Surface Enhanced Raman Scattering from a molecular impurity model

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Surface-enhanced Raman scattering (SERS) allows the fingerprinting of single molecules via their vibrational degrees of freedom. Inspired by its analogy with the field of cavity optomechanics [1], a first model was proposed considering the optomechanical dynamics between plasmonic electric fields and molecular vibrations [2]. This molecular optomechanical approach allowed both, to describe new effects in the field of SERS arising from the dynamical backaction and to offer new possibilities in cavity optomechanics due to the resulting large coupling strengths involved – orders of magnitude larger than in previous configurations. Despite recent experimental works evidencing such optomechanical nature of SERS, large spectral discrepancies have arisen with current theoretical predictions [3] that call for new mechanisms for its understanding. Inspired by the microscopic molecular Hamiltonian [4], in this work we propose an optomechanical SERS model that considers the internal mechanisms of the molecule. In this model, the electronic transitions involved in the Raman processes are treated as a set of two-level systems that mediate the interaction between plasmons and molecular vibrations via electron-vibron couplings [4]. Since such electronic levels typically lie in the ultra-violet range, we can adiabatically eliminate them and recover the original optomechanical Hamiltonian [2]. Beyond such adiabatic approximation, we further consider a near-resonant transition coexisting with the off-resonant ones, showing interesting cooperative behaviours such as enhancements of anti-Stokes lines and modifications of spectral widths. For ultrastrong interaction scenarios with electron-vibron couplings close to the mechanical frequency, we consider the resulting phonon-dressed states in the master equation that show incoherent contributions to the anti-Stokes peaks, decisive for understanding the spectrum. Our model shows the importance of treating the molecular degrees of freedom with equal footing in SERS and offers new perspectives of the mechanisms involved in molecular optomechanics.

References

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