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ABSTRACT

Strong coupling between surface plasmons and molecular excitons may lead to the formation of new hybrid states—polaritons—that are part light and part matter in character. A key signature of this strong coupling is an anti-crossing of the exciton and surface plasmon modes on a dispersion diagram. In a recent report on strong coupling between the plasmon modes of a small silver nano-rod and a molecular dye, it was shown that when the oscillator strength of the exciton is large enough, an additional anti-crossing feature may arise in the spectral region where the real part of the permittivity of the excitonic material is zero. However, the physics behind this double anti-crossing feature is still unclear. Here, we make use of extensive transfer matrix simulations to explore this phenomenon. We show that for low oscillator strengths of the excitonic resonance, there is a single anti-crossing arising from strong coupling between the surface plasmon and the excitonic resonance, which is associated with the formation of upper and lower plasmon–exciton polaritons. As the oscillator strength is increased, we find that a new mode emerges between these upper and lower polariton states and show that this new mode is an excitonic surface mode. Our study also features an exploration of the role played by the orientation of the excitonic dipole moment and the relationship between the modes we observe and the transverse and longitudinal resonances associated with the excitonic response. We also investigate why this type of double splitting is rarely observed in experiments.

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I. INTRODUCTION

Strong coupling between excitonic resonances and surface plasmons is a fascinating and potentially important interaction between light and matter[1–4] and is of interest in many areas including non-linear optics[5] and chemical reactivity.[6] In the strong coupling interaction, the uncoupled excitonic and plasmonic resonances lose their uncoupled identity as two new hybrid states—polaritons—are formed. The formation of hybrid polariton states via strong coupling is accompanied by a single avoided crossing between the photon and the exciton, such an anti-crossing is usually known as Rabi-splitting. One feature that makes these hybrid polaritons states so fascinating is the fact that they inherit the properties of both the photon and exciton from which they are formed. One can, thus, see the strong coupling process as a way for excitons to acquire a coherent spatial extent and as a way for photons to acquire mass.

Strong coupling between surface plasmons and excitons, for example, of dye molecules has become an intense field of study.[7] In a recent study of strong coupling between the J-aggregated dye molecules and the surface plasmon modes supported by silver nanorods, Beane *et al.*[8] found a puzzling inconsistency between the results from their experiments and the results from their

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numerical simulations; in their experimental data, they observed a single anti-crossing, while in their model data, they saw two avoided crossings. The origin of this double anti-crossing is still not clear, in part because the model used by Beane *et al.* was based on a Lorentz oscillator model of the J-aggregated dye [5,6-dicholoro -2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)-benzimida-zol-2-ylide-ne]-propenyl]-1-ethyl-3-(4-sulphobutyl)-benzimida-zolium hydrox-ide (TDBC)][9] that involved two resonances. Beane *et al.* suggested that one explanation for the double anti-crossing they saw was the twofold excitonic transition of the dye layer. They also suggested that the linewidth of the excitonic resonance is the main parame-ter that determines whether a single or double anti-crossing will be observed. We show here that the double anti-crossing occurs even for a single excitonic resonance, and we explore the conditions under which such a double anti-crossing may occur.

The double splitting phenomenon of interest here has been known for nearly 40 years, and it was observed in experiments by Pockrand *et al.*,[10] who attributed the double splitting to surface plasmon modes coupling with the transverse and longitudinal reso-nances of the excitonic transition.[10] Some years earlier, Agranovich and Malshukov showed through calculation that a surface plasmon can undergo a double splitting at frequencies for a system of a metal layer coated with a thin film of material possessing a resonance, e.g., an excitonic resonance.[11]

In this paper, we show that, as originally predicted by Agra-novich and Malshukov,[11] surface plasmons can indeed strongly cou-ple to a single excitonic species at two different energies and that the energies of these two anti-crossings correspond to the longitudinal and transverse resonance energies associated with the excitonic tran-sition. In addition, and with the help of calculations of field profiles, we show that this interaction may produce three modes: an upper polariton, a lower polariton, and an excitonic surface mode.

II. ORIGIN OF DOUBLE SPLITTING

The system we investigate here comprises a semi-infinite sil-ver medium over-coated with a 30 nm thick excitonic layer, and this could represent, for example, a 30 nm layer of dye molecules sus-pended in a host matrix[1,2] [see Fig. 1(a)]. The thickness of the dye layer is chosen to be thick enough to lead to strong coupling, but not so thick as to support guided modes or to support an epsilon near zero (ENZ) mode.[12]

We take the permittivity of air to be 1.0, the permittivity of sil-ver is taken from the work of Rakić *et al.*,[13] and the permittivity of the dye layer as a function of photon energy, $\varepsilon(E)$, can in its simplest form be represented using a Lorentz oscillator model. For clarity, we took a single oscillator model using just the strongest oscillator in the two-oscillator model used by Gentile *et al.*[9] and upon which the work of Beane *et al.*[8] was based; our permittivity here is given by

$$\varepsilon(E) = \varepsilon_b + \frac{fE_o^2}{E_o^2 - E^2 - iE\gamma}, \tag{1}$$

where ε_b is the background permittivity, f is the oscillator strength, E_o is the exciton transition energy, and γ is the damping factor. We took the parameters to be E_o = 2.10 eV, γ = 0.053 eV, f = 0.3, and ε_b = 2.25. A plot of the real and imaginary parts of this com-plex permittivity is shown in Fig. 1(b). At this point, it is worth clarifying some nomenclature. The excitonic transition represented by the Lorentzian oscillator has a resonance energy (frequency) of E_o = 2.10 eV, which is sometimes known as the transverse resonance. Materials having a zero in the real part of their permittivity can also support a longitudinal resonance;[10,11,14] in our case, the trans-verse resonance occurs at 2.10 eV, while the longitudinal resonance occurs at 2.24 eV [see Fig. 1(b) and also Sec. S1 of the supplementary material for further details].

We used a transfer matrix based model to obtain the Fres-nel transmission amplitude of p-polarized light as a function of the photon energy and in-plane wavevector for the structure, for light incident from the air side. The results for three different oscillator strengths of the dye layer are shown in Fig. 2.

Figure 2(a) shows the calculated modulus of the transmission amplitude of p-polarized light in which we can see the dispersion of the surface plasmon mode for the case when there is no excitonic resonance present in the system, i.e., for f = 0. The dark slanted region is the air light-line, while the surface plasmon mode (bright region) is visible beyond the light-line, which is non-radiative. When the oscillator strength is non-zero but low, as shown in Fig. 2(b), for which f = 0.05, an avoided crossing between the surface plasmon mode and the exciton occurs. This is as expected when the sur-face plasmon strongly couples to the exciton, producing two hybrid polaritons. When the oscillator strength is sufficiently strong, f = 0.3, two avoided crossings can be seen: one at 2.1 eV and the other at a higher energy 2.24 eV.

A simple explanation for these anti-crossing phenomena can be seen from the permittivity of the dye. The avoided crossings in Fig. 2(c) correspond to the two resonance energies discussed above. The first is the transverse resonance energy, E_t = 2.1 eV, where the imaginary part of permittivity is the maximum, and the other is the

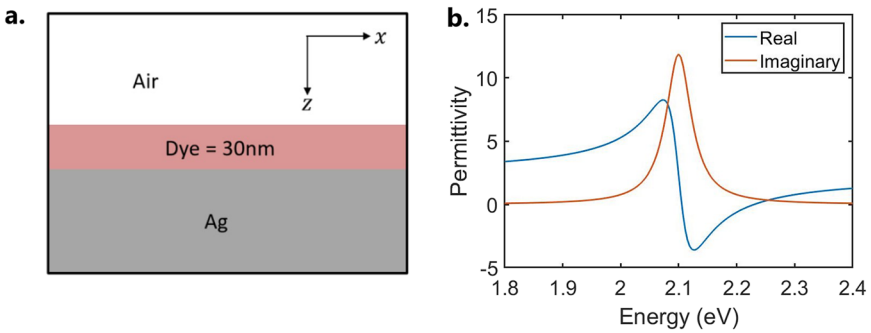

FIG. 1. (a) Schematic of the system stud-ied: a thin (30 nm) dye layer on a semi-infinite silver film in air. (b) Complex per-mittivity of the dye layer, modelling as a Lorentz oscillator [Eq. (1)] with parame-ters E_o = 2.10 eV, γ = 0.053 eV, f = 0.3, and ε_b = 2.25.

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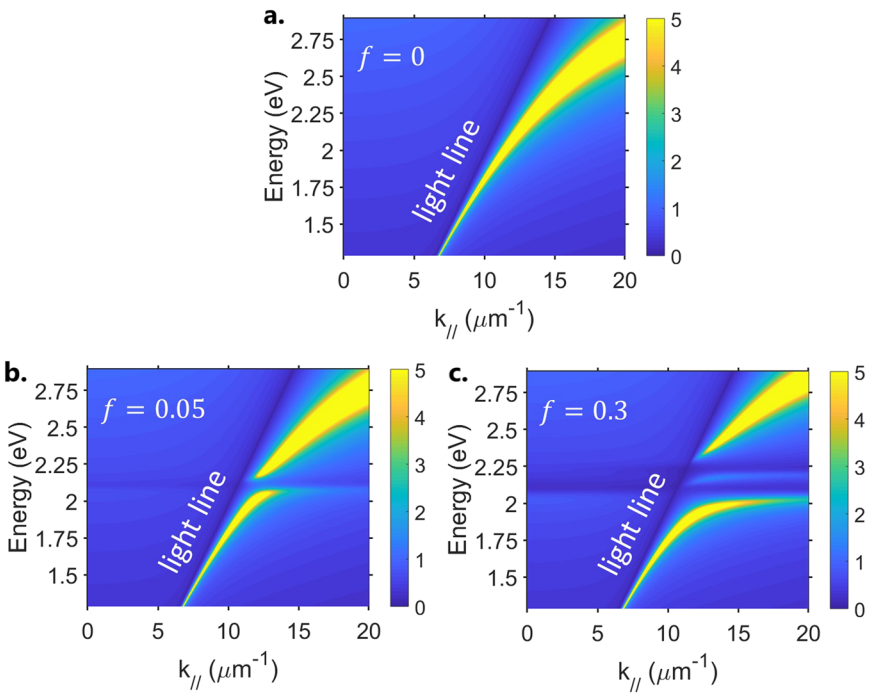

FIG. 2. Fresnel transmission amplitude of p-polarized light for an air/dye/Ag structure (Fig. 1) with the dye layer's oscillator strength set to (a) $f = 0$, (b) $f = 0.05$, and (c) $f = 0.3$.

longitudinal resonance energy, $E_l = 2.24$ eV, where the real part of permittivity is zero.

III. THE MIDDLE MODE

When two material resonances are both strongly coupled to a photonic mode, three hybrid polariton modes are typically formed: an upper polariton, a middle polariton, and a lower polariton (examples can be found in excitonic[15,16] and vibrational resonances).[17,18] An inspection of Fig. 2(c) does show what appears to be a "middle" mode of some kind, which is tempting to think that this feature is a middle polariton. However, the situation here is very different. We do not have two material resonances, and instead, we have one excitonic transition for which two very different modes of behavior (transverse and longitudinal oscillation) are possible.

To understand the origin of this "middle" mode, we need to follow the consequences of our dye-based material having a negative permittivity in this spectral region [see Fig. 1(b)]. Materials with a negative permittivity may look metallic[19] and, under appropriate conditions, may support a surface mode bound to the interface between the dye layer and the air.[9,20–23] Rather confusingly, this mode is also known as a polariton (in this case, a surface exciton polariton). (The rather problematic multiple different uses of the word polariton are discussed in the supplementary material.) The existence condition for such a mode at the interface between the two media, labeled 1 and 2, is[24]

$$\frac{\varepsilon_1}{k_{z,1}} = -\frac{\varepsilon_2}{k_{z,2}}, \tag{2}$$

where $k_{z,i}$ is the z-component (normal to the interface) of the wavevector in medium i. In addition, for such a mode to be considered a propagating mode, we require that absorption is not dominant, i.e., $|\Re(\varepsilon_2)| > |\Im(\varepsilon_2)|$. For $f = 0.3$, these conditions may be satisfied in our system, suggesting that the "middle" mode here is indeed a surface mode.

To examine whether the explanation outlined above is appropriate, i.e., to check that we have an upper avoided crossing due to the longitudinal resonance associated with our excitonic transition, a surface exciton polariton in the spectral region where the dye permittivity is negative, and a lower avoided crossing due to the transverse resonance associated with our excitonic transition, we calculated the electric field distributions associated with these features using a well-established technique.[25,26] For an in-plane wavevector of $k_\parallel = 15\ \mu\text{m}^{-1}$, and for energies corresponding to the three features at this in-plane wavevector, i.e., 2.53 eV, 2.18 eV, and 2.00 eV, the calculated profiles are shown in Fig. 3.

The electric fields of the upper and lower polaritons (top and bottom rows) are very similar in character to each other. Their in-plane electric field component (left column) decays away from the air–dye interface, while the out-of-plane electric field component (right column) involves both interfaces in a more complex way. For the "middle mode" (middle row), the situation is rather different. Both of the electric field components decay away from the air/dye interface, revealing the surface exciton polariton nature of this mode.[9]

Although the field distributions help identify the "middle mode" as being of different character to the upper and lower modes, there is another aspect that we explore next. Pockrand *et al.* observed that it is the out-of-plane component of the surface plasmon electric field that interacts with the longitudinal resonance, while the in-plane electric field component interacts with the transverse resonance.[10] As a result, we calculated another set of dispersion plots,

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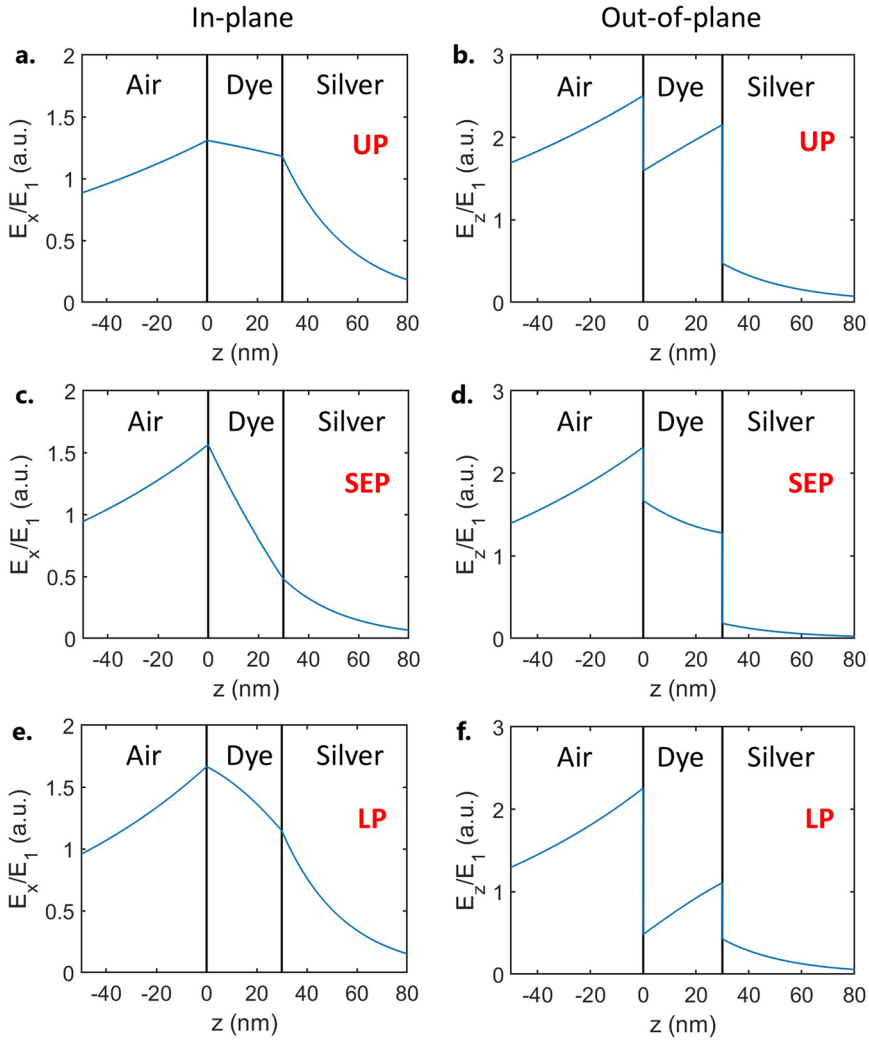

FIG. 3. In-plane (a), (c), and (e) and out-of-plane (b), (d), and (f) electric field distributions of the modes seen in Fig. 2(c) at $k_{||} = 15\ \mu m^{-1}$ for (a) and (b) the upper polariton mode (2.52 eV), (c) and (d) the surface exciton polariton (2.18 eV), and (e) and (f) the lower polariton mode (2.00 eV).

similar to Fig. 2, but with the dipole moment of the dye molecules lying first in the plane of the film and then perpendicular to the plane of the film. To do this, we made use of a uniaxial transfer matrix model, and the results are shown in Fig. 4.

Two dispersion plots are shown in Fig. 4. In Fig. 4(a), the in-plane permittivity of the dye is set equal to that used for the data shown in Fig. 1, while the out-of-plane permittivity is simply set equal to the background permittivity. In Fig. 4(b), the situation is

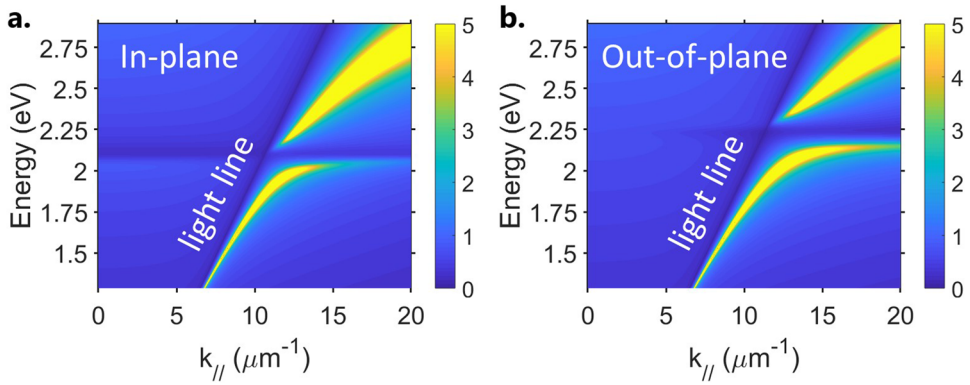

FIG. 4. Fresnel transmission amplitude (p-polarization) for the air/dye/Ag system. Here, the dye is uniaxial, the oscillator strength is $f = 0.3$, and the damping is $\gamma = 0.053$ eV. The dipole moment lies (a) in the plane (the anti-crossing occurs at 2.10 eV) and (b) perpendicular to the plane (the anti-crossing occurs at 2.24 eV).

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reversed, and here, the in-plane permittivity is set equal to the background permittivity, while the out-of-plane permittivity is set to be equal to that used for the data shown in Fig. 1. From these data, we see that when the dipole moments lie in the plane of the film, an anti-crossing associated with the transverse resonance occurs, while for dipole moments normal to the plane, an anti-crossing associated with the longitudinal resonance occurs. The results of these calculations are thus consistent with the work of Pockrand *et al.*[10] The absence of a surface exciton polariton feature in Fig. 4 is a consequence of the rather complex dependence on the existence such modes have when the medium involved is anisotropic (for details, see the work of Hartstein *et al.*).[27]

To show that the phenomenon of anti-crossing at different resonance energies associated with a single excitonic transition is not unique to the strong coupling of surface plasmons and excitons, we calculated the dispersion of the modes (p-polarization) associated with a microcavity filled with a dye layer, for which the dye layer placed between the two (silver) mirrors is uniaxial. A schematic diagram is shown in Fig. 5(a). Figure 5(b) shows the calculated transmittance of a cavity when there is no excitonic resonance present. Figure 5(c) shows the result when the dye layer is isotropic for a microcavity of 160 nm thick. Figure 5(d) shows the data for the same cavity, but here the dipole moment of the dye is in the plane of the cavity. Here, an avoided crossing occurs at 2.1 eV. Finally, in Fig. 5(e), for which the dipole moments are oriented out-of-plane, an anti-crossing occurs around 2.24 eV, consistent with the result shown in Fig. 4(b). The magnitude of the splitting when the dipole moment lies in-plane is similar to the isotropic case and is larger than the splitting for the case when the dipole moment is oriented out-of-plane. This reduced splitting is because the electric field in the microcavity is dominated by the in-plane electric-field component.[28]

IV. EFFECT OF DAMPING AND OSCILLATOR STRENGTH

In this section, we show the results from calculations to observe the effect of varying the oscillator strength and the damping factor on the double anti-crossing phenomenon, in particular, on the "middle" mode.

Figure 6(a) shows the transmission amplitude for the system depicted in Fig. 1(a), but for a range of oscillator strengths, all with the in-plane wavevector set at $k_{\parallel} = 15\ \mu\text{m}^{-1}$, and for these data, the damping factor is held constant, $\gamma = 0.053$ eV. We see that when the oscillator strength is large, three distinct modes can be observed with two well separated transmission amplitude minima between each mode. As the oscillator strength is reduced, the strength of the middle mode falls and the two minima eventually converge to 2.1 eV,

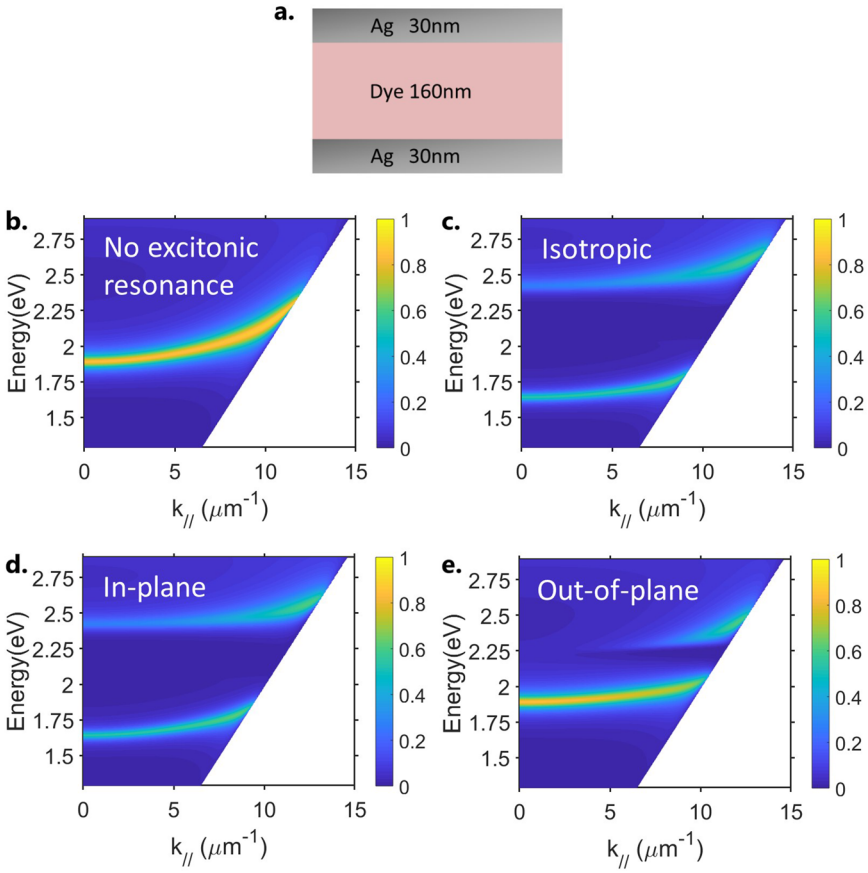

FIG. 5. (a) Schematic diagram of the microcavity with the dye layer (thickness 160 nm) sandwiched between two silver mirrors (each of thickness 30 nm). (b)–(d) Transmittance (p-polarization) of the microcavity with (b) isotropic dye, $f = 0$; (c) isotropic dye, $f = 0.3$; (d) uniaxial dye, $f = 0.3$, in-plane dipole moment; and (e) uniaxial dye, $f = 0.3$, out-of-plane dipole moment.

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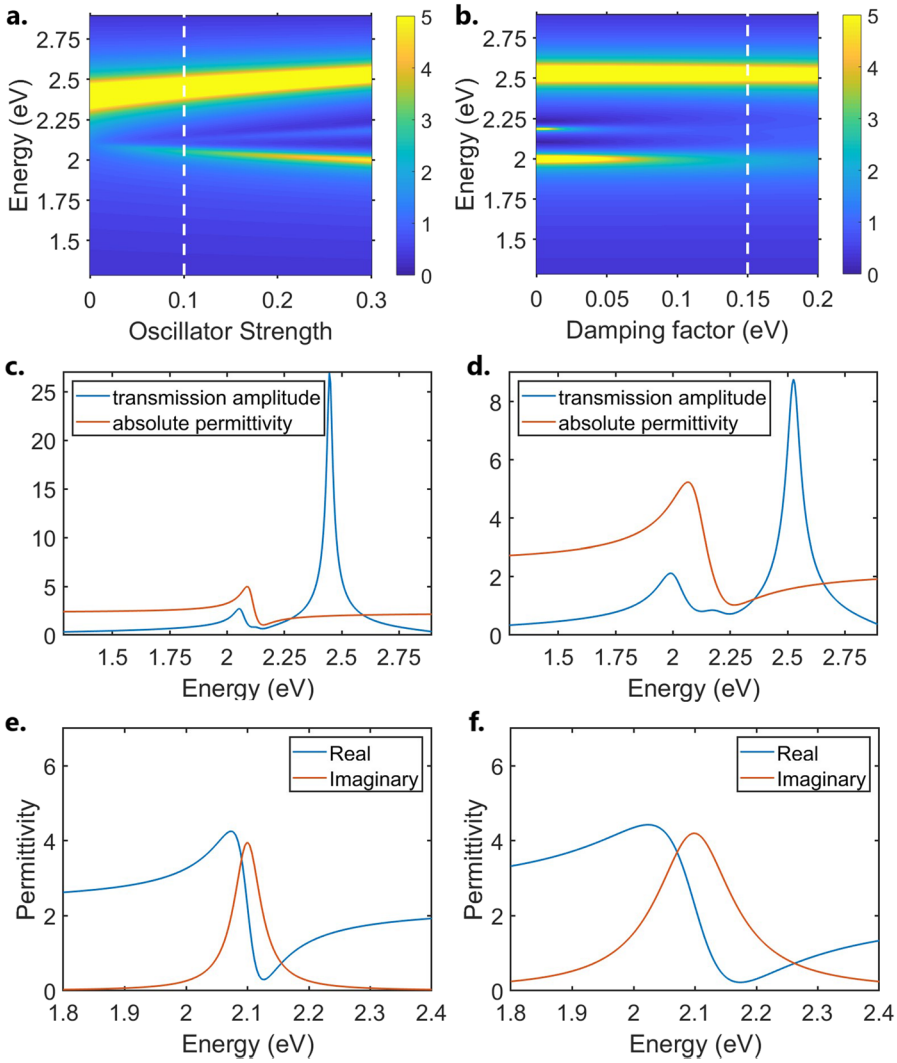

FIG. 6. The effect of oscillator strength and damping. The p-polarized Fresnel transmission amplitude at $k_{\parallel} = 15\ \mu m^{-1}$ is shown in (a) as a function of the oscillator strength while keeping the damping fixed, $\gamma = 0.053$ eV. In (b), the p-polarized Fresnel transmission amplitude at $k_{\parallel} = 15\ \mu m^{-1}$ is shown as a function of the damping factor while keeping the oscillator strength fixed, $f = 0.3$. In (c), a line plot is shown corresponding to the white dashed line at ($f = 0.1$) in (a), together with the absolute permittivity of the dye. In (d), a line plot is shown corresponding to the white dashed line at ($\gamma = 0.15$) in (b), together with the absolute permittivity of the dye. (e) and (f) are the permittivity of the dye in (c) and (d), respectively.

the transverse resonance energy of the molecule. In Fig. 6(c), we extracted a transmission amplitude line plot of Fig. 6(a) for $f = 0.1$, shown in Fig. 6(a) as a white dashed line. The peaks at 2.45 eV and 2.06 eV are the upper and lower polariton branches. Between the two main peaks seen in Fig. 6(c), two minima can be observed: one at 2.1 eV, the transverse resonance energy, and the other at 2.15 eV, the longitudinal resonance energy. What is interesting here is that the real part of the permittivity is strictly positive for this value of the oscillator strength [see Fig. 6(e)] so that there is no energy for which the real part of the permittivity is zero. In Fig. 6(c), the absolute permittivity is plotted in conjunction with the transmission amplitude, and we can see that the minimum of the absolute permittivity corresponds well with a minimum of the transmission amplitude. From these calculations, we see that features associated with the longitudinal resonance do not undergo a sudden disappearance when the permittivity goes from negative to positive. Instead, as the oscillator strength is reduced further, the transverse and longitudinal resonances appear to become degenerate.

The oscillator strength is not the only factor that determines whether a double anti-crossing is seen, but the damping factor also plays an important role. Even when the oscillator strength is strong such that the energies corresponding to the maximum and minimum values of the absolute permittivity are well separated, the middle mode is not necessarily seen. Figure 6(b) shows the transmission amplitude at $k_{\parallel} = 15\ \mu m^{-1}$ for a range of damping factors while keeping the oscillator strength fixed at $f = 0.3$. We see that the anti-crossing energies do not vary with the damping factor; however, as the damping increases, the strength of the middle mode decreases. Figure 6(d) shows a line plot of the transmission amplitude when the damping factor is $\gamma = 0.15$ eV. Three modes are still seen even when the permittivity is strictly positive [Fig. 6(f)]. We also plotted the absolute permittivity on top of this transmission line plot, from which we see that the extrema in the absolute permittivity correspond reasonably well with the associated features in the transmission amplitude data.

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What should we make of the fact that we see a (residual) middle mode even when the permittivity is not strictly negative? More specifically, is this consistent with our assignment of the middle mode being a surface mode, specifically a surface exciton polariton? To address this issue, we calculated the absorption spectra of the polariton modes by employing a prism-coupling geometry, and the results are shown in Fig. 7. The prism-coupling geometry and transmission amplitude of the structure are shown in Sec. S3 of the supplementary material. Figure 7(a) shows the absorption of the system when the dye layer has the same permittivity as for Fig. 1. As there is a spectral region of negative permittivity in the dye layer, the conditions for surface mode to exist are satisfied; hence, there are three distinct absorption peaks, which are the upper polariton, the surface mode, and the lower polariton. In Figs. 7(b) and 7(c), the permittivity of the dye is taken to be the same as for Figs. 6(c) and 6(d), where the permittivity is strictly positive. From these data, we see that even if the transmission amplitude shows three distinct peaks, the absorption spectrum shows only two distinct peaks, corresponding to the upper and lower polariton, while the absorption associated with the middle mode is barely discernible. This is as expected, and the fact that we see a weak feature here despite the lack of a negative permittivity simply follows from the dispersion of the permittivity. As the parameters are adjusted so that the permittivity becomes negative, this middle mode starts to show an appreciable absorption.

Strong coupling between surface plasmons and J-aggregates has been reported many times, but it appears that only a single avoided crossing is usually seen.[1] There are several factors that contribute to this. First, J-aggregates are long-chain molecules that tend to lie flat on a surface.[29] This typically leads to J-aggregate films being uniaxial with the dipole moment of the J-aggregates lying in the plane of the surface.[30] As we have seen above, when the film is highly uniaxial and the dipole moment is in-plane, we only observe a single splitting at the transverse resonance frequency, i.e., the transition frequency of the molecule. Even if there is some component of the dipole moment normal to the surface, it is usually weak compared to the in-plane component.[30] Second, the middle mode is rather weak in intensity due to the high absorption of the dye in this spectral region. There may also be uncoupled molecules that contribute to the absorption in this spectral range.[31] Finally, J-aggregate films may be somewhat rough, having different domains in the same film.[32] This roughness will lead to surface scattering, further reducing the middle mode's visibility.

V. SUMMARY AND CONCLUSION

When surface plasmons strongly couple with an excitonic species, hybridization occurs and an anti-crossing emerges between the two new hybrid states that form. We have shown that when the excitonic material has a high enough oscillator strength together with a narrow enough linewidth, an additional anti-crossing occurs. The energies where the two anti-crossings occur correspond to the transverse resonance and the longitudinal resonance. The transverse resonance corresponds to the energy of the excitonic transition, while the longitudinal resonance corresponds to the energy at which the real part of the permittivity is zero. Furthermore, we have shown that molecular dipole moments that are parallel to the surface of the material contribute to the splitting at the transverse resonance, while the dipole moments oriented normal to the surface contribute to the splitting at longitudinal resonance. The interaction of surface

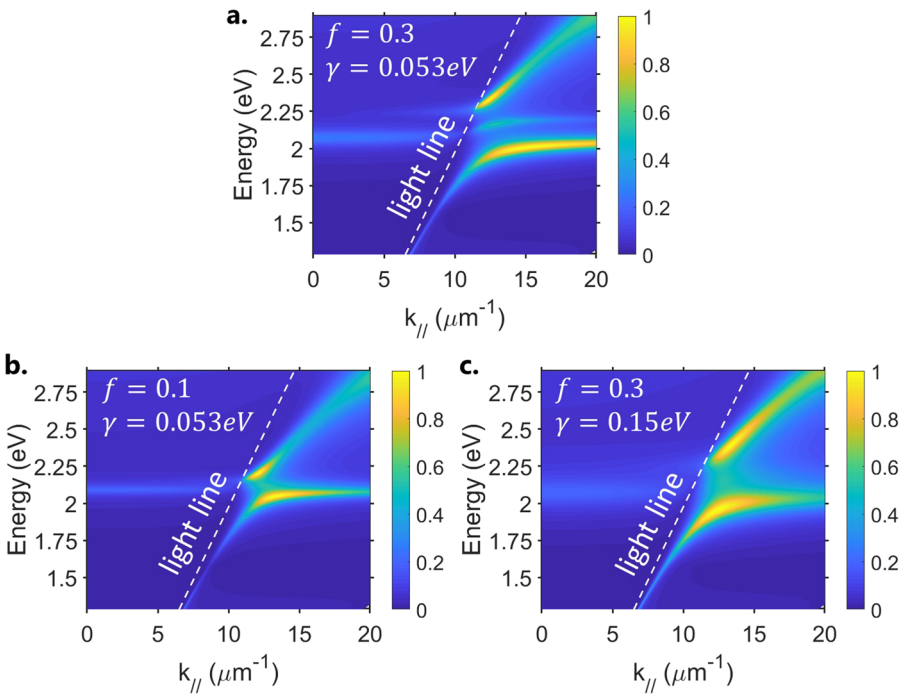

FIG. 7. Absorption (p-polarization) of the 30 nm silver film with the 30 nm dye layer on top in the prism geometry (schematic shown in Fig. S1). The dye has an oscillator strength and a damping factor of (a) f = 0.3 and γ = 0.053 eV; (b) f = 0.1 and γ = 0.053 eV; and (c) f = 0.3 and γ = 0.15 eV.

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plasmons with such an excitonic material gives rise to three different modes: the upper polariton, surface exciton polariton, and lower polariton.

We have also showed that the separation between the transverse and longitudinal resonance is affected by the oscillator strength, while the strength of interaction of the electric field with the longitudinal resonance is weak for the material with larger damping.

We concluded that this phenomenon is rarely observed experimentally as the dye layer is uniaxial with the dipole moment lying in-plane, and the roughness of the organic dye layer scatters the surface exciton polariton, which reduces its intensity.

SUPPLEMENTARY MATERIAL

See the supplementary material for further details on transverse and longitudinal resonance, nomenclature of polariton, and absorption calculation of the middle mode when the permittivity is strictly greater than zero.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material and from the corresponding author upon reasonable request. The research data supporting this publication are openly available from the University of Exeter's institutional repository.

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