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 system composed of a molecular junction bridging a plasmonic cavity. More explicitly, we relate transport and optical properties through a model system consisting of a conductive bridge linking two gold 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 its conductance, G, through the geometrical parameters of the system. Therefore, for a given size of the linker, we modify the conductivity of the junction varying the number n of quanta of conductance, nG_0 ($G_0 \equiv 2e^2/h \cong 77.5\text{mS}$). Maxwell's equations are solved via a boundary element method (BEM) [5] to obtain the electromagnetic fields and the optical extinction spectra.

We find two regimes in the optical response (see Figure 1). For the short wavelength regime, we first notice a broadening of the plasmon resonance as conductance is increased, followed by a slight blue-shift until a saturation point is reached. Then, the resonance becomes narrower again as conductance continues to be increased but its wavelength remains unaltered. We call this plasmon resonant mode the Bonding Dimer Plasmon (BDP). For the long wavelength regime, there is no appreciable change when conductance takes small values. However, for very large values of conductance, a new highly red-shifted resonance emerges. We call this resonance the Charge Transfer Plasmon (CTP) and its main feature is its tunability.

We use a simple resistor model to explain both the initial decrease of the optical extinction intensity of the BDP and its progressive recovery for further increase of the conductance. We also notice a slight blue-shift which corresponds to a screened Coulomb interaction at the junction between the gold shells. Moreover, we identify a threshold value of the conductance when the optical properties of the junction start being affected by the transport properties. This threshold conductance relates the time of flight of the electrons involved in the transport process with the time of the optical cycle of the plasmonic resonances of the cavity.

We believe that the study of this kind of spectral changes in plasmonic cavities might serve as a probe of molecular conductance and transport processes in the visible part of the spectrum, a range which is not accessible through electrical measurements.

References

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Figures

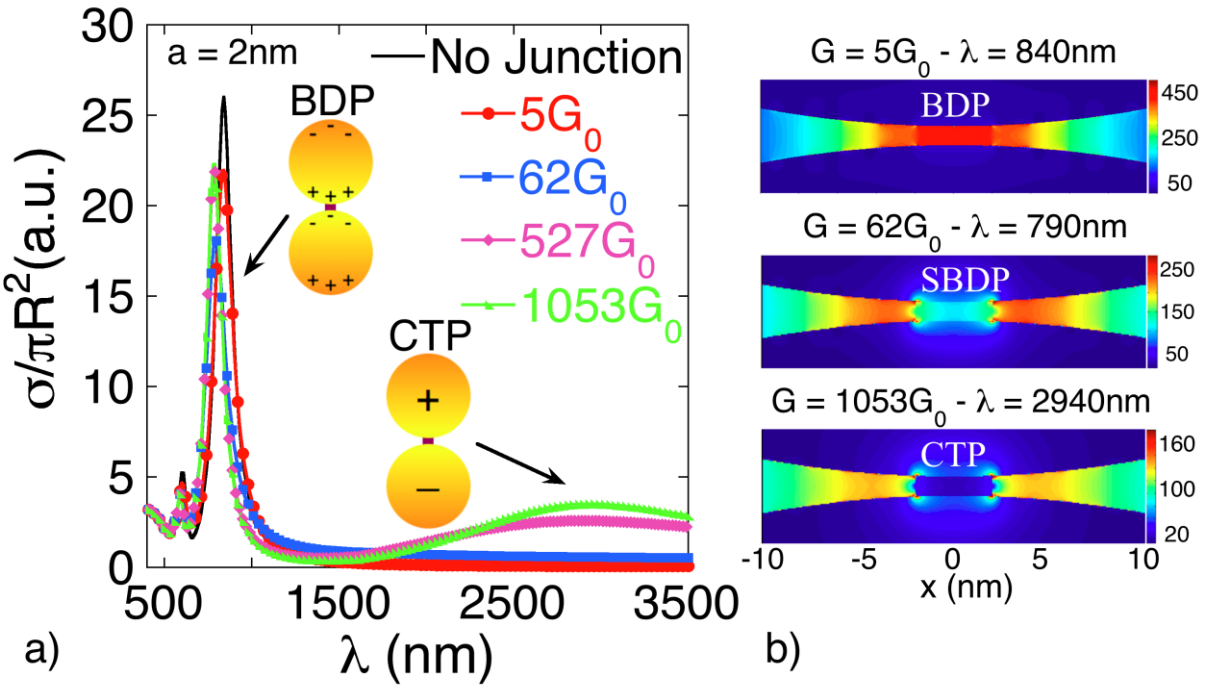

Figure 1: (*Left*) - Optical extinction spectra of a nanoshell dimer bridged by a conductive molecular junction of radius a = 2nm as conductivity is increased via the increment of conductance. We can observe the variations in the behaviour of the plasmon resonance (BDP) and the emergence of the new resonance (CTP) in the IR part of the spectrum. (*Rigth*) - Near-fields patterns corresponding to the short wavelength regime (*top and middle*) and to the long wavelength regime (*bottom*), where the progressive expelling of the electric field out of the junction can be observed.