

Coupling between Molecular and Plasmonic Resonances: Effect of Molecular Absorbance

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In this work, we show using both experiments and classical electrodynamic simulations that plasmon splitting in resonant molecule-coated nanoparticles increases linearly as the square root of absorbance of the molecular layer. This linear relationship shows the same universal behavior established in analogous systems such as cavity-polariton and surface plasmon polariton systems. To explain this behavior, a simple physical mechanism based on linear dispersion and absorption is proposed. The insights obtained in this study can be used as a general principle for designing resonant molecule-coated nanoparticles for realizing tunable nanophotonic devices and molecular sensing.

The past two decades have witnessed tremendous research focused on understanding the interactions between electromagnetic radiation and metal nanostructures. The motivation stems from the promise that localized surface plasmon resonance (LSPR) will provide significant advances in areas such as molecular imaging, biological sensing, and nanophotonic devices.^{1–3} Many of these applications require control over LSPR wavelength, which can be achieved using changes in shape, size,^{4–8} electron density,^{9,10} interparticle distance,^{11,12} and surrounding refractive index.^{7,13–16} Currently, it is widely recognized that frequency-independent dielectric material positioned on a metal nanoparticle will linearly red-shift the LSPR wavelength.^{3,8,17} However, it is only recently that a metal nanoparticle covered with a layer of resonant molecules has attracted interest in the plasmonics community. It has been shown that the presence of strongly absorbing molecules on the metal nanoparticle surface result in resonant coupling between molecular and plasmonic resonances.^{18–23} Resonant coupling is characterized by the formation of new hybridized states in the extinction spectra, and the energy of these states can be engineered significantly by controlling the spectral overlap between the plasmonic and molecular resonances, similar to the vacuum-field Rabi splitting observed in cavity-polariton systems.²⁰ Such control over hybridized states paves a way to enhance the application of plasmonics in realizing tunable nanophotonic devices,²⁴ molecular sensing,²⁰ and plasmonic resonance energy transfer (PRET) methods.²⁵

Kometani et al.¹⁸ were among the first to observe resonant coupling effects in resonant molecule-coated plasmonic nanostructures. They observed an absorption dip in the extinction spectra of J-aggregate-coated silver and gold nanoparticles. Wiederrecht et al.¹⁹ later explained that this observation arised from coherent coupling between molecular excitons and electronic polarizations of noble metal nanoparticles. The effects of resonant coupling as a function of spectral overlap were

experimentally reported by Wurtz et al. who used J-aggregate molecules on nanowire assemblies with tunable LSPR.²⁶ Ni et al.²⁷ later extended these ideas to solution-bound gold nanorods. Using nanoshells and J-aggregates, Fofang et al.²⁸ observed similar behavior in both dipolar and quadrupolar plasmonic resonances. From these studies, it is clear that the extinction spectra of nanoparticles covered with resonant molecules are not a simple sum of absorption contributions, but rather strongly influenced by the strength of resonant coupling, which is maximized at the spectral overlap of the resonances.

The successful application of resonant coupling for various applications mentioned above relies on maximizing the splitting between hybridized states at the spectral overlap. Fofang et al.²⁸ reported an increase in the splitting by controlling the concentration of dye in plasmon-exciton nanostructures. They speculated that the thickness of the molecular layer controlled the magnitude of splitting. For cavity-polariton and other analogous systems, factors affecting the splitting have been thoroughly studied over the past decade. It has been shown both theoretically (quantum mechanical²⁹ and classical³⁰) and experimentally^{31,32} that the splitting can be controlled by the absorbance of the absorber used in the cavities.³³ One would therefore expect similar behavior in resonant molecule-coated plasmonic nanoparticle systems. In this work, we experimentally show that the splitting observed in resonant molecule-coated plasmonic nanostructures can be controlled by changing the absorbance, A , of the molecular layer. A linear relationship between \sqrt{A} and the splitting is observed in the experiments. Using classical electrodynamic simulations, we confirm this relationship and establish a simple physical mechanism based on linear dispersion and absorption.

To understand the plasmon splitting due to hybridization, we studied the extinction spectra of a resonant molecule-coated plasmon nanostructure that consisted of gold nanorod and J-aggregates as a function of the molecular absorbance by varying the concentration. A schematic of the J-aggregate-coated nanorods together with the molecular structure of the J-aggregate is shown in the inset of Figure 1. Bare gold nanorods with diameter 35 nm and length 90 nm were purchased from Nanopartz Co. (Salt Lake, UT) and used in the experiments

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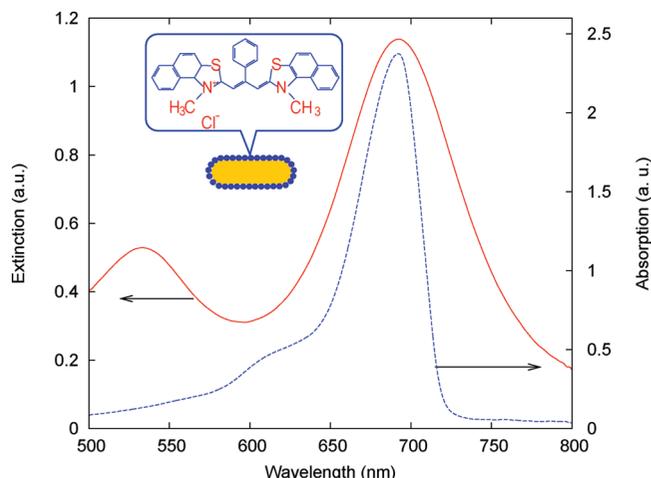


Figure 1. Extinction spectra of gold nanorods and absorption spectra of J-aggregates. The inset shows a schematic of a resonant molecule-coated plasmonic nanostructure consisting of gold nanorod and J-aggregate molecules.

without any further modification. These nanorods exhibited a transverse plasmon resonance at 533 nm and a longitudinal plasmon resonance at 692 nm (Figure 1). The J-aggregate used in the experiments was 2, 2'-dimethyl-8-phenyl-5,6,5',6'-dibenzothiaicarbocyanine chloride, and was characterized by a strong absorption at 693 nm upon aggregation on a nanorod surface. This absorption wavelength overlaps with the LSPR of the gold nanorods (Figure 1). The absorbance of the molecular layer was controlled by using various amounts of dye solutions (prepared in a mixture of water/ethanol, 50:50 by volume) that were added to the nanorod solution. The mixture was stirred for 5 min and was kept undisturbed for 36 h to allow aggregation of molecules on the nanorod surface.

Figure 2a shows the extinction spectra of the J-aggregate-coated nanorods as a function of concentrations of dye solution used. From the extinction spectra, we see clearly the splitting of the plasmon band into two distinct peaks at positions different from the peak positions of the isolated molecular resonance and the plasmon band of the nanorods. It is also shown in Figure 2a that the splitting increases as higher concentrations of the molecules are used. This increased splitting can be explained by increased coverage of the resonant molecules on the nanoparticle surface. Recently, Ni et al.²⁷ and Zhao et al.³⁴ reported plasmon shift of nanorods and nanoprisms, respectively, as a function of the concentration of resonant molecules. However, these systems did not exhibit hybridization-induced plasmon splitting. In the case of Ni et al.,²⁷ who used nanorods similar to the work presented here, a minor peak in the molecular adsorption precluded the observation of the splitting.

The observed larger splitting at higher molecular concentration is a result of stronger absorption of the molecular layer since more molecules are adsorbed on the nanoparticle. The molecular absorbance of a monolayer is given by $A = \sigma \times N_0 \times \theta$, where σ is the absorption cross section of the resonant molecules, N_0 is the saturated coverage, and θ is the coverage of the resonant molecules on the nanoparticle surface.^{35,36} The coverage follows a Langmuir isotherm given by $\theta = (aC_s)/(1 + aC_s)$, where a is the adsorption equilibrium constant and C_s is the concentration of the adsorbate in solution. For a given resonant molecule and constant surface area of nanoparticles, the absorbance only varies with θ since σ and N_0 are fixed. Thus, to calculate A as a function of concentration we assume N_0 , σ , and a to be 1, 1, and $1.45 \mu\text{M}^{-1}$, respectively. These

values were chosen to normalize \sqrt{A} such that $\sqrt{A} = 1$ for $\theta = 1$, i.e., complete monolayer, and when $\sqrt{A} = 0$ no molecular layer is present. The actual values used in the calculation only change the magnitude of absorbance but not the dependence on concentration. To obtain the magnitude of splitting as a function of concentration we fitted the two peaks in the extinction spectra using two Lorentzians and a third-order polynomial function. The splitting between the two hybridized states as a function of \sqrt{A} is plotted in Figure 2b. We see that the splitting is linearly dependent on \sqrt{A} , as expected from its similarities with microcavity-polariton systems^{29–33} and surface plasmon-polariton systems.^{37,38} Therefore, by simply changing the absorbance of the molecular layer, either by increasing the coverage as demonstrated here or using dye molecules with different absorption cross sections, it is possible to tune the coupling between the plasmon and molecule resonances.

In order to understand the plasmon splitting as a function of \sqrt{A} , we calculated the extinction spectra of a prolate spheroid covered with a layer of resonant molecules using classical electrodynamics. The nanoparticles used in this work is small enough that they had a dipolar response to incident light, thus, a quasi-static approximation is appropriate. The polarizability in the quasi-static limit for a two-layer prolate spheroid embedded in a dielectric medium is given by³⁹

$$\alpha = \frac{V((\epsilon_2 - \epsilon_m)[\epsilon_2 + (\epsilon_1 - \epsilon_2)(L^{(1)} - f_v L^{(2)})] + f_v \epsilon_2 (\epsilon_1 - \epsilon_2))}{([\epsilon_2 + (\epsilon_1 - \epsilon_2)(L^{(1)} - f_v L^{(2)})][\epsilon_m + (\epsilon_2 - \epsilon_m)L^{(2)}] + f_v L^{(2)} \epsilon_2 (\epsilon_1 - \epsilon_2))} \quad (1)$$

where V is total volume of the system, f_v is the fraction of the total volume occupied by the nanorod, $L^{(1)}$ and $L^{(2)}$ are the geometric parameters for metal and molecular spheroids, respectively, and ϵ_1 , ϵ_2 , and ϵ_m are the dielectric functions of the gold nanorods, molecular layer and the surrounding medium, respectively. From the polarizability, the extinction efficiency is straightforwardly given by³⁹

$$\sigma(\omega) = \frac{k}{\pi R^2} \text{Im}[\alpha(\omega)] \quad (2)$$

where k is $(2\pi)/(\lambda)$.

To model the gold nanorods, we used a spheroid with a spherical radius, R , of 23.97 nm with an aspect ratio of 3.14 so as to match the experimental LSPR of 692 nm. The dielectric constant of gold were described by a Drude model

$$\epsilon_1(\omega) = \epsilon_{\infty 1} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (3)$$

where $\epsilon_{\infty 1}$ is the contribution from the bound electrons in the metal (9.84), ω_p is the bulk plasmon frequency of gold (9 eV), and γ is the plasmon relaxation constant (67 meV).⁴⁰ To compensate for various inhomogeneous broadening effects in the experimentally observed extinction spectra, the value of γ was multiplied by a factor of 2.4. The dielectric constant of the molecular layer was modeled as a one-oscillator Lorentzian model given by

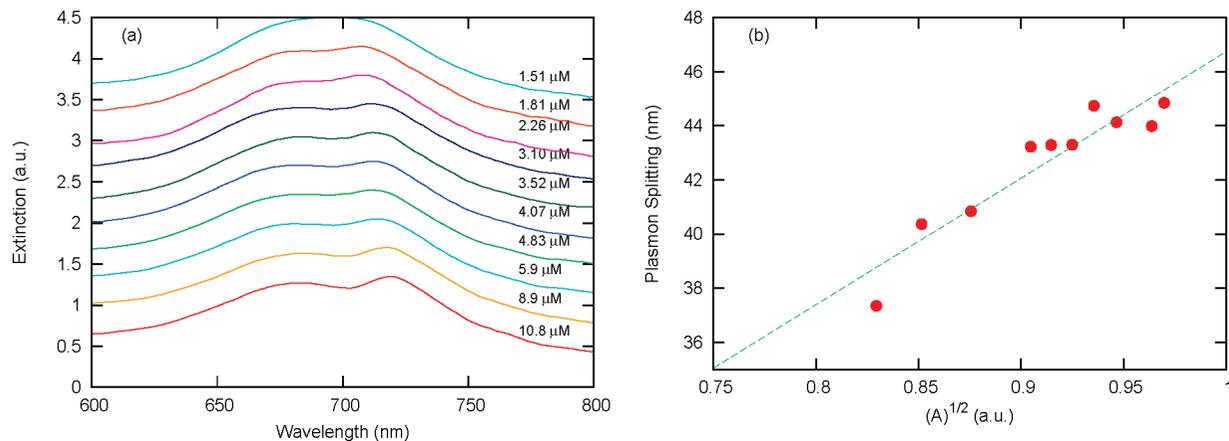


Figure 2. (a) Experimental extinction spectra of J-aggregate-coated nanorods using different concentrations of dye solution. (b) Plasmon splitting as a function of \sqrt{A} . The dotted line is a linear fit of the form $y = ax$

$$\varepsilon_2(\omega) = \varepsilon_2(\omega)' + \varepsilon_2(\omega)'' = \varepsilon_{\infty 2} + \frac{f\omega_2^2}{\omega_2^2 - \omega^2 - i\omega\Gamma} \quad (4)$$

where $\varepsilon_{\infty 2}$ is the high-frequency component of the dielectric constant (1.768), ω_2 is the molecular excitation frequency (1.789 eV), Γ is the excitation line width (52 meV), and f is the reduced oscillator strength, which we will vary in the calculations to simulate different absorption cross sections.²⁸ In all simulations, the surrounding medium was assumed to be water with a dielectric constant of 1.768.

In the experiments, the absorption coefficient was constant since we only studied one kind of molecule and assumed a monolayer of molecules; thus the absorption only varied with the coverage. However, in the simulations we relate the absorption to $A = \alpha' \times t_m$, where α' is the absorption coefficient and t_m is the thickness of the molecular layer. In this way, we can simulate the splitting both as a function of thickness and the absorption coefficient. The absorption coefficient is related to the imaginary part of the refractive index as, $\alpha' = \kappa(4\pi)/(\lambda)$, where $\kappa = \text{Im}(\sqrt{\varepsilon_2})$, is a function of ω_2 , $\varepsilon_{\infty 2}$, f , and Γ . At $\omega = \omega_2$,

$$\kappa = \left[\frac{\left[\varepsilon_{\infty 2}^2 + \left(\frac{f\omega_2}{\Gamma} \right)^2 \right]^{1/2} - \varepsilon_{\infty 2}}{2} \right]^{1/2} \quad (5)$$

To investigate the relationship between splitting and \sqrt{A} , we calculated the extinction spectra of resonant molecule-coated nanorods for various absorbance levels by changing the magnitude of the oscillator strength, f , and the thickness of the molecular layer, t_m . In Figure 3b, we plot the extinction spectra calculated using eq 1 for a gold nanorod covered with a layer of resonant molecules of thickness $t_m = 0.06R$ (1.44 nm) at different oscillator strengths ranging from 0.02 to 0.07. The magnitudes of thickness and oscillator strength are consistent with previous reports on J-aggregate-coated nanoparticles.^{26,28} We see from Figure 3a that the plasmon band splits into two peaks, representing the two hybridized states resulted from resonant coupling. As the oscillator strength, f , of the molecular layer increased, the absorbance of the molecular layer also increased and, thus, the plasmon splitting increased as well. The splitting as a function of \sqrt{A} obtained from the simulations is shown in Figure 3b where a linear dependence is found. To investigate further the dependence of the splitting on the

absorption we calculated the extinction spectra using different values of molecular layer thickness for different oscillator strengths (ranging from 0.02 to 0.07). The plasmon splitting as a function of \sqrt{A} is plotted in Figure 4 for the different molecular layer thicknesses. We see that the splitting follows a similar linear relationship as a function of absorbance for various thickness of the molecular layer. This is expected since as the molecular layer became thicker, the magnitude of absorbance increased, resulting in increased splitting for a given oscillator strengths. The calculated linear relationship between plasmon splitting and \sqrt{A} is in excellent agreement with what is observed in the experiments.

The linear dependence of the plasmon splitting on \sqrt{A} found in the experiments, and classical electrodynamic simulations can be explained by considering the linear dispersion and absorptive properties of the resonant molecular layer. Due to incident radiation, free electrons within the bare gold nanoparticles oscillate. At specific wavelengths of radiation the response and incident radiation are 90° out of phase, which leads to the enhancement of the electric field and strong absorption characterized by a peak in the extinction spectrum, the plasmon peak.² At this point the incident field do not change the restoring force on the conduction electrons, and they oscillate at their intrinsic frequency, i.e., the plasmon frequency. Therefore, we can examine this condition as a means to understand the resonances in complicated systems such as resonant molecule-coated nanoparticles. For the nanorods covered with resonant molecules we find that the phase condition happens at multiple frequencies. This is shown in Figure 5, where we plot the phase shift and corresponding extinction spectra for bare nanorods covered with resonant molecules calculated using the quasi-static approximation model for different absorbance. To illustrate the phase relation, we used a molecular layer with a nonabsorbing, yet dispersive, resonant molecule (i.e., $\varepsilon_2(\omega) = \varepsilon_2(\omega)'$). Obviously, in reality we cannot neglect $\varepsilon_2(\omega)''$ since it is directly related to the real part using the Kramer–Kronig transformation; however, we can use this as a model to explain the plasmon splitting. In the case of the nanorods covered with resonant molecules, the dispersion of the real part of the refractive index of the molecule layer, $n_m = \text{Re}(\sqrt{\varepsilon_2})$, causes the phase to be out of phase by 90° three times (indicated by vertical arrows) due to different boundary conditions (a shell layer with dispersive material). This results in three resonance positions or three peaks in the extinction spectra and can be seen from Figure 5 where the phase shift and extinction spectra are shown. The central peak position is at the spectral overlap and the other

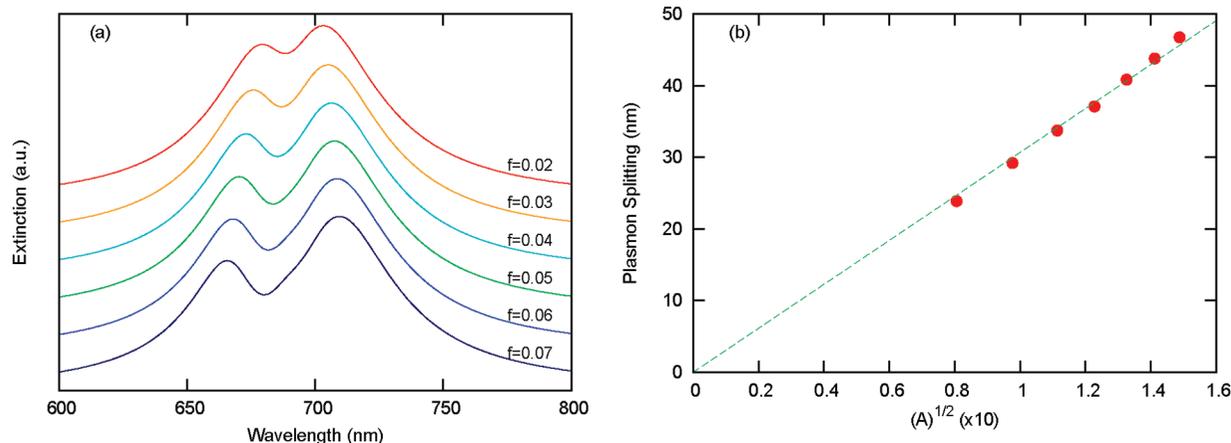


Figure 3. (a) Extinction spectra calculated using eq 1 for various oscillator strengths. (b) Calculated splitting as function of \sqrt{A} . The dotted line is a linear fit of the form $y = ax$.

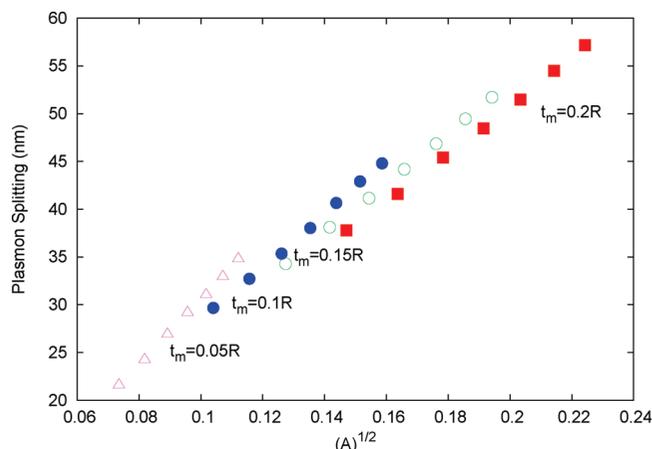


Figure 4. Calculated splitting as function of \sqrt{A} for various thickness ($0.05R$ – $0.2R$) and oscillator strength of the molecular layer (0.02 – 0.07).

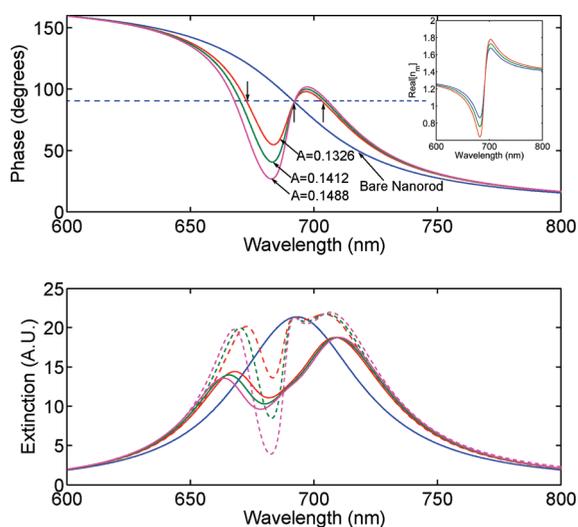


Figure 5. (a) Phase shift between the incoming radiation and response of resonant molecule-coated nanoparticle. The inset shows the refractive index $n_m = \text{Re}(\sqrt{\epsilon_2})$ as a function of oscillator strength. (b) Extinction spectra of bare nanorods and nanorod covered with resonant molecules for various absorbance levels without (dotted lines) and with (solid lines) the imaginary part considered.

two peaks (longer and shorter resonance wavelengths) are positioned on either sides of spectral overlap. It can be seen from the inset of Figure 5a that as the absorbance of the molecular layer is increased (by increasing the oscillator

strength), the molecule's refractive index at shorter resonance wavelength decreases (at longer resonance wavelength it increases). However, there is no change in the refractive index with absorbance at the molecular resonance wavelength. The increase (decrease) in the refractive index at the longer wavelength (shorter wavelength) resonance condition causes a red-shift (blue-shift) of the peak positions. These shifts are similar to the shifts observed in nanoparticles covered with a thin dielectric layer, where an increase in the refractive index causes the redshift of the resonance and a decrease in the refractive index causes a blue-shift. Therefore, as the oscillator strength increased, the molecular layer became more dispersive, the wavelengths where the 90° phase difference occurred moved away from the spectral overlap, and thus the splitting increased (dotted lines in Figure 5b). When we included $\epsilon_2(\omega)$ into the quasi-static approximation model, the layer of resonant molecules absorbs the incoming radiation and the central peak is canceled (solid lines in Figure 5b). This contributes further to the shifting of the wavelength where the 90° phase difference occurred, resulting in increased splitting. Therefore, as the oscillator strength of the resonant molecule increases, the molecular layers become more dispersive and absorb more of the incoming radiation, which leads to larger splitting. On the other hand, increasing the thickness of the molecular layer leads to increased absorption of the incoming radiation, which in turn cancels the central peak more effectively and drives larger splitting. Considering these mechanisms, the end result is that an increase in absorbance will lead to larger splitting since it is directly related to both the oscillator strength and the thickness of the molecular layer.

In conclusion, we have demonstrated experimentally and theoretically that the magnitude of plasmon splitting in resonant molecule-coated nanoparticles due to hybridization can be controlled by the molecular absorbance. The measured extinction spectra of J-aggregate-coated gold nanorods exhibited a linear relationship between the plasmon splitting and \sqrt{A} , similar to that observed in systems such as microcavity-polariton and surface plasmon-polariton systems. Using electrodynamic simulations based on the quasi-static approximation, we found a similar linear dependence on absorption either by increasing the oscillator strength of the molecule or the thickness of the molecular layer. A simple physical mechanism showed that the splitting is caused by the dispersion in the real part of the molecular dielectric constant and absorbance from the imaginary part, both increases as the absorption increases. The insights gained from this study will be useful in improving applications

of resonant coupling, including tunable nanophotonic devices, molecular sensing, and PRET methods.

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References and Notes

- (1) Ozbay, E. *Science* **2006**, *311*, 189.
- (2) Maier, S. A.; Atwater, H. A. *J. Appl. Phys.* **2005**, *98*, 011101.
- (3) Maier, S. A. *Plasmonics: Fundamentals and Applications*; Springer: New York, 2007.
- (4) Kreibig, U.; Volmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, New York, 1995.
- (5) Kelly, K. L.; Coronado, E. A.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.
- (6) Grand, J.; Lamy de la Chapelle, M.; Bijeon, L.; Adam, P.-M.; Vial, A.; Royer, P. *Phys. Rev. B* **2005**, *72*, 033407.
- (7) Noguez, C. *J. Phys. Chem. B* **2007**, *111*, 3806.
- (8) Zheng, Y. B.; Jensen, L.; Yan, W.; Walker, T. R.; Juluri, B. K.; Jensen, L.; Huang, T. J. *J. Phys. Chem. C* **2009**, *113*, 7019.
- (9) Mulvaney, P.; Pérez-Juste, J.; Giersig, M.; Liz-Marzán, L.; Pecharromán, C. *Plasmonics* **2006**, *1*, 61.
- (10) Juluri, B. K.; Zheng, Y. B.; Ahmed, D.; Jensen, L.; Huang, T. J. *J. Phys. Chem. C* **2008**, 7309.
- (11) Sidhaye, D. S.; Kashyap, S.; Sastry, M.; Hotha, S.; Prasad, B. L. V. *Langmuir* **2005**, *21*, 7979.
- (12) Park, S. Y.; Lee, J. S.; Georganopoulou, D.; Mirkin, C. A.; Schatz, G. C. *J. Phys. Chem. B* **2006**, *110*, 12673.
- (13) Haes, A. J.; Zou, S.; Schatz, G. C.; VanDuyne, R. P. *J. Phys. Chem. B* **2004**, *108*, 109.
- (14) Hanarp, P.; Kall, M.; Sutherland, D. S. *J. Phys. Chem. B* **2003**, *107*, 5768.
- (15) Miller, M. M.; Lazarides, A. A. *J. Phys. Chem. B* **2005**, *109*, 21556.
- (16) Hsiao, V. K. S.; Zheng, Y. B.; Juluri, B. K.; Huang, T. J. *Adv. Mat.* **2008**, *20*, 3528.
- (17) Zheng, Y. B.; Juluri, B. K.; Mao, X.; Walker, T. R.; Huang, T. J. *J. Appl. Phys.* **2008**, *103*, 014308.
- (18) Kometani, N.; Tsubonishi, M.; Fujita, T.; Asami, K.; Yonezawa, Y. *Langmuir* **2001**, *17*, 578.
- (19) Wiederrecht, G.; Wurtz, G.; Hranisavljevic, J. *Nano Lett.* **2004**, *4*, 2121.
- (20) Ambjörnsson, T.; Mukhopadhyay, G.; Apell, S. P.; Käll, M. *Phys. Rev. B* **2006**, *73*, 085412.
- (21) Sugawara, Y.; Kelf, T. A.; Baumberg, J. J.; Abdelsalam, M. E.; Bartlett, P. N. *Phys. Rev. Lett.* **2006**, *97*, 266808.
- (22) Uwada, T.; Toyota, R.; Masuhara, H.; Asahi, T. *J. Phys. Chem. C* **2007**, *111*, 1549.
- (23) Kelley, A. M. *Nano Lett.* **2007**, *7*, 3235.
- (24) Zheng, Y. B.; Yang, Y.-W.; Jensen, L.; Fang, L.; Juluri, B. K.; Flood, A. H.; Weiss, P. S.; Stoddart, J. F.; Huang, T. J. *Nano Lett.* **2009**, *9*, 819.
- (25) Liu, G.; Long, Y.; Choi, Y.; Kang, T.; Lee, L. *Nat. Methods* **2007**, *4*, 1015.
- (26) Wurtz, G.; Evans, P.; Hendren, W.; Atkinson, R.; Dickson, W.; Pollard, R.; Harrison, W.; Bower, C.; Zayats, A. *Nano Lett.* **2007**, *7*, 1297.
- (27) Ni, W.; Yang, Z.; Chen, H.; Li, L.; Wang, J. *J. Am. Chem. Soc.* **2008**, *130*, 6692.
- (28) Fofang, N. T.; Park, T.-H.; Neumann, O.; Mirin, N. A.; Nordlander, P.; Halas, N. J. *Nano Lett.* **2008**, *8*, 3481.
- (29) Norris, T. B. *Confined Electrons and Photons*; Plenum: New York, 1995.
- (30) Zhu, Y.; Gauthier, D. J.; Morin, S. E.; Wu, Q.; Carmichael, H. J.; Mossberg, T. W. *Phys. Rev. Lett.* **1990**, *64*, 2499.
- (31) Lidzey, D.; Bradley, D.; Skolnick, M.; Virgili, T.; Walker, S.; Whittaker, D. *Nature* **1998**, *395*, 53.
- (32) Hobson, P. A.; Barnes, W. L.; Lidzey, D. G.; Gehring, G. A.; Whittaker, D. M.; Skolnick, M. S.; Walker, S. *Appl. Phys. Lett.* **2002**, *81*, 3519.
- (33) Holmes, R.; Forrest, S. *Org. Electron.* **2007**, *8*, 77.
- (34) Zhao, J.; Jensen, L.; Sung, J.; Zou, S.; Schatz, G. C.; Duyne, R. P. V. *J. Am. Chem. Soc.* **2007**, *129*, 7647.
- (35) Shaw, A. M.; Hannon, T. E.; Li, F.; Zare, R. N. *J. Phys. Chem. B* **2003**, *107*, 7070.
- (36) Ingle, J. D., Jr.; Crouch, S. R. *Spectrochemical Analysis*; Prentice Hall: New York, 1998.
- (37) Bellessa, J.; Bonnand, C.; Plenet, J. C.; Mugnier, J. *Phys. Rev. Lett.* **2004**, *93*, 036404.
- (38) Dintinger, J.; Klein, S.; Bustos, F.; Barnes, W. L.; Ebbesen, T. W. *Phys. Rev. B* **2005**, *71*, 035424.
- (39) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; John Wiley and Sons: New York, 1983.
- (40) Sönnichsen, C. Ph.D. thesis, Ludwig-Maximilians-Universität München, München, 2001.

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