

Molecular Optomechanics with Plasmons : backaction at the nanoscale

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The discovery of the giant enhancement of Raman scattering from single molecules via surface plasmon had a transformative impact on spectroscopy and chemical analysis. Over the past decades a range of theories have been developed to describe the scattering of the amplified Raman signal. However recent experiments, where maximal enhancement is achieved under excitation with a laser precisely blue-detuned from the plasmon resonance, have revealed unexplained large nonlinear effects. We developed in our work a novel theory shedding light on the physics of surface enhanced Raman scattering (SERS) by mapping the problem to cavity optomechanics¹.

We show that the Raman-active vibrational modes of a molecule acting as nanoscopic mechanical oscillators are parametrically coupled to the plasmonic cavity via an optomechanical interaction. Moreover, since the plasmon decay time can have a value comparable to the vibrational period (both tens of femtoseconds), the theory predicts that the localized plasmons in SERS are not only responsible for a huge electromagnetic field enhancement but should also exert a delayed backaction force on the molecular vibration. Under detuning, one component of this force is modulating the amplitude of the vibrational motion which for blue detuned excitation means amplification of the molecular vibration. Our calculations reveal that dynamical backaction effects, leading to coherent amplification of the molecular motion, can take place in real systems.

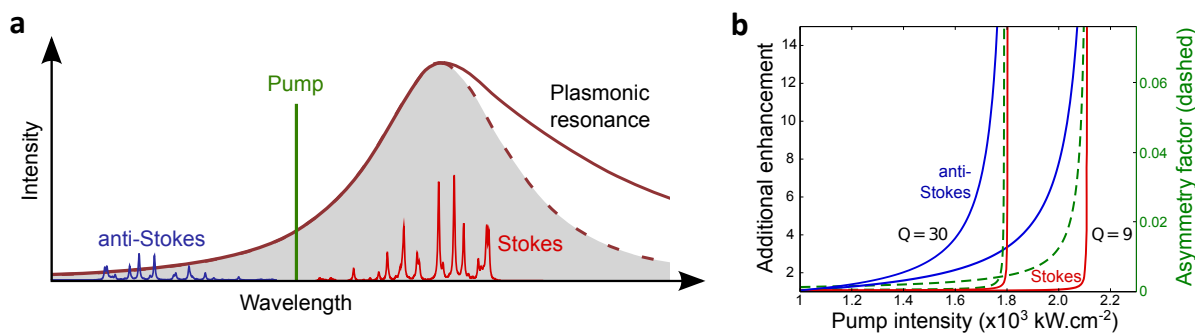


Fig. 1 – (a) Dynamical Backaction Amplification (DBA) occurs under blue-detuned excitation of the plasmon, which leads to resonant enhancement of Stokes scattering over anti-Stokes, and thereby to a coherent build-up of vibrational excitation. (b) The corresponding additional enhancement factor is plotted on the right for two plasmonic quality factors Q . The threshold power for the onset of regenerative oscillations (“phonon lasing”) is lower for higher Q . For these two cases the anti-Stokes/Stokes ratio (green dashed line, right scale) is also given for completeness.

These new insights are of major relevance for the design of novel nanostructures pushing the limits in sensitivity and resolution of nano-scale Raman imaging. More radically, the theory lays the foundations of molecular cavity optomechanics and opens the way to experimentally unforeseen research directions. The rich physics of cavity optomechanics promises to be accessible in systems of nanometric dimensions featuring coupling rates several orders of magnitude higher than state-of-the-art microfabricated devices and mechanical modes near their quantum ground states at room temperature.

1. Roelli, P. Galland, C. Piro, N. & Kippenberg, T. J. *Molecular cavity optomechanics as a theory of plasmon-enhanced Raman scattering*, Nature Nanotechnology 11, 164–169 (2016)