Addressing atomic-scale resolution and nonlinear effects in plasmon-enhanced molecular spectroscopy

Javier Aizpurua

Center for Materials Physics (CSIC-UPV/EHU) and DIPC, Donostia / San Sebastián, Spain

Optical cavities show the ability to enhance light emission from molecules by modifying the electromagnetic local density of states where the emitter is positioned. Among the variety of optical cavities, plasmonic gaps allow for beating the diffraction limit and reducing effective mode volumes to the extreme, thus boosting light-matter interaction. In this context, different approaches from condensed matter theory as well as from cavity quantum electrodynamics (QED) serve to address the complex dynamics of molecular emission in plasmonic cavities [1]. First, the importance of the atomic scale in molecular light emission in a tunneling cavity will be presented: a full quantum chemistry description of the molecular electronic states, interacting with the inhomogeneous spatial distribution of plasmonic states, reveals the importance of considering light emission beyond the point-dipole approximation [2]. This approach describes more accurately molecular exciton dynamics and allows for a correct interpretation of atomic-scale resolution in molecular fluorescence. Secondly, a cavity-QED description of light emission within a simplified molecular picture is shown to reveal the complex dynamics from emitters in plasmonic antennas and sets up as a powerful theoretical platform to address the non-linear regime of molecular optomechanics, as in surface-enhanced Raman scattering [3,4]. Experimental examples of these effects will illustrate the validity of the different quantum approaches.

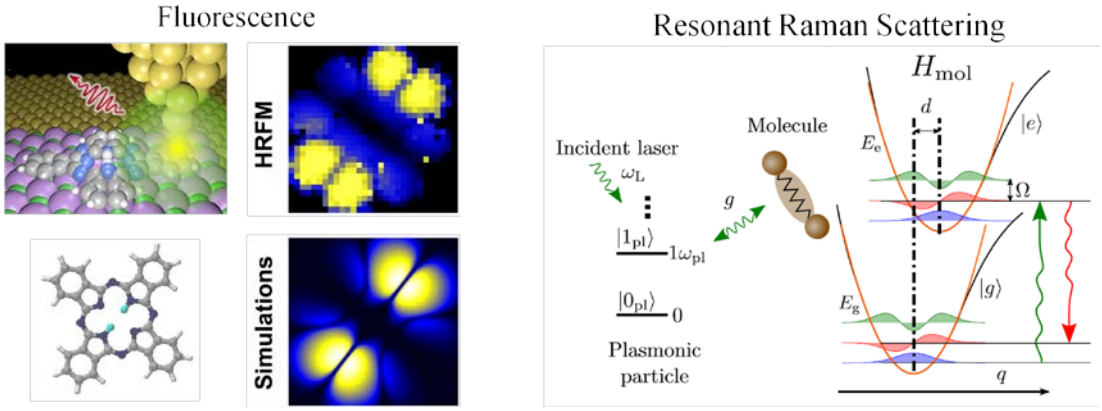

Figure 1. Left: Light emission from a single free-base phthalocyanine (H_2Pc) molecule in a tunneling junction. Experimental hyper-resolved fluorescence map (HRFM, top), and quantum-chemistry simulations of the emission (bottom). Right: Vibronic scheme of energy levels in surface-enhanced resonant Raman scattering (SERRS) within a cavity-QED theoretical framework.

[1] T. Neuman and J. Aizpurua, Optica **5**, 1247-1255 (2018).
[2] T. Neuman *et al*. Nano Lett. **18**, 2358-2367 (2018).
[3] M. Schmidt *et al*., ACS Nano 10, 6291-6298 (2016).
[4] F. Benz *et al*. Science **354**, 726-729 (2016).