Driving surface-enhanced molecular spectroscopy to the atomic scale

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Plasmonic nanocavities are formed at the junction of two metallic interfaces and provide a great opportunity to explore atomic-scale morphologies and complex photochemical processes by optically monitoring the excitation of their intense surface plasmonic modes. In recent years, optical spectroscopy of these cavities has proven to be extremely sensitive to atomic-scale features that determine the chemistry and the optoelectronics in the gaps. Quantum theoretical approaches can be exploited to address the optics of metallic nanogaps when the separation distances are taken to the extreme, reaching Ångstrom-scale dimensions. In this regime, classical theories fail to address the fine details of the optical response, and more sophisticated quantum theories are needed [1-2]. Several examples of how atomic features determine the optical response in plasmon-enhanced spectroscopy, and how the size of molecules can set the performance of single molecular emitters in strongly inhomogeneous plasmonic fields will be provided [3].

The extreme subnanometric localization of light also allows to understand ultraresolution in molecular vibrational spectroscopy, as recently achieved in intramolecule-resolved Surface-Enhanced Raman Spectroscopy [4]. The small effective volumes associated to these special optical 'picocavities' are of particular interest in quantum nano-optics, as they provide particularly large values of the coupling strength of the plasmons with excitons of an emitter, or with mechanical vibrations of a molecule located in the cavity [5-6]. This opportunity of large coupling can be exploited in molecular optomechanics of single molecules to obtain strong non-linear responses, enhancement of signals due to detuning, or to study Stokes/anti-Stokes correlations.

References: