

# Effect of Stokes Shift on Polariton Dynamics

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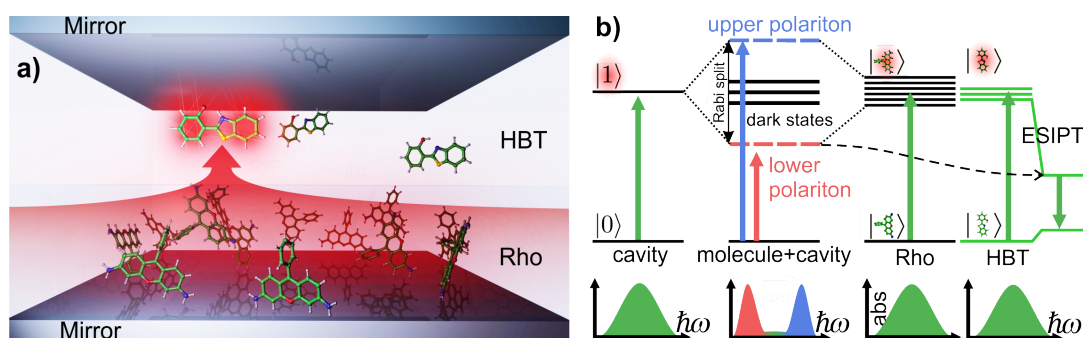
The strong coupling between photoactive molecules and confined light, like surface plasmon polaritons (SPP) or cavity photons (CP), manifests itself by Rabi splitting in the absorption spectrum at the matching energy of the molecular absorption and the light mode. The split is due to formation of hybrid polariton states between the light and the molecules [1]. These states change the energy landscape of the molecules and thus also their chemical behavior. This has evolved to a new field of research called *polariton chemistry* [2,3]. However, the polariton relaxation pathways within a strongly coupled system are not well known yet, even it is highly important question since it can reveal whether the claimed long polariton lifetime is sufficient for the suggested control.

We have studied the dynamics of polaritons by analyzing their emission in two different cases including SPPs or optical cavities [4]. While the emission of SPP is purely transverse magnetic (TM), the strong coupling with molecules induces transverse electric (TE) component to the emission of a SPP-molecule polariton. In the case of randomly oriented molecules the TM/TE ratio of the polariton emission clearly follows its molecular contribution. In addition, we show that the Stokes shift of the molecule influences the emission - the larger the shift the lower the TE emission. For optical cavities, the angle dependent emission of molecule-CP polaritons reveals different relaxation pathways depending on the Stokes shift. While molecules with high Stokes shift seem to undergo regular molecular relaxation and emit a polariton at the fluorescence wavelength, the system with no Stokes shift will relax to the lower polariton via coupling to vibrational states.

Our recent quantum mechanical molecular dynamic simulations show that in the case of high Stokes shift the polariton indeed very rapidly localizes to a single molecule excitation and decays to the fluorescing state [5]. This supports well the experiments and above explanation, and can be also directly utilized in for example for coherent polaritonic light harvesting [6].

**Figure 1:**

a) Illustration of polaritonic light harvesting in a Fabry-Pérot microcavity.  
b) The cavity mode is resonant with both chromo-



phores and thus upper polariton, lower polariton and 'dark' states are formed. HBT can undergo ultrafast excited-state intra-molecular proton transfer where the energy drops below the lower polariton (dashed arrow). Therefore, the excitation localizes on a single HBT.

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