Extreme Nanooptics for Atomic-Scale, Single-Molecule Surface-Enhanced Molecular Spectroscopy

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Electronic excitations and vibrations of molecules can be efficiently excited and enhanced by the action of optical resonators which improve the interaction between light and matter. Among the variety of optical resonators, plasmonic cavities emerge as a special type which reduce the electromagnetic effective mode volumes down to the nanoscale, thus dramatically increasing light-matter interactions, and bringing molecular spectroscopy such as fluorescence or Raman scattering to the extreme of single intra-molecular resolution [1]. Furthermore, atomic-scale morphological features in plasmonic nanogaps produce the ultimate confinement of light reaching effective mode volumes below 1 nm^3 [2], thus enabling sub-nanometric access and control of single-molecule electronic excitations in tip-enhanced electroluminescence [3] or non-linear optomechanical control of molecular vibrations in surface-enhanced Raman scattering [4,5]. To describe the interaction of light and matter in this extreme regime of localization, quantum theoretical frameworks are needed which often involve methodologies from condensed matter physics to describe the response of the plasmonic cavity [2], from quantum chemistry to describe molecular excitations [6], or from quantum optics to account for the quantization of electromagnetic fields and their coherent dynamics [7]. The combination of several of these approaches allows for addressing novel non-linear and coherent effects in surface-enhanced molecular spectroscopy as reported in this talk.

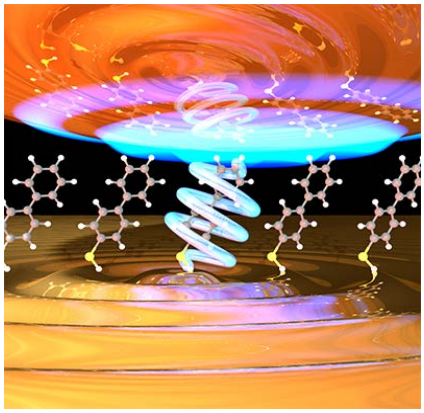

Figure 1: Artistic schematics of a nanometric optical cavity formed by a plasmonic nanoparticle-on-a-mirror (NPoM) configuration which creates a nanogap with a set of self-assembled biphenyl-4-thiol molecules in it. The induced inhomogeneous plasmonic field at the nanogap is responsible for the emergence of non-linear and coherent effects in molecular fluorescence as well as in vibrational spectroscopy of molecules.

References

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