Induced correlation between molecules in different plasmonic fields

Yoshiki Osaka, Nobuhiko Yokoshi, Hajime Ishihara
Department of Physics and Electronics, Osaka Prefecture University, 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka, 599-8531, Japan
E-mail: osaka@pe.osakafu-u.ac.jp

Abstract. We theoretically examine the optical responses of two molecules near gold nanoblocks which generate strongly localized near-fields due to localized surface plasmon resonance. The molecules located in the near-fields efficiently interact with light. As a result, we find that correlations between the molecules exist, even though the molecules are distantly positioned. Because these correlations are of importance to collective behaviors of the molecules such as superradiance and superfluorescence, this result implies the possibility of these collective behaviors being generated through the plasmonic fields. Besides, correlations between molecules must be taken into account with regards to device applications of metallic nanostructure arrays.

1. Introduction
Superfluorescence (SF) is the cooperative light emission from an ensemble of initially uncorrelated molecules (or atoms) [1, 2]. The molecule ensemble spontaneously creates a macroscopic dipole through the common emission field, and then gives rise to an SF pulse. The maximum intensity of the pulse is proportional to $N^2$ and the time duration is proportional to $N^{-1}$, where $N$ represents the number of excited coherent molecules. Therefore, in general, SF occurs in high-density systems where the correlation between the molecules is large. On the other hand, metallic nanostructures, e.g., nanoparticles and nanoblocks, generate strongly localized near-fields due to localized surface plasmon resonance and the efficient interactions of molecules near the metal with light [3]. In other words, the metallic nanostructures play the role of an optical antenna and enlarge the effective scattering cross-section of the molecules for the incident light [4]. In particular, dimeric-arranged metal nanoblocks with a few nm-sized gap width provide enhanced near-fields near the gap with $\sim 10^4$ times greater intensities than that of the incident light [5]. An array of such the metallic nanostructure, which is actually produced experimentally, enables us to efficiently excite a number of molecules [6]. Then, we can expect that the molecules will exhibit collective behavior.

To date, we have theoretically examined optical responses of a single molecule located near the gap of such a single dimer-type metallic nanostructure and have found that a high-efficiency interaction between the incident light and the molecule is realized [7, 8]. In this work, we analyze the optical responses of two molecules near four gold nanoblocks arrayed in a dimer-type, and investigate the correlation between the efficiently excited molecules near the metallic antenna. As a result, we find that correlations between the molecules exist, even though the molecules are distantly positioned.
Figure 1. (a) Schematic figure of the assumed positions of the metallic nanostructures. We arrange four gold nanoblocks with a 2.83 nm gap. Each nanoblock is 20 nm \times 20 \times 4 \text{ nm}.

(b, c, d) Electric field intensity map of the metallic nanostructures. The orange arrow indicates the direction of polarization of the incident light.

2. Theory

We theoretically analyze the optical responses of four gold nanoblocks, arranged as shown in Fig. 1(a). For a clear demonstration, we assume the metal blocks to be thin so that the mode volume of localized light fields is not much larger than the molecular volume. The size of each block is 20 \times 20 \times 4 \text{ nm}^3, and the gap width is 2.83 nm. In order to obtain the optical response fields, we solve the discretized integral form of Maxwell’s equation by applying the discrete dipole approximation (DDA) [9]. In this calculation, we divide the space containing the metal blocks into small cubic cells, where microscopic quantities such as the electric field and polarization in each cell are averaged by the volume of the cell. Additionally, the self-interaction can be evaluated analytically. The integral equation is given as

\[ E_i = E_i^0 + \sum_{j=1}^{n} G_{i,j}^f P_j V_j, \]

where \( n \) represents the total number of cells, \( i \) and \( j (= 1, ..., n) \) are the cell number. \( \chi_j \) and \( V_j \) are the optical susceptibility and the volume of the \( j \)-th cell, respectively. \( E_i \) is the total response field and \( E_i^0 \) is the incident field. The free space Green’s function, \( G_{i,j}^f \), has both transverse and longitudinal electromagnetic components. The metal blocks are assumed to have a Drude-type dielectric function with the parameters of gold [10, 11]. As for the susceptibility of the molecule, we assume that it is of Lorentzian-type, i.e., \( \chi_j^m = \frac{(|d|^2/V_j)}{(\hbar \Omega^m - \hbar \omega - i\gamma)} \), where \( d \) is the dipole moment, \( \hbar \Omega^m \) is the eigenenergy, and \( \gamma \) is the nonradiative damping constant.

Figures 1(b, c, d) show the electric field intensity map of the metallic nanostructures when the light polarized along the direction of the orange arrows is irradiated. One can see the field enhancement at the gap. Therefore, when the molecules are near to the gap, the plasmonic fields excite the molecules efficiently.

In this work, we assume that two molecules, A and B, are positioned near the metal (Fig. 2(a)), and investigate the correlation between molecules A and B. We calculate the absorption cross section of molecule A according to the definition

\[ \sigma_{abs} = 4\pi(\omega/c) \int_V d^3r |E(r)|^2 |\text{Im}\{\chi(r)\}|/|E_0(r)|^2, \]

and estimate the correlation between molecules A and B from the spectra of the absorption cross section.
3. Results

Figure 2(a) gives the top view of the metallic nanostructures and demonstrates the variation of the position of molecule B. The position of molecule A is fixed near one of the gaps. In Fig. 2(b), we show the absorption spectra of molecule A when molecule B is placed at positions 1, 2, and 3 in Fig. 2(a). The black dotted line represents the absorption spectrum of molecule A when molecule B is absent. Only when molecule B is sited at position 2, corresponding to the neighborhood of the other gap, do we observe the red shift of absorption spectrum of molecule A. We can consider that this peak shift originates from the interaction energy with molecule B efficiently excited by enhanced field near the gap. Therefore, we can see that molecule A correlates with molecule B placed at position 2.

In Fig. 3, we discuss the relationship between the shift of the absorption spectrum of molecule A and the position of molecule B in more detail. Figures 3(b, c, d) show the absorption peak position of molecule A against the position of molecule B for three cases of polarization of incident light. The horizontal axis for the solid red (dashed blue) line represents the position of molecule B from the point P along the dashed red (blue) arrow in Fig. 3(a). As shown on the red line in Fig. 3(b), we find large shifts when molecule B is located near the gap. On the other hand, we find small shifts on the blue line in Fig. 3(b). Therefore, the condition dictating the appearance of the large shift corresponds to cases where both molecules are located in enhanced fields (see Fig. 1(b)). In Fig. 3(c), we cannot see the shifts, because molecule A is not located in the enhanced fields (see Fig. 1(c)). We find a large shift on both the red and blue lines in Fig. 3(d), because enhanced fields are generated in all of the gaps (Fig. 1(d)). In conclusion, these results state that the correlation between the molecules is strengthened when both molecule A and molecule B are located in enhanced fields near the gaps.

4. Conclusion

We have investigated the correlation between two molecules near four gold nanoblocks and found that these molecules are strongly correlated with each other when they are excited by the enhanced near-fields. Because the correlations between the molecules are of importance to their collective behavior, the results of this study suggest the possibility of generating cooperative phenomena through plasmonic fields. In addition, we believe that device applications of metallic nanostructure arrays must take correlation between molecules into account.
Figure 3. (a) Dashed red and blue arrows represent the variations in the position of molecule B. Figures 3(b, c, d) show the absorption peak position of molecule A against the position of molecule B for the incident light with different polarizations, represented by the orange arrows in the insets. The horizontal axis for the solid red (dashed blue) line represents the position of molecule B from the point P along the dashed red (blue) arrow in Fig. 3(a). The vertical dotted gray line denotes the gap position.

Acknowledgements
This work was partially supported by Grant-in-Aid for JSPS Fellows 25-9308 from MEXT, Japan.

References
[1] Dicke R H 1954 Phys. Rev. 93 99
[2] Bonifacio R and Lugliato L A 1975 Phys. Rev. A 11 1507
[3] Anger P, Bharadwaj P and Novotny L 2006 Phys. Rev. Lett. 96 113002
[4] Bharadwaj P, Deutsch B and Novotny L 2009 Adv. Opt. Photon. 1 438
[5] Tanaka Y, Ishiguro H, Fujiwara H, Yokota Y, Ueno K, Misawa H and Sasaki K 2011 Opt. Express 19 7726
[6] Ueno K, Juodkazis S, Shibuya T, Yokota Y, Mizeikis V, Sasaki K and Misawa H 2008 Journal of the American Chemical Society 130 6928
[7] Ishihara H, Nobuhiro A, Nakatani M and Mizumoto Y 2011 Journal of Photochemistry and Photobiology A: Chemistry 221 148
[8] Osaka Y, Yokoshi N, Nakatani M and Ishihara H 2014 Phys. Rev. Lett. 112 133601
[9] Purcell E M and Pennypacker C R 1973 Astrophys. J. 1186 705
[10] Johnson P B and Christy R W 1972 Phys. Rev. B 6 4370
[11] Antoine R, Brevet P F, Girault H H, Bethell D and Schiffrin D J 1997 Chem. Commun. 1901