

Unconventional optical properties of an antenna-molecule coupled system

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For enhancing the interaction between light and small objects, highly localized photon modes based on metal nano- and microstructures has attracted considerable attention, and it has been extensively investigated with regard to its application to highly sensitive sensing, few-molecule detection, etc., by using a strongly magnified light field. Further, with the emergence of recent state-of-the-art nanofabrication technologies, accurately controlled metallic nanogaps have been successfully fabricated to realize an extremely localized and enhanced electromagnetic field [1]. In such systems, the metal structures serve as light-harvesting antennas, and two-photon induced chemical reactions occur, for example, at the nanogap, even through a very weak excitation by an incoherent light source [2]. Thus, a metal-molecule (quantum dot) coupled system can be potentially employed to efficiently excite nano-objects that are extremely small, as compared to the light wavelength; an optical antenna with a large cross section harvests the light and efficiently transfers its excitation energy to a nano-object with a small cross section.

Although the metal antenna has the advantage of a large cross section, its use results in drawbacks such as a large scattering loss and nonradiative dissipation, which reduce the light harvesting efficiency. The key concept in order to overcome such drawbacks is a quantum mechanically coherent coupling that invokes strong feedback interplay between the antenna and the molecules, i.e., the coupling affects not only the optical response of the molecular system but also that of the metal system. The purpose of this contribution is to propose an approach for exploiting the full potential of the antenna-molecule coupled system by regarding the antenna system and molecules as a quantum mechanically coupled system.

We demonstrate that controlling their coupling and interference yields distinctive energy transparency effects that drastically reduce energy dissipation in the weak excitation process [3] as well as population inversion of the two-level system due to the nonlinear effect in the strong excitation process. The former mechanism overcomes the drawback stated above and the latter indicates the potential of this system to realize various optical processes beyond conventional understanding, such as direct conversion to coherent light (e.g., superfluorescence from incoherent pump light) and unconventional lasing schemes.

In the present demonstration, we consider the model of metallic blocks as depicted in Fig. 1. We assume that a molecular dimer is located in the vicinity of a metal nanogap. 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). In this calculation, we assume the Drude-type dielectric function for the metal structure and use the parameters for the molecule similar to the value for the porphyrin. Because of the dipole-dipole interaction between the monomers, two split states are formed, i.e., the optically allowed (OA) state and the optically forbidden (OF) state. The latter is not active in the usual long wavelength

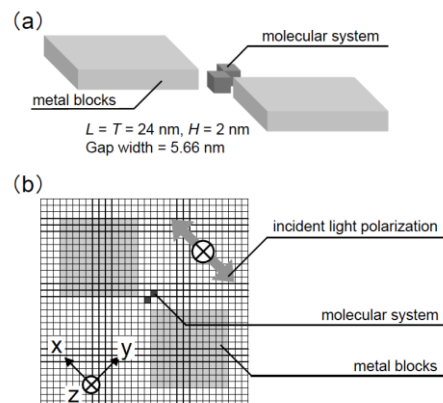


Figure 1: (a) Schematic picture of the metal structures and molecular systems. (b) Top view of the model for the calculation. Grids show the cells for DDA calculation.

approximation (LWA) condition because the excitation pattern is quadrupole-type. Near the nanogap, the absorption of the OA state is greatly enhanced as compared with that in the free space and also exhibits a wide broadening in its spectral peak because of the strong interaction with the localized electromagnetic field. Further, the OF state becomes also prominent, which is due to the breakdown of LWA by the steep gradient of the intensity of the localized field. Interestingly, a pronounced suppression of the absorption of the metal structure occurs near the molecular resonance energy (Fig. 2), wherein the absorption is greatly suppressed and the metal blocks behave as a transparent material. 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 phenomenon is because of the feedback-interplay between the metal structures and molecules.

The above energy transparency effect can be understood by considering the interference between the metal-molecule coupled modes (Fig. 3). The metal antenna and molecular system can be 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 these oscillators Oscillator 1 and Oscillator 2. These two oscillators form two eigenstates; Eigenstate A and B. In Eigenstate A, the two oscillators oscillate in phase, and in Eigenstate B, they oscillate out of phase. Near the resonance, the relative phase between Eigenmodes A and B is almost inverted, and 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.

A more remarkable feature of this system appears in the nonlinear excitation regime. Namely, for a certain range of detuning between the resonance energies of the two kinds of two-level systems: System 1 and System 2 corresponding to the metal antenna and the molecule, respectively, the population inversion is created at System 2 when System 1 is pumped. This effect contradicts conventional understanding that the population inversion cannot be created for the two-level system, and also, we can expect a wide variety of potential applications of this mechanism such as a direct conversion to a coherent light like superfluorescence from incoherent pump light, and unconventional lasing scheme. Thus, this study can contribute to a significant increase in the degrees of freedom for controlling the microscopic energy flow and energy conversion in nanosystems, thereby facilitating the development of next generation energy technologies.

References

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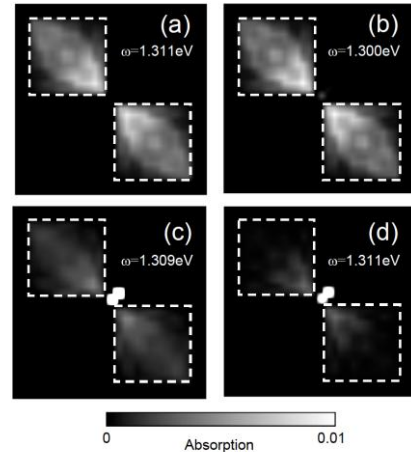


Figure 2: Spatial map of absorption. (a) Absorption in the absence of a molecular dimer. Energy is tuned to the gap plasmon resonance. (b) Absorption in the presence of a molecular dimer. Energy is shifted from the molecular resonance. (c) Absorption in the presence of a molecular dimer. Energy is tuned to the OF resonance. (d) Absorption in the presence of a molecular dimer. Energy is tuned to the OA resonance.

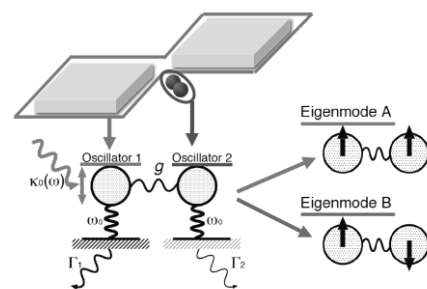


Figure 3: Schematic illustration of the coupled harmonic-oscillator model. Oscillators 1 and 2 model the metal antenna and the molecular system, respectively. It is assumed that Oscillator 1 alone is pumped and that the damping constant of Oscillator 1 is much larger than that of Oscillator 2. In Eigenmodes A and B, Oscillators 1 and 2 oscillate in phase, and out of phase, respectively.