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Vacuum Rabi splitting for surface plasmon polaritons and Rhodamine 6G molecules

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ABSTRACT

We report on strong coupling between surface-plasmon polaritons and Rhodamine 6G molecules at room temperature. As a reference to compare with, we first determine the dispersion curve of (uncoupled) surface plasmon polaritons on a 50 nm thick film of silver. Consequently, we determine the dispersion curve of surface plasmon polaritons strongly coupled to Rhodamine 6G molecules, which exhibits vacuum Rabi splitting. Depending on the Rhodamine 6G concentration, we find splitting energies between 0.05 eV and 0.13 eV.

Keywords: surface plasmon polariton, vacuum Rabi splitting, strong coupling, dispersion curve

1. INTRODUCTION

The combination of Surface Plasmon Polaritons (SPPs) with emitters, such as dye molecules, ions and quantum dots, is a heavily studied field of research. In many cases, the interactions between SPPs and emitters are governed by the weak coupling regime.^{1–5} In the strong coupling regime, interesting phenomena occur that cannot be described with Fermi's golden rule, such as vacuum Rabi splitting. Rabi splitting has been shown in for example microcavities^{6–8} and in plasmonic systems with SPPs coupled to J-aggregates,^{9–11} rhodamine (R6G) molecules,¹² and quantum dots.^{13,14} Here, we show double vacuum Rabi splitting for the strongly coupled SPP-Rhodamine 6G dye molecule system. We explore the system studied by us¹² further in a new experimental setup. We provide numerical simulations to analyze the data and a detailed description of the sample fabrication process.

2. EXPERIMENTS

A classic Kretschmann-type setup,¹⁵ shown in Fig. 1, was used to study strong coupling of SPPs with R6G molecules. A collimated beam of white light, coming from a tungsten source, is used as a probe. The width of the beam was controlled by an adjustable slit, set to 0.5 mm. A polarizer is inserted in the path of the light source to obtain p-polarized light. The reflected light, having interacted with the sample, is focused into a fiber and analyzed with a spectrometer (Oriel Linespec model 77480 spectrometer with a model 78854 CCD array).

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Figure 1. Kretschmann-type setup to determine the white light reflectivity of the layered Ag/PMMA+R6G molecules structures. A collimated beam of white, p-polarized light from a tungsten source is led to the sample and used to excite SPPs. The reflected light, used to probe the sample, is subsequently focused into a multimode fiber (not shown) and analyzed with a spectrometer. The sample substrate and the prism both have a refractive index $n = 1.5230$ and are brought in contact with each other by immersion oil with the same refractive index.

For comparison, the dispersion curve of (uncoupled) SPPs was measured first. The SPPs were excited in a 50 nm thick layer of bare silver, deposited onto a glass microscopy slide by e-beam evaporation. The theoretical dispersion curve for non- or weakly interacting SPPs on an interface of a semi-infinite metal slab and a dielectric is given by¹⁵

$$k_x = \frac{\omega}{c} \left(\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m} \right)^{1/2}, \quad (1)$$

where ω is the frequency of the light in rad/s, c is the speed of light and ε_d and ε_m are the dielectric constants of the dielectric and the metal, respectively. For thin (metal) films, embedded between two semi-infinite dielectrics, the reflectivity of p-polarized light is given by Fresnel's equations,¹⁵

$$r^p = \frac{r_{01} + r_{12} e^{2ik_{z1}d}}{1 + r_{01}r_{12}e^{2ik_{z1}d}} \quad (2)$$

with d the thickness of the middle layer and

$$r_{jk} = \left(\frac{k_{zj}}{\varepsilon_j} - \frac{k_{zk}}{\varepsilon_k} \right) / \left(\frac{k_{zj}}{\varepsilon_j} + \frac{k_{zk}}{\varepsilon_k} \right). \quad (3)$$

Possible combinations of j and k are $jk = 01$ or $jk = 12$. The indices 0 and 2 stand for the semi-infinite dielectric materials whereas index 1 signifies the middle layer. Furthermore, k_{zj} and k_{zk} are the z-component of the k-vector in material j and k , respectively, with relative permittivities ε_j and ε_k .

Figure 2. Typical reflection curve as obtained with the setup as shown in Fig. 1. The corresponding angle of incidence was $45.0 \pm 0.2^\circ$. Shown is also a fit with a Gaussian curve to accurately determine the location of the reflection minimum, here 477 ± 1 nm.

Figure 3. Measured and theoretical dispersion curves of SPPs on a 50 nm thick silver layer. The measured dispersion curve (circles) is for the SPP on the metal/air interface. The white drawn curve is the result of a calculation of the dispersion curve of SPPs on an infinitely thick silver layer, whereas the gray scale contours are an indication of the relative surface plasmon resonance strength, calculated with Eq. 2. This calculation also results in the second visible curve, which is the dispersion of the SPP on the silver/glass interface. This SPP is inaccessible with a Kretschmann-type setup. The dielectric data for silver was taken from Johnson and Christy.¹⁶ Note that the calculations do not contain any free parameters. The error bars are based on a $\pm 0.2^\circ$ error interval in the angle, including alignment, and a ± 1 nm error interval for the location of the minimum, which exceeds the 99% confidence interval.

The spectrum of the reflected white light was recorded as a function of incident angle. A sample measurement is shown in Fig. 2, corresponding to an incident angle of $45.0 \pm 0.2^\circ$. A clear minimum is visible in the spectrum, the fingerprint of surface plasmon resonance (SPR). We checked that the minimum did not show with s-polarized light. A Gaussian is fitted to the minimum in order to accurately determine the location of the minimum in the reflection spectrum. Tracking the wavelength at which the minimum occurs as a function of incident angle then yields the dispersion curve of the SPP on the silver film.

The experimentally determined dispersion curve for a 50 nm thick silver layer, obtained with the procedure described above, is displayed in Fig. 3. Also shown are computed dispersion curves of SPPs on an infinitely thick layer (white curve, Eq. 1) and a 50 nm thick silver layer sandwiched between glass ($n = 1.5230$) and air ($n = 1$) dielectrics (gray scale contours, Eq. 2). The frequency-dependent data on the electric permittivity of silver was taken from Johnson and Christy.¹⁶ The calculations do not contain any free parameters. Within the accuracy of the measurement, the data shows excellent agreement with the theoretical curves.

In order to study the interaction of the R6G molecules with SPPs, samples were prepared containing a layered structure on top of a microscopy slide as a substrate. A full description of the sample preparation procedure is given in Appendix A, a short description is given here. A layer of silver, of 50 nm thickness, was evaporated onto the substrate by e-beam evaporation. Rhodamine 6G molecules are first dissolved into ethanol and mixed with poly(methylmethacrylate) (PMMA), dissolved in anisole. By spin coating and afterwards drying on a hot plate, thin films of PMMA with a thickness of 20–40 nm, containing R6G molecules, were obtained on top of the silver layer. The resulting concentrations of R6G molecules in the PMMA layer were 100 and 200 mM respectively, for the different samples.

To model our samples, a similar (semi-classical) calculation as performed for the single silver layer (Fig. 3) was carried out for a two-layer system embedded between two semi-infinite dielectric materials. The two layers were comprised of silver and PMMA with embedded R6G molecules, respectively. The layer of polymer, containing the R6G molecules, was approximated with a homogenous, frequency-dependent effective refractive index. This effective refractive index was derived from absorption measurements of R6G in solution, with the subsequent application of the Kramers-Kronig equations.¹⁷ The result of the calculation of the dispersion curve for the strongly coupled SPP/R6G system is shown in Fig. 4. Though the dispersion curve thus obtained resembles the dispersion curve of the non-interacting SPP for a large range of frequencies, a distinct gap in the dispersion

Figure 4. Theoretical dispersion curve of SPPs on a 50 nm thick silver layer, strongly coupled to R6G molecules. A clear gap is present around $3.5 \cdot 10^{15}$ rad/s due to strong coupling. The layer of polymer, containing the R6G molecules, was approximated with a homogenous, frequency-dependent effective refractive index. The inset shows the measured absorbance of a 0.0667 mM Rhodamine 6G solution in anisole containing 2 w-% PMMA, on which the calculation of the effective refractive index is based.

curve for the stratified silver/PMMA+R6G system is visible around $3.35 \cdot 10^{15}$ rad/s, due to strong coupling. This is the vacuum Rabi splitting which could be also obtained by a full quantum calculation.¹⁸ In the context of semi-classical treatment, it is often also called the normal mode splitting.

Samples with both silver and a PMMA layer with embedded R6G molecules in 100 and 200 mM concentrations were measured in the same fashion as the sample with just a silver film. Similarly, tracking the minima that occur when the incident angle is scanned over a range from 44° to 63° yields the dispersion curve for the coupled SPP/R6G system. The dispersion curves for the two concentrations are displayed in Fig. 5 (100 mM sample) and Fig. 6 (200 mM sample). A distinct double split in the dispersion curve is visible in both cases, which is absent in the measured dispersion curve for the uncoupled SPPs in Fig. 3. For the 100 mM sample, splitting energies of 0.05 ± 0.03 eV and 0.13 ± 0.04 eV are found around $3.4 \cdot 10^{15}$ rad/s and $3.9 \cdot 10^{15}$ rad/s, respectively.

Figure 5. Measured dispersion curve of the coupled SPP/R6G system. The sample had an effective R6G concentration of 100 mM. Clearly visible is the double splitting, once at $3.4 \cdot 10^{15}$ rad/s (2.2 eV) and once at $3.9 \cdot 10^{15}$ rad/s (2.6 eV). The splitting energies for this sample are 0.05 ± 0.03 eV and 0.13 ± 0.04 eV for the gaps at lower and higher frequency, respectively. The error bars are based on a $\pm 0.2^\circ$ error interval for the angle, including alignment, and a 99% confidence interval for the locations of the minima in the reflection spectra, obtained by fitting.

Figure 6. Measured dispersion curve of the coupled SPP/R6G system. The sample had an effective R6G concentration of 200 mM. Clearly visible is the double splitting, once at $3.4 \cdot 10^{15}$ rad/s (2.2 eV) and once at $4.0 \cdot 10^{15}$ rad/s (2.6 eV). The splitting energies for this sample are 0.09 ± 0.03 eV and 0.13 ± 0.04 eV for the gaps at lower and higher frequency, respectively. The error bars are based on a $\pm 0.2^\circ$ error interval for the angle, including alignment, and a 99% confidence interval for the locations of the minima in the reflection spectra, obtained by fitting.

The 200 mM sample shows splitting energies of 0.09 ± 0.03 eV and 0.13 ± 0.04 eV around $3.4 \cdot 10^{15}$ rad/s and $4.0 \cdot 10^{15}$ rad/s, respectively. The location of the lower energy split coincides with the R6G absorption maximum, and the higher energy one is close to a shoulder in the R6G absorption spectrum.¹⁹ The double split does not show in the result of our calculation, as shown in Fig. 4, since the calculated effective refractive index for the PMMA+R6G layer is based on an absorption measurement of R6G in solution. The absorption measurement shows the shoulder (see the inset in Fig. 4), but it is not a strong enough feature to appear in the calculations. However, R6G is known to form aggregates easily, of mostly dimers, which results in an additional absorption maximum that strongly overlaps with the absorption shoulder of the monomer.^{10,19} The samples in Figs. 5 and 6 may contain a considerable amount of dimers in addition to monomers, contributing to the strong splitting observed around $4 \cdot 10^{15}$ rad/s. The locations of the splits agree quite well with our earlier studies,¹² however, care has to be taken when comparing the numerical values of the R6G concentrations, as the materials used there differ from the materials used in this study. See also section A.3.

3. CONCLUSION

We have shown that, in contrast to the dispersion curve of uncoupled SPPs, the dispersion curve of the coupled SPP/R6G molecule system shows vacuum Rabi splitting due to strong coupling. The concentration-dependent splitting energies found are between 0.05 eV and 0.13 eV. With increasing concentration, the lower frequency energy splitting increases as well. The higher frequency energy gap however remains constant within the accuracy of the measurement. It is likely to contain a contribution from dimers. Shown elsewhere, the splitting energy is also affected by the interaction time of the SPP and the molecule: by restricting the area of interaction, the interaction time can be controlled with sub-fs precision.¹²

APPENDIX A. SAMPLE PREPARATION

A.1 Preparation of Rhodamine 6G Solution

The preparation of the Rhodamine 6G solution is a two-step process. In the first step, the required amount of R6G (Sigma Aldrich, CAS: 989-38-8) was weighed and dissolved into ethanol (Etax aA 99.5 w-%, Altia) in an orbital shaker for 1 h. The concentration of R6G in ethanol was 66.68 mM. In the next step, R6G in ethanol was mixed with a positive e-beam resist (PMMA A1 MW 950, MicroChem) to obtain the desired concentrations. Due to purity considerations this step was conducted in an ISO4 standard clean room. In order to get a uniform solution the sample was left to stir overnight. Typically, a stock solution of 200 mM was prepared and from

this all other concentrations could be prepared by further diluting with PMMA. The solutions were stored in a refrigerator at 6°C. It was observed that dissolving the R6G directly into the resist (resin Anisole) resulted in low-quality solutions, containing a large amount of aggregates.

A.2 Preparation of Substrates

Before spin-coating R6G films, microscope cover glass substrates (Schott D 263 M cover glass, thickness 0.170 ± 0.005 mm, size 22x22 mm) were cleaned by both wet and dry processes. The cover glasses, inserted into a rack, were incubated in hot acetone for 10 minutes followed by a 20 minute ultrasonication step (in acetone) in a water bath. Ultrasonication was performed twice, but during the second time, the rack with cover glasses was placed into distilled water. The sonication time in distilled water was 10 min. After sonication, the cover glasses were dried with nitrogen. The wet cleaning process was followed by a reactive ion etching cleaning step with an oxygen plasma (Oxford Plasmalab 80 Plus RIE, 100 W, 200 mTorr, 45 ccm O₂ and 5 ccm Ar flows, 1 minute). Immediately after the ion etching cleaning processes, a 50 nm silver film was deposited on the substrates by standard e-beam evaporation techniques. Evaporation of the metal was started at $2\text{--}4 \cdot 10^{-7}$ mbar pressures. Evaporation rates of 3.0–4.2 Å/s were used.

A.3 Rhodamine 6 G film preparation

A Rhodamine 6G/PMMA A1 film was formed on top of evaporated silver film by spin coating with 3000 rpm for 60 s. The film was baked on a hot plate set to 170°C for 5 minutes to remove the remaining solvents. Depending on the Rhodamine concentration, the thickness of the film was measured with a profilometer to be between 20–40 nm. The R6G concentrations given in the text above are the effective concentrations in solid PMMA, i.e., mol/l solid PMMA. These effective concentrations in the sample were calculated as follows: we assume that the mass density of the solution is equal to the mass density of pure anisole. Then, given a x M solution of R6G in PMMA A1 (1 w-% PMMA in anisole), this is equivalent to having x mol/0.995 kg, using a mass density of anisole of 0.995 kg/l. The fraction of PMMA is 1%, which gives $x/(0.995 \cdot 10^{-2})$ mol/kg solid PMMA. With a mass density of PMMA of 1.18 kg/l, an effective concentration of $x \cdot 1.18/(0.995 \cdot 10^{-2})$ mol/l solid PMMA is obtained. From our solutions of 0.833 mM R6G in PMMA A1 and 1.667 mM R6G in PMMA A1, it follows that the effective concentration R6G in the baked samples is 100 mM and 200 mM, respectively.

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