Optical spectroscopy of conductive molecular junctions 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 adjacent nanoshell pairs have been explained using exact numerical calculations and hybridization models [3]. Recent simultaneous measurements of electronic conduction and Raman spectroscopy in molecular junctions have suggested the possibility of sensing individual molecules [4], connecting both fields.

We study theoretically this connection between molecular electronics and plasmonics in a model system composed of a conductive molecular junction bridging two nanoshells. The nanoshells are formed by a silica core surrounded by a gold shell and the molecular junction is modelled as a cylinder of radius a linking both nanoshells. The conductivity of the junction, σ, is related to conductance, G, through the geometrical parameters of the system. So, for a given size of the linker, we modify the conductivity of the junction varying the number *n* of quanta of conductance, nG_0 ($G_0 \equiv 2e^2/h \cong 77.5$mS). Maxwell's equations are solved via a boundary element method (BEM) [5] to obtain the electromagnetic fields and the optical extinction spectra.

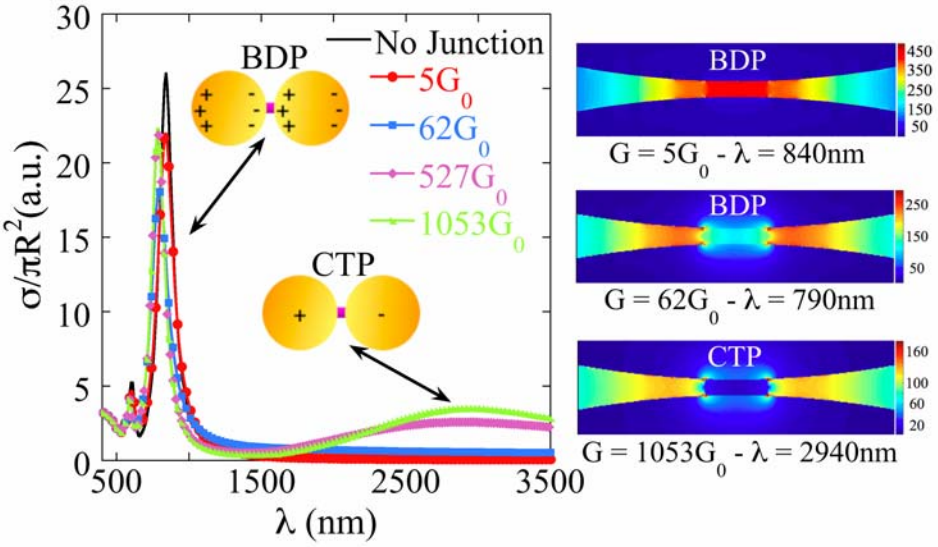

Figure: (*Left*) - Optical extinction spectra of a nanoshell dimer bridged by a conductive molecular junction of radius a = 2nm, as conductivity is increased via the increment of conductance. We can observe the variations in the behaviour of the plasmon resonance (BDP) and the appearance of the new resonance (CTP) in the IR part of the spectrum. (*Rigth*) - Near-fields patterns corresponding to the short wavelength regime (*up and*

medium) and to the long wavelength regime (*down*), where the progressive expelling of the electric field out of the junction can be observed.
We find two regimes in the optical response (see Figure). For the short wavelength regime, we first notice a broadening of the plasmon resonance as conductance is increased until a saturation point is reached. Then, a slight blue-shift takes place and the plasmon resonance becomes narrower again. We call this resonance the Bonding Dimer Plasmon (BDP). For the long wavelength regime, when conductance takes small values, there is no appreciable change. However, for very large values of conductance, a new highly red-shifted resonance appears. We call this resonance Charge Transfer Plasmon (CTP) and its main feature is its tunability.

We believe that the study of spectral changes in plasmonic cavities might serve as a probe of molecular conductance and transport in the visible, a regime not accessible through electrical measurements.

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