Resonance Quenching and Guided Modes Arising from the Coupling of Surface Plasmons with a Molecular Resonance

Wei-Hsun Yeh, Joseph W. Petefish, and Andrew C. Hillier*

Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, United States

ABSTRACT: In this paper, we describe experimental and modeling results that elucidate the nature of coupling between surface plasmon polaritons in a thin silver film with the molecular resonance of a zinc phthalocyanine dye film. This coupling leads to several phenomena not generally observed when plasmons are coupled to transparent materials. The increased absorption coefficient near a molecular resonance leads to a discontinuity in the refractive index, which causes branching of the plasmon resonance condition and the appearance of two peaks in the p-polarized reflectance spectrum. A gap exists between these peaks in the region of the spectrum associated with the molecular resonance and reflects quenching of the plasmon wave due to violation of the resonance condition. A second observation is the appearance of a peak in the s-polarized reflection spectra. The initial position of this peak corresponds to where the refractive index of the adsorbate achieves its largest value, which occurs at wavelengths just slightly larger than the maximum in the molecular resonance. Although this peak initially appears to be nondispersive, both experimental data and optical modeling indicate that increasing the film thickness shifts the peak position to longer wavelengths, which implies that this peak is not associated with the molecular resonance but, rather, is dispersive in nature. Indeed, modeling shows that this peak is due to a guided mode in the film, which appears in these conditions due to the abnormally high refractive index of the film near the absorbance maximum. Results also show that, with increasing film thickness, numerous additional guided modes appear and move throughout the visible spectrum for both s- and p-polarized light. Notably, these guided modes are also quenched near the location of the molecular resonance. The quenching of both the plasmon resonance and the guided modes can be explained by a large decrease in the in-plane wave propagation length that occurs near the molecular resonance, which is a direct result of the film’s large absorption coefficient.

The resonance conditions of surface plasmons (SPs) at a metal/dielectric interface are highly sensitive to the local environment. This behavior has led to their extensive use in thin-film and adsorption sensing.1−3 The majority of these applications have involved measurements with transparent films or adsorbates possessing a negligible optical absorption coefficient. Changes in the resonance condition in response to a simple dielectric material can be readily explained in terms of the metal’s refractive index and the optical thickness of the dielectric layer.4 In the presence of a film with a dielectric constant larger than that of the surroundings, the increased optical density results in a decrease in the energy associated with the SP resonance and a corresponding red shift in the resonance position.

For adsorbates possessing a molecular resonance, the coupling with SPs is much more complex and also information rich. The complexity of this coupling has been demonstrated with propagating SPPs (or surface plasmon polaritons) in thin metal films. Early studies with SPPs showed that the coupling of Langmuir−Blodgett dye assemblies using attenuated total reflection on thin silver films leads to branching of the dispersion curves near the molecular resonance.5−7 Notably, studies of SPP−adsorbate interactions benefit from the ability to directly measure dispersion relations via simple angle and wavelength scanning. A number of studies involving the coupling of SPPs with J-aggregates and other absorbing materials have been published.8−10 In analytical applications, the interaction of SPPs and molecular adsorbates has led to various advanced forms of surface plasmon spectroscopy.11,12 Examples of these advancements include spectral fingerprinting, enhancements in sensitivity for SPR thickness shifts,13,15 and signal enhancement for absorbance detection.16

The interaction of molecular resonances with localized surface plasmon resonance (LSPR) at nanoparticles has received increasing attention.17 Details of the interaction between a molecular resonance and the LSPR at nanoparticles are strongly influenced by the size (and shape) of the nanoparticle, as well as the degree of overlap between the LSPR and the molecular resonance.18 Indeed, the coupling leads not only to variation in the magnitude of the LSPR shifts, but also to resonance quenching, which has been exploited for detection methods such as plasmon resonance energy transfer.19,20 In addition to the ability to exploit plasmon−molecule interactions to improve the efficiency of photochemical and photoelectrochemical processes,21 molecule−plasmon coupling can be used to perform active optical switching.22,23 A merging of local and extended surface plasmon coupling with molecular
resonances, via ordered arrays of nanostructures, can potentially lead to even greater flexibility and control of SP–molecule coupling and the resulting phenomena.24,25

To more fully understand the interaction between a molecular resonance in an adsorbed material and an SP in a metal film, we describe the results of a series of experiments and optical modeling studies that demonstrate the coupling between propagating SPPs in a thin silver film and the molecular resonance associated with thin films of a zinc phthalocyanine (ZnPC) dye. The optical reflection of thin films of ZnPC on silver is examined in the Kretschmann configuration as a function of the wavelength and angle of incidence. The well-defined SP resonance on a bare silver film red-shifts in the presence of a thin ZnPC film. With increasing thickness, the SP resonance overlaps with the Q-band of the ZnPC film. In the region of the spectrum where the ZnPC Q-band absorbance lies, the SP resonance is quenched, and the SP is split into a low- and high-energy state, evidenced by the appearance of two separate peaks in the reflectance of p-polarized light. Under these same conditions, an additional peak appears in the s-polarized spectrum. Optical modeling is used to verify the origins of this SP resonance quenching and also to assist in interpreting this new peak, which is the consequence of a guided wave in the dye film and is not directly related to the molecular resonance. Also, the presence of the molecular resonance leads to quenching of both plasmon and guided modes within the spectral region associated with the large optical absorbance in the film as a result of the decreased propagation length of the plasmon wave.

**EXPERIMENTAL SECTION**

Materials and Reagents. ZnPC, hydrogen peroxide solution (30%), and sulfuric acid were purchased from Sigma-Aldrich (St. Louis, MO). Glass slides were purchased from Fisher Scientific (Pittsburgh, PA). Index matching fluid and BK7 prisms were purchased from Edmund Optics (Barrington, NJ). Silver (99.999%), tungsten wire baskets, and alumina-coated tungsten evaporation baskets were purchased from Ted Pella, Inc. (Redding, CA). Deionized water with electrical resistivity greater than 18 MΩ · cm was used during the rinsing and cleaning procedures (NANOPure, Barnstead, Dubuque, IA).

Sample Preparation. Metal and dye films were deposited using thermal evaporation onto planar glass slides. Fresh piranha solution (mixture of 3:1 concentrated sulfuric acid to 30% hydrogen peroxide solution) was used to clean the glass slides. Caution: piranha solution reacts violently with organic compounds! Following the cleaning, the glass slides were rinsed vigorously with deionized water and dried under nitrogen. The slides were subsequently placed in a vacuum chamber (model Bench Top Turbo III, Denton Vacuum, Moorstown, NJ) for deposition of ~45 nm of silver by resistive heating from a tungsten wire basket at a rate of 0.1 Å s⁻¹ and a pressure of <10⁻⁵ Torr. The Ag-coated slides were then immediately transferred to a second vacuum chamber (model DV502A, Denton Vacuum). Thin films of ZnPC were slowly (<0.1 Å s⁻¹) deposited on Ag-coated slides under a pressure of <10⁻⁵ Torr from alumina-coated tungsten evaporation baskets.

Atomic Force Microscopy (AFM) Imaging. AFM imaging of the sample surfaces was performed with a Dimension 3100 scanning probe microscope and a Nanoscope IV controller (Veeco Metrology, LLC, Santa Barbara, CA). Imaging was performed in tapping mode using silicon TESP7 AFM tips (Veeco Metrology) with a spring constant of ~70 N m⁻¹ and a resonance frequency of ~280 kHz. Film thicknesses were determined by using a razor blade to remove a region of film, and a line profile along this boundary was used to determine the height difference between the substrate and film.

Surface Plasmon Resonance Reflection Measurements. A computer-controlled variable-angle ellipsometer (Multiskop, Optrel GbR, Sinzing, Germany) was modified to perform broadband reflection measurements by removing the compensator, replacing the He–Ne laser with a fiber-coupled, broad-band, tungsten–halogen light source (OSL1, Thor Lab, Newton, NJ), and mounting an optical fiber spectrophotometer (HR4000CG-UV-NIR, Ocean Optics, Inc., Dunedin, FL) as the detector. Control of the angle of incidence was achieved with the instrument’s motorized two-circle goniometer. Reflection measurements were performed in the Kretschmann configuration, with metal-coated glass slides attached to a 45° BK7 prism using index matching fluid. Reflectance values were reported in terms of p-polarized (R_p) or s-polarized (R_s) reflectance, which is calculated by dividing the reflected light intensity (p or s) by the s-polarized reflectance from an uncoated silver (47 nm) surface at the same angle of incidence (θ).

Spectroscopic Ellipsometry. Rotating analyzer ellipsometry (RAE) was performed in the polarizer–sample–analyzer (PSA) configuration using the optical system described above. Light from a tungsten–halogen light source was polarized at 45° and reflected by the sample surface at an incident angle of 70°. The analyzer was rotated from 0° to 180°, and a fiber-optic spectrometer was used to capture spectra of reflected intensities at 5° intervals. The measured intensity spectra were numerically integrated over the range of analyzer angles to obtain the ellipsometry parameters Δ and Ψ between 400 and 1000 nm. The values of Δ and Ψ were then converted into equivalent optical thicknesses using an N-phase model (vide infra). The optical constants of the silver substrate (refractive index n and absorption coefficient κ) were first determined using a three-phase model (air/silver/BK7) with the AFM-measured silver thickness (47 nm). The optical constants of the ZnPC films were then found by fitting a four-layer model (air/ZnPC film/silver/BK7) using the AFM-measured thicknesses for the Ag (47 nm) and ZnPC (19 nm).

Optical Modeling. N-phase Fresnel calculations were used to model reflection and transmission through the multilayer air/ZnPC film/silver/BK7 prism system as a function of the wavelength, angle of incidence, and polarization state of the incident light. Scripts were written in MATLAB (The MathWorks, Inc., Natick, MA) to calculate reflection for three-phase (BK7/silver/air) or four-phase (BK7/silver/ZnPC film/air) models. Wavelength-dependent reflective indices of BK7 glass were used in the calculations. The dispersion of BK7 glass was estimated using the Sellmeier equation:

\[
n(\lambda) = 1 + \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} + \frac{B_3\lambda^2}{\lambda^2 - C_3}
\]  

where \(n\) is the refractive index of BK7, \(\lambda\) is the wavelength of light (μm), and the values of the constants were taken from Schott glass: \(B_1 = 1.03961212, B_2 = 2.31792344 \times 10^{-4}, B_3 = 1.01046945, C_1 = 6.00069867 \times 10^{-3} \mu m^2, C_2 = 2.00179144 \times 10^{-2} \mu m^2, C_3 = 1.03560653 \times 10^{-2} \mu m^2\). The refractive index values for silver (Figure S3, Supporting Information) and ZnPC (Figure S4, Supporting Information) were derived from fitting

\[dx.doi.org/10.1021/ac202855a\]
the experimental spectroscopic ellipsometry results (Figure S2, Supporting Information) from the experimentally prepared thin films.

## RESULTS AND DISCUSSION

Organic dyes such as ZnPC have generated considerable interest due to their large molar absorptivities and potential use as artificial pigments and in applications such as memory storage, catalysis, and optoelectronics.\(^{27}\) In solution, ZnPC exhibits a strong molecular resonance near 680 nm associated with the dye’s Q-band (Figure 1). When formed as a thermally evaporated thin film on silver, there is a slight red shift of this peak to \(~710\) nm (Figure 1).

The coupling of this ZnPC film, with its strong molecular resonance, with an SP in the Ag substrate was studied by measuring the optical reflection of p-polarized (\(R_p\)) and s-polarized (\(R_s\)) light with the sample in the Kretschmann configuration (Figure 2A). The uncoated silver film (47 nm thick) exhibits the expected sharp decrease in reflectivity for p-polarized light associated with the formation of an SP. At an incident angle of 48°, the reflectance minimum occurs at a wavelength of \(~437\) nm (Figure 2B). Reflection of s-polarized light under these conditions results in a high reflectivity (Figure 2C), consistent with conditions of total internal reflection. The addition of a thin (6 nm) ZnPC film to the silver results in a red shift of the SP to 492 nm and no change in the s-polarized response. The behavior of a thicker (19 nm) ZnPC film shows several notable features. The reflectance minimum in p-polarized light has red-shifted, but it has also split into two distinct minima, one appearing at \(~561\) nm and the other at 792 nm. In addition, reflection of s-polarized light now shows an unusual reflectance minimum, albeit a weak one, at 716 nm.

More detail about the nature of these features can be illustrated with reflection images taken at several different incident angles (Figure 3). These reflection images for the bare silver film (Figure 3A) show the expected behaviors: the s-polarized image (\(R_s\)) is uniform, and a strong resonance minimum appears in the p-polarized image (\(R_p\)). The dispersive nature of the SP in the p-polarized image is highlighted by the red-shifting of the reflection minimum with decreasing angle (Figure 3A). Reflection images of the 19 nm ZnPC film on silver show two clearly resolved minima, with a gap in between (Figure 3B). The peak that appears at longer wavelengths displays clear dispersive behavior by shifting to longer wavelengths with decreasing angle. The shorter wavelength peak also shifts, but to a lesser degree. A notable feature in this image is that the SP resonance is completely quenched between the two minima at all angles. The minimum in the s-polarized image (Figure 3B) is also apparent, and this feature appears nondispersive under these conditions, with its position unaffected by the changing angle. However, this peak is indeed dispersive, as we will show in subsequent data and calculations (vide infra).

![Figure 1. Absorbance spectra of ZnPC in solution (50 \(\mu\)M in CHCl\(_3\)) and as a 19 nm film on Ag-coated (47 nm) glass.](image1.png)

![Figure 2. (A) Schematic of the Kretschmann configuration used for measurement of reflectance spectra. Reflectance spectra for 0, 6, and 19 nm thick ZnPC films in air on a 47 nm Ag/BK7 prism in the Kretschmann configuration at a 48° angle of incidence: (B) p-polarized reflectance (\(R_p\)) and (C) s-polarized reflectance (\(R_s\)).](image2.png)

![Figure 3. Measured reflectance images for p-polarized (\(R_p\)) and s-polarized (\(R_s\)) light as a function of the angle of incidence and wavelength for (A) a 47 nm Ag film and (B) with an additional 19 nm ZnPC layer in the Kretschmann configuration. The intensity ranges correspond to 0 < \(R_p\) < 1.2 and 0.9 < \(R_s\) < 1.1.](image3.png)
Red-shifting of the resonance peak in the p-polarized data associated with film formation is the behavior typically seen with SPs. Therefore, the appearance of two peaks, and the quenching of the resonance in the spectral region near the molecular resonance, must be associated with the coupling that occurs between the molecular resonance and the SP resonance. This behavior can be explained by considering the nature of the plasmon and the impact of the molecular resonance on the SP matching condition (vide infra). The appearance of a minimum in the s-polarized spectra near a molecular resonance has not been reported, although a recent publication has highlighted an enhanced transmission through a nanohole metal array when coated with a thin dye film.25 We believe that the peak appearing in that result and the peak appearing here have the same fundamental origin, which is the emergence of a guided wave in the thin adsorbed film (vide infra).

To more fully understand the coupling of the molecular resonance of ZnPC and the SP in the silver film, we completed a series of optical modeling calculations. The optical constants of silver and ZnPC were determined by combining the film heights, as measured by atomic force microscopy (see the Supporting Information, Figure S1) with spectroscopic ellipsometry of the two films (Supporting Information, Figures S2, S3 and S4). A four-phase optical model was then used to calculate the reflection of transverse magnetic (TM = p-polarized) and transverse electric (TE = s-polarized) light as a function of the ZnPC thickness, wavelength, and angle for the BK7 prism/Ag/ZnPC/air multilayer. Modeling results for a bare 47 nm Ag film and also with an additional 19 nm ZnPC layer at 48° are shown in Figure 4. A comparison between the calculated reflectance spectra in Figure 4 with the experimental results in Figure 2 shows a significant similarity. The bare silver films show a nearly identical resonance minimum in the p-polarized spectrum (Figure 4A) and little of note in the s-polarized result (Figure 4B). The addition of a 19 nm ZnPC film shows the same red-shifting and splitting of the resonance in the p-polarized spectrum, with fine structure nearly identical to that seen in the experimental results. Notably, the strong resonance minima in the p-polarized spectra are completely outside the region of the spectrum where the ZnPC Q-band absorbance lies (denoted by the dotted box in Figure 4), indicating the same quenching behavior as the experimental results. The new minimum observed in the s-polarized data with the 19 nm ZnPC layer is also apparent in the calculated results. Thus, both of these behaviors can be explained by standard optical theory and are the direct result of the optical properties of the ZnPC dye and how they interact with the SP in the Ag film.

The splitting of the SP resonance and the quenching that occurs near the molecular resonance of the ZnPC film can be explained by considering the wave vector ($k_{SP}$) of the SP parallel to the ZnPC/Ag interface. For a macroscopically thick ZnPC film, this wave vector can be described by the following relationship:

$$k_{SP} = \frac{2\pi}{\lambda} \sqrt{\epsilon_m \epsilon_d / (\epsilon_m + \epsilon_d)}$$

where $\epsilon_m$ is the dielectric constant of the silver and $\epsilon_d$ is the dielectric constant of the ZnPC film. In a general case, $k_{SP}$ is a complex number:

$$k_{SP} = k_{SP}' + ik_{SP}''$$

For this SP to exist and propagate along the metal/film interface, the propagation length ($L$),4 as defined by

$$L = \frac{1}{k_{SP}''}$$

must have a nonzero value. This propagation length can be readily calculated by considering the wavelength-dependent optical constants of the metal and dielectric films. The refractive index ($n$) and absorption coefficient ($\kappa$) for ZnPC (Figure 5A,B) illustrate the resonance associated with the Q-band. The absorption coefficient goes through a maximum in this region ($\sim$700 nm), and as is consistent with the Kramers–

**Figure 4.** Calculated reflectance ($R$) spectra for 47 nm Ag (dashed lines) and 47 nm Ag + 19 nm ZnPC (solid red lines) films in the Kretschmann configuration at a 48° angle of incidence using TM (p-polarized) and TE (s-polarized) light. The dotted box denotes the region of the visible spectrum enclosing the molecular resonance for ZnPC.

**Figure 5.** (A) Refractive index ($n$) and (B) absorption coefficient ($\kappa$) for ZnPC as determined by spectroscopic ellipsometry of a 19 nm film. (C) Calculated propagation length ($L$) for the optical wave along the interface of silver and ZnPC.
Kronig relation, the refractive index decreases when approaching this absorbance from smaller wavelengths and then exhibits a discontinuity to reach a maximum value just to the right of the absorbance maximum, before decreasing again. Using these optical parameters for ZnPC, along with the dielectric properties of Ag, allows one to calculate \( L \) for this interface as a function of the wavelength (Figure 5C). These results indicate that \( L \) obtains nonzero values between \(~400\) and \(550\ nm\) and then again above \(~750\ nm\). However, between \(550\) and \(750\ nm\), \( L \) approaches zero. These results indicate that the SP can exist above and below this spectral region, but is unable to propagate near the molecular resonance. This behavior is primarily the result of the large value of the absorption coefficient \( \kappa \) for ZnPC in this region, which makes the imaginary part of \( \varepsilon_d \) large and consequently creates a large value for \( k_{\text{SP}} \) and a vanishing value for \( L \). Similar calculations using a nonabsorbing material (Supporting Information, Figure S7A,B) show only an increasing \( L \) with increasing wavelength, which supports the presence of a propagating SP over much of the visible spectrum. An idealized absorbing material, with a Lorentzian absorbance peak, gives a value of nearly \( L = 0 \) over the entire spectral region associated with the absorbance peak (Supporting Information, Figure S7C,D).

For a metal/film interface, the SP wave vector can be simplified. At energy levels well away from the plasma frequency for a given metal, the imaginary part of the metal’s dielectric constant takes on large, negative values, which allows \( \kappa_{\text{SP}} \) to be approximated by

\[
k_{\text{SP}} \approx \frac{2\pi}{\lambda} \sqrt{\varepsilon_d}
\]

Far from the molecular absorbance (or for a nonabsorbing material), where the absorption coefficient of the film is zero, this wave vector can be written as

\[
k_{\text{SP}} \approx \frac{2\pi}{\lambda} n_d
\]

which is a purely real number, indicating that the propagation constant \( L \) is very large and that the plasmon is supported at this interface. However, near the molecular resonance, the imaginary part of the film’s dielectric constant goes through an inflection that tracks the value of \( n \) (\( \varepsilon_d'' = 2\pi\kappa \)), while the real component approaches the negative square of the absorption coefficient (\( \varepsilon_d'' = \varepsilon'' - \kappa^2 \)). Thus, the plasmon wave vector can be approximated as

\[
k_{\text{SP}} \approx \frac{2\pi}{\lambda} \sqrt{\kappa}
\]

and the propagation length approaches the limit of

\[
L = \frac{1}{2\pi\kappa}
\]

Thus, the larger the value of \( \kappa \), the smaller the wave propagation length. Therefore, a molecular resonance will result in the extinguishing of the SP.

The second feature in both experimental and modeling results was the appearance of a new peak in the s-polarized spectrum. More detail regarding the nature and origins of this peak can be deduced through some additional experimental data and complementary optical modeling results. The results from Figure 3B show that the minimum in the s-polarized data does not change wavelength with the angle, which would suggest that it is a nondispersive peak and is somehow related to the molecular absorbance. However, increasing the thickness of the film suggests that this peak is indeed dispersive. Figure 6 shows experimental reflectance spectra for ZnPC films of various thicknesses between 6 and 160 nm on Ag. The absence of a peak is noted in the 6 nm film, followed by the first appearance of the peak with a 19 nm film. With larger ZnPC film thicknesses, the peak position is seen to red-shift significantly. The peak magnitude also increases as the film thickness increases from 19 to 121 nm. The red-shifting of the peak position for the 19 nm film from its initial value at 716 nm to the final peak position of \(~920\) nm for the \(166\) nm ZnPC film clearly shows that this peak is dispersive. Additional evidence of dispersion can be seen in Figure 6B for the \(166\) nm thick ZnPC film, which shows a red-shift in the peak position with decreasing angle of incidence. A second peak, whose origin is similar to that of the first peak (vide infra), is also observed in the two thickest ZnPC films at wavelengths near \(~510\) nm.

Optical modeling supports the behavior seen in these experimental data. Figure 7 depicts a series of computed reflectance spectra using s-polarized (TE) light as a function of the ZnPC thickness. Spectra are plotted for film thicknesses between 0 and 140 nm, at increments of 10 nm. The thinnest films show only an increasing \( L \) with increasing wavelength, which supports the presence of a propagating SP over much of the visible spectrum. An idealized absorbing material, with a Lorentzian absorbance peak, gives a value of nearly \( L = 0 \) over the entire spectral region associated with the absorbance peak (Supporting Information, Figure S7C,D).

![Figure 6. Measured reflectance spectra with s-polarized light (R) for (A) ZnPC films of increasing thickness on a 47 nm Ag layer in the Kretschmann configuration at a 48° angle of incidence. (B) Reflectance image for s-polarized (R) light as a function of the angle of incidence and wavelength for a 166 nm ZnPC film on a 47 nm Ag layer.](image-url)

dx.doi.org/10.1021/ac202855a1143
Figure 7. Calculated reflectance spectra using TE light (s-polarized) for increasing ZnPC film thickness on Ag in the Kretschmann configuration. Line plots showing reflectance spectra with increasing ZnPC film thickness from 0 to 100 nm. The inset shows an expanded view of the films with 0, 10, 20, and 30 nm ZnPC thicknesses.

than 30 nm, the peak grows in magnitude and also shifts appreciably to the red. Thus, the dispersive nature of this peak is confirmed with the large red shift with increasing thickness. Although the original peak position was located near the maximum in the molecular absorbance, the dispersive nature of the peak confirms that this initial peak position being near the molecular absorbance was coincidental. As we will prove in the following passages, the origin of this peak is ultimately that of a guided mode within the ZnPC layer, which is excited by an SP in the silver film.

With increasing ZnPC thickness, the SP that is excited at the silver/ZnPC interface is able to couple to a guided mode within the ZnPC layer, which produces a peak in the s-polarized spectra. The location and magnitude of this guided mode are impacted by the coupling between the SPP in the Ag film and the molecular resonance on the ZnPC layer. The propagation of this guided mode is also hindered by the quenching of the SPP associated with the molecular resonance, which explains the reduced amplitude of the peaks when they are located near the molecular resonance.

Evidence that numerous guided modes can be excited by both s- and p-polarized light at increasing film thickness can be shown by additional model results. As an illustration, Figure 8 depicts computed p- and s-polarized spectra with ZnPC films of thicknesses between 0 and 500 nm. Numerous guided modes appear in these spectra, and labels for particular modes have been included. The peaks observed in the experimental data of Figure 6 correspond to the TE0 mode (Figure 8B). For TE0, the first peak to appear at small film thicknesses is near 700 nm. It then red-shifts with increasing film thickness. As the film thickness reaches ~80 nm, a second peak appears in the TE0 mode at small (~400 nm) wavelengths. This peak also shifts to longer wavelengths with increasing film thickness. This second peak in the simulated results for TE0 corresponds to the second peak observed near ~510 nm for the 121 and 166 nm thick films in the experimental data.

It should be noted that several features in the waveguide modes depicted in Figure 8 differ from what would be observed in a typical nonabsorbing waveguide layer. The modes shown here are highly nonlinear with thickness and are quenched near the molecular resonance so that their magnitudes go to zero. In contrast, the location of a guided mode in a nonabsorbing dielectric slab waveguide would vary linearly with the thickness and appear over the entire spectral region. To illustrate this further, a slab waveguide sandwiched between two perfect mirror layers, for example, would support guided modes for TE excitation that satisfy the relationship

\[
\frac{2\pi}{\lambda} n_d h_d \cos(\theta) = m\pi \tag{9}
\]

where \(n_d\) is the dielectric constant of the waveguide layer, \(h_d\) is the waveguide thickness, \(\theta\) is the incident angle, and \(m = 1, 2, ...\) are the modes of the TE-guided wave. The increase in wavelength with increasing film thickness would be strictly linear in this case, with the slope increasing for higher modes (increasing \(m\)). Numerical results for an asymmetric waveguide slab, as is the case here, with a nonabsorbing, dielectric film in the Kretschman configuration on a 47 nm Ag film, also exhibit a linear increase in wavelength with thickness (Supporting Information, Figure S9).

Although the complete solution describing the matching conditions for an asymmetric waveguide is more complex, the general behavior for the ZnPC film system can still be interpreted with eq 9. As noted, the peaks in Figure 8 are nonlinear. However, they approach linearity far from the molecular absorbance (high and low wavelengths). In these near-linear regions, the peaks exhibit an increasing slope with increasing mode number, which is consistent with eq 9. A simple explanation for the nonlinear shape of the modes near the molecular resonance comes from the fact that the layer height (\(h_d\)) and the refractive index (\(n_d\)) are inversely proportional in the guided mode (eq 9). By simply inverting the refractive index curve for ZnPC from Figure SA, one can reproduce the shape of the curves in Figure 8. The most notable consequence of this behavior in the experimental
results is that the guided mode appears in the s-polarized spectra at much smaller film thicknesses with ZnPC than would be the case with a nonabsorbing, dielectric material because of the abnormally high value of $n_d$ provided by the molecular resonance.

Ultimately, for a guided mode to persist, it must be able to propagate within the waveguide layer. However, the conditions that lead to quenching of the SP also lead to quenching of the guided modes. The increased absorption coefficient near the molecular resonance in the ZnPC film diminishes the propagation length of the guided modes so that they are also quenched. Nevertheless, all other features of these modes are consistent with what would be observed in a traditional dielectric waveguide.

**CONCLUSIONS**

The interaction of surface plasmons with a molecular resonance leads to the appearance of several new features not typically observed with SPs that are coupled to transparent materials. The molecular resonance in a ZnPC dye film, for example, causes the SP in a silver layer to split into two branches. The gap between these branches reflects quenching of the SP. The origin of this quenching is due to the decreased propagation length for the SP due to the large absorption coefficient for the dye near the molecular resonance. The magnitude of the quenching is a strong function of the strength of the molecular resonance, as well as the degree of overlap between the SP and that of the adsorbed molecule.

The appearance of a guided mode in the s-polarized spectra is a feature that occurs with this particular dye, but also appears in transparent films. In a transparent film, this guided mode is also quenched near the molecular resonance, and the resulting dispersion curve is highly nonlinear near the resonance location. However, the nature of this dispersion relation follows what would be expected on the basis of the optical properties, particularly the refractive index, of the molecular film.

The coupling of molecular resonances to surface plasmons provides an information-rich system for optical sensing and the ability to tune the optical response through the degree of overlap with the molecular resonance. The novel features exhibited by this type of system have been used in the design of new analytical and sensing schemes in both nanoparticle (LSPR) and thin-film (SPP) systems. One could envision exploiting these features further in the development of new optical spectroscopies and sensor systems and in optoelectronic devices.

**ASSOCIATED CONTENT**

* Supporting Information
Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Corresponding Author
*E-mail: hillier@iastate.edu.

**ACKNOWLEDGMENTS**

This work was supported by the National Science Foundation (Grant CHE 0809509) and the W.M. Keck Foundation through the W.M. Keck Laboratory for High Throughput Atom-Scale Analysis at Iowa State University.

**REFERENCES**

(13) Zangeneh, M.; Doan, N.; Sambriski, E.; Terrill, R. H. Appl. Spectrosc. 2004, 58, 10−17.