ABSENCE OF MUTUAL POLARITON SCATTERING FOR STRONGLY COUPLED SURFACE PLASMON POLARITONS AND DYE MOLECULES WITH A LARGE STOKES SHIFT

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Phys. Rev. B 88 (2013) 085425.

Abstract

We have studied strong coupling between surface plasmon polaritons (SPP) and molecular excitations (ME) of various dye molecules [1,2]. Clear Rabi splittings have been observed on the dispersion curves recorded via reflectance geometry. However, in addition to the scattered light from the SPP-ME hybrid modes, the fluorescence of the MEs is observed in the luminescence measurements of the samples. This reveals the coexistence of strongly coupled SPP-ME polaritons and non-coupled MEs, and is observed with all the molecules tested.

As the molecular fluorescence is directly related to the ME occupation, it provides an ideal tool for studying the polariton dynamics and scatterings among the MEs and hybrid modes. Here we have utilized dye molecules with an especially large Stokes shift, i.e. Nile Red (NR), to demonstrate the absence of scatterings among the hybrid modes and to show that the modes decay via dephasing and internal relaxation of the molecules to a fluorescing state of the dye [2]. This result provides essential information on the dynamics of the strongly coupled modes.

During the last decades surface plasmons polaritons (SPPs) have attracted vast interest because of their strongly enhanced light-matter interactions, which opens routes towards optical devices beyond the diffraction limit allowing nanoscale integration of photonics. Of particular interest is also strong coupling between SPPs and molecular excitations (ME) exhibiting Rabi splittings even up to several hundreds of meV depending on the molecular species and concentration [3]. The obtained new hybrid modes could provide the needed non-linearity to enable interactions between photons/plasmons, essential for any active all optical components.

Earlier studies of strongly coupled SPP-ME systems have reported that the luminescence of polaritons with an energy higher than the ME, the so-called upper polariton branch (UPB), is usually very weak despite the large incoupled intensity monitored via reflectance [1,3]. Despite these clear and consistent observations, the relaxation dynamics of the plexitons into the non-coupled MEs, as well as scatterings among them are still not fully understood [4].

Experimental setup

Fig 1: Shematics of the measurement setup and the samples. The sample is mounted on the surface of the rotatable hemicylindrical prism by index matching oil. The excitation of SPPs is done by polarized and collimated white light and both the reflected signal (detection 1) and the luminescence signals (detection 2) were collected to a fibre guiding the radiation to a spectrometer. φ is the angle of incidence as well as the detection angle in detection 1. Lower left part represents the structure of the sample consisting of two layers, silver and SU-8 polymer with the Nile Red dye embedded, at the top of a glass substrate. Thickness of the silver and polymer layers were about 50 nm.

Absorption and dispersion curves

The measured absorptions from the samples NR1, NR2 and NR3 are shown in figure 2 together with the fittings subsequently used for modelling the dielectric function of the polymer layer. The absorption consists of two overlapping maxima at energies $E_1 = 2,34$ eV and $E_2 = 2.10$ eV, and needs to be fitted with two Gaussian peaks. Figure 3 presents the center wavelengths of the excited modes, i.e. observed dips in the reflectance measurements (D1), for all the three samples as a func-

tion of the excitation angle, together with the reflectance coeficients calculated by the transfer matrix method using the parameters fitted from the absorptions. The measured data are in good agreement with the calculations.
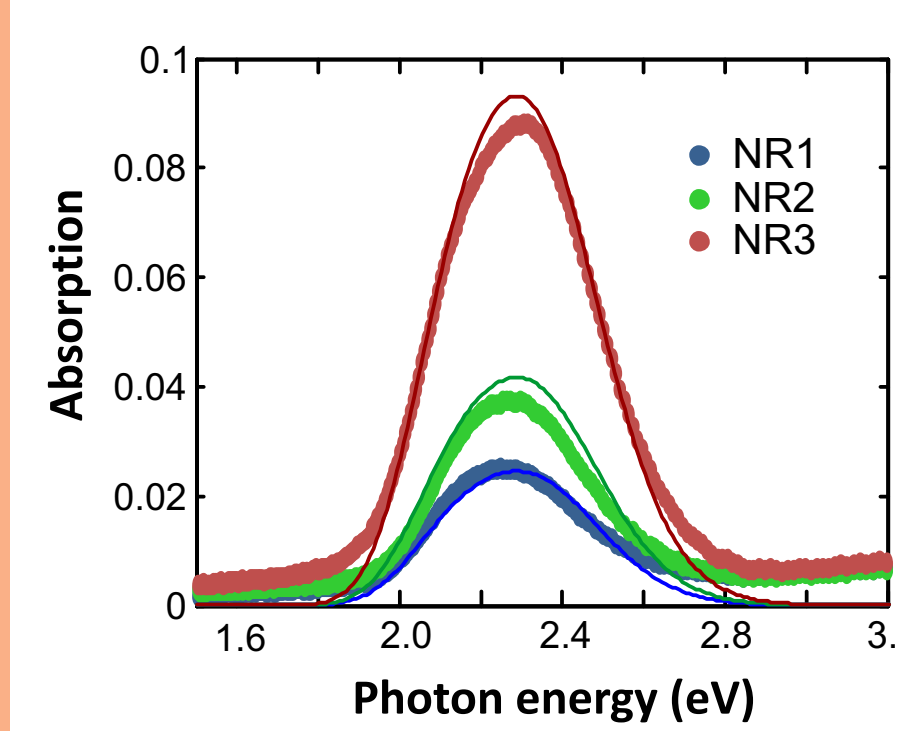

Fig. 2: Measured absorptions from the samples NR1, NR2 and NR3 shown as blue, green and red circles, respectively, together with the Gaussian fits.
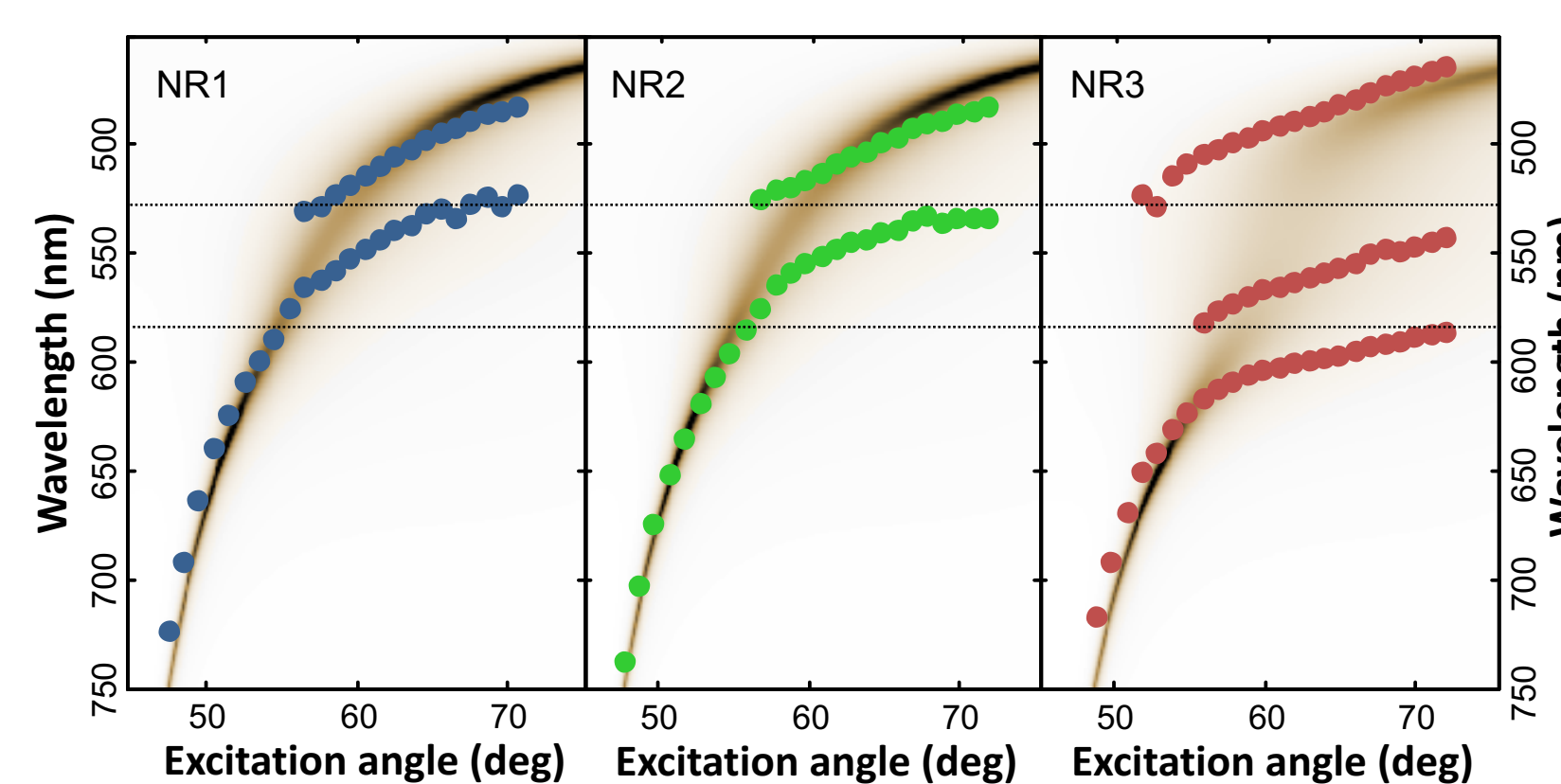

Fig. 3: Energies of the measured dips (circles) in the reectivity (D1) as a function of excitation angle, showing clear Rabi splittings in the dispersion curves for all three samples NR1, NR2, and N3. The parameters from the absorbtions were used in a transfer matrix calculation, overlayed as colorscale. Dotted horizontal lines show the energies of the molecular excitations.

Luminescence measurements

To study the scattering dynamics, the fluorescence data were measured as a function of the SPP incoupling angle. To separate it from the luminescence of the polaritons, the D2 data were collected via an additional polarizer (see Fig. 1). The results from the sample NR2 are shown in Fig. 4a. Since the SPPs as well as the polaritons have always a TM character, the measured TE signal is purely due to the ME fluorescence. As the molecules are randomly oriented the fluorescence is unpolarized and the luminescence of the genuine polaritons can be obtained by subtraction of spectra TM-TE, as shown in Fig. 4b.
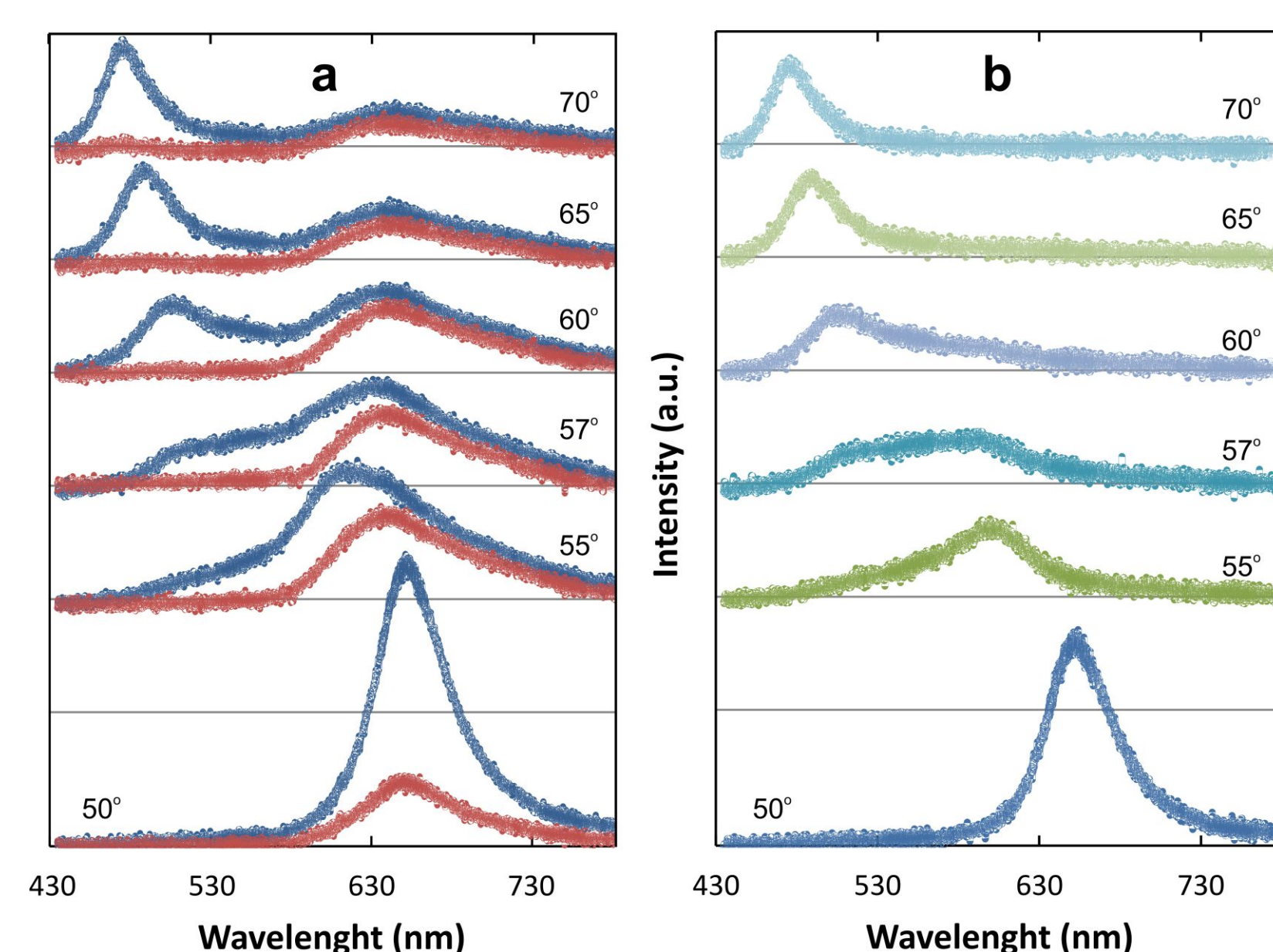

Fig 4: a: Measured TE (red) and TM (blue) D2-spectra at different angles.The TE spectra match well the measured fluorescence spectrum of the NR b: Pure polariton luminescence obtained by subtraction of the spectra TM - TE. Note that the spectra with different angles are shifted vertically for clarity.

As a measure of the excited molecular population, we integrate the total fluorescence of the TE-spectra as a function of the incoupling angle. The results shown in figure 5a reveal a clear maximum around an angle of 55° which is attributed to an effcient energy transfer to the MEs. Also the calculations based on the transfer mat-

rix method are shown. The Poynting vector was used to compute the energy transported into the NR film, where it becomes absorbed and subsequently decay to fluorescence. To understand better the physics of the increased energy transfer around 55°, we employ a generic quantum mechanical three-level model:

$$H = \begin{pmatrix} E_{\text{SPP}}(k) & C_1 & C_2 \\ C_1 & E_1 & 0 \\ C_2 & 0 & E_2 \end{pmatrix},$$

in the basis of eigenstates of SPP and the two molecular excitations. The polariton eigenstates are obtained from the Hamiltonian via diagonalization and fitted to the measured dispersions by using the coupling constants C_i as a fitting parameters,

$$|\Psi_n(k)\rangle = \alpha_n(k)|\text{SPP}\rangle + \beta_n(k)|\text{ME}_1\rangle + \gamma_n(k)|\text{ME}_2\rangle,$$

By assuming decoherence via pure dephasing one can now calculate the fluorescence intensity as $\alpha^2(\beta^2+\gamma^2)$, where α^2 is related to the probability of excitation and the term in parenthesis of ME. The calculated results are shown in figure 5b.
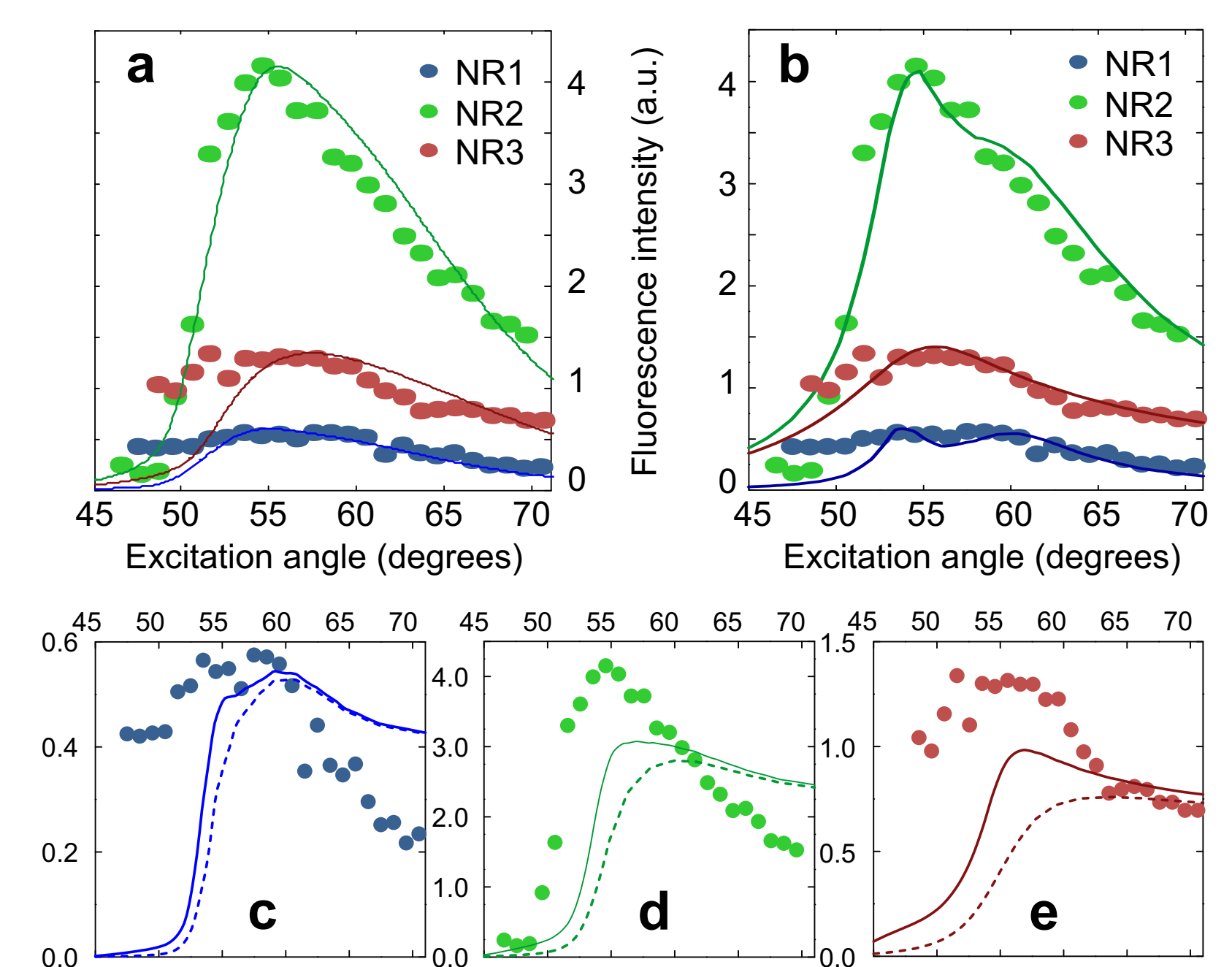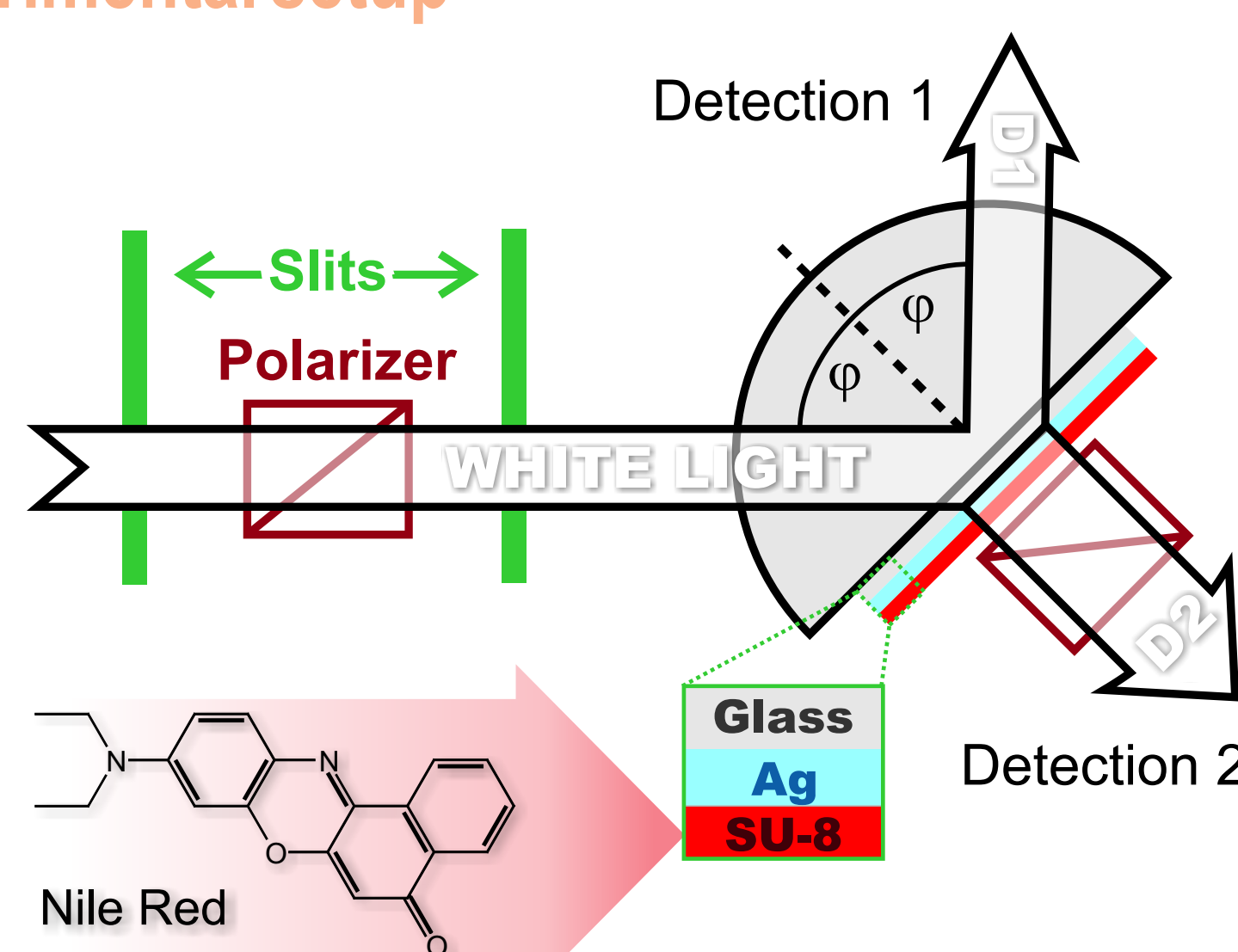

Fig. 5: Fluorescence as a function of the incoupling angle. a: Measured total fluorescence for the three samples NR1, NR2, NR3, together with the theoretical transfer matrix calculations (solid lines). b: Measured total fluorescence together with the results of the quantum mechanical three state model (solid lines). c-e: Measured total fluorescence of NR1 (c), NR2 (d) and NR3 (e) together with the results of the three state model including relaxation and thermalization of the hybrid modes (dashed lines), as well as decoherence via thermalization (solid lines). As seen from the figures these models do not fit to the measured results.

Conclusions

We have shown that the polariton hybrid modes of strongly coupled SPPs and molecular excitations of Nile Red, solely decay through an internal molecular relaxation, and the process occurs in absence of any prior mutual scatterings among the hybrid states or relaxation. In addition, single wavelength SPP studies further clarify that there is a negligible amount of energy transfer between the polariton branches, and the commonly observed decrease of the upper polariton branch luminescence is due to a fast decay to the molecular states.

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