First-principles study of plasmon-molecule coupling in metallic cluster dimers

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Metallic clusters behave as nanoscale plasmonic resonators, and can serve to build up optical cavities where light is amplified and localized into nanoscale volumes. When an emitter, such as a molecule, is placed in a cavity formed by a cluster dimer, the optical response of the whole system depends greatly on the atomistic shape and relative orientation of both the clusters and the molecule [1, 2]. Atomistic ab-initio methods allow for an accurate description of the coupling between clusters and molecules, capturing the physics of the plasmonic response [3]. We present preliminary results of the atomistic optical spectra of porphyrin molecules coupled to silver nanodimers, using the ab-initio SIESTA [4] software to obtain the ground-state of the system, and the linear-response TDDFT code PyNAO [5] to compute the optical excitations. The results show the emergence of a Fano spectral line in absorption spectroscopy near the plasmonic resonance, a characteristic feature of the weak light-matter coupling regime. The strength of the coupling varies drastically with the gap geometry, as well as with the orientation of the molecule. Moreover, our simulations also reveal the existence of a Charge Transfer Plasmon at lower frequencies.

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FIGURES

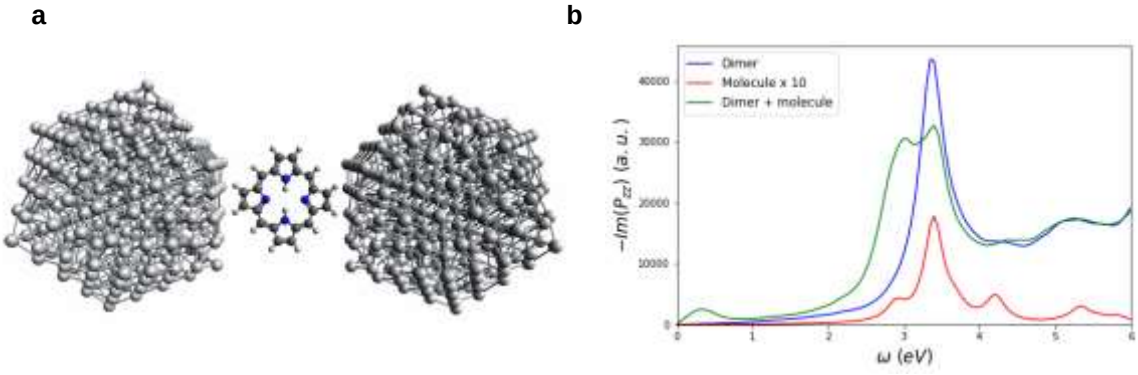

Figure 1: a) Atomistic structure of the studied system, composed of two Ag309 clusters with a 2,3-Dihydroporphyrin molecule placed in the gap between them. **b)** Imaginary part of the optical polarizability along the dimer axis direction for the bare silver dimer (blue), the bare single molecule (red), and the coupled dimer and molecule system (green).