

Anomalous Dispersion in Coupled Surface Plasmons and Excitons

Leila Hesami, Md G. R. Chowdhury, M. A. Noginov

Center for Materials Research, Norfolk State University, Norfolk, VA 23504, USA
mnoginov@nsu.edu

Abstract: We studied dispersion in Rhodamine laser dyes (in the Kretschmann geometry) and found multi-branch “staircase” dispersion curves, emergence of the new dispersion “fork” branch, and effect of the energy transfer on the strong coupling.

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Introduction Controlling of light with matter is of great importance for both fundamental science and applications, including control of emission, energy transfer, chemical reactions, resistivity, surface potentials, polaritonic lasers, nanophotonics and many others [1,2].

Although less stable than many inorganic media, dye-doped polymers (e.g., Rh590-PMMA or Rh610-PMMA), are routinely used in nanophotonic research because of their strong absorption and emission, high optical gain, stimulated emission, and coupling with surface plasmons [1,2], cavities or other molecules. Thorough studies of these phenomena are reported below.

Summary of studies Although reflection and transmission are among the most studied strong coupling phenomena, we have observed their highly unusual dispersion behavior in single doped (with Rh590 dye or Rh610 dye) and co-doped PMMA polymers, which, according to our knowledge, was newer reported in the literature.

We fabricated a series of Kretschmann geometry samples and dye doped PMMA films on glass, with concentrations of Rhodamine dyes (Rh590 and Rh610) in the polymer (PMMA) ranging between 0 g/L and 1260 g/L and studied their absorption and reflection spectra (Fig. 1). The angular and spectral positions of the dips in the experimental reflection spectra resulted in the dispersion curves discussed below.

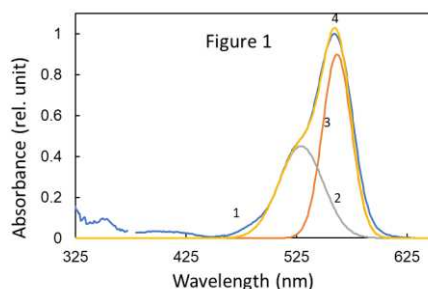


Figure 1. Absorption spectra of Rh610: PMMA; Trace (1) - Experiment (normalized to unity); Traces (2) and (3) - Fits of the experimental spectrum with two Gaussian functions; Trace (4) - Sum of traces (2) and (3).

In brief, we have observed (i) multi-branch “staircase” dispersion curves of surface plasmon polaritons at high dye concentrations (Fig. 2), (ii) emergence of a new “fork” branch of the dispersion curve (Fig. 3), (iii) effect of energy transfer on strong coupling in co-doped donor-acceptor system (Fig. 4), and (iv) effect of dye-dye interaction on spectral positions of the absorption bands, explained in terms of the second order perturbation theory (Fig. 5).

Anomalous dispersion of surface plasmons Experimentally, in pure PMMA (no dye) the dispersion curve consists of a single branch, in agreement with the literature [1,2]. At modest Rh590: PMMA and Rh610: PMMA dye concentrations ($n=4$ g/l or 8 g/l), the dispersion curve has two branches and one Rabi splitting, whose spectral position corresponds to the maximum of the dye’s absorption band [1,2]. At higher Rh590 dye concentration (16 g/l), the dispersion curve has three branches and two Rabi splits, appropriately corresponding to the peak and the shoulder of the dye absorption band [1,2]. Note that at nominally the same Rh610 dye concentration ($n=16$ g/l), the dispersion curve still had two branches and one Rabi splitting, similarly to Rh590 dye at lower concentration. At $n=64$ g/L and $n=128$ g/l, the Rh590 and Rh610 dispersion curves have four branches and three Rabi splittings. Intriguingly, in Rh590: PMMA at $n=64$ g/l and $n=128$ g/l, the upper dispersion branch features a “fork” splitting (Fig. 3). This is the evidence of emergence (or birth) of the fourth branch of the dispersion curve. In pure dyes (without PMMA), the dispersion curve in Rh590 splits into six branches (Fig. 2) and that in Rh610 splits into four branches.

Coupling and dispersion in donor-acceptor systems We then compared the dispersion curves in the mixture of Rh590: PMMA/Rh610: PMMA dye-doped polymers with those of the same dyes taken separately and found that, as a rule, branches of individual dyes can be found in the dispersion curves of the mixtures. Vice versa, the dispersion branches in the mixtures can be found in one of the dispersion curves of individual dyes. An exception from this rule is encircled in Fig.4, where one of the top branches of the mixture does not exist in Rh590: PMMA or Rh610: PMMA taken separately. Thus, the dispersion

curve of the Rh590: PMMA/Rh610: PMMA mixed samples can be more than simple “geometrical” summation of the Rh590: PMMA or Rh610: PMMA dispersion curves, suggesting an important role played by donor-acceptor energy transfer in a strong coupling regime.

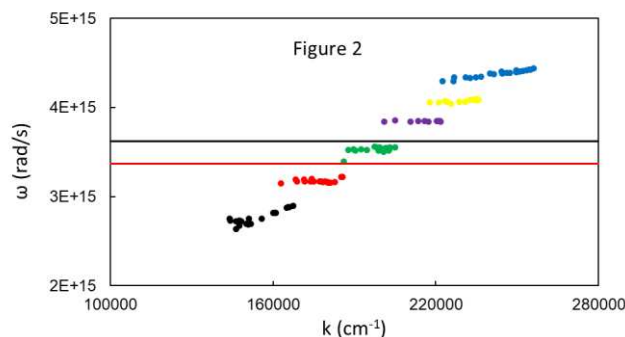


Figure 2. Multi-segment dispersion curve in pure Rh590 (no PMMA) at maximal dye concentration ($n=1260$ g/L). Horizontal lines correspond to the main peak and the shoulder in the Rh590 absorption spectrum.

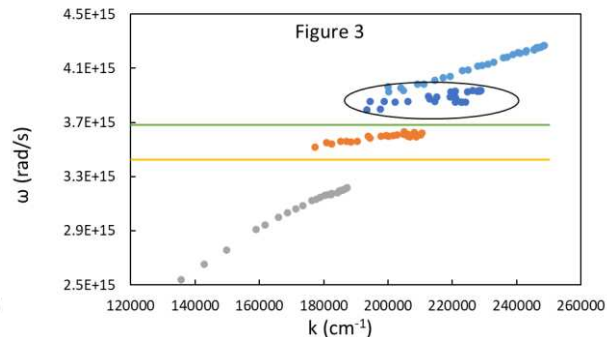


Figure 3. Emergence of the new dispersion branch in Rh590, at $n=128$ g/L. Horizontal lines correspond to the main peak and the shoulder in the Rh590 absorption spectrum.

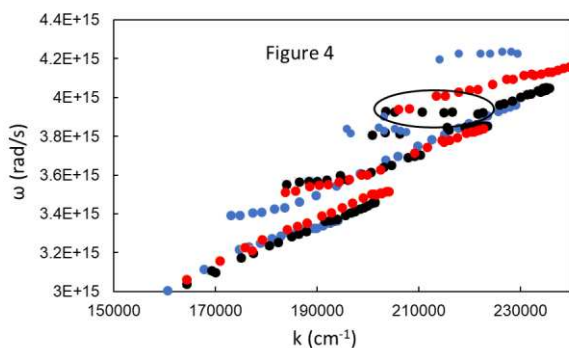


Figure 4. Dispersion curve of the 16 g/L Rh590 (red), Rh60 (blue) and mixture of Rh590 and Rh610 (black). In circled area, the dispersion curve of the mixture is different from the sum of the components.

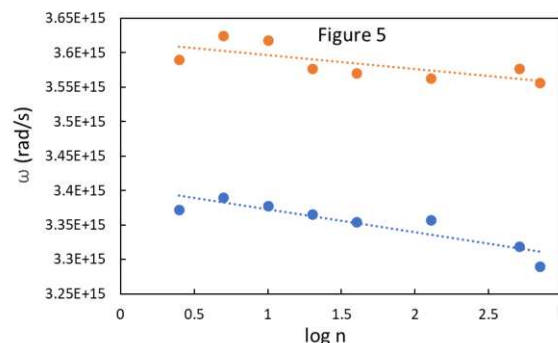


Figure 5. Concentration dependence of the spectral position of the main peak (circles) and shoulder (squares) in Rh5610:PMMA.

Effect of strong coupling in individual Rh590 and Rh610 molecules According to Ref. [3], the S0-S1 absorption band of R6G dye (very similar to Rh590) consists of a major electronic transition peak and a vibronic shoulder peak. Below, we study the concentration dependence of both transitions.

Experimentally, we prepared a series of Rh590: PMMA and Rh610: PMMA thin films, measured their absorption spectra, and fitted them with two Gaussian functions. We found that the maximum of the major Gaussian peak is close to the maximum of the experimental absorption band. At the same time, the shoulder peak is much weaker and its strength growth with increase of the dye concentration, in agreement with Ref. [3] (Fig.1). Next, we measured maximal spectral positions of the main peak and the shoulder and plotted them as the function of the dye concentration. We found that with increase of the dye concentration, (i) the spectral maxima of both the main peak and the shoulder are shifted to smaller frequencies and (ii) the energy splitting between the main peak and the shoulder was getting larger. While the latter phenomenon can be qualitatively explained in terms of non-degenerate second order perturbation model, the former requires thorough theoretical analysis. It can possibly be explained by the existence of the S0-S2 absorption band at 350 nm; however, the latter band appears to be too small (Fig. 1).

More experimental results and theoretical analysis will be presented at the conference.

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