

Electromagnetic interactions of anisotropic dye molecules surrounding a nanosphere

Baptiste Auguie* and Eric C. Le Ru

School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600 Wellington, New Zealand

*Presenting author (baptiste.auguie@vuw.ac.nz)

Nanostructures such as metal colloids can substantially affect the absorption and emission of light by vicinal molecules, raising considerable interest for such diverse applications as light-harvesting in solar cells, or surface-enhanced spectroscopies. The topic is also of great relevance to more fundamental pursuits such as strong coupling between light and molecules. Recent experimental results have revealed that molecular absorption can undergo considerable spectral changes when a molecule is adsorbed on a metal surface [1]. Such changes may be attributed to a variety of causes, some of a more chemical nature – a modification of the molecule interacting with the metal surface – and some that fall in the realm of classical electromagnetic scattering.

This contribution will present an original and rigorous computational model to describe the electromagnetic interactions between collections of anisotropic dye molecules and a core nanosphere in experimentally-relevant configurations. Our model extends the coupled-dipole approximation, which predicts important effects of orientation-dependent dye-dye interactions in a homogeneous medium [2], with a rigorous multipolar description of dye-nanosphere interactions based on a generalised multipolar Mie theory [4]. The predictions of this model reveal a rich interplay between the relative orientation of the dye molecules, their concentration, and their interaction with the metallic core that strongly modifies the local electric field, in amplitude and polarisation. The model qualitatively confirms the results of a simpler core-shell approximation where the dyes are described as a homogeneous effective-medium shell [1,3], but provides a much finer microscopic description of dye-dye interactions for different relative dye orientations and distances, and better insights into the subtle effects of dye-nanoparticle electromagnetic interactions.

References

- [1] Darby, B. L., B. Auguie, M. Meyer, A. E. Pantoja, and E. C. Le Ru, 2016: Modified optical absorption of molecules on metallic nanoparticles at sub-monolayer coverage. *Nat. Photon.* **10**, 40–45.
- [2] Auguie, B., and E. C. Le Ru, 2018: Optical absorption of dye molecules in a spherical shell geometry. *J. Phys. Chem. C* **122**, 110–115.
- [3] Tang, C., B. Auguie, and E. C. Le Ru, 2018: Modeling molecular orientation effects in dye-coated nanostructures using a thin-shell approximation of Mie theory for radially anisotropic media. *ACS Photon.* **5**, 5002–5009.
- [4] Auguie, B., B. L. Darby, and E. C. Le Ru, 2019: Electromagnetic interactions of dye molecules surrounding a nanosphere (submitted).

Preferred mode of presentation: Oral