Hidden nonlinear optical susceptibilities in linear polaritonic spectra

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ABSTRACT:

Molecular polaritons arise from strong coupling (SC) between an ensemble of $N = 10^6 - 10^{12}$ molecules and electromagnetic modes of a cavity. SC involves multiple exchanges of excitation between cavity and matter and is expected to leverage nonlinear optical transitions in the molecules, reminiscent of quantum control schemes. However, several polaritonic phenomena, including but not limited to the linear spectra, are well-described within the framework of classical linear optics. In this work, we address this paradox from a spectroscopic perspective. We derive a general expression for polaritonic linear spectra, which reveals that the widely used classical optics-based expression has a hierarchy of finite-size $1/N$ quantum corrections encoding signatures of vacuum fluctuations mediated nonlinear optical processes, such as Raman scattering. An emergent timescale separation in polaritonic dynamics is responsible for the absence of spectroscopic fingerprints of these nonlinearities in commonly used low-Q cavities; they are expected to emerge in high-Q, single-mode cavities, where enhanced spectral resolution allows these slow processes to manifest. Understanding these nonlinear effects is crucial for harnessing genuine cavity-induced molecular processes beyond classical linear optics.

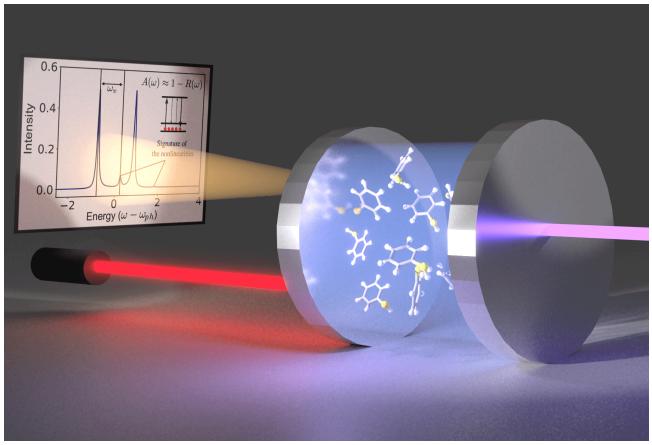

Fig. 1: A schematic of a typical polaritonic linear response setup

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