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Collective vibrational response in Surface Enhanced Raman Spectroscopy

The enhancement of the Raman signal induced by plasmonic resonances has been typically modelled in Surface Enhanced Raman Spectroscopy (SERS) using a simple classical expression, which indicates that the signal scales to first approximation with the fourth power of the local electric field enhancement at the position of the molecule and linearly with laser intensity. A semiclassical extension to this treatment indicates an additional quadratic scaling of the signal with laser intensity due to vibrational pumping [1].

On the other hand, an alternative quantum description treats the coupling between the molecular vibrations and the plasmonic modes as an optomechanical interaction, leading to a molecular optomechanical framework that is able to recover the classical and semiclassical behavior, and that also suggest a variety of new phenomena [2-6]. Notably, this approach indicates that under adequate conditions the molecules in the system cease to respond independently of each other, because the molecule-molecule coupling introduced by the optomechanical interaction needs to be taken into account [2,7-9].

Here, we present the molecular optomechanical framework of SERS [6] and emphasize the emergence of collective effects due to optomechanically-induced molecule-molecule coupling. We present experimental evidence indicating that these collective effects can be observed in current experimental platforms [8, 9], and that they can facilitate the optical control of vibrational energies, populations and effective losses, opening new prospects in SERS.

References

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