

Chemical reactivity of vibrational polaritons in the ultrastrong coupling regime

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Recent experiments have demonstrated that the interaction with quantized electromagnetic fields can modify the chemical reactivity of molecules inside optical and infrared cavities [1,2]. Chemical reactions inside liquid phase infrared cavities with giant Rabi splittings in linear transmission have been shown to proceed very differently from a cavity-free scenario, but the origins of such modifications are still not well understood. It was recently shown that inside infrared cavities, simple chemical concepts such as the dissociation energy and the bond length depend on the state of the cavity field, and also become strongly dependent on the behavior of the electric dipole function along the entire reaction pathway, not only around equilibrium configurations [3].

We further develop this intuition by studying the static and dynamical properties of vibrational polaritons in the ultrastrong coupling regime, for anharmonic Morse vibrations that are either polar at equilibrium (e.g. R-CO, R-OH), or non-polar at equilibrium (e.g. CO₂). Using numerically exact methods (MCTDH [4]), we classify the intracavity reactivity of molecular species according to the ultrafast evolution of the vibrational energy for a coupled system initially in the vacuum. We show that anharmonic polar bonds have an enhanced tendency to break under experimentally relevant values of the light-matter coupling strength, in comparison with free space. We also show that such enhanced intracavity reactivity can be detected by measuring the far-field photocount statistics of leaked cavity photons over picosecond timescales. Our work may thus serve to develop protocols for quantum control of polariton-assisted chemical processes in the liquid phase, and used as a benchmark in future developments of numerical methodology to study the complex chemical dynamics of vibrational polaritons.

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