Spectral signature of molecular linkers in plasmonic cavities

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In the last decade fundamental advances have been achieved in the fields of molecular electronics [1] and plasmonics [2]. In particular, the optical properties of plasmonic dimers with different shapes have been deeply studied and explained using exact numerical calculations and hybridization models [3]. Recent experiments, such as the simultaneous measurements of electronic conduction and Raman spectroscopy in molecular junctions [4], have suggested the possibility of sensing individual molecules, connecting both fields.

Following this emerging connection, we related optical properties to transport processes in a recent letter using a model consisting of a conductive bridge linking two gold nanoshells [5]. For the sake of simplicity, we modelled the linker as a pure conductor with real conductivity so that the variation of conductivity affected only the imaginary part of the dielectric function characterizing the junction. Now, boosted by the recent interest in molecular switches [6], we have improved this simple model to make it more realistic. In this work, we study the effect on the optical response of a molecular junction bridging a gold nanoparticle dimer, where the dielectric response of the junction is characterised by a Lorentz model, which takes into account the resonant frequency ω_0 of the linking molecule. In this work, both the real and imaginary parts of the dielectric function characterizing the junction are affected by the nature of the linker.

As a first step, we have considered junctions with transition frequency ω_0 = 1.51eV - (λ_0 = 820nm), corresponding to rotaxane molecules [6]. Fixing the radius of the gold particles (R = 50nm) and the separation distance between them (d = 1nm), the plasmonic resonance of the disconnected dimer is found at λ_p = 665nm, below the transition wavelength of the molecular linker. Then, we connect the gold particles with a cylindrical molecular region of radius a mimicking the molecules, and we observe the evolution of the far-field and near-field properties of the whole system as the bridge becomes wider. Electromagnetic fields and optical extinction spectra are obtained by solving Maxwell's equations exactly with the Boundary Element Method (BEM) [7].

Figure 1(a) shows the evolution of the optical extinction spectra of our system as the radius of the molecular junction is increased up to 35 nm. As for the pure conductor, we observe that the Bonding Dimer Plasmon (BDP) mode, arising from the coupling between the dipole modes of the individual nanoparticles (initially found around λ_{BDP} = 665nm), is slightly blue-shifted as the radius of the linker is increased. In contrast to our previous study, for longer wavelength values, in addition to the appearance of a Charge Transfer Plasmon (CTP) mode around λ_{CTP} = 970nm, where a real charge transfer between the particles occurs, we also observe the emergence of a new resonance between the BDP and the CTP modes.

For small molecular junctions, in contrast to the pure conductor case, where the CTP mode vanishes with a dramatic red-shift towards longer wavelength values as size is decreased, the CTP mode disappears slightly blue-shifting as the linker size is reduced. These BDP and CTP resonances are prominent for small sizes of the molecular linker, whereas the new resonance gains spectral weight dramatically as the linker size is increased, suggesting a strong influence of the molecular transition in the optical behaviour of the system. The nature of the three different resonances described above is analyzed with the help of near-field contour plots.

The results are generalized to consider molecular linkers presenting different resonances in the range of λ_0 = 400-1200 nm (Figure 1(b)). In this case, where we have fixed the radius of the molecular linker to 5 nm, we observe that the position of the BDP remains unaltered, whereas its intensity is stronger for longer λ_0 values. In contrast, the CTP mode presents a parabolic red-shift and loss of spectral weight as the resonance of the connecting molecules λ_0 is found at longer wavelength values.

We believe that the study of this kind of spectral changes in plasmonic cavities connected by molecular linkers might lead to control the switch on and off of the different emerging plasmon modes.

References

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Figures

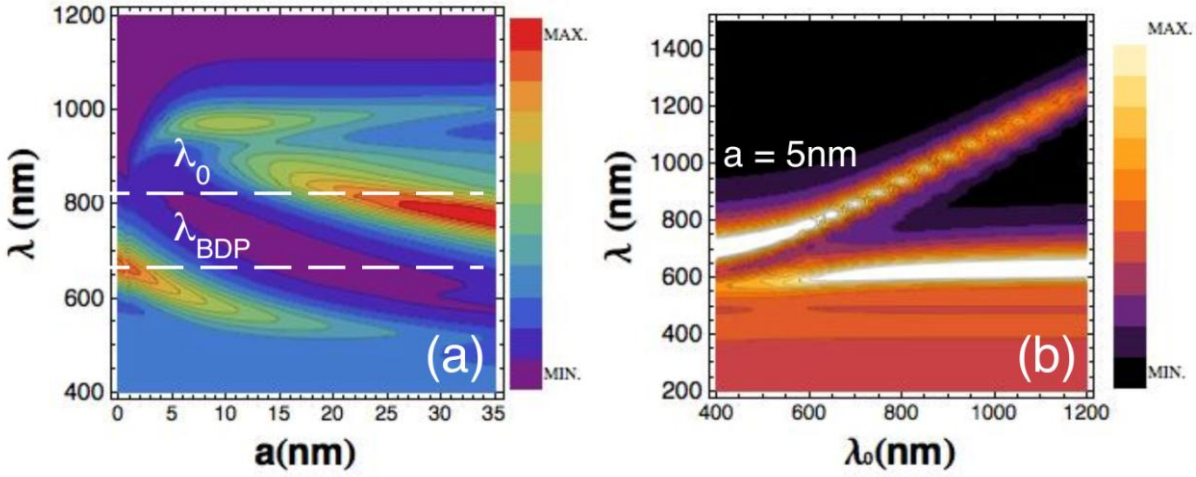

Figure 1: (a) Evolution of the optical extinction spectra of a molecular junction bridging a gold nanoparticle dimer as the radius of the molecular linker a is increased. The dashed lines indicate the spectral position of the considered molecular transition at 1.51eV (λ_0) and the initial spectral position of the BDP mode (λ_{BDP}), which also appears when the dimer is disconnected. (b) Plasmonic resonances of a gold nanoparticle dimer connected by a molecular bridge of radius a = 5 nm formed by different molecules, as a function of their resonance wavelengths.