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

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INTRODUCTION

When an emitter, such as a molecule, is placed in a cavity formed by a cluster dimer, the resulting coupling strongly modifies the optical response of the system.

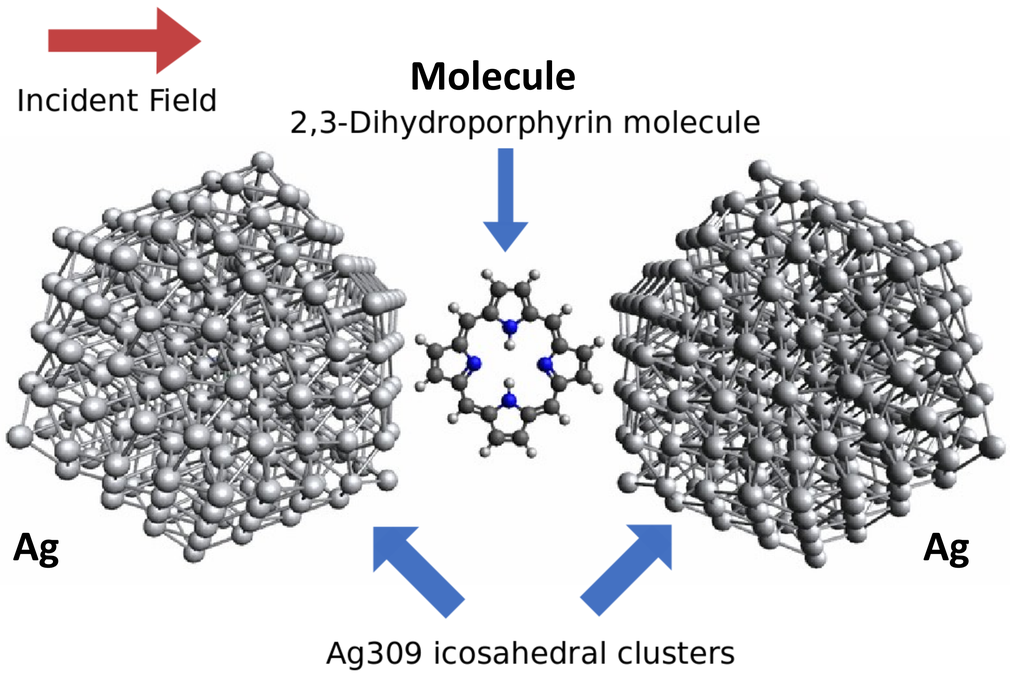
Atomistic ab-initio methods allow for an accurate description of the coupling between clusters and molecules, capturing the physics of the plasmonic response.

We present preliminary results of the atomistic optical spectra of porphyrin molecules coupled to silver nanodimers, using the ab-initio SIESTA software to obtain the ground-state of the system, and the linear-response TDDFT code PyNAO to compute the optical excitations.

A Fano spectral line emerges 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.

We also notice the appearence of a Charge Transfer Plasmon (CTP) at lower frequencies.

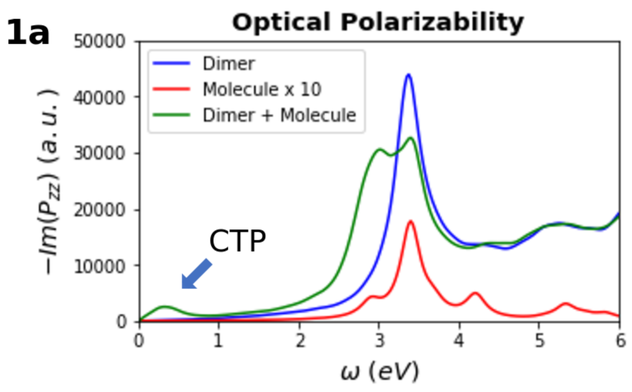
STRUCTURE

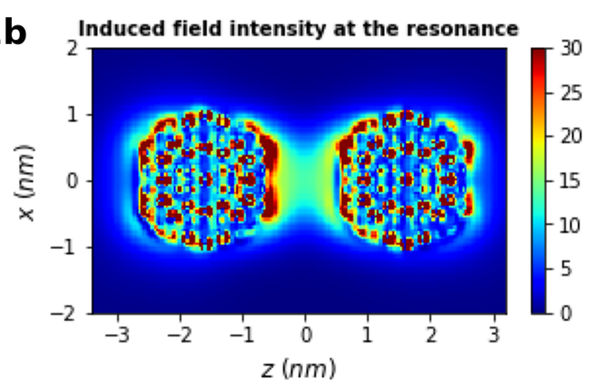


RESULTS

Effect of the gap geometry

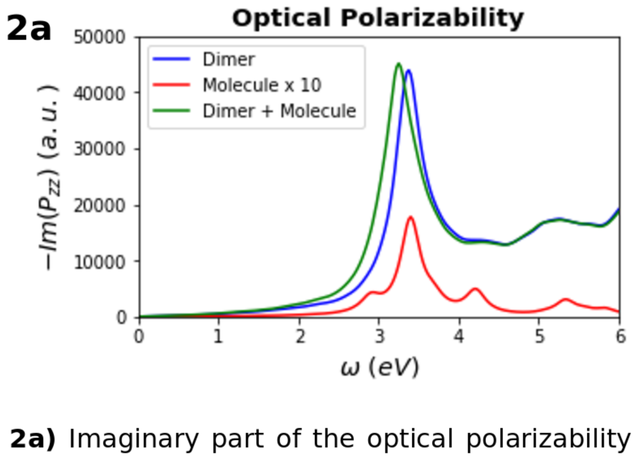
Facet-to-facet

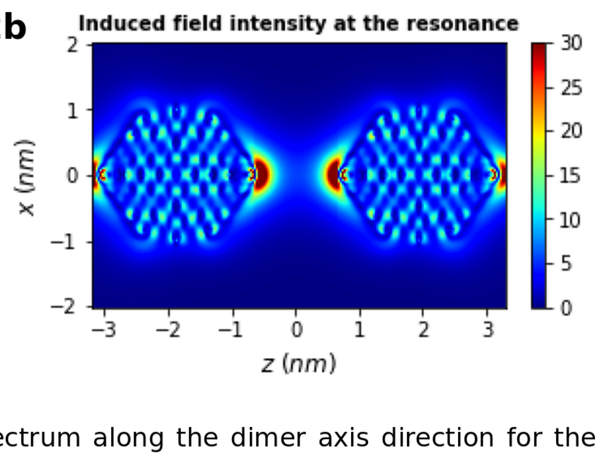




1a) Imaginary part of the optical polarizability spectrum along the dimer axis direction for the bare silver dimer (blue), the bare single molecule (red), and the coupled dimer and molecule system (green). The configuration of the dimer is facet-to-facet. Notice the splitting at the resonance and the Charge Transfer Plasmon (CTP) at lower frequencies.
1b) Induced field intensity at the resonance for the bare dimer. The field is homogeneously distributed inside the gap.

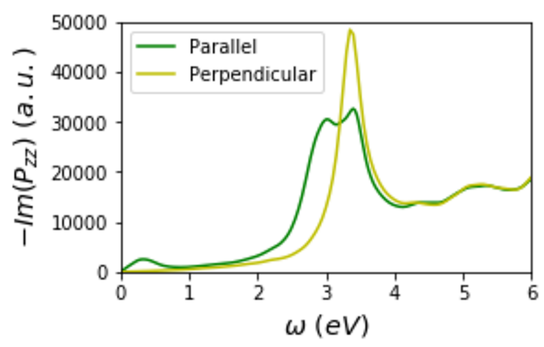
Tip-to-tip





2a) Imaginary part of the optical polarizability spectrum along the dimer axis direction for the tip-to-tip configuration of the dimer. In this case, there is no splitting nor CTP.
2b) Induced field intensity at the resonance for the bare dimer. The field is extremely confinated around the vertices.

Effect of the molecule orientation

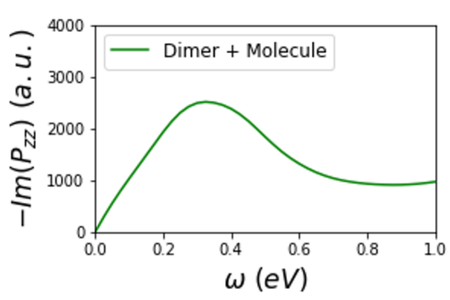


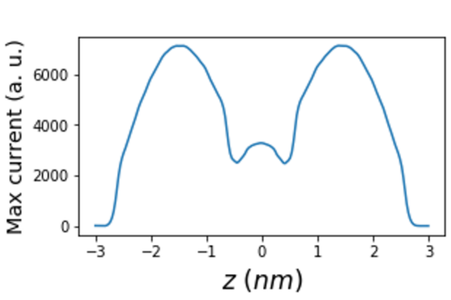
Optical polarizabilities obtained for two different orientations of the molecule.

Parallel (green): both coupling and Charge Transfer Plasmon (CTP).

Perpendicular (yellow): neither coupling nor CTP.

Charge Transfer Plasmon





a) Emergence of the Charge Transfer Plasmon (CTP) at around 0.3 eV.
b) Maximal current flowing through a plane of fixed z for the CTP mode.

CONCLUSION & OUTLOOK

Atomistic linear-response TDDFT allows for a precise simulation of the coupling between the dimer and the molecule.

Convergence tests are still being developed.

Comparison with the results of a Coupled Dipole model variyng the orientation of the molecule and the distance between the clusters.

Analysis of the required computational resources.

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