

Excitation Resonance of Raman Scattering with the hybridized States of Localized Surface Plasmons and Excitons of Molecules at Electrified Interface

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Recent attempts to improve the efficiency of photochemical and photoelectrochemical processes have focused on control of the interaction between photons and molecules. Optimized perturbation of photons to excite molecules can be applied when both of the energy and the polarization direction of the electromagnetic field is tuned to match those of the electronic states of molecular orbitals. However, the intrinsic cross section of molecules for interaction with photons limits the probability of the electronic excitation. We need completely different strategy to break the limit of the reactivity of conventional photochemical systems. Most important target is to alter the cross sections of the molecules with photons. We should construct novel system in which the interaction between photons and molecules are drastically improved. Localized plasmons allow the localization, energy, phase, and wave vector of the field to be controlled by changing the structure of the metal on a nanometer scale. Such highly localization can also alter the photoexcitation process of the electrons in the electronic. Surface-enhanced Raman scattering (SERS) is a promising tool for detecting the interaction between molecules and localized plasmons. Over the past three decades numerous studies on SERS have shown that it can be applied as a versatile probe to detect molecules with ultra-high sensitivity. Although the electromagnetic enhancement by localized plasmons in the SERS process has been quantitatively evaluated and shows good agreement with numerical results obtained by finite-difference time-domain calculations of the field, this explanation cannot account for the fact that there are SERS-active and SERS-inactive molecules. To explain the molecular specificity of the enhancement, the contribution of highly localized photoexcitation process at the interface between molecule and metal, charge transfer resonance involving electron transfer between the molecules and metal, has been considered from the early stages of study on SERS. Due to uncertainties in the mechanism of the huge enhancement, there is still controversy concerning the concept of single-molecule SERS. It seems to relate those with unclear understanding of the photoexcitation process induced by highly localized electromagnetic field [1, 2]. In this paper, we discuss possibility of the modification of the photoexcitation process induced by localized plasmon. We attempt to control of the electronic excitation of molecules by introduce the metal-nanodimer with controlled nanogap distance under light illumination. Highly localized electric field at the gap leads to the formation of the hybridized states of plasmons and excitons of molecules. Observation of intensity dependence on the resonance with the states implies modification of the energy of the photoexcitations.

### References

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