Multipole resonance in the interaction of a spherical Ag nanoparticle with an emitting dipole*

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The effect of multipole resonance in the interaction between a spherical metallic nanoparticle (MNP) and an emitting dipole is studied with the Mie theory. The results show that the absorption peak of the MNP with respect to the field of the emitting dipole is blue-shifted with the decrease of the spacing between MNP and emitting dipole due to the enhanced multipole resonance. At a short distance, the enhanced multipole terms of scattering are not obvious compared with the dipole term. For the decay rate of the emitting dipole, multipole resonance brings about the enhancement of it largely at short spacing. For the radiative decay rate, the behavior is quite different. The dipole term is dominant at a short spacing, and the multipole term is dominant at a larger spacing.

Keywords: Mie theory, multipole resonance, absorption, decay rate

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1. Introduction

Much work has been done to study the mechanism of the interaction between a noble metallic nanoparticle (MNP)/film and an excited luminescent molecule in order to enhance the emission of the molecule.[1–10] The enhancement can be achieved through two processes, i.e., excitation and emission. For the excitation process, the incident light can be enhanced on the surface of the MNP due to the excitation of localized surface plasmon resonace (LSPR). The enhanced field can increase the excitation rate of the molecule, which can be achieved with both a metallic nanoparticle and a film. In some researches, the field can be enhanced up to 100 times.[11] For the emission process, it is believed that the decay rate of luminescent molecules would be affected when the emission spectrum of luminescent molecules overlaps with the scattering or absorption band of the nanoparticle.[12] The energy of an excited molecule couples to the LSPR mode on the MNP and then the LSPR mode is scattered as far field, which presents a new decay channel. The purpose of this paper is mainly to investigate the interaction between the excited molecule and the MNP. In general, the excited molecule is treated as an oscillating electric dipole in theory. The field of the emitting dipole with moment $\boldsymbol{p}$ at $\boldsymbol{r}$ is in the form of

$$\boldsymbol{E}_{\mathrm{d}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\left[(\hat{\boldsymbol{r}}\times\boldsymbol{p})\times\hat{\boldsymbol{r}}\frac{k^2}{\boldsymbol{r}} + (3\hat{\boldsymbol{r}}(\hat{\boldsymbol{r}}\cdot\boldsymbol{p}) - \boldsymbol{p}) \times\left(\frac{1}{r^3} - \frac{\mathrm{i}k}{r^2}\right)\right]\exp(\mathrm{i}kr). \quad (1)$$

The MNP scatters and absorbs the far and near field of the dipole, and then affects the decay rate of the dipole. However, unlike the plane wave used to study the optical property of a nanoparticle, the amplitude of the emitting dipole field decreases sharply at a short distance ($\sim r^{-3}$). The non-uniformity of the field at the location of the MNP will lead to the enhancement of the multipole resonance of the MNP. To obtain the role of multipole resonance in the interaction between emitting dipole and MNP, the Mie method is used.

Mie theory is a kind of method to deal with the problem of interaction between a nanosphere and a plane electromagnetic wave initially.[13,14] It has been widely used to calculate the scattering and extinction properties of nanospheres. In 1981, Ruppin improved it to deal with the problem between a nanoparticle and an emitting dipole.[15] Compared with quasi-static approximation and the G–N method,[16] the improved Mie theory is more exact, because the former two methods are only applicable for the nanoparticle with a size far smaller than a wavelength.

2. Method

In Mie theory, the source field which satisfies the Laplace equation can be expanded with four series of orthogonal functions.[16] Suppose that the position of the dipole is at (0, 0, R) in the Cartesian coordinates and the nanoparticle with radius a at the origin, and let ε_1 and ε_{m} be the relative permittivity of the surrounding medium and nanoparticle respectively, then the field of the emitting dipole with orientation radial or

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tangential to MNP will be written as[15]

$$\boldsymbol{E}_d = \begin{cases} \sum_{n=1}^{\infty} (B_{o\zeta n}^{(3)} M_{o\zeta n}^{(1)} + A_{e\zeta n}^{(3)} N_{e\zeta n}^{(1)}), & r < R, \\ \sum_{n=1}^{\infty} (B_{o\zeta n}^{(1)} M_{o\zeta n}^{(3)} + A_{e\zeta n}^{(1)} N_{e\zeta n}^{(3)}), & r > R, \end{cases} \tag{2}$$

with

$$\zeta = \begin{cases} 0, & \text{adial}, \\ 1, & \text{tangential}. \end{cases}$$

The expansion coefficients are in the following form:

$$A_{e0n} = \begin{cases} \mathrm{i}(2n+1) \dfrac{pk_1^2}{4\pi\varepsilon_1\varepsilon_0} \dfrac{\mathrm{h}_n(k_1R)}{R}, & r < R, \\ \mathrm{i}(2n+1) \dfrac{pk_1^2}{4\pi\varepsilon_1\varepsilon_0} \dfrac{\mathrm{j}_n(k_1R)}{R}, & r > R, \end{cases}$$

$$B_{o0n} = 0,$$

$$A_{e1n} = \begin{cases} \dfrac{\mathrm{i}(2n+1)}{n(n+1)} \dfrac{pk_1^2}{4\pi\varepsilon_1\varepsilon_0 R} \dfrac{d(k_1R\mathrm{h}_n(k_1R))}{d(k_1R)}, & r < R, \\ \dfrac{\mathrm{i}(2n+1)}{n(n+1)} \dfrac{pk_1^2}{4\pi\varepsilon_1\varepsilon_0 R} \dfrac{d(k_1R\mathrm{j}_n(k_1R))}{d(k_1R)}, & r > R, \end{cases}$$

$$B_{o1n} = \begin{cases} \dfrac{\mathrm{i}(2n+1)}{n(n+1)} \dfrac{pk_1^3}{4\pi\varepsilon_1\varepsilon_0} \mathrm{h}_n(k_1R), & r < R, \\ \dfrac{\mathrm{i}(2n+1)}{n(n+1)} \dfrac{pk_1^3}{4\pi\varepsilon_1\varepsilon_0} \mathrm{j}_n(k_1R), & r > R, \end{cases}$$

where j_n and h_n are the Bessel function of the first kind and the third kind (Hankel function) respectively, k_1 is the wave vector in the surrounding medium, while superscripts 1 and 3 represent that the Bessel functions that are contained by $\boldsymbol{M}$, $\boldsymbol{N}$, and the expansion coefficients A, B in Eq. (2) are of the first and third kind respectively. The magnetic field can be obtained from Maxwell's equations.

Due to the orthogonality of Mie basis functions, the field of scattering E_{S} should have the expressions as

$$\begin{cases} \boldsymbol{E}_{\mathrm{S}} = \sum_{n=1}^{\infty} (B_{o\zeta n}^{(3)} b_n M_{o\zeta n}^{(3)} + A_{e\zeta n}^{(3)} a_n N_{e\zeta n}^{(3)}), \\ H_{\mathrm{S}} = -\dfrac{\mathrm{i}k}{\omega\mu_1\mu_0} \sum_{n=1}^{\infty} (B_{o\zeta n}^{(3)} b_n N_{o\zeta n}^{(3)} + A_{e\zeta n}^{(3)} a_n M_{e\zeta n}^{(3)}), \end{cases} \tag{3}$$

$$a_n = \frac{[m\rho\mathrm{j}_n(m\rho)]'\mathrm{j}_n(\rho) - m^2[\rho\mathrm{j}_n(\rho)]'\mathrm{j}_n(m\rho)}{m^2[\rho\mathrm{h}_n(\rho)]'\mathrm{j}_n(m\rho) - [m\rho\mathrm{j}_n(m\rho)]'\mathrm{h}_n(\rho)},$$

$$b_n = \frac{[\rho\mathrm{j}_n(\rho)]'\mathrm{j}_n(m\rho) - [m\rho\mathrm{j}_n(m\rho)]'\mathrm{j}_n(\rho)}{[\rho\mathrm{h}_n(\rho)]'\mathrm{j}_n(m\rho) - [m\rho\mathrm{j}_n(m\rho)]'\mathrm{h}_n(\rho)}.$$

Here $\rho = k_{\mathrm{m}}a$; a_n and b_n could be obtained based on the boundary conditions on the surface of nanoparticle; $m = n_{\mathrm{m}}/n_1$, with n_{m} and n_1 being the refractive indices of a nanoparticle and the surrounding medium respectively.

By adding a new boundary, the problem of the core–shell structure can also be solved with this method.

The far-field emission can be obtained by integrating a Poynting vector on the surface enclosed dipole and nanoparticle, and expressed as

$$P_{\mathrm{r}} = \frac{\pi}{2\omega\mu\mu_0 k} \sum_{n=1}^{\infty} (|A_{e\zeta n}^{(1)} + A_{e\zeta n}^{(3)} a_n|^2 + |B_{o\zeta n}^{(1)} + B_{o\zeta n}^{(3)} b_n|^2) n^2(n+1)^2 \frac{2}{2n+1}. \tag{4}$$

The absorption and scattering power can be obtained by integrating the Poynting vector on the surface enclosed MNP. They are expressed as

$$P_{\mathrm{abs}} = \frac{\pi}{2\omega\mu\mu_0 k} \sum_{n=1}^{\infty} (|B_{o\zeta n}^{(3)}|^2(-\mathrm{Re}(b_n) - |b_n|^2) + |A_{e\zeta n}^{(3)}|^2(-\mathrm{Re}(a_n) - |a_n|^2)) n^2(n+1)^2 \frac{2}{2n+1}, \tag{5}$$

$$P_{\mathrm{scat}} = \frac{\pi}{2\omega\mu\mu_0 k} \sum_{n=1}^{\infty} (|A_{e\zeta n}^{(3)} a_n|^2 + |B_{o\zeta n}^{(3)} b_n|^2) n^2(n+1)^2 \frac{2}{2n+1}. \tag{6}$$

The total power loss of the emitting dipole is in the form of

$$P_{\mathrm{tot}} = P_{\mathrm{r}} + P_{\mathrm{abs}} + P_{\mathrm{intr}} \frac{1-q_0}{q_0}, \tag{7}$$

the relative decay rate $\Gamma/\Gamma_0 = q_0 P_{\mathrm{tot}}/P_{\mathrm{intr}}$, where Γ is the decay rate of the emitting dipole in the vicinity of the nanoparticle, Γ_0 and q_0 are the decay rate and quantum yield of the free emitting dipole respectively, q_0 is 1 in the calculations that we do below, and P_{intr} is the emitting power of the free emitting dipole.

The relative radiative decay rate can be expressed as

$$\frac{\Gamma_{\mathrm{r}}}{\Gamma_0} = q_0 \frac{P_{\mathrm{r}}}{P_{\mathrm{intr}}}. \tag{8}$$

where Γ_{r} is the radiative decay rate of the emitting dipole in the vicinity of the nanoparticle. The relative absorption decay rate and the relative scattering decay rate $\Gamma_{\mathrm{abs}}/\Gamma_0$ and $\Gamma_{\mathrm{scat}}/\Gamma_0$ are treated in a way similar to that of treating the relative radiative decay rate in Eq. (8).

With the above equations, the role of multipole resonance in the interaction between a spherical silver nanoparticle (AgNP) and an emitting dipole is studied. The surrounding refraction index is $n_1 = 1$. The index of Ag is measured experimentally[17] and the correction is done for the small size effect.[18] The calculation is performed with Matlab. All the figures below are plotted with software origin 8.5.

3. Results and discussion

The absorption properties of AgNP with radius $a = 30$ nm to the field of the emitting dipole are studied. The results show the absorption peaks of AgNP to the fields of the radial and tangential emitting dipole are blue-shifted compared with that of the plane wave at spacing $s = 2$ nm as shown in Fig. 1(a). The normalized curves for the radial and tangential emitting dipole have similar shapes. From Eq. (1), the near field of the emitting dipole is dominant, and the electric fields of the emitting dipole with radial and tangential orientations at the location of AgNP have similar forms but their phase difference is π. Therefore, the normalized absorption

curves of AgNP to the fields of the radial and tangential emitting dipole nearly coincide. To make a thorough investigation of multipole resonance, the expansion of the absorption spectrum is done and shown in Figs. 1(b)–1(d). For the absorption of AgNP to a plane wave in Fig. 1(b), the dipole term ($n = 1$) is dominant. For the absorption of AgNP to the field of the emitting dipole, even the term of $n = 40$ is larger than the dipole term. It reveals that the absorption increases sharply as spacing decreases, which should be the reason for the emission quenching at the short distance.[19,20] The peak of multipole resonance is at a shorter wavelength, which leads to the blue-shift of the total absorption peak. Moreover, the tangential term has a similar shape to the radial term, but with a lower value.

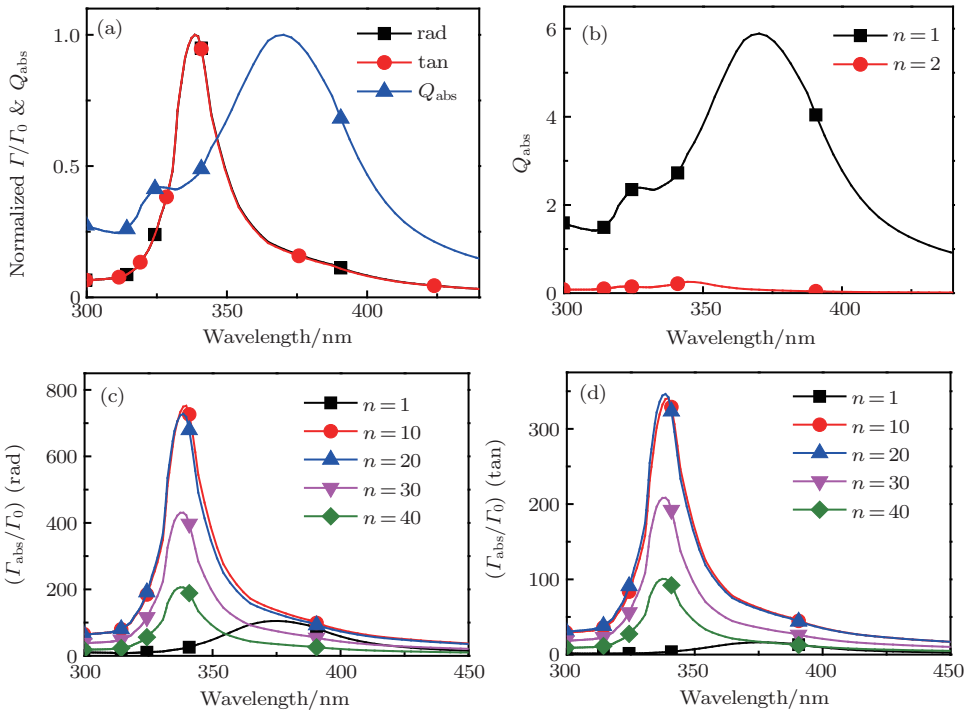


Fig. 1. (color online) Comparisons between the absorption properties of AgNP to the field of the emitting dipole and the plane wave for $s = 2$ nm. (a) Normalized total absorption, Q_{abs} is the absorption coefficient of AgNP. The normalized curves for the cases of tangential and radial orientations are much the same. (b) Expansion of absorption for the case of a plane wave. (c) Expansion for the case of a radial emitting dipole. (d) Expansion for a tangential emitting dipole (plotted with software origin 8.5).

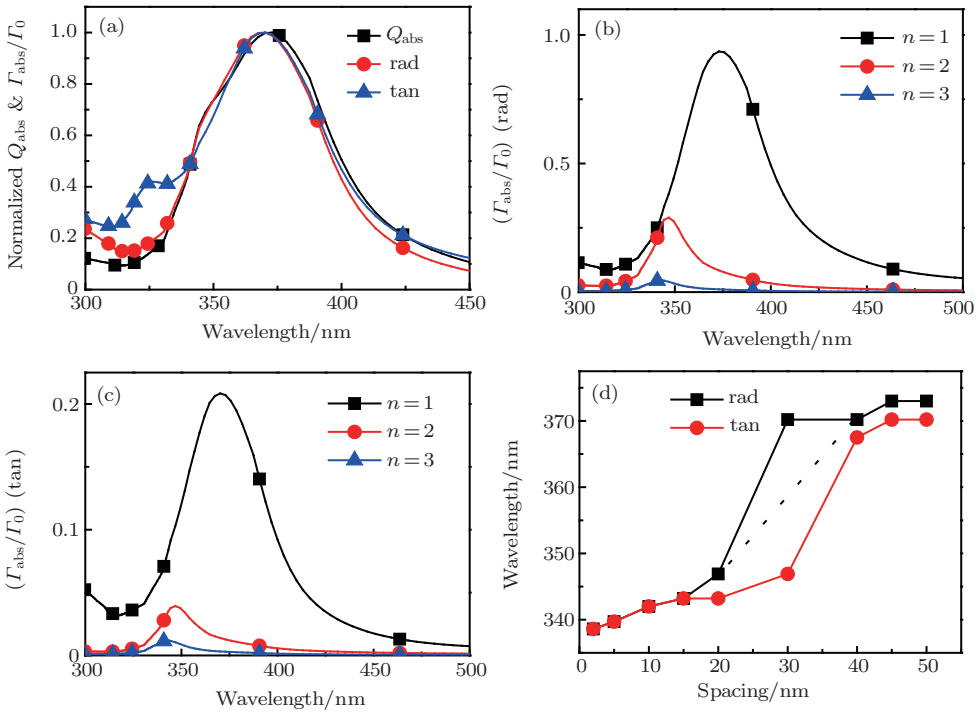


Fig. 2. (color online) Comparisons between the absorption properties of AgNP to the field of emitting dipole and plane wave for $s = 50$ nm and spacing dependence of the peak location. (a) Normalized total absorption, (b) radial, (c) tangential, and (d) peak location of absorption for the cases of a radial and tangential emitting dipole. The dash line is used for spacing from 20 nm to 40 nm because the intensities of multipole and dipole resonance peaks are comparable. At the other spacing, there is only one major peak (plotted with software origin 8.5).

The absorption property for spacing $s = 50$ nm is studied and shown in Fig. 2. From Fig. 2(a), the absorption peak for the case of the plane wave is only slightly higher than those of the radial and tangential emitting dipole. That is because the influence of multipole resonance on the absorption of AgNP declines and is less obvious than the dipole term compared with the case of $s = 2$ nm, as shown in Figs. 2(b) and 2(c). Simultaneously, the influence of multipole resonance is still larger than that of the plane wave. That is why the peak location of $Q_{\rm abs}$ is at a longer wavelength than that of an emitting dipole field. Also, the results for radial and tangential emitting dipoles are similar to each other. Therefore, only the radial case is discussed below. Besides, the spacing dependences of the peak location of absorption for the cases of radial and tangential emitting dipoles are shown in Fig. 2(d). As spacing increases, the absorption peak is red-shifted. The dotted line is used because the peak for spacing from 20 nm to 40 nm is not a single one due to the decline of multipole resonance.

As has been discussed above, the multipole resonance plays an important role in the absorption property of AgNP to the emitting dipole for short spacing. For the scattering case, the peak basically remains the same at different spacings. In order to reveal it, the multipole resonance of scattering is studied, and the results are shown in Fig. 3. The results show that the proportion of multipole resonance in the total scattering is far less than the dipole term, even though it can increase a lot for short spacing. The dipole term is dominant.

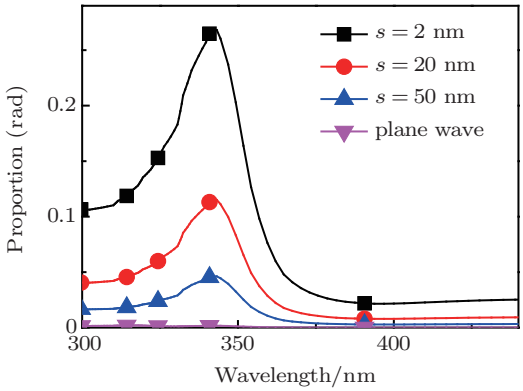


Fig. 3. (color online) Proportion of multipole resonance in the scattering of AgNP to the radial emitting dipole field (plotted with software origin 8.5).

The multipole resonance in the decay rate of the radial emitting dipole is studied, and the results are shown in Fig. 4. Like the case of absorption, multipole resonance is dominant for short spacing, as shown in Fig. 4(a). The term of $n = 60$ is also obvious. For short spacing, the dipole term is dominant, as shown in Fig. 4(b). The peak locations of decay rates for radial and tangential emitting dipoles are shown in Fig. 5 and they are red-shifted as the spacing increases. The dotted line is used here for the same reason as in Fig. 2(d). The peak locations for radial and tangential cases are the same for short spacing ($s < 15$ nm). Difference arises for the case of larger spacing, and the peak in the radial case is at a longer wavelength.

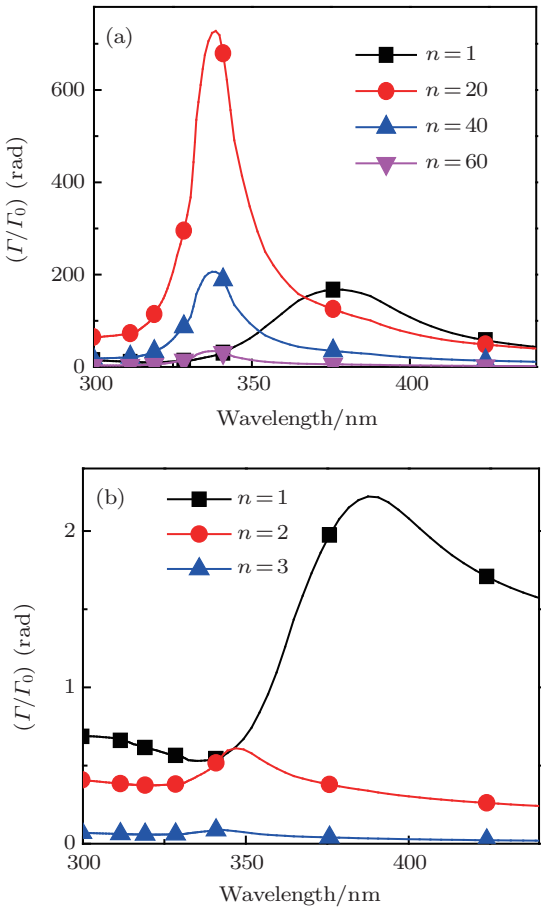


Fig. 4. (color online) Relative decay rates of the emitting dipole for $s = 2$ nm (a) and 50 nm (b) (plotted with software origin 8.5).

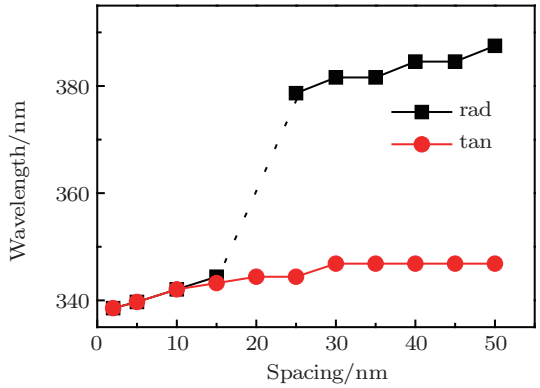


Fig. 5. (color online) Peak locations of the decay rate of radial and tangential emitting dipoles (plotted with software origin 8.5).

The radiative decay rate of radial emitting dipole is calculated, and the results are shown in Fig. 6. Quite unlike the absorption or the decay rate above, the relative radiative decay rate shows a novel property. The dipole term is dominant at $s = 2$ nm and it is nearly equal to the total radiative decay rate. In addition, the influence of the multipole term also declines as the spacing decreases, which is shown in Fig. 7. The behavior is quite different from the case of the decay rate or scattering, in which the effect of multipole resonance is more obvious at a short distance.

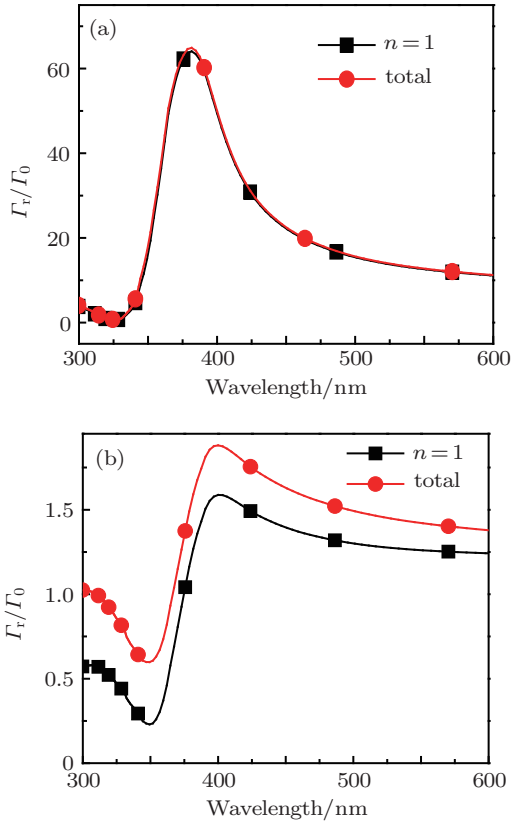


Fig. 6. (color online) Comparisons of relative radiative decay rates between dipole term and the total for $s = 2$ nm (a) and 50 nm (b) (plotted with software origin 8.5).

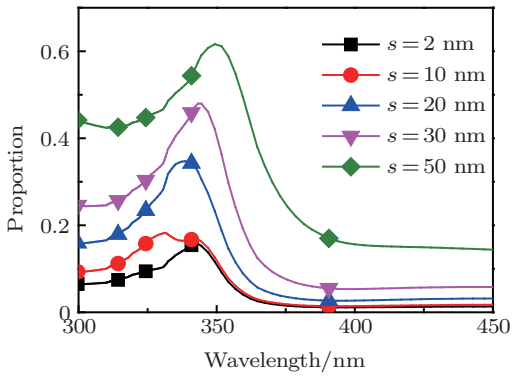


Fig. 7. (color online) Proportions of multipole resonance in the radiative decay rate (plotted with software origin 8.5).

4. Conclusion

The influence of multipole resonance in the interaction between spherical AgNPs is studied with Mie theory. The absorption rate of AgNP and the decay rate of the emitting dipole are both blue-shifted as the spacing between the AgNP and the emitting dipole decreases due to the enhanced multipole resonance. The dipole term is dominant for scattering at spacings ranging from 2 nm to 50 nm, even though the multipole resonance is enhanced more compared with the dipole term. For the radiative decay rate, the dipole term is dominant and nearly equal to the total radiative decay rate for short spacing, and the multipole resonance becomes more obvious as the spacing increases. It is quite different from the case of the decay rate.

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