Driving Plasmon-Enhanced Molecular Spectroscopy to the Atomic Scale

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Electronic transitions and vibrations of molecules can be more effectively excited under 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 allows for reduction of the electromagnetic effective mode volumes down to the nanoscale, thus allowing to bring molecular spectroscopy such as fluorescence or Raman scattering to extreme regimes of resolution and interaction strength.
Furthermore, atomic-scale morphological features in plasmonic cavities produce the ultimate confinement of light, setting sub-nanometric access and control of single-molecule electronic excitations as well as nanoscale molecular optomechanics. To describe the interaction between light and matter at this ultraconfined level, quantum theoretical frameworks which involve methods of condensed matter physics, quantum chemistry and quantum optics are needed.

Furthermore, the inhomogeneous plasmon field distribution in the proximity of a metallic nanoantenna where a molecular emitter is located, provides a special situation in cavity optics which requires the emitter to be studied beyond the dipolar approximation, contrary to commonly considered in molecular fluorescence. To address the limitations of point-dipole approaches we perform full quantum chemistry calculations of electronic transitions in organic molecules of interest located in plasmonic cavities which reveal quantitative and qualitative differences in the coupling strength and emission dynamics with respect to point-dipole approaches.
A similar situation can be found in Raman spectroscopy of similar molecules under the influence of inhomogeneous plasmonic fields. Such fields break selection rules and improve the strength of optomechanical interactions, producing nonlinear Raman signals.
The use of extreme plasmonic fields as shown here provides a new platform to push light-matter interactions in molecular spectroscopy to the atomic scale limit.

References

[1] M. Barbry *et al.*, Nano Lett., 15 (2015) 3410.
[2] T. Neuman et al., submitted (2018).
[3] F. Benz *et al.*, Science, 354 (2016) 726.
[4] A. Lombardi, Phys. Rev. X, 8 (2018) 011016.

Figures

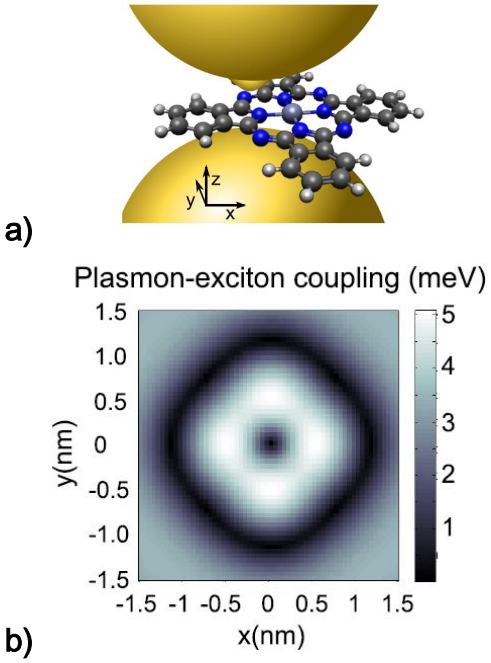

Figure 1: (a) Schematics of an organic molecule (ZnPc) in a plasmonic cavity. (b) Spatial map of the plasmon-exciton coupling strength for the situation depicted in (a). The plasmonic cavity scans the molecule horizontally (XYplane).