Thesis Subject

Name of the laboratory: Centre Interdisciplinaire de Nanosciences de Marseille – CINaM

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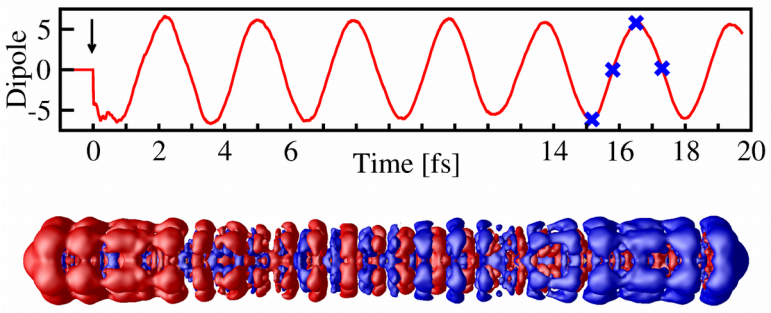
Subject's title: **Simulation of Optical Properties of Noble-Metal Clusters**

An astounding number of **applications and advanced materials exploit the localized surface-plasmon resonance (LSPR)** which dominates the near-UV and visible ranges of the absorption spectra **of noble-metal nanoparticles (NPs) and clusters,** ranging from plasmonics to bio-labeling and -sensing, catalysis, surface-enhanced Raman spectroscopy (SERS) and a multitude of other applications. The LSPR and most exploitable **properties depend sensitively on** NP size [1], structure [2,3], composition [4], and, in particular, **the environment.**

However, the fundamental **physical understanding of intermediate-sized clusters (around 2nm) and their optical properties is still rather poor,** experimental benchmark results are only beginning to be available. Recent cutting-edge experiments highlight the importance of the environment [5,6].

Monolayer-protected clusters, in which the metal core is surrounded and stabilized by ligands, can be produced atomically precise, measured and, in many cases, crystallized, which enables the experimental determination of the precise structure. Unlike free clusters, these "cluster compounds" allow for definite studies, in particular concerning the information content of optical spectra [7,8] and the transition from the molecular-like spectra of tiny clusters to the metallic behavior of larger clusters and nanoparticles [9].



Snapshot of the time-dependent density of an excited gold nanorod, reflecting a LSPR dipole mode, from Ref. [3]

In the proposed thesis work, we will study the influence of the environment and, in particular, of the nature and the arrangement of ligand molecules on the **optical properties of monolayer-protected clusters,** mostly of gold. This will be done primarily **using Time-Dependent Density-Functional Theory (TDDFT)** [10] in atomistic calculations.

Results are highly interesting on the one hand for the fundamental understanding of the physics of these clusters, and on the other hand for the optimization of the many existing applications and the conception of new ones. This field is extremely active, at the moment, with many groups studying these systems.

The work will be carried out at the CINaM, Marseille. It will profit from close participation with members of the **department "Theory and Numerical Simulation"** of the CINaM. It will be part of the larger project of H.-Ch. Weissker on the properties of metallic nanostructures and be inserted in the network of **national** (Lyon, Orsay) and **international** (Madrid; San Antonio, Texas) collaborations, both **theoretical** and **experimental**, as well as from the implication of the supervisor in national and international research networks (GDR REST; GDR OR-Nano; ETSF).

Candidates should have a solid background in condensed matter physics and/or quantum chemistry, with working knowledge on computational and numerical methods. Research experience at MSc level is required, preferably in the development and/or application of *ab initio* modeling tools. Furthermore, the candidate should be enthusiastic about the prediction and theoretical understanding of quantum phenomena concerning light-matter interaction at the nanoscale. He/she must be interested and able to work within international teams.

Interested candidates are invited to contact H.-Ch. Weissker. A formal dossier of application to the Ecole Doctorale 352 will have to be prepared in which the profile/quality of the candidate has a large weight. Necessary documents for the application are: a CV with the grades of previous education (in particular during MSc) and two letters of recommendation, as well as a letter of motivation.

[1] H.-Ch. Weissker and C. Mottet. Optical properties of pure and core-shell noble-metal nanoclusters from TDDFT: The inuence of the atomic structure. Phys. Rev. B , **84,** 165443 (2011).

[2] S.-M. Mullins, H.-Ch. Weissker, R. Sinha-Roy, J.J. Pelayo, I.L. Garzón, R.L. Whetten, X. López-Lozano, Chiral symmetry breaking yields the I-Au 60 perfect golden shell of singular rigidity, Nature Commun. **9,** 3352 (2018).

[3] X. Lopez-Lozano, H. Barron, C. Mottet & H.-Ch. Weissker. Aspect-ratio and size-dependent emergence of the SPR in Au nanorods: an ab initio TDDFT study. Phys. Chem. Chem. Phys. **16** 1820(2014).

[4] X. Lopez-Lozano, C. Mottet, and H.-Ch. Weissker. Effect of alloying on the optical properties of Ag/Au nanoparticles. The Journal of Physical Chemistry C , **117,** 3062 (2013).

[5] J. A. Scholl, Ai Leen Koh, and J.A. Dionne. Quantum plasmon resonances of individual metallic nanoparticles. NATURE , **483,** 421 (2012).

[6] H. Haberland. Looking from both sides. NATURE , **494,** 7435 **(**2013).

[7] H.-Ch. Weissker, H. Barron Escobar, V. D. Thanthirige, K. Kwak, D. Lee, G. Ramakrishna, R.L Whetten, and X. Lopez-Lozano. Information on quantum states pervades the visible spectrum of the ubiquitous Au144 gold nanocluster. Nature Communications, DOI: 10.1038/ncomms4785, (2014).

[8] H.-Ch. Weissker, O. Lopez-Acevedo, R. L. Whetten, and X. Lopez-Lozano. Optical spectra of the special Au144 gold-cluster compounds: Sensitivity to structure and symmetry. J. Phys. Chem. C , **119,** 11250 (2015).

[9] Xóchitl López-Lozano, G. Plascencia-Villa, G. Calero, R. L. Whetten, & H.-Ch. Weissker. Is the largest aqueous gold cluster a superatom complex? Electronic structure & optical response of the structurally determined Au146(p-MBA)57; Nanoscale, 2017, **9,** 18629–18634.

[10] See, e.g., C. Ullrich, Time-Dependent DFT: Concepts and Applications (Oxford Graduate Texts) 1st Edition.