Large Optical-Frequency Shift of Molecular Radiation via Coherent Coupling to an Off-Resonance Plasmon

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We demonstrate coherent optical coupling between molecular and plasmon resonances that are well separated in energy. In the presence of metallic nanoparticles, the second harmonic spectrum of organic dyes no longer peaks at the absorption wavelength but is instead blueshifted by 25 nm towards the localized plasmon resonance. The phase of the light generated by the dyes displays a large modulation across the plasmon resonance and no change across the molecular one. The second harmonic signal contributed by the nanoparticles, which is peaked at the plasmon frequency when no molecules are present, similarly displays a shift towards the molecular resonance in their presence. A model based on the interplay of the nonlinear optical near fields is able to account for these observations.

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Thanks to field magnification and enhancement of light-matter interactions through plasmon resonances, metal nanostructures are ideal candidates for the development of light-on-a-chip devices [1] and extremely valuable tools to characterize and tune the optical response of dyes in their proximity [2–6]. The most pronounced interaction effects in organometallic systems are observed when the frequency of the plasmon mode matches that of molecular emission, as in nanoantennas [7], or absorption [8], in which case hybridization of the optical modes may take place [9–14]. Apart from modification of the molecular absorption, emission, and conversion efficiency or lifetime, other interesting effects have been reported such as changes in the spectral, polarization, and angular emission profiles of the radiated light [4–7,15,16] and even strong optical mode coupling leading to large Rabi shifts [9–14]. The coherent character of the optical coupling between molecular and plasmon resonances has been hard to access directly, and it has been demonstrated only in the strong-coupling regime characterized by the hybridization of the plasmon and exciton modes, which may take place only when the two are nearly degenerate [14].

Here we demonstrate the coherent optical coupling between molecular and plasmon resonances that are separated by as much as 150 nm. In the presence of the nanoparticles, the peak efficiency of second harmonic conversion by the dyes no longer matches the frequency of the molecular absorption but is instead significantly blueshifted towards the plasmon. Experiments with larger nanoparticles show that their second harmonic signal is similarly (red)shifted towards the molecular resonance. The phase of the nonlinear field exhibits in both cases a modulation only across the plasmon resonance. All these findings can be rationalized by considering the interplay of the nonlinear near fields generated by the dyes and

nanoparticles, a phenomenon that might allow active tailoring of coherent light generation at the nanoscale.

We carried out extinction and second harmonic (SH) spectroscopy experiments on films of a nonlinear dye (crystal violet) deposited onto silver nanoparticles of two different sizes. Small (10 nm diameter) silver colloids were immobilized onto glass surfaces previously functionalized with an amino-silane layer, while films of larger nanoparticles (50 nm average diameter) were spin-cast from dispersions of poly(vinylpyrrolidone)-coated colloids in 1,2-propanediol and annealed to 400 K to desorb the organic material. Molecular films were deposited by immersion in 1-propanol solutions of the dye. A tunable pulsed source was employed for SH experiments, consisting of an optical parametric oscillator pumped by a frequency-tripled *Q*-switched Nd-Yag laser operating at 1064 nm, with 4.2 ns pulse duration and 10 Hz repetition rate. The idler beam of the optical parametric oscillator could be tuned throughout the near infrared and was focused onto the sample at 45° incidence angle. The phase of the generated SH light was measured by SH interferometric spectroscopy [17] using the setup described in Ref. [18]. To correct for laser fluency, the SH intensity spectra were normalized to the nonlinear signal of a thin urea sample obtained by immersion of a glass slide into a urea solution in 1-propanol. The reference for SH interferometry was an 80-nm thick indium tin oxide layer, which provided a relatively flat phase profile in the spectral range of interest [19].

The extinction spectra of molecular films on glass and onto the smaller nanoparticles are shown in Fig. 1(a), together with that of the nanoparticle film. The absorption feature at 400 nm corresponds to the dipolar plasmon resonance. On both substrates, the molecular film exhibits two broad absorption features—possibly linked to different dye isomers—as observed in solid phases and solutions of

FIG. 1 (color online). (a) Extinction spectra of the nanoparticles (dashed line) and of the dyes on glass (bold line) and on top of the nanoparticles (thin line). (b) SH spectra of the same samples (markers). Continuous lines are theoretical predictions from Eq. (1) (see the text).

the same dye [20,21]. These features do not undergo any visible change in width, relative intensity, or spectral position when the dyes are deposited onto the nanoparticles. The corresponding SH intensity spectra are shown in Fig. 1(b). Although a nonlinear resonance might be expected in correspondence to each absorption band [22,23], the SH spectrum of the molecular film on glass exhibits only a single peak around 540 nm matching the band at lower wavelength, which indicates that the nonlinear susceptibility of the film is dominated by the latter resonance.

A single SH peak is observed also for the dyes deposited on the nanoparticles, in which case, however, the spectral maximum is significantly blueshifted. Since the extinction spectrum is unmodified, the observed blueshift does not reflect a change in the molecular electronic states but rather a modification of the frequency-doubling process in the presence of the plasmonic nanoparticles. By themselves, these small nanoparticles did not generate any appreciable SH signal. Remarkably, the observed shift is of the same order of magnitude of the Rabi shifts observed in organometallic systems in the strong-coupling regime [9–14]. Contrary to the strong-coupling phenomenology, our resonances are far apart, and the spectral shift is observed only in the nonlinear spectrum.

To gain further insight we measured the phase of the SH signals. Examples of SH interferograms acquired with a molecule-nanoparticle sample are shown in Fig. 2(a), where the sinusoidal dependence of the SH signal upon the distance d between the sample and the indium tin oxide reference can be observed [17]. The three upper curves display a maximum for $d = 0$, indicating that SH generation from the sample is in phase with that of the reference along wavelengths and, thus, that the sample's SH phase profile is here spectrally flat. Only interferograms recorded at shorter wavelengths (such as 420 nm) are characterized by a different phase. The phase (respectively, intensity) of the field generated by the dyes with and without the nanoparticles, as extracted from sinusoidal fits to the interferograms, is plotted as a function of the wavelength in Fig. 2(b) (respectively, in the inset). The phase measured on the pristine molecular film undergoes a change of

FIG. 2 (color online). (a) SH interferograms acquired on a dye-nanoparticle sample at the indicated wavelengths and corresponding sinusoidal fits. (b) SH phase profile for the dye on glass (empty circles) and on top of the nanoparticles (dots); inset: SH intensity profile of the latter sample (markers). Theoretical profiles from Eq. (1) are shown as continuous lines.

approximately 2 rad in correspondence with the maximum of generation, slightly less than the value π expected from the Kramers-Kronig relations. The SH phase of the dyes on top of the nanoparticles is instead remarkably flat near maximum generation, while it displays a large modulation near the plasmon wavelength. The intensity profile exhibits a blueshift consistent with that of Fig. 1(b).

The phase change near the plasmon resonance proves that the nanoparticles play an active role in SH conversion by the dyes. As stated previously, metallic nanoparticles can strongly affect radiation from nearby dyes [4–7]. The fluorescence spectrum of dyes near nanoparticles is significantly shifted when the emission is nearly resonant with the plasmon [6], while it exhibits a secondary maximum at the plasmon wavelength when the latter is spectrally far [4]. These observations were rationalized in terms of a modified density of optical states near the plasmon resonance [4,6]. In our case the probe is fully coherent, and we observe a shift (rather than a double-peak feature) for off-resonance conditions, accompanied by an important modification of the phase profile. These findings hint to a *coupled* polarization of the dye-nanoparticle system. The fact that the coupling affects only SH conversion, and not absorption, is quite remarkable. The large separation between the two eigenfrequencies excludes the formation of hybrid bands, which are indeed not observed in extinction. On the other hand, SH generation is a driven radiative phenomenon, and for frequencies intermediate between the two resonances the polarization induced in the dyes can interact optically with the highly polarizable nanoparticles that may thus contribute to the conversion process.

Molecular SH generation is due to the nonlinear polarization of electrons in the anharmonic potential well of valence orbitals [22,23]. In order to describe cooperative SH conversion by the dye-nanoparticle system, we extend this model to include the near-field coupling to the

FIG. 3 (color online). Three-dimensional plot of the modulus squared (a) and phase (b) of the nonlinear molecular polarization $P_M^{2\omega}$ versus the SH wavelength and the product $b_M b_{NP}$. The lines correspond to the theoretical curves in the upper part and the inset of Fig. 2(b).

nanoparticles. The resulting equations, which include the effect of resonant field enhancement close to the plasmon resonance frequency ω_{NP} , are

$$\begin{aligned} \ddot{P}_M + \gamma_M \dot{P}_M + \omega_M^2 P_M &= -D_M P_M^2 + \frac{e^2 n_M}{2m} (E_{NP}^{2\omega} + E^\omega), \\ \ddot{P}_{NP} + \gamma_{NP} \dot{P}_{NP} + \omega_{NP}^2 P_{NP} &= -D_{NP} P_{NP}^2 + \frac{e^2 n_{NP}}{2m} (E_M^{2\omega} + E^\omega). \end{aligned} \quad (1)$$

Here ω_M is the frequency of molecular absorption, P_M and n_M (respectively, P_{NP} and n_{NP}) are the polarization and number densities of the molecules (respectively, nanoparticles), and the D coefficients represent the nonlinear susceptibilities [22]. The two polarization densities have a linear term oscillating at ω and a nonlinear one at 2ω and are coupled through the near fields that they generate at 2ω . These may be written as $E_M^{2\omega} = -2\omega i b_M P_M^{2\omega}$ and $E_{NP}^{2\omega} = -2\omega i b_{NP} P_{NP}^{2\omega}$, where the b coefficients are geometrical factors linking the field intensities to their respective sources [24]. The near-field coupling is relevant only at the SH frequency, as linear (as well as two-photon) absorption processes result only in a different final state of the molecule or nanoparticle and not to a coherently oscillating polarization.

The theoretical SH intensity and phase profiles are given by the modulus squared and phase of the molecular nonlinear polarization, $P_M^{2\omega}$. If $E_{NP}^{2\omega}$ is zero, the first equation in (1) reduces to that of a forced anharmonic oscillator with resonance frequency ω_M in both the linear and nonlinear responses [22,23]. The predictions of this uncoupled theory are compared with the SH spectra of the pristine molecular film in Figs. 1(b) and 2(b), by using the values $\omega_M = 5.55 \times 10^{14}$ Hz and $\gamma_M = 0.8 \times 10^{14}$ Hz that best reproduce the intensity spectrum. Although the predicted phase change (by π) is larger than the observed value, good overall agreement with the experiment is found. For comparison's sake, we have used the uncoupled equations to fit

also the intensity spectrum of the sample with the nanoparticles, leaving ω_M free to vary from its value observed in absorption, and thereby determined an effective spectral shift of 25 nm.

Figure 3 shows the theoretical dependence of the SH intensity and phase on the product $b_M b_{NP}$, which is a measure of the near-field intensity [17]. The nonlinear susceptibility D_{NP} of the nanoparticles was set to zero due to their vanishing nonlinear activity, and ω_{NP} (7.5×10^{14} Hz) and γ_{NP} ($\approx \gamma_M$) were estimated from the plasmon extinction peak. While for zero coupling the theoretical SH intensity (a) is peaked at the molecular absorption, this maximum shifts towards the blue with increasing coupling strength. Eventually, a second component arises at lower wavelength (near the plasmon resonance), which for yet stronger coupling merges with the first one halfway between the two bare resonances. The phase of the SH light (b), which at zero coupling displays a variation across the molecular peak, gradually becomes flat in this wavelength region to become more and more modulated near the plasmon resonance. The model and experiment are compared in panel (b) of Figs. 1 and 2 for specific values of the b and n parameters [17]. The theory provides a rather good approximation, reproducing, in particular, the blueshift of the intensity maximum and the phase change across the plasmon resonance. The model further predicts a weak secondary shoulder at short wavelengths that is not observed experimentally in Fig. 1(b) and is only partially visible in the inset in Fig. 2(b), which could be due to the lower signal intensity in this spectral range or indicate that more details of the system need to be taken into account.

Equation (1) is appropriate also in the case where the nanoparticles generate a SH signal comparable with that of the dyes. The model predicts that SH generation by nanoparticles in the vicinity of dyes should also be shifted [Fig. 3(a)]. To verify this, we characterized films of larger nanoparticles with higher hyperpolarizability. The scanning electron microscopy image of such a film, which

FIG. 4 (color online). (a) Extinction spectra of a molecular film on glass and on top of large nanoparticles (inset: scanning electron microscopy image of the nanoparticle film). (b) SH intensity spectrum of a dye-nanoparticle sample, compared with those of pure nanoparticle and dye films. (c) SH phase profile of the nanoparticles, in both the presence and absence of dyes. In (b) and (c), continuous lines are theoretical curves.

displayed the plasmon absorption at 420 nm, is shown in the inset in Fig. 4(a). The dyes' absorption features remained unchanged also on top of these larger nanoparticles [Fig. 4(a)]. The SH intensity and phase spectra of the nanoparticle film before and after dye deposition are shown in Figs. 4(b) and 4(c), respectively. The nonlinear field generated by the nanoparticles alone displays an intensity maximum and a phase shift of approximately π at the plasmon wavelength. The uncoupled theory derived from Eq. (1) with $E_M^{2\omega} = 0$ provides a good fit of both profiles. To the best of our knowledge, this is the first experimental report of the spectral behavior of SH generation from metal nanoparticles.

The SH intensity spectrum of the nanoparticle-dye sample exhibits two features, both shifted with respect to the bare resonances (b). The fit to the intensity spectrum using Eq. (1) is displayed on top of the corresponding data. Visual inspection shows that the blueshift of the molecular feature by 20 nm [consistent with Fig. 1(b)] is larger in magnitude than the redshift of the nanoparticles feature (of the order of 10 nm). The phase spectrum of the same sample (c) displays a large steplike modulation in correspondence with the plasmon resonance and almost none near the molecular resonance, as in Fig. 2(b). The redshift of the nanoparticle's feature is also clearly visible in the phase data of Fig. 4(c). We point out that an explanation only in terms of a modified density of states near the plasmon resonance would not account for such a redshift.

Our results show that quadratic nonlinear optical conversion, thanks to its unique coherence and interface sensitivity, can provide unprecedented insight into optical emission and coupling in nanoscale systems and may prove a powerful tool to probe optical hybridization, e.g., in strong-coupling systems. The large shift of molecular emission induced by coupling to a plasmon mode that is well separated in frequency is remarkable, as it shows that coherent optical interaction effects arise also for off-resonance conditions. This phenomenon may open new possibilities for tailoring optical responses at the nanoscale (e.g., in nanoantenna systems); in particular, the

characteristic phase profile of the emitted light suggests that a phase modulation of the driving fundamental light might be effective in enhancing or tuning the spectral shift, which is attractive for active photonics components.

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- [24] The (collective) SH near field inside the film can be relatively large and depends on the local molecular arrangement; in Eq. (1), we consider for simplicity a position-independent average.