

表面増強分光における準放射プラズモン共鳴の寄与

Contribution of sub-radiant plasmon resonance to surface-enhanced spectroscopy

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The electromagnetic (EM) mechanisms of surface-enhanced spectroscopy e.g. surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence (SEF) have been examined using superradiant plasmon resonance, such as the dipole or dipole–dipole (DD) coupled plasmon resonance localized at the gaps between small and symmetric metallic nanoparticle (NP) dimers [1]. The large EM enhancement of DD-coupled resonance at the gaps, namely hotspots (HSs), has received considerable attention because HSs exhibit exotic phenomena such as cw laser excited nonlinear emissions, ultrafast SEF, vibrational pumping, and the field gradient effect [2]. Furthermore, the EM coupling energy between DD-coupled plasmons and a molecular excitons at the HSs exceeds several hundred millielectronvolts, resulting in new physics and chemistry e.g. strong coupling, molecular optomechanics, and polariton chemistry [2,3].

However, higher-order plasmon resonance, such as the dipole–quadrupole (DQ) coupled plasmon resonance, which is subradiant, mainly determines the EM enhancement for large or asymmetric NP systems. Thus, clarifying the contribution of the subradiant resonance to EM enhancement is important for evaluating various plasmonic systems for SERS related spectroscopies and phenomena [4-7].

First, the contribution of DQ coupled plasmon resonance to EM enhancement is explained using the spectral uncorrelation between the experimentally obtained SERS with ultrafast SEF and the Rayleigh scattering spectra of silver NP dimers [4]. Second, the radiation properties of the SERS light generated by the DQ coupled resonance were determined through EM calculations [5]. Third, the importance of absorption spectroscopy in the evaluation of DQ coupled resonance is clarified based on quantum optics [6]. Finally, we introduce a method to directly evaluate the EM enhancement factors induced by DQ coupled resonance using ultrafast SEF [7].

References

- [1] T. Itoh, Y. S. Yamamoto, and Y. Ozaki, *Chem. Soc. Rev.* 2017, **46**, 3904-3921.
- [2] T. Itoh, M. Prochazka, Z.-C. Dong, W. Ji, Y. S. Yamamoto, Y. Zhang, and Y. Ozaki, *Chem. Rev.* 2023, **123**, 1552-1634.
- [3] T. Itoh, and Y. S. Yamamoto, *Nanoscale* 2021, **13**, 1566-1580.
- [4] T. Itoh, and Y. S. Yamamoto, *J. Phys. Chem. C* 2023, **127**, 5886–5897.
- [5] T. Itoh, and Y. S. Yamamoto, *J. Phys. Chem. B* 2023, **127**, 4666-4675.
- [6] T. Itoh, and Y. S. Yamamoto, *J. Chem. Phys.* 2023, **159**, 2 034709.
- [7] T. Itoh, and Y. S. Yamamoto, *J. Chem. Phys.* 2024, **160**, 024703.