains of different length [4,5,9]. The description of the clusters in terms of simple chains does not only explain qualitatively the nature of the different modes supported by the structures, but it also allows for understanding the observed redshifts. Moreover, based in this description we have developed a simple semi-analytical composite dipole model (CDM) [5] to gain information about the experimental clusters otherwise difficult to obtain. The CDM gives an effective length of the long chain modes and an effective proportion of spheres that contribute to this long chain resonance.

Last, we use the calculated behavior of straight chains to better understand the Raman measurements of complex clusters. When a fixed laser is used as excitation, both theory and experiments indicate that it is generally favorable for SERS to select structures of a particular size that results in the excitation of

the lowest energy mode by the illumination wavelength. The optimal size depends on the diameter of the spheres, due to the different redshifts pointed out above. More interesting from a theoretical perspective is the case when the excitation wavelength is not fixed, but can be tuned to maximize the Raman signal for a particular size of the structure and particle diameter. In this case, chain simulations show that there is still an optimal length [10] that depends on the diameter, with long chains being favorable for the smaller particles, and short chains or even dimers for the larger ones. We explain this observation by a simple model that considers a radiative correction, which significantly increases losses for long chains of large particles. This effect should also be important to explain the experimental optics of clusters.

**References**


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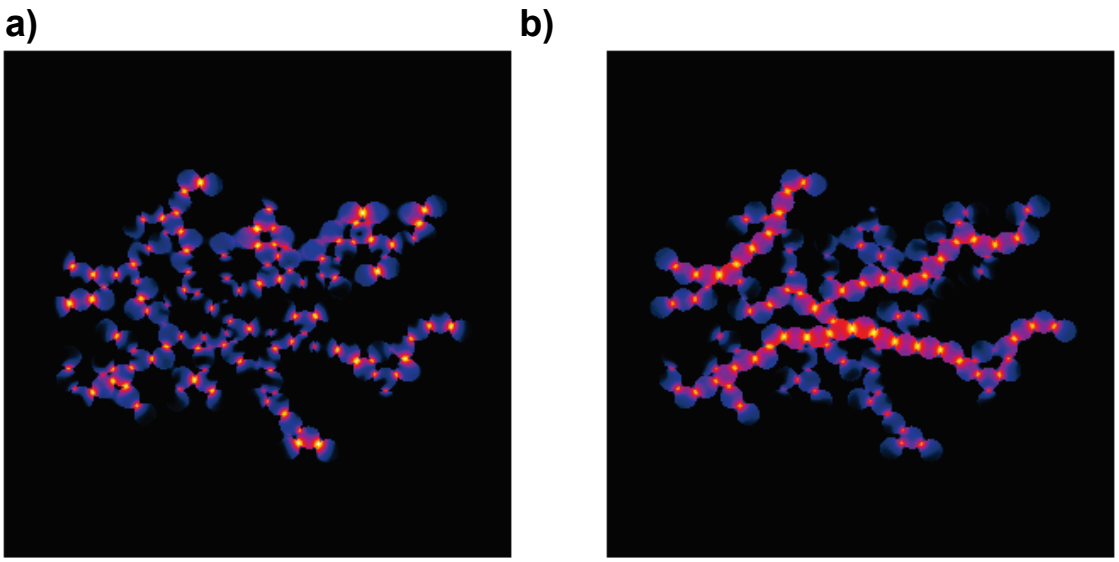
**Figures**




Displacement field D on a 2-dimensional aggregate of 100 spheres of 40nm diameter, illuminated by a plane wave at a wavelength of a) 645nm and b) 850nm. Strong fields extend over considerably longer chains for the larger wavelength, while they are mostly confined to dimers and small chains at the periphery of the aggregate for the larger energy. Logarithmic scale is used for the color scale.