Molecular cavity optomechanics:
A new theory of plasmon-enhanced Raman scattering

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We present a new theory of plasmon-enhanced Raman scattering by mapping the problem onto the canonical model of cavity optomechanics, in which a bi-directional interaction takes place between molecular vibration and plasmon. The optomechanical coupling rate, from which we derive the Raman cross-section, is computed from the Raman activity of the molecules and the plasmonic field distribution. When the excitation is blue-detuned from the plasmon onto the anti-Stokes vibrational sideband, the electromagnetic force can lead to parametric amplification of molecular vibrations, revealing an enhancement mechanism never contemplated before. The optomechanical theory (i) provides a quantitative framework for the calculation of enhanced cross-sections; (ii) recovers known results; and (iii) enables the design of novel systems that leverage dynamical backaction to achieve additional, mode-selective enhancement. Finally, it yields a new understanding of plasmon-enhanced Raman scattering and opens a route to *molecular quantum optomechanics*.
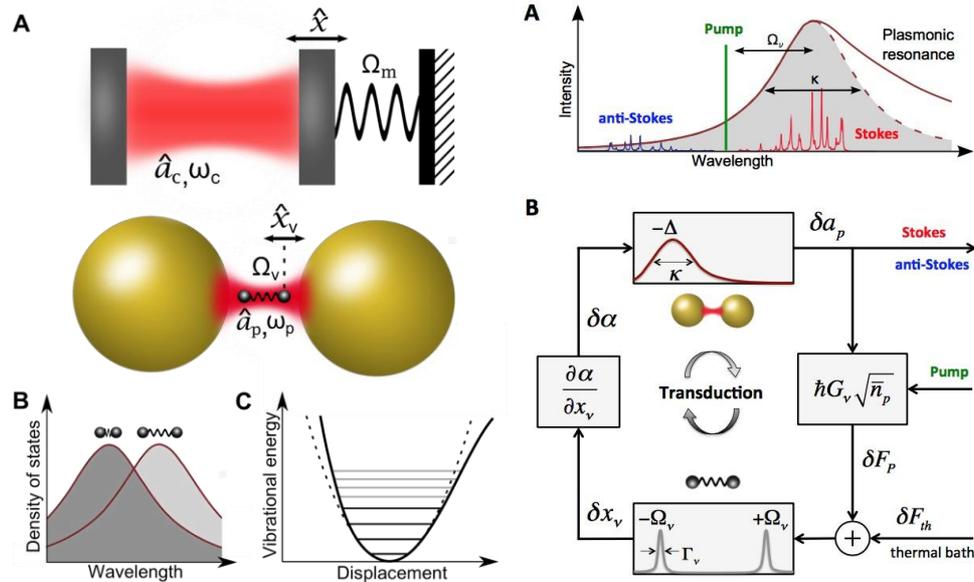
Figure 1 (adapted from Ref. [7]): **Left panel** : **Cavity-optomechanical model of the interaction between plasmon and molecular vibration**. (A left) Schematic mapping between a cavity with a mechanically compliant mirror (top) and a molecule – with internal vibrational mode sketched as two masses connected by a spring – coupled to the plasmonic resonance of a metal dimer (bottom). Operators and frequencies are introduced in the text. (B left) During vibrational motion the change in polarizability of the molecule leads to a shift of the plasmon resonance frequency (Eq. 1). (C) Schematic shape of the molecular potential as a function of the generalized coordinate for a vibrational mode in a realistic poly-atomic molecule. The harmonic oscillator description is valid for small amplitudes (low excitation numbers, dark lines) but anharmonicity must be taken into account under high amplification (higher levels, gray lines). **Right panel : Feedback in the SERS process**. (A right) Schematic Raman spectrum. When the pump is blue-detuned by approximately the vibrational frequency, $\Delta \sim \Omega_v$, the Stokes process (red) is selectively enhanced over the anti-Stokes process (blue) by the plasmonic resonance (brown line) described by a Lorentzian in the model (shaded area). (B right) Equivalent feedback diagram of the system. Variables (fluctuations from average) are indicated along the arrows and boxes represent transfer functions. The equations of motion have been linearized and frequencies are relative to the pump laser. The pump power controls the amplification factor (via n_p) in the transduction from the plasmonic field to the force acting on the molecular displacement.

Our model is based on the insight that the change in polarizability of a molecule under deformation (Raman tensor) leads to an optomechanical coupling [8] to the plasmonic cavity, which is typically a localized surface plasmon (sometime called a "hot spot"). Since the plasmon decay time can have a value comparable to the vibrational period (both tens of femtoseconds) this model predicts that the localized plasmons in surface- and tip- enhanced Raman scattering are not only responsible for a huge electromagnetic field enhancement but should also exert a delayed "backaction" force on the molecular vibration. When the incoming excitation laser is blue detuned from the plasmonic resonance, this force leads to amplification of the molecular vibration (Fig. 1, right panel), while red detuned excitation leads to its damping (or "cooling"). Quantifying the optomechanical coupling rate by density-functional theory (DFT) and finite-element modeling (FEM) numerical simulations, we find that efficient dynamical backaction can occur in realistic systems, leading to parametric amplification of the molecular motion.

This new insight is of major relevance for the design of novel nanostructures pushing the limits in sensitivity and resolution of nanoscale Raman spectroscopy and imaging. In particular it suggest counter-intuitive guidelines such as the search for narrow (i.e. high-Q) plasmonic resonances not overlapping with the excitation wavelength. More radically, the theory lays the foundations of *molecular cavity optomechanics* and opens unforeseen research directions. The rich physics of cavity optomechanics is now accessible in systems of nanometric dimensions featuring coupling rates several orders of magnitude higher than state-of-the-art microfabricated devices.

References

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