MODULATION OF INTRAMOLECULAR VIBRATIONAL ENERGY FLOW IN AN OPTICAL CAVITY

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Recent experiments in polariton chemistry indicate that reaction rates can be significantly enhanced or suppressed inside an optical cavity. One possible explanation for the rate modulation involves the cavity mode altering the intramolecular vibrational energy redistribution (IVR) pathways in the vibrational strong coupling (VSC) regime. In this study, motivated by a recent work of Ahn et al (Science, 380, 1165 (2023)), we present our classical and quantum dynamical IVR results on a model effective Hamiltonian. We show that tuning the cavity frequency to a key reactant stretching mode results in a strong perturbation of the cavity-free IVR pathways. Thus, in the VSC regime, an appropriately tuned cavity mode can efficiently scramble the initial zero-photon state over the molecular quantum number space. Further support comes from the behaviour of the Shannon entropy and participation ratio distributions. The extent of IVR, however, is strongly mode-specific and dependent on the cavity frequency. Interestingly, good classical-quantum correspondence is seen even for low total cavity-molecule excitations.