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Anomalous optical response of metal–molecule coupled system

Hajime Ishihara*, Atsushi Nobuhiro, Masatoshi Nakatani, Yoshihiko Mizumoto

Department of Physics and Electronics, Osaka Prefecture University, 1-1, Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

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ABSTRACT

We theoretically investigate the optical response of a coupled system composed of a molecular dimer and metal structures forming a nanogap. The metal structures serve as a light harvesting antenna; a localized light field is strongly enhanced by the plasmon resonance at the nanogap, and the molecular dimer is strongly coupled with the antenna via this enhanced field. Through numerical calculations, we find that photon energies received by the metal antenna are concentrated into the molecules without being absorbed by the metal structures under particular resonance conditions. This metal-transparency effect can be understood by considering the interference between the eigenmodes of the metal–molecule coupled system.

1. Introduction

The control of light–matter interaction has been a topic of great importance in various research fields. Two main types of approaches have been considered for control of light–matter interaction. In one approach, the matter wavefunction is controlled through the design of nanostructures, molecules, and so on, to increase the matter oscillator strength; in the other, the light mode is modified using microstructures such as microcavities, photonic crystals, and metamaterials [1]. Recent developments in nano- and micro-fabrication technologies enable us to accurately control both light modes and matter wavefunctions simultaneously, greatly increasing the degree of freedom in “designing” the light-matter coupling. Interestingly, these technologies allow control of the interaction between the resonance states of light field and matter system, where strong feedback-interplay causes anomalous optical effects that cannot be expected by considering one-sided interaction. Numerous examples have been reported recently for the nano-to-bulk crossover size regime: a large nonlinear response of nondipole-type excitonic states [2], an anomalous radiative shift of confined excitonic states [3], an ultrafast radiative decay with a couple of tens of femtoseconds [4], and so on. In these phenomena, the interplay between the spatial structures of light waves and those of the polarization waves is crucial; for understanding this interplay, it is important to describe the motions of light and matter system self-consistently through an equal footing theory [5,6].

The metal nano- and microstructures generating a highly localized light field (LLF) in a nanoscale region are also expected to be a typical system where the light–matter feedback-interplay causes peculiar optical effects. Thus far, LLF by metal structures has been studied with regard to its application in a highly sensitive sensing, few-molecule detection, and so forth, by means of a strongly magnified light field [7]. Further, accurate control of the geometrical structures of a gold nanogap has been achieved recently, resulting in the realization of very strong light–molecule coupling [8,9]. In such systems, the metal structures serve as a light harvesting antenna, and two-photon induced chemical reactions occur at the nanogap even through a very weak excitation by an incoherent light source [10]. These pioneering demonstrations indicate how greatly an electric field is enhanced and how strongly it affects the target molecules. However, the potential of the metal–molecule (or quantum dot) coupled system has not been fully exploited yet. The role of the feedback-interplay between metal structures and molecules in the vicinity of the nanogap becomes considerably important as compared with that in free space; this is because this interplay strongly affects the optical response of metal structures, and vice versa. This leads to unconventional optical responses as observed in the nano-to-bulk crossover size regime and provides a high degree of freedom to control the microscopic energy flow between the metal structures and molecules. The purpose of this paper is to theoretically study this aspect of the metal–molecule (quantum dot) coupled system and to demonstrate the peculiar energy flow between metal structures and molecules.

The rest of this paper is organized as follows: In the next section, we explain our model and theoretical method. The calculated results are shown in Section 3. In Section 4, the results are explained

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* Corresponding author. Tel.: +81 72 254 9268; fax: +81 72 254 9268.
E-mail address: ishi@pe.osakafu-u.ac.jp (H. Ishihara).

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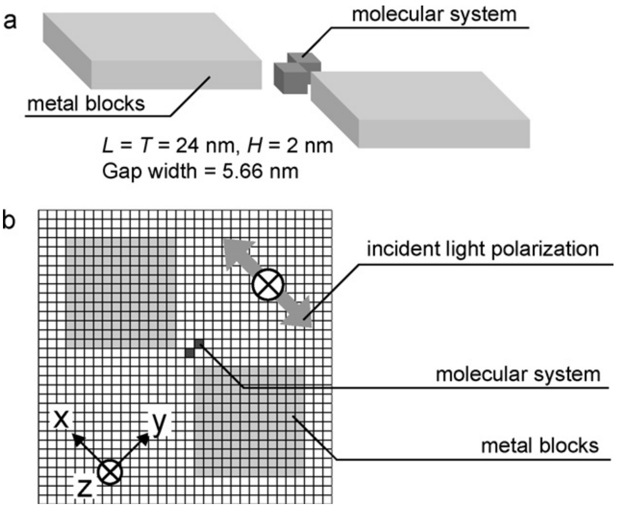

Fig. 1. (a) Schematic picture of the metal structures and molecular systems. The size of each block is $L = T = 24$ nm and $H = 2$ nm. The nanogap width is 5.66 nm. (b) Top view of the model for the calculation. Grids show the cells for DDA calculation which are 2 nanometers on a side. Black cells show the position of a molecular dimer, where each monomer occupies a single cell. We assume a dipole along x-axis to be active in each monomer. The gray double-headed arrow shows the direction of incident light polarization.

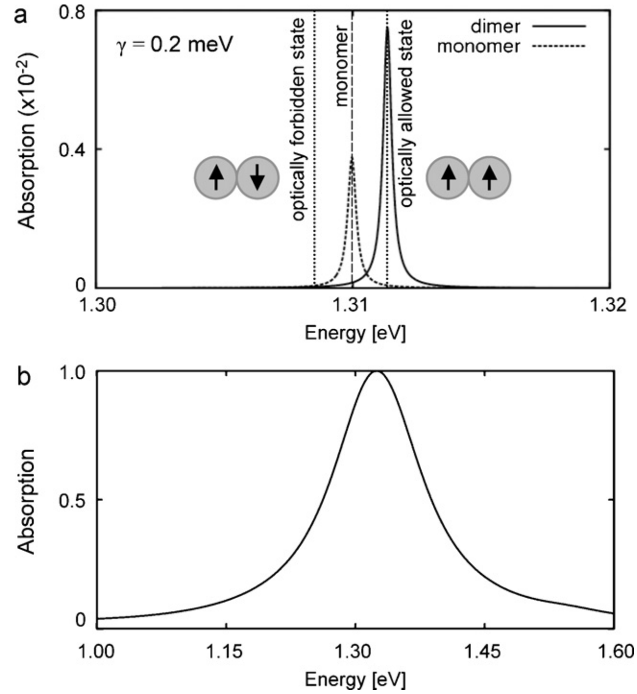

Fig. 2. (a) Absorption spectra of a molecular dimer and a monomer in free space. The vertical dashed line indicates the monomer eigenenergy. The vertical dotted lines indicate the OA state (upper line) and OF state (lower line). Black arrows represent the phase relation between the dipoles in respective monomers in a molecular dimer. (b) Absorption spectrum of metal structures. In (a) and (b), absorption values are normalized by the maximum value of the metal absorption. We assume $\gamma = 0.2$ meV.

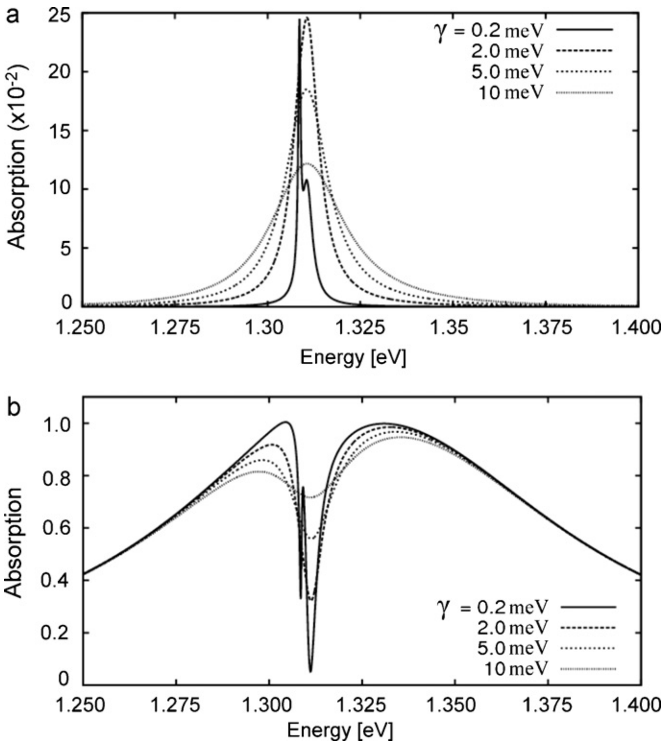

Fig. 3. (a) Absorption spectra of a molecular dimer whose position is indicated in Fig. 1(b). (b) Absorption spectra of metal structures in the presence of the molecular dimer.

using a coupled oscillator model. The conclusion is given in the last section.

2. Model and theory

As mentioned in the previous section, the metal structures with an accurately controlled nanogap serve as an efficient light-harvesting antenna, and the generated LLF can be used in various applications. It should be noted, however, that the metal antenna system has a large photo-emission rate and that the metal itself has a large dephasing rate. Avoiding these dissipations is a crucial aspect in the design of a highly efficient antenna system, and the consideration of feedback-interplay is essential for this study. In the present demonstration, we consider the model of metallic blocks as depicted in Fig. 1; this model is similar to those fabricated in Ref. [10]. We assume that a molecular dimer is located in the vicinity of a metal nanogap. Although we refer to the photon absorbers as "molecules" hereafter, we can also regard them as quantum dots depending on their parameters. In order to discuss optical response and microscopic energy flow, we calculate the absorption of this molecular dimer and the metal structures.

To obtain the response field, we solve the discretized integral form of Maxwell's equation being based on discrete dipole approximation (DDA) [11]. In this calculation, we divide the space including the metal blocks into small cubic cells, where microscopic quantities such as electric field and polarization in each cell are averaged by the volume integral in the analytical evaluation of the self-interaction. The integral equation is given as

$$\mathbf{E}_i = \mathbf{E}_i^0 + \sum_{j=1}^{N} \mathbf{G}^f_{i,j}\mathbf{P}_j V_j, \qquad (1)$$

where $\mathbf{P}_j = \chi_j \mathbf{E}_j$ is satisfied at each cell. χ_j is the optical susceptibility; i, the index of a cell at an observation position ($i = 1, \ldots, N$); j, the index of a cell at a source position ($j = 1, \ldots, N$); $\mathbf{E}_i$, the total response field; $\mathbf{E}_i^0$, the incident field; $\mathbf{G}^f_{i,j}$, the free space Green's function with both the transverse and longitudinal electromagnetic components; and V_j, the volume of the j th cell. The metal

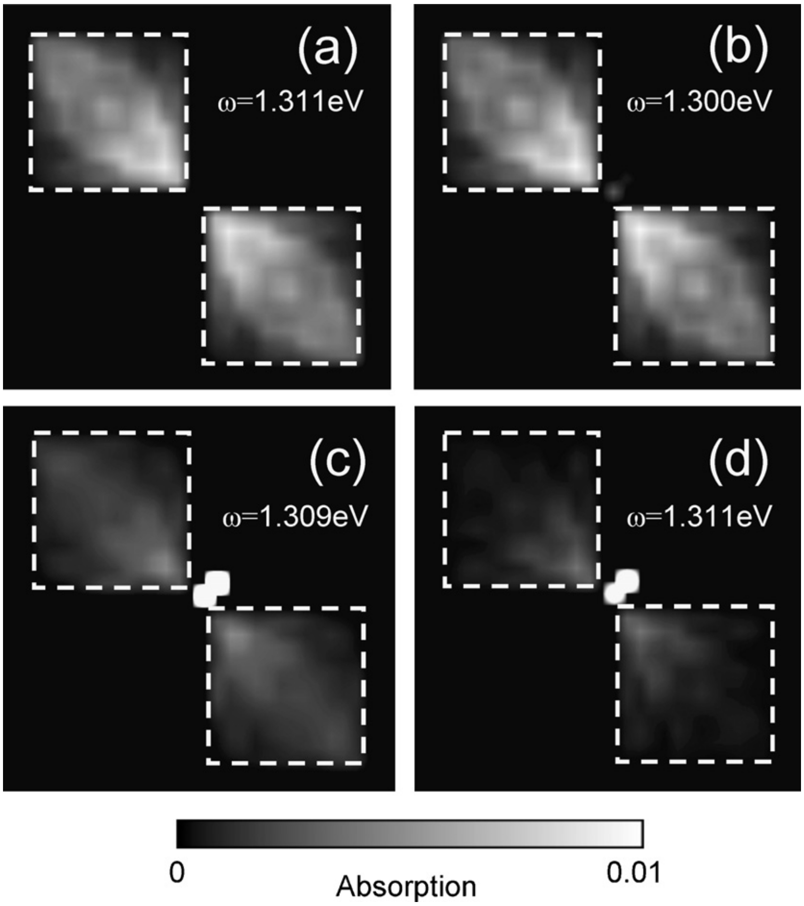

Fig. 4. Spatial map of absorption. (a) Absorption in the absence of a molecular dimer. Energy is tuned to the gap plasmon resonance. (b) Absorption in the presence of a molecular dimer. Energy is shifted from the molecular resonance. (c) Absorption in the presence of a molecular dimer. Energy is tuned to the OF resonance. (d) Absorption in the presence of a molecular dimer. Energy is tuned to the OA resonance. For (a)–(d), $\gamma = 0.2$ meV is assumed. For easy view of the contrast in metal absorption, the range of the displayed absorption value is limited within 0–0.01, though the value at the molecules exceeds this range.

blocks are assumed to have a Drude-type dielectric function with parameters of gold [12,13]. For a clear demonstration of the role of feedback-interplay, we assume the metal blocks to be thin so that the mode volume of LLF is not much larger than the molecular volume. Further, for discussing the essential aspects of the phenomena, we assume a simple model of a molecular dimer that has Lorentzian-type susceptibility, i.e., $\chi_j^m = (|d|^2/V)/(\hbar\Omega^m - \hbar\omega - i\gamma)$, where d is the dipole moment of constituent monomers, $\hbar\Omega^m$ is the eigenenergy of the non-coupled monomer resonance state, and γ is the nonradiative damping constant of the monomer. On solving Eq. (1), we obtain the formal solution, $\mathbf{P} = \mathbf{X}\mathbf{E}^0$, where $\mathbf{X}$ is the inverse of the coefficient matrix of the simultaneous equations. From this expression, we understand that the roots of $\mathrm{DET}[\mathbf{X}^{-1}] = 0$ provide eigenenergies of the molecular system interacting with the photon field. These eigenenergies are generally shifted from that of a non-coupled molecule because of the inter-monomer interaction via a longitudinal field (dipole–dipole coupling) and because of the self-interaction of the respective dimer states. The former interaction causes the energy splitting of coupled dimer states, and the latter induces a shift in eigenenergies and a change in their width of these dimer states. It should be noted that the magnitude of this self-interaction of these dimer states is greatly different from that in free space because of the strong coupling with the metal structures. We assume that the incident light has a k-vector along z-axis and polarization along the gap direction.

3. Results

First, we observe the basic absorption spectra of the molecular dimer and metal structures. Fig. 2(a) shows the absorption spectra of the molecular dimer in free space. In this case, we use the following parameters: $d = 7.2$ debye [14], which is similar to the value for the porphyrin, and $\hbar\Omega^m = 1.2933$ eV, which we choose for the tuning to the local plasmon resonance in the present model. Because of the dipole–dipole interaction between the monomers, two split states are formed. In this spectrum, the peak structure corresponding only to the higher state appears. In this state, the dipoles in the respective monomers oscillate in phase with each other; this state is termed the optically allowed (OA) state. The lower state, on the other hand, is the optically forbidden (OF) state, where the dipoles in the respective monomers oscillate out of phase. Fig. 2(b) shows the spectrum of metal structures in the absence of the molecules, where we can see a very broad peak structure due to the gap plasmon resonance.

Next, we examine how these spectra are modified by their interaction. Fig. 3(a) shows absorption spectra of a molecular dimer located near the nanogap for several different values of the damping constant. In the case of small damping ($\gamma = 0.2$ meV), characteristic features can be seen for the OA and OF states (The precise position of a molecular dimer is indicated in Fig. 1(b)). The absorption of the OA state is enhanced as compared with that in the free space and also

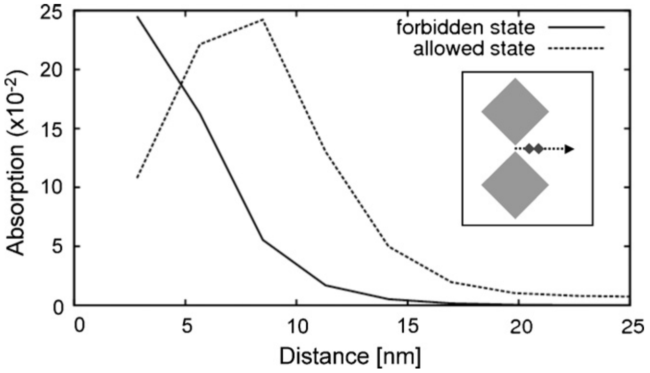

Fig. 5. Position dependence of the absorption of a molecular dimer. The horizontal axis indicates the distance between the center of the nanogap and that of the molecular dimer. The inset indicates how the position of the molecular dimer is changed. For this calculation, we assume $\gamma = 0.2$ meV.

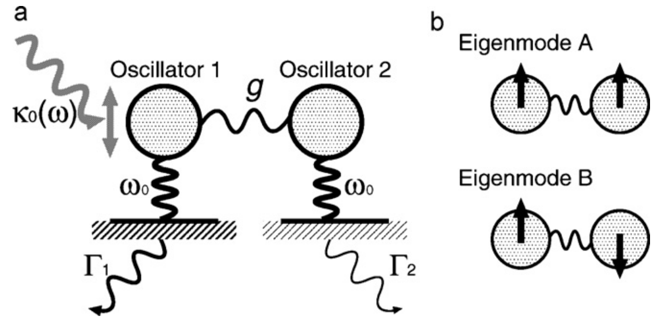

Fig. 6. Schematic illustration of the system. (a) Coupled harmonic-oscillator model. Oscillators 1 and 2 model the metal antenna and the molecular system, respectively. It is assumed that Oscillator 1 alone is pumped by the rate κ_0 and frequency ω and that the damping constant of Oscillator 1 is much larger than that of Oscillator 2 ($\Gamma_1 \gg \Gamma_2$). (b) Phase relation of oscillators in respective coupled eigenmodes. In Eigenmodes A and B, Oscillators 1 and 2 oscillate in phase and out of phase, respectively.

exhibits a wide broadening in its spectral peak. The enhancement is due to the antenna effect of the metal structures that concentrates the photon energies into the molecules. The remarkable broadening arises from the modification of the self-interaction by the strong metal–molecule interaction via the LLF. It should be noted that the peak structure of the OF state is also prominent, which is due to the breakdown of the long wavelength approximation by the steep gradient of the LLF intensity. Because the interaction with LLF for the OF state is smaller than that for the OA state, the peak of the OF state is very sharp and the maximum value is higher than that in the OA state, thus demonstrating the high Q character of this state. With the increase in the damping of molecules, the structure of the OF state rapidly disappears. On the other hand, interestingly, the integral absorption of the OA state tends to increase with the damping.

Fig. 3(b) shows another aspect of the above effect, namely, the absorption spectra of the metal blocks. A pronounced suppression of the absorption occurs near the molecular resonance energy. This phenomenon is clearly because of the feedback-interplay between the metal structures and molecules. Particularly, in the case of the small damping, the absorption is greatly suppressed and the metal blocks behave as a transparent material at the molecular resonance energy. In other words, under this condition, the photon energies received by the metal antenna are concentrated into the molecules without a large dissipation in the metal blocks. This situation is clearly observed in the spatial maps of absorption, shown in Fig. 4. In the present parameters, the absorption cross section of the metal blocks is much larger than that of the molecular dimer if blocks lie separately in the free space. In particular, for the OF state of the molecular dimer, the absorption cross section is negligibly small as compared with that of the metal blocks. However, at the molecular resonance energy, the absorption of the directly pumped metal blocks almost disappears, whereas that of the OF state becomes prominent if the molecular damping is small. This energy transparency effect at the metal structures can be understood by considering the interference between the metal–molecule coupled modes, which is explained in detail in the next section. In the present demonstration, we assume thin metal blocks to extract the essential features of the effect clearly, which is not the case for the sample in Ref. [10]. However, even in the case of thicker metal blocks, a similar effect of the energy transparency occurs over the entire metal structure if the molecular ensemble or aggregate occupies the space of the mode volume of the localized field; we do not treat such a case here to avoid unessential complications due to the many states of the molecular system.

Finally, we demonstrate how the quenching effect is different between the OA and OF states. Fig. 5 shows the position dependence of the absorption of the molecular dimer. In general, the photoemission probability of luminescent objects is greatly enhanced near the LLF. However, as is well known, if the object is too close to the metal, quenching occurs because of the energy transfer from the object to the metal. In Fig. 5, we can see such a behavior of the OA state; its absorption becomes maximum at a particular distance from the metal nanogap. On the other hand, interestingly, the position of the maximum absorption of the OF state is closer to the nanogap and the maximum value becomes larger than that of the OA state. Observing this effect, we understand that the OF state with a small damping serves as a good energy absorber, where the received photon energies by the metal antenna are effectively transferred and accumulated in the molecules.

4. Discussions

As we demonstrated above, by considering the feedback-interplay between the metal structures and a molecular system, we find an interesting energy flow between these objects. In particular, we observed the possibility that the photon energy received by the metallic antenna is strongly concentrated into the molecule without being absorbed by the metal blocks if the molecular damping is much smaller than that of the metallic antenna. This effect can be understood if we consider the coupled harmonic-oscillator model. In this model, the metal antenna and molecular system are modeled by harmonic oscillators with large damping and small damping, respectively. The oscillator with large damping is strongly coupled with an external field, whereas that with small damping is not. We call them “Oscillator 1” and“Oscillator 2”, respectively. We assume that the two oscillators are coupled with each other (Fig. 6(a)), as the metal structures and the molecular system are coupled via LLF.

The Hamiltonian of this model is given as

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_{\rm ex}(t), \tag{2}$$

where

$$\hat{H}_0 = \sum_{n=1,2} \hbar\omega_0 \hat{c}_n^\dagger \hat{c}_n + \hbar g(\hat{c}_1^\dagger \hat{c}_2 + \hat{c}_1 \hat{c}_2^\dagger), \tag{3}$$

$$\hat{H}_{\rm ex}(t) = \hbar\kappa_0(\hat{c}_1^\dagger {\rm e}^{-i\omega t} + \hat{c}_1 {\rm e}^{i\omega t}). \tag{4}$$

In these expressions, $\hat{c}_{1,2}$ are annihilation operators for Oscillators 1 and 2, ω_0 is the common eigenfrequency of these oscillators, and g is the coupling constant between these oscillators. Since the absorption cross section of the molecule is considerably smaller than that of the metal antenna, we assume that Oscillator 1 alone is pumped by the rate κ_0 and frequency ω. We describe the motion of the den-

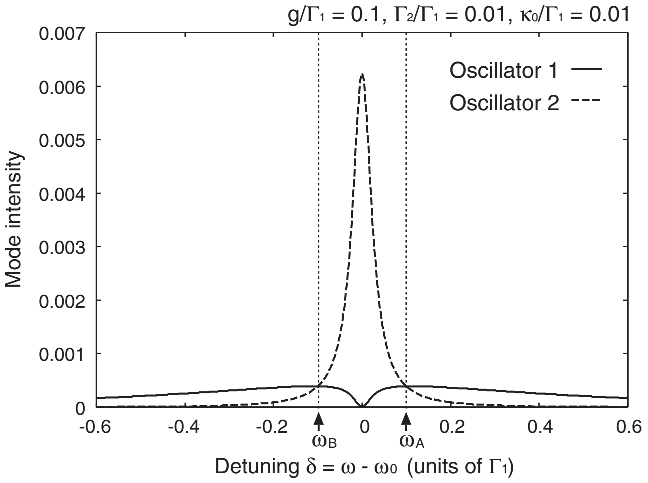

Fig. 7. Mode intensity of oscillators. Near resonance frequency ($\delta \simeq 0$), the excitation of Oscillator 1 is suppressed (solid line), whereas Oscillator 2 is strongly excited (broken line). Vertical dotted lines indicate the eigenfrequencies, ω_A and ω_B.

sity operator $\hat{\rho}$ of this system by the following Markovian quantum master equation [15]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\hat{H}(t), \hat{\rho}(t)\right] + \sum_{n=1,2}\Gamma_n\left[\hat{c}_n\hat{\rho}(t)\hat{c}_n^{\dagger} - \frac{1}{2}\{\hat{c}_n^{\dagger}\hat{c}_n, \hat{\rho}(t)\}\right]. \quad (5)$$

Considering the large difference in the damping constant between the metal structures and the molecular system, we assume $\Gamma_1 \gg \Gamma_2$, where $\Gamma_{1,2}$ are the damping constants of Oscillators 1 and 2, respectively. Now, we express the operators for the respective oscillators as

$$\hat{c}_1 = \frac{1}{\sqrt{2}}(\hat{c}_A + \hat{c}_B), \quad (6)$$

$$\hat{c}_2 = \frac{1}{\sqrt{2}}(\hat{c}_A - \hat{c}_B). \quad (7)$$

Here, the operators $\hat{c}_{A,B}$ are the annihilation operators of eigenmodes of $\hat{H}_0$, which diagonalize the system as $\hat{H}_0 = \hbar\omega_A\hat{c}_A^{\dagger}\hat{c}_A + \hbar\omega_B\hat{c}_B^{\dagger}\hat{c}_B$, where $\omega_A = \omega_0 + g$ and $\omega_B = \omega_0 - g$ are the eigenfrequencies of Eigenmodes A and B. In Eigenmodes A and B, Oscillators 1 and 2 oscillate in phase and out of phase, respectively, as illustrated in Fig. 6(b).

Fig. 7 shows the detuning ($\delta = \omega - \omega_0$) dependence of the mode intensity of the respective oscillators $|\langle\hat{c}_{1,2}\rangle|^2$ in the steady state. As explained below, the superposition between Eigenmodes A and B is essential for the energy transparency effect. For this superposition, the spectrum of one of these two oscillators should be broader than the coupling constant (g) between these oscillators. Otherwise, there is no overlap between these two coupled modes. Further, the spectral width of the oscillator corresponding to the energy absorber (Oscillator 2) should be small in order to hold the energy. Considering these conditions, we choose the value as $g/\Gamma_1 = 0.1$, $\Gamma_2/\Gamma_1 = 0.01$, and $\kappa_0/\Gamma_1 = 0.01$. With regard to the relation between g and Γ_2, g should be larger than Γ_2. As shown in Fig. 3, metal transparency does not appear at the OF resonance if the molecular damping of this state is large though this transparency appears at the OA resonance. From Fig. 7, we know that near resonance frequency ($\delta \simeq 0$), the excitation of Oscillator 1 (corresponding to the gapmode by the metal structures) is suppressed (solid line), whereas Oscillator 2 (corresponding to the molecule) is strongly excited (broken line), i.e., the energy transparency occurs. This can be understood if we consider an interference effect between Eigenmodes A and B because Oscillators 1 and 2 are expressed as superpositions of these modes, as indicated by Eqs. (6) and (7).

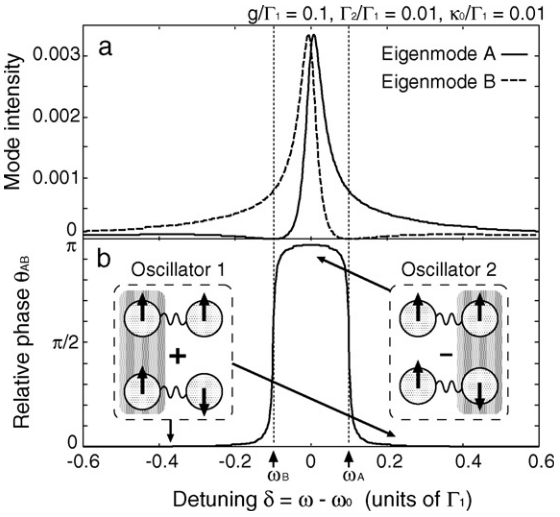

Fig. 8. (a) Mode intensity of coupled eigenmodes. Eigenmodes A and B have a high mode intensity near the resonance (solid and broken lines, respectively), and they are overlapped. The vertical dotted lines indicate the eigenfrequencies ω_A and ω_B. (b) Relative phase between coupled eigenmodes. The relative phase θ_{AB} is almost inverted near the resonance region $\omega_B < \omega < \omega_A$, where the amplitudes of Oscillator 1 are superposed destructively and those of Oscillator 2 are superposed constructively.

Actually, as indicated in Fig. 8, the relative phase θ_{AB} between Eigenmodes A and B is almost inverted near the resonance region $\omega_B < \omega < \omega_A$. In the region of $\theta_{AB} \simeq \pi$, the amplitudes of Oscillator 1 are superposed destructively and those of Oscillator 2 are superposed constructively. Thus, we have a peculiar effect where the pumped Oscillator 1 is not excited while the unpumped Oscillator 2 is excited. This well explains the energy transparency effect that occurs in the metal–molecule coupled system demonstrated in the previous section.

As explained above, the energy transparency effect is due to the interference between the coupled modes formed by the metal antenna and the molecular system. In the real system, the gapmode of the metal structures has many degrees of freedom, and hence, it is expected that a larger amount of energy can transparently flows from the metal to the molecule.

5. Conclusions

We theoretically demonstrate an optical response of a coupled system comprising metal structures and a molecular dimer. The metal structures generate a highly localized light field (LLF) near its nanogap and the molecular dimer is located there. The molecular dimer has two split states, an optically allowed (OA) state and an optically forbidden (OF) state due to the dipole–dipole interaction between monomers. Near the nanogap, the absorption by the OA state is enhanced and exhibits a considerable broadening of its peak structure due to the interaction with the metal structures. Further, the OF state also exhibits a prominent response due to the breakdown of the long wavelength approximation. It should be noted that the energy transparency effect occurs at the molecular resonance, i.e., the excitation energy received by the metal structures is concentrated into the molecules without strong dissipation in the metal. This effect is more remarkable when the the molecular resonance is narrower. We explain this mechanism by using the coupled harmonic-oscillator model. Under particular resonance conditions, only the molecules are excited even if only the metal structures are pumped by the external field; this phenomenon is due to the interference between the metal–molecule coupled modes.

In the present demonstrations, we only show the typical cases with particular conditions. However, we remark that similar effects can be obtained even if we relax the conditions. For example, in the case that the resonance energy of the molecule is shifted from that of the gapmode, a Fano-type spectral shape appears near the molecular resonance and energy concentration also occurs. Therefore, we can expect that energy concentration occurs in a wider range of frequency if several molecules with different resonance energies are coupled with the metal structures. We will discuss such possibilities in future studies. From the present demonstrations, we understand that the nanostructure design with the consideration of the feedback-interplay between constituent elements such as metal structures and molecules (quantum dots) will help in developing new technologies for manipulating microscopic energy flow.

Acknowledgments

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