Plasmon-exciton coupling and charge transfer plasmons in metallic cluster dimers

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Recent results have shown that atomistic ab-initio methods allow for an accurate description of the coupling between metallic clusters and molecules, capturing the physics of their plasmonic response [1]. We have studied the optical spectra of porphyrin molecules coupled to silver cluster dimers, using the ab-initio SIESTA [2] software to obtain the ground-state of the system, and the linear-response TDDFT code PyNAO [3] to compute the optical excitations. The results show the emergence of a Fano spectral line in the absorption spectra near the plasmonic resonance, a characteristic feature of the weak light-matter coupling regime. The strength of this coupling is very dependent on the geometric features of the system, such as the separation between the clusters or the orientation of the molecule. Our simulations also reveal the existence of a Charge Transfer Plasmon at lower frequencies for the smallest nanocavity sizes. These states are predicted to emerge when a molecular energy level is resonant with the Fermi level of the clusters [4]. By applying a shift of the local potential around the atoms belonging to the molecule, we control the energies of the molecular level relative to those of the metal clusters, allowing for the tuning of the strength of the charge transfer modes.

References

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[3] P. Koval, M. Barbry, and D. Sánchez-Portal, Computer Physics Communications, 236, (2019), 188.

[4] V. Kulkarni and A. Manjavacas, ACS Photonics, 2, 7, (2015) 987.

Figures

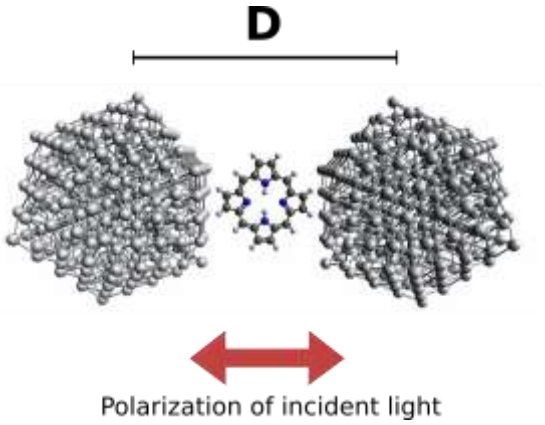

Figure 1: Atomistic structure of the studied system. It is composed of two Ag_{309} clusters with a 2,3-Dihydroporphyrin molecule placed in the gap between them.

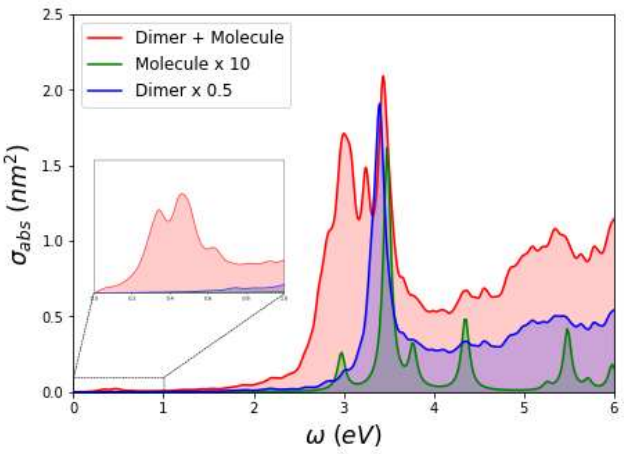

Figure 2: Absorption spectra of the bare silver dimer (blue), the bare single molecule (green), and the complete dimer and molecule system (red). The inset shows the Charge Transfer Plasmon emerging at low frequencies.