# Atomic-scale interactions in plasmon-enhanced molecular spectroscopy

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Surface-enhanced molecular spectroscopy relies on the effect of enhanced electromagnetic fields to boost the signal from electronic and vibrational molecular excitations. Through the years, techniques such as fluorescence, infrared absorption, or Raman scattering have taken advantage of plasmonic nanoantennas to achieve such a signal enhancing effect. As fabrication and chemical synthetic methods are standardly reaching atomic-scale configurations, for instance in plasmonic nanogaps, more sophisticated theoretical methods are needed to address the quantum nature of electronic states, or to account for the quantization of plasmonic fields. Here, we report the effect of strongly inhomogeneous fields, localized at the atomic scale, as in tunneling gaps or in nanoparticle-on-a-mirror (NPoM) configurations, to modify fluorescence in molecules, as well as selection rules in plasmon-enhanced Raman scattering [1]. The presence of "picocavities" in plasmonic gaps redefines the landscape of Raman molecular activit. By adopting *ab-initio* methods to obtain the electronic structure and vibrational fingerprints of organic molecules, the effect of these field inhomogeneities can be properly considered, providing an understanding of relevant spectral information, including strong coupling of molecular emitters, and molecular optomechanics. On the other hand, the quantization of plasmonic fields, following cavity-Quantum Electrodynamics (QED) methods [2], can be also considered to reveal the complex dynamics of molecular fluorescence from hybrid molecule-cavity polaritonic branches, or to trace the population of vibrations interacting with a plasmonic cavity, pumped by a detuned external laser field. Strong non-linear effects and correlations in the emission can be identified in both types of photon emission thanks to the quantum nanooptics framework [3]. The quantum regime in surface-enhanced molecular spectroscopy is currently at hand, and accurate quantum theories can reveal a new variety of phenomena with implications in the control of quantum molecular states, as well as in plasmon-induced chemical reactivity.

## References

[1] T. Neuman, R. Esteban, D. Casanova, F. J. García-Vidal, and J. Aizpurua, Nano Lett. **18**, 2358-2367 (2018)
[2] M.K. Schmidt, R. Esteban, A. González-Tudela, G.Giedke, and J. Aizpurua, ACS Nano **10**, 6291-6298 (2016)
[3] F. Benz, M. K. Schmidt, A. Dreismann, *et al*. Science **354**, 726-729 (2016) .

## Figures

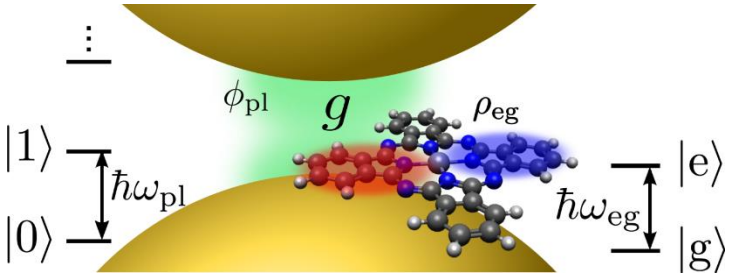


**Figure 1.** Schematic representation of a plasmonic cavity where an optical resonance at energy $\hbar\omega_{\rm pl}$ produces an electromagnetic potential $\phi_{\rm pl}$, which interacts at a coupling rate $g$, with an excitonic state of a molecule with energy $\hbar\omega_{\rm eg}$, characterized by an electronic transition density $\rho_{\rm eg}$.