Dynamics of strongly coupled modes between surface plasmon polaritons and photoactive molecules: the effect of the Stokes shift

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Already for some time the coupling between surface plasmon polaritons (SPP) and molecules has been utilized in plasmonics. In addition to regular absorption and emission, the regime of strong coupling has been demonstrated for a variety of molecules and plasmonic systems [1]. This strong coupling manifests itself by the appearance of an avoided crossing, i.e. Rabi splitting, in the SPP dispersion at the point of the molecule absorption, due to formation of new hybrid polariton states.

We have investigated the dynamics of these polariton states by analyzing their scattered emission [2]. While the scattered emission of SPP is purely transverse magnetic (TM) polarized, the strong coupling with molecules induces transverse electric (TE) component to the emission via the partial molecular nature of the hybrid state. We observe that the TM/TE ratio of the polariton emission follows the contribution of the molecular states in this hybrid mode, which is determined by the coupling strength. In addition, the Stokes shift of the molecule fluorescence seems to influence the polarization of the emission - the larger the shift the lower the TE polarized emission.

We argue that due to random orientation of the molecules, the emission of a fully coherent SPP-molecule polariton should be purely TM-polarized, like SPP. However, as result of the unique microenvironments of the molecules in combination with thermal motion, this symmetry may break for individual excitations, providing a route to the TE emission. The experimental results agree qualitatively with this model including the symmetry breaking as shown in Figure 1. Furthermore, the relaxation rate of the polariton correlates with the Stokes shift, so that TE emission can only occur if the Stokes shift is small and consequently the lifetime is long enough. Theoretical models that include microscopic details of the molecules will be essential to systematically exploit strong coupling for plasmonics or even controlling chemical reactions.

Fig. 1. Schematics of the experiments on the strongly coupled polariton modes between SPPs and molecules. The measurements are carried out via prism coupling in Kretschmann geometry and arrows point the polarizations of interest. Inset shows the measured polarization ratio as a function of the wave vector, kx, together with a fit by the developed theory.

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