Theory of plasmon enhanced molecular absorption: Effects of plasmon hybridization due to multiple metal nano-particle arrangement

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ABSTRACT

It is vitally important for opto-electronic organic devices to optimize the photo-excitation efficiency. One strategy would be the arrangement of molecules in the vicinity of metal nano-particles (MNPs) and the enhancement of photon absorption or emission due to the coupling of molecular transitions to MNP plasmon excitations. If two or more MNPs are placed in the proximity of a single molecule it would couple to the hybrid plasmon levels of the MNPs. The energetic position of these levels is directly related to the MNP arrangement and, thus, can be easily adopted to the molecular transitions. Using a density matrix methodology we investigate molecular excitation dynamics upon photon absorption in a dye molecule placed in the vicinity of spherical MNPs. Firstly, a system of two identical MNPs is considered and an absorption enhancement of three orders of magnitude is demonstrated. Secondly, a system of four identical MNPs symmetrically placed around the dye molecule is investigated. The different plasmon hybrid levels originated by different arrangements of MNPs make it possible to choose a large variety of molecules to be excited with high efficiency. This would be of particular interest for future applications.

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1. Introduction

Metal nano-particles (MNPs) are particularly interesting nano-scale systems which exhibit special optical and electronic properties. When a small spherical MNP is irradiated by light the external field causes the conduction electrons to oscillate coherently forming so-called plasmons [1]. This high electronic polarizability results in a local field enhancement, an effect which found numerous applications in Raman spectroscopy [2], biomedicine [3,4], bio-sensing [5], nano-photonics [6], photo-voltaics [7,8] and so on. In the recent decade, enhancement effects due to MNP surface plasmons attracted also some interests in material science [9—11].

There are numerous studies either theoretically or experimentally which confirm such enhancement effects (see for example [12—17] and references therein). Focusing on MNPs and a dye molecule placed on a TiO_2 cluster, one of the present authors theoretically studied the plasmon enhancement of photoinduced charge injection from the dye into the TiO_2 cluster [18,19]. It was found that the charge injection can be strongly affected by the

photoexcitation of the MNPs. Here, we will concentrate on the energy transfer coupling between the dye molecule and the MNPs, neglecting charge injection into the supporting layer (the TiO_2 cluster). Up to four MNPs placed in different special arrangements are considered. We investigate the interrelation between the MNP spatial arrangement, the resulting hybrid plasmon level scheme and the molecular photoexcitation enhancement. The paper is organized as follows. In the next section we introduce the model of the molecule-MNP system and describe the applied density matrix theory. In Section 3 we discuss the results, and some concluding remarks are given in Section 4.

2. Model and method

We consider a system of a single dye molecule in the proximity of two or four MNPs. The dynamics of the molecular excitation is described in the framework of a density matrix theory particularly suited to consider molecule-MNP systems [14,20].

In order to do this we first introduce the Hamiltonian and the states of interest. The Hamiltonian of the combined molecule and MNP system is expanded with respect to the product states of the electronic state of the molecule and that of the MNPs. Accordingly, the states of the coupled system is represented by the product

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states. The overall ground-state of the coupled system is

$$|\psi_g\rangle = |\varphi_g\rangle \times \prod_m |m0\rangle. \tag{1}$$

Here, $|\varphi_g\rangle$ is the electronic ground-state of the dye molecule, and $|m0\rangle$ is the electronic ground-state of the mth MNP. Conveniently, the energy related to $|\psi_g\rangle$ is set equal to zero. We assume that the externally applied laser field is weak enough, so that only singly excited states of the molecule-MNP system are of interest. The molecular excitation is accounted for by

$$|\psi_e\rangle = |\varphi_e\rangle \times \prod_m |m0\rangle, \tag{2}$$

with $|\varphi_e\rangle$ as the molecular excited state. The excited state energy of the molecule is denoted as E_e, and we have $E_e = \varepsilon_e$. The excitation of MNP plasmons is described by

$$|\psi_{mI}\rangle = |\varphi_g\rangle \times |mI\rangle \prod_{n\neq m} |n0\rangle, \tag{3}$$

where $|mI\rangle$ is the lowest lying excited state of the mth MNP. Since we consider spherical MNPs these states are dipole plasmons which can be counted by Cartesian coordinates $I = x,y,z$ fixing the spatial dipole plasmon polarization (see below and, e.g. [20]). The energies of the MNP plasmon excitations are

$$E_{mI} = \varepsilon_{pl}. \tag{4}$$

ε_{pl} is the dipole plasmon energy. Since we assume that the inter-MNP surface to surface distance as well as the molecule MNP distance is of some nanometer the restriction to dipole plasmon is justified (also when considering the formation of hybrid plasmon states; see reasoning below).

Based on the above given description, the related Hamiltonian takes the form (a ground-state contributions does not appear because the energy has been assumed to equal zero)

$$H(t) = E_e|\psi_e\rangle\langle\psi_e| + \sum_{m,I} E_{mI}|\psi_{mI}\rangle\langle\psi_{mI}| + H_{mol-mnp} + H_{mnp-mnp}$$
$$+ H_{field}(t). \tag{5}$$

The molecule-MNP coupling can be written as

$$H_{mol-mnp} = \sum_{m,I} J_{mI,e}|\psi_{mI}\rangle\langle\psi_e| + \text{H.c.} . \tag{6}$$

The coupling matrix element $J_{mI,e}$ is taken in the dipole-dipole approximation [18]

$$J_{mI,e} = \frac{(\boldsymbol{d}_{I0}^{(m)}\cdot\boldsymbol{d}_{eg}^*)}{|\boldsymbol{X}|^3} - \frac{3(\boldsymbol{d}_{I0}^{(m)}\cdot\boldsymbol{n})(\boldsymbol{n}\cdot\boldsymbol{d}_{eg}^*)}{|\boldsymbol{X}|^3}, \tag{7}$$

where $\boldsymbol{d}_{I0}^{(m)} = d_{pl}\boldsymbol{e}_I$ is the mth MNP dipole moment, and $\boldsymbol{e}_I$ denotes the unit vectors of a Cartesian coordinate system. Throughout the paper it is assumed that the MNPs are identical, that they are made by Au, and that they have a diameter of 20 nm. Moreover, $\boldsymbol{d}_{eg} = d_{mol}\boldsymbol{e}$ is the molecular transition dipole moment. Values of d_{pl} and d_{mol} are presented in Table 1. Finally, $\boldsymbol{X}$ is the vector connecting the centers of mass of the molecule and the MNP ($\boldsymbol{n} = \boldsymbol{X}/|\boldsymbol{X}|$). In a comparable way we can describe the coupling between the mth MNP and the nth MNP as

Table 1
Used parameters (for explanation see text).

d_{mol}	3 D
d_{pl}	2925 D
$\hbar\gamma_{pl}$	28.6 meV
r_{mnp}	10 nm
$\tau_p(t_p)$	20 fs (30 fs)
E_0	5×10^5 V/m
ε_e	2.6 eV
ε_{pl}	2.6 eV
$\hbar\omega_0$	2.6 eV

$$H_{mnp-mnp} = \sum_{m,I} \sum_{n,I'} J_{mI,nI'}|\psi_{mI}\rangle\langle\psi_{nI'}| + \text{H.c.} . \tag{8}$$

The coupling matrix element $J_{mI,nI'}$ looks similar to $J_{mI,e}$, Eq. (7), but with $\boldsymbol{d}_{eg}$ replaced by $\boldsymbol{d}_{I'0}^{(n)}$ (now, $\boldsymbol{X}$ is the vector connecting the centers of mass of both MNPs). The coupling to the radiation field takes the standard form

$$H_{field}(t) = -\boldsymbol{E}(t)(\boldsymbol{d}_{eg}|\psi_e\rangle\langle\psi_g| + \sum_{m,I} \boldsymbol{d}_{I0}^{(m)}|\psi_{mI}\rangle\langle\psi_{m0}|) + \text{H.c.} , \tag{9}$$

with

$$\boldsymbol{E}(t) = \boldsymbol{n}_E E(t)\exp(-i\omega_0 t) + \text{c.c.} . \tag{10}$$

$\boldsymbol{n}_E$ is the field polarization, ω_0 is the carrier frequency, and $E(t)$ is the field envelope. The latter has a Gaussian shape $E(t) = E_0\exp(-2(t - t_p)^2/\tau_p^2)$, with amplitude E_0, pulse center at t_p, and duration τ_p. To stay in a time region where the plasmon decay can be resolved we only consider pulses with a duration of $\tau_p = 20$ fs (all used parameters can be also found in Table 1).

To account for the fast nonradiative decay of MNP plasmons, the temporal behavior of the photoinduced molecule-MNP excitations has to be studied in the framework of an open system description. Consequently, our simulations are based on the introduction of a reduced density operator $\widehat{\rho}(t)$ and the related density matrix

$$\rho_{\alpha\beta}(t) = \langle\psi_\alpha|\widehat{\rho}(t)|\psi_\beta\rangle , \tag{11}$$

where α and β label the different states introduced beforehand. $\rho_{\alpha\beta}$ shall obey the following quantum master equation

$$\frac{\partial}{\partial t}\rho_{\alpha\beta} = -i\tilde{\omega}_{\alpha\beta}\rho_{\alpha\beta} - \frac{i}{\hbar}\sum_\gamma (v_{\alpha\gamma}(t)\rho_{\gamma\beta}(t) - v_{\gamma\beta}(t)\rho_{\alpha\gamma}(t))$$

$$-\delta_{\alpha,\beta}\sum_\gamma (k_{\alpha\to\gamma}\rho_{\alpha\alpha}(t) - k_{\gamma\to\alpha}\rho_{\gamma\gamma}(t)). \tag{12}$$

The complex transition frequencies are given by the diagonal part of the Hamiltonian $H(t)$, Eq. (5), and read $\tilde{\omega}_{\alpha\beta} = \omega_{\alpha\beta} - i(1 - \delta_{\alpha,\beta})r_{\alpha\beta}$, with $\hbar\omega_{\alpha\beta} = E_\alpha - E_\beta$ and the dephasing rates $r_{\alpha\beta} = 1/2 \sum(k_{\alpha\to\gamma} + k_{\beta\to\gamma})$. Since the plasmon decay is fast compared to all other decay processes the set of transition rates is reduced here to $k_{I\to g} = 2\gamma_{pl}$, where γ_{pl} is the plasmon dephasing rate (cf. Table 1). The coupling matrix $\hbar v_{\alpha\beta}(t)$ covers all coupling elements, namely the molecule-MNP energy transfer coupling $J_{mI,e}$, the inter-MNP coupling $J_{mI,nI'}$ and the coupling to the time-dependent external field via $-\boldsymbol{E}(t)\boldsymbol{d}_{eg}$ and $-\boldsymbol{E}(t)\boldsymbol{d}_{I0}$.

To characterize the temporal response of the system on the laser pulse excitation we compute the population of the molecule-MNP ground-state