Controlling the Nonadiabatic Electron-Transfer Reaction Rate through Molecular-Vibration Polaritons in the Ultrastrong Coupling Regime

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Controlling chemical reactions is one of the ultimate goals in the field of chemistry. Recent experiments showed that the chemical reactions can be modified, either increased or decreased, by strongly coupling a nuclear vibration mode to the single mode of an optical cavity [1]. Motivated by these experiments, we investigated how the rate of a nonadiabatic electron-transfer reaction changes by varying the molecule-cavity coupling strength in the hitherto unexplored ultrastrong coupling regime, where the coupling strength is comparable in magnitude with both the vibrational and the cavity frequencies.

We found two main factors that determine the modification of the reaction rate: the relative shifts of the energy levels induced by the coupling, and the mixing of ground and excited states of molecular vibration in the ground state of the hybrid molecule-plus-cavity system [2]. The former is the dominant factor if the molecule-cavity coupling strengths for the reactant and product states differ significantly from each other, and it gives rise to an increase in the reaction rate over a wide range of system's parameters. The latter dominates if the coupling strengths and energy levels of the reactant and product states are close to each other, and it leads to a decrease in the reaction rate. The effect of the mixing of molecular vibrational states on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton. In contrast, the effect of the relative shifts of the energy levels should be essentially independent of the number of molecules coupled to the cavity.

The rapid progress in the realization of strong and ultrastrong couplings between molecules and optical cavities is likely to open a new door to the physical control of chemical reactions and dynamical processes that, unlike Floquet engineering [3] and other approaches using intense laser fields, is based on the zero-point quantum fluctuation of the vacuum state of the cavity field.

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[2] N. T. Phuc, P. Q. Trung, and A. Ishizaki, *Scientific Reports* **10**, 7318 (2020).
[3] N. T. Phuc and A. Ishizaki, *J. Phys. Chem. Lett.* **9**, 1243 (2018); N. T. Phuc and A. Ishizaki, *Phys. Rev. B* **99**, 064301 (2019).