Molecular decay rates and emission frequencies in the vicinity of an anisotropic metamaterial

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ABSTRACT

The decay rates and emission frequencies of a fluorescing molecule in the vicinity of an anisotropic metamaterial are studied within a phenomenological model. A special kind of indefinite medium recently shown to have a broadband all-angle negative refraction is studied for its interaction with the emitting dipole in the long wavelength limit at close molecule-substrate distances. In addition, materials of alternating metal-dielectric stratified layers are also studied. For the first kind which consists of a composite of metallic nanowires and a dielectric host, the results show that large molecular decay rates (hence exceedingly short lifetimes) occur when negative refraction takes place within the medium; and large blue-shifts can occur for the emission frequencies of the admolecules. For the stratified layered system, abrupt changes in both the emission lifetimes and frequencies can also take place upon negative refraction, although to a much less extent. These abrupt changes can thus provide signatures for probing the transition to such unusual optical property for the medium via surface-fluorescence experiments.

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1. Introduction

The recent explosion in the study of optical interaction with various metamaterials has revealed many interesting phenomena such as negative refraction, reversed Doppler effect, perfect lensing,...etc. [1]. Since the first successful fabrication of these materials employing the split ring resonator structure [2], many different approaches have been developed to create such metamaterials including metal-wire composites [3] as well as stratified systems of alternating metal-dielectric layers [4]. These two general approaches, namely, via composite materials and photonic crystals, have been well-established since the beginning of this decade [5]. An interesting feature with these systems is that negative refraction can be achieved merely from the anisotropic nature of the permittivity, and is possible even with non-magnetic materials [3,4,6]. One of the most exciting developments in the fabrication of each of these two types of materials is the recent 3D realization of negative refraction in each of the two systems at optical wavelengths [7,8].

While just like any new class of optical materials in which interaction with both far and near sources will be of great

interest to be explored, most of the optical phenomena involving metamaterials studied thus far have considered incident plane waves from distant sources [9]. Thus it would be of interest to study the possibility of probing these materials alternatively using near light sources such as fluorescing molecules located in the vicinity of these materials. Although this approach of probing many solid surfaces (especially metallic ones) has been in practice for decades [10], it is not yet well explored in the case of these new metamaterials. Theoretically, however, there have been several recent studies [11–15] on the emission of two-level systems in the vicinity of these new materials, although most of these were limited to *isotropic* materials where the formulation for the molecule-substrate interaction is simpler, with the molecule being modeled as a radiating dipole. Nevertheless, there is a large class of these metamaterials (e.g. the two types of materials aforementioned) which possesses strong anisotropic properties and will render the formulation on the molecule-substrate interaction complicated.

In this work, we will present a simplified formulation of this problem (i.e. dipole-anisotropic substrate interaction) by applying existing models in the literature [10,16] to study the decay rates (inverse lifetimes) and emission frequencies of these admolecules in the presence of two different types of nonmagnetic anisotropic metamaterials, namely, the metal-wire composite and the metal-dielectric stratified alternating layer systems. We shall

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follow the recent works [3,4] applying effective medium theories to describe the dielectric response of these indefinite systems (i.e. not all the components in the dielectric tensor are of the same signs), and shall limit to close molecule–material distances so that the long-wavelength approximation can be implemented.

2. Theoretical formulation

Following Chance, Prock and Silbey [10], let us consider a molecular emitter of dipole moment (p) embedded in an isotropic medium of dielectric ε_1 and located at a distance $z = d$ from the interface of an anisotropic medium filling $z < 0$ with dielectric tensor $\vec{\varepsilon}$ of the following form:

$$\vec{\varepsilon} = \begin{pmatrix} \varepsilon_x & 0 & 0 \\ 0 & \varepsilon_x & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix}. \quad (1)$$

By modeling the dipole as a damped harmonic oscillator (with dipole moment p) driven by the reflected field (E_R) from the interface [10], the modified decay rate and emission frequency shift of the molecule can be obtained in the form of two coupled equations (normalized to the free decay rate):

$$\hat{b} \equiv \frac{b}{b_0} = 1 + \frac{3\varepsilon_1}{2k_1^3} \left(\frac{1}{1 + \left(\frac{b_0}{\omega_0}\right) \Delta\omega} \right) \text{Im} \left(\frac{E_R}{p} \right), \quad (2)$$

$$\Delta\omega \equiv \frac{\Delta\omega}{b_0} = \frac{\omega_0}{b_0} \left[\sqrt{1 - \frac{e^2}{m\omega_0^2} \text{Re} \left(\frac{E_R}{p} \right) - \frac{b_0 b}{2\omega_0^2} + \frac{b^2}{4\omega_0^2}} - 1 \right], \quad (3)$$

where $b_0 = \frac{2e^2 k_1^3}{3m\varepsilon_1 \omega_0}$ is the free decay rate (with e and m being the electronic charge and mass, respectively), $\Delta\omega = \omega - \omega_0$ is the shift from the free molecule emission frequency, k_1 is the emission wave number, and we have assumed unity intrinsic quantum yield for the molecule. Note that the surface effects are completely accounted for via the term $\left(\frac{E_R}{p}\right)$ which is essentially the Green function of the reflection problem. In the limit when both $b_0 \ll \omega_0$ and $b \ll \omega_0$, Eqs. (2) and (3) can be decoupled to the following simplified form [10]:

$$\hat{b} \approx 1 + \frac{3\varepsilon_1}{2k_1^3} \text{Im} \left(\frac{E_R}{p} \right), \quad (4)$$

$$\Delta\omega \approx \frac{b^2}{8b_0\omega_0} - \frac{b}{4\omega_0} - \frac{3\varepsilon_1}{4k_1^3} \text{Re} \left(\frac{E_R}{p} \right) \approx -\frac{3\varepsilon_1}{4k_1^3} \text{Re} \left(\frac{E_R}{p} \right). \quad (5)$$

Furthermore, in the long wavelength limit $d \ll \lambda$, electrostatic approximation can be applied. By matching the appropriate boundary conditions at the interface, the reflected field at the dipole site ($z = d$) per unit dipole moment can be obtained in the following form [10,16,17]:

$$\frac{E_R}{p} = \frac{\theta}{d^3} \frac{\sqrt{\varepsilon_x \varepsilon_z} - \varepsilon_1}{\sqrt{\varepsilon_x \varepsilon_z} + \varepsilon_1}, \quad (6)$$

where θ is an orientation parameter with $\theta = \frac{1}{8}$ for perpendicular dipole and $\theta = \frac{1}{16}$ for parallel dipole, respectively. Before we apply Eqs. (2)–(6) to study the emission characteristics of the molecule, we shall first provide a brief summary of the dielectric properties of the two metamaterial systems [3,4] in the following with the application of various effective medium theories (EMT).

In the type of metal-dielectric composite metamaterial (Fig. 1(a)), a matrix of metallic nanorods is embedded in a dielectric host [3,7], and in the long wavelength limit, an effective dielectric

Fig. 1. Geometries of the two different types of metamaterials studied in this work: (a) the metal-wire composite, and (b) the alternating metal-dielectric stratified system.

function for the system can be obtained via the application of the Bruggeman theory in the form [3]:

$$\varepsilon_{\text{eff}}(D) = \frac{\Delta \pm \sqrt{\Delta^2 + 4D\varepsilon_a\varepsilon_m}}{2D}, \quad (7)$$

where D is a geometric parameter and $\Delta = f(1 + D)(\varepsilon_m - \varepsilon_a) + D\varepsilon_a - \varepsilon_m$, with real $\varepsilon_a (>0)$ and complex $\varepsilon_m (\text{Re } \varepsilon_m < 0)$ being the dielectric function of the host and metal, respectively, and f the volume fraction of the metal. Note that the root in Eq. (7) is taken so that ε_{eff} will have a positive imaginary part [3]. For cylindrical metal rod with axis along the z direction, the dielectric tensor in (1) can be described as follows [3]:

$$\vec{\varepsilon} = \begin{pmatrix} \varepsilon_{\text{eff}}(1) & 0 & 0 \\ 0 & \varepsilon_{\text{eff}}(1) & 0 \\ 0 & 0 & \varepsilon_{\text{eff}}(\infty) \end{pmatrix}, \quad (8)$$

with $\varepsilon_{\text{eff}}(\infty) = f\varepsilon_m + (1 - f)\varepsilon_a$.

For the other type of metamaterials which contains stratified alternating metal-dielectric layers (Fig. 1(b)) [4,8], an effective dielectric function can be derived via the application of the characteristic matrix formulation of the optical response for each layer in the form of Eq. (1) with

$$\varepsilon_x = \frac{\varepsilon_1 + \eta\varepsilon_2}{1 + \eta}, \quad (9)$$

Fig. 2. Effective permittivity for a Ag-wire and Al_2O_3 composite system. Note that negative refraction occurs for $\lambda > 750$ nm when we have $\text{Re } \epsilon_z < 0$.

$$\epsilon_z = \frac{\epsilon_1 \epsilon_2 (1 + \eta)}{\epsilon_2 + \eta \epsilon_1}, \quad (10)$$

where $\eta = \frac{d_2}{d_1}$ is a geometric parameter, while ϵ_i and d_i are the dielectric function and thickness of each of the two materials, respectively. In what follows, we shall apply Eq. (2) to (6) to study the emission characteristics of the admolecule on a metamaterial with anisotropic dielectric responses described by Eqs. (7) and (8), as well as those by Eqs. (9) and (10), respectively. We have found that Eqs. (2) and (3) will give acceptable results for relatively small surface effects so that the square root in (3) remains real; hence yielding physical results which are essentially very close to those obtained from the approximate model in Eqs. (4) and (5).

3. Numerical results and discussion

We have studied both the modified decay rates and emission frequencies of a dipole located in vacuum near the surface of each of the two types of metamaterials described above with geometry as depicted in Fig. 1. The dielectric materials are taken as Al_2O_3 in the composite case and MgF_2 in the multilayer case. These are the same materials used in the recent fabrication breakthrough of 3D metamaterials at optical frequencies [7,8], and their dielectric constants can be found from Ref. [18]. Note that the “fishnet” structure in Ref. [8] is not accounted for in the present modeling. The metal in these structures is taken as Ag throughout and is described by the following Drude function:

$$\epsilon_m = \epsilon_r - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}, \quad (11)$$

where the interband dielectric constant, plasmon frequency and the damping constant are chosen to have values equal to 4.039, 1.39×10^{16} rad/s, and 3.14×10^{13} rad/s, respectively [19].

We first study the metal-wire composite system with the volume fraction of the metal fixed at $f = 0.1$. Fig. 2 shows the real and imaginary parts of the dielectric functions as described in Eq. (8) for a Ag wire- Al_2O_3 system in which we clearly observe the three dielectric characteristics for such a system, namely: the transverse plasmon resonance (~ 400 nm); the longitudinal plasmon resonance (~ 750 nm) at which $\text{Re } \epsilon_z \sim 0$; and negative refraction ($750 \text{ nm} < \lambda$) for which we require $\text{Re } \epsilon_z < 0$ and $\text{Re } \epsilon_x > 0$ [3]. Fig. 3 shows the decay rate spectrum for a molecular dipole at two regimes of distance from the metamaterial surface. We show only the case of a perpendicular dipole with very similar results expected for parallel dipoles at such close distances when the decay is predominated by

Fig. 3. Normalized decay rates as a function of emission wavelength for a perpendicular molecular dipole at two regimes of distance from the metamaterial described in Fig. 2.

nonradiative energy transfer into the material. Aside from the peak lifetimes (corresponding to very small decay rate values) in the neighborhood of the transverse plasmon resonance, the most interesting feature is the abrupt increase in molecular decay rates at the onset of negative refraction. This increase of decay rate is due mainly to the large nonradiative transfer on account of processes similar to the perfect lens effect: the radiations from the dipole are mostly “collimated” to focus into the material, thus providing a close-to-perfect nonradiative channel for the molecule to decay. This resembles somewhat the strong coupling effects between an emitting dipole at very close proximity to a metal nanoparticle (MNP) [20]; with the effects weakened appreciably at farther molecule-substrate distances [Fig. 3(b)]. Note that the physical mechanisms corresponding to such strong coupling are quite different in our case compared to the case with MNPs. In the latter case it arises mainly from the resonant excitation of the collective oscillation of the free electrons at the MNP surface, while here it is originated mainly from negative refraction. Fig. 4 shows the frequency-shift spectrum, again for two distance regimes, from which it is seen that while red-shifts take place most of the time, large blue-shifts occur at the onset of negative refraction at a wavelength close to the longitudinal plasmon resonance of the composite system, indicating the reflected field at the molecule being strongly out-of-phase with respect to the oscillation of the dipole. Both this and the abrupt decrease of lifetimes from

Fig. 4. Normalized frequency-shifts as a function of emission wavelength for the same system as in Fig. 3. We have plotted here $\Delta\omega = \omega - \omega_0$ which is the shift from the free molecule emission frequency.

Fig. 6. Normalized decay rates as a function of emission wavelength for a perpendicular molecular dipole at two regimes of distance from the metamaterial described in Fig. 5.

Fig. 5. Effective permittivity for a Ag-MgF₂ multilayer system. Note that negative refraction only occurs for a short range of wavelengths from about 270 nm to 320 nm for which $\text{Re } \epsilon_z < 0$.

fluorescing molecules at such a metamaterial surface can provide signatures for negative refraction to occur with these materials.

Next we show the results from a corresponding study with the stratified system of metamaterials [Fig. 1(b)] for which we have fixed the Ag-MgF₂ volume ratio to be $\eta = \frac{2}{3}$. Figs. 5–7 show the corresponding results for the dielectric functions, the decay rates, and the frequency-shifts for admolecules near such a metamaterial. Note that in this case the conditions for negative refraction are the same as those for the previous composite case, i.e. $\text{Re } \epsilon_z < 0$ and $\text{Re } \epsilon_x > 0$ [21]; and one observes from Fig. 5 that there exists only a small frequency range (λ in the neighborhood of ~ 270 – 320 nm) for this to take place. Hence we have negative refraction take place in the short wavelength regime in the spectra shown for this system; whereas for the composite case [Fig. 1(a)] this occurs at long wavelengths. Moreover, one still observes the abrupt increases in decay rates and frequency-shifts when this occurs as in the metal-wire composite system, though the magnitude of the increase in this case is much less. The distinct effects from negative refraction in the two cases can be understood from the two effective dielectric functions ϵ_z , i.e. $\epsilon_{\text{eff}}(\infty) = f\epsilon_m + (1-f)\epsilon_a$ in Eq. (8) and ϵ_z in Eq. (10). We first note that the Drude function Eq. (11), i.e. ϵ_m in (8) or, say, ϵ_2 in (10) will have a negative real part for $\omega < \sqrt{\omega_p^2 - \gamma^2}$. Thus this will imply from Eq. (8) that the composite system will fulfill the negative refraction condition for long enough wavelengths as revealed from Fig. 2. However, the situation is quite different for the layered system since the effective

Fig. 7. Normalized frequency-shifts as a function of emission wavelength for the same system as in Fig. 6.

ε_z depends on the *quotient* of the Drude function as seen from Eq. (10). This results only for a very small range of wavelengths that the negative refraction condition can be satisfied as revealed from Fig. 5, which showed the real part of ε_z a kind of anomalous dispersion feature. Hence the distinction in the negative refraction behavior between the two systems is deeply rooted in the two very different effective dielectric functions of the systems. Note that for the layered system only the longitudinal resonance prevails at which the molecular lifetimes are lengthened; and for longer wavelengths, the system just behaves like ordinary metal which again damps the molecule seriously at such close distances [10].

4. Discussion and conclusion

In this study we have examined the abrupt changes in the spectrum of a fluorescing molecule when placed in close proximity

to a highly anisotropic nonmagnetic metamaterial. We have found that the molecular lifetimes can become exceedingly short and emission frequencies can experience large blue-shifts when negative refraction occurs in a material made of metallic nanowire composite. Similar changes also take place with the other type of material with photonic crystal structures, though to a much lesser extent. Our modeling results should provide experimental signatures for negative refraction to be probed from these systems via optical interactions between these materials and near-field sources such as emitting molecules. Future theoretical studies will aim at developing a fluorescence model which will allow both electric and magnetic response from the metamaterial of arbitrary anisotropy to be included. We believe this will open up more channels for probing these unusual optical properties for a broader class of metamaterials.

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