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Absorption and spontaneous emission of light by molecules near metal nanoparticles in external magnetic field

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Abstract

The frequency dependence of dipole polarizabilities of diamagnetic metal nanoparticles in a constant magnetic field B of various values is investigated. It is shown that with change of a magnetic field induction optical spectrums of absorption, scattering and radiation of nanosystems are transformed. It occurs as for nanoparticles, and molecules located near a surface of these particles. Influence of a magnetic field on absorption rate of photons by a cluster "molecule-nanoparticle", and also on the rate of spontaneous radiation a molecule near a nanoparticle is established.

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Keywords: metal nanoparticle (NP); magnetic field; two-particle cluster; dipole polarizability; radiation characteristics; plasmon resonance.

1. Introduction

In recent years there were many works devoted to research of influence of metal nanoparticles (NPs) on radiation transitions in molecules [Rusinov, Kucherenko et al. (2014), Kucherenko et al. (2015), Zeinidenov et al. (2014), Sun et al. (2009), Suvorova et al. (2012), Alaa EL-din et al. (2013), Kucherenko, Nalbandyan (2014), Bryukhanov et al. (2012), Santhi et al. (2004), Klimov et al. (2001), Mukha et al. (2011), Jing Zhao et al. (2007), Klimov (2009)]. In particular, dependences of absorption rate, spontaneous and induced radiation on the sizes and the form NPs and also from average distance between them and molecules of a luminophor are defined. Dependences of radiation characteristics of the molecules placed, mainly, about globular metal NPs in the transparent mediums on configuration, spectral and dielectric parameters of such systems [Rusinov, Kucherenko et al. (2014), Kucherenko et al. (2015)] are investigated. In this regard, many different theoretical models are proposed, which addressed

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luminescence molecules placed in the vicinity of the metal NPs. So, in works [Zeinidenov et al. (2014), Sun et al. (2009), Suvorova et al. (2012), Alaa EL-din et al. (2013), Kucherenko, Nalbandyan (2014), Bryukhanov et al. (2012), Santhi et al. (2004), Klimov et al. (2001), Mukha et al. (2011), Jing Zhao et al. (2007)] found that inclusion of silver NPs in optically transparent mediums significantly influences the spontaneous and stimulated transitions in molecules of organic dyes. Nonmonotonic change of the fluorescence intensity of dye with increase in concentration of particles was observed. At an optimum ratio of concentration intensity of a molecules luminescence increased in the presence of silver particles several times. Investigate in detail changes in the spectra of the polarizability conductive NPs and two-particle cluster [Kucherenko, Nalbandyan (2014)] in constant external magnetic fields of various value of induction at different mutual orientation between the field vector and the cluster axis. It is established that intensity of light absorption of nanoparticles on different parts of the spectrum can be adjusted by means of the magnetic field. The spectra of the real and imaginary parts of the polarizabilities of nanoparticles and clusters are significantly deformed: splitting occurs of individual spectral bands and appearance of new resonances, "running up" in frequency with increasing magnetic field \mathbf{B} [Kucherenko, Nalbandyan (2014)]. At the same time it should be noted that works to the devoted influence of an external magnetic field on the above-mentioned radiation processes happening in molecules near NP are not numerous [Artemyev et al. (2012)].

1.1. Configuration of the studied system

In Fig. 1 shows the configuration of the system, where NP - spherical metallic nanoparticle of radius R ; M is the molecule with the dipole moment vector \mathbf{p} whose direction is given by angle t with respect to the vector \mathbf{B} ;

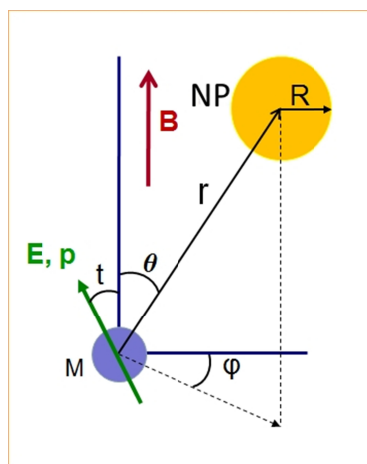


Fig.1. Geometrical configuration of the system "molecule-nanoparticle" in the optical field with a vector strength \mathbf{E} and a constant magnetic field with induction \mathbf{B} .

\mathbf{B} is the induction vector of the external magnetic field; \mathbf{E} is the intensity vector of the high-frequency electric field that interacts with the system "molecule-NP"; \mathbf{r} - radius-vector directed from the molecule to the center of the particle, its orientation is specified by the angles θ and φ . This system is placed in a transparent medium with permittivity $\varepsilon_m = 1$. In problems of absorption and induced radiation vectors \mathbf{p} and \mathbf{E} are generally oriented from each other arbitrarily, but in calculations, for simplicity reasons (for decrease number of independent parameters) these vectors are accepted by the collinear.

2. The absorption rate of photons by a molecule, located near the nanoparticle

The simple model transformation of the stimulated and spontaneous dipole transitions in organic molecules located in the area of individual metallic NP is proposed [Rusinov, Kucherenko et al. (2014), Kucherenko et al. (2015), Zeinidenov et al. (2014)]. This model can be used to explain the experimentally observed changes in the

electronic absorption spectra, as well as spontaneous and stimulated emission of dyed solutions with metal nanoparticles. Under this model, absorption rate of photons in the presence of an external magnetic field induction B is given by

$$w(\omega) = 2 \frac{|\mathbf{p}[\bar{\mathbf{I}} + \bar{\mathbf{G}}(\mathbf{r})\bar{\alpha}(\omega|\mathbf{B})]\mathbf{E}(\omega)|^2}{\hbar^2} \frac{\gamma_L}{(\omega - \omega_f)^2 + \gamma_L^2}, \quad (1)$$

where $\mathbf{E}(\omega)$ - the electric field vector of the excitation, γ_L is the width of the Lorentz contour of the molecule absorption band, ω_f is the resonance frequency of the transition between the ground i and the excited f states of the molecule, $\bar{\mathbf{G}}$ - quasi-static dyadic Green's function of a point dipole source [Kucherenko, Nalbandyan (2014)]

$$\bar{\mathbf{G}}(\mathbf{r}) = \frac{1}{r^3} \begin{pmatrix} 3 \cos^2 \varphi \sin^2 \theta - 1 & 3 \sin^2 \theta \sin \varphi \cos \varphi & 3 \cos \theta \cos \varphi \sin \theta \\ 3 \sin^2 \theta \sin \varphi \cos \varphi & 3 \sin^2 \theta \sin^2 \varphi - 1 & 3 \cos \theta \sin \varphi \sin \theta \\ 3 \cos \theta \cos \varphi \sin \theta & 3 \cos \theta \sin \varphi \sin \theta & 3 \cos^2 \theta - 1 \end{pmatrix}. \quad (2)$$

The permittivity of metal is a second rank tensor, its nonzero components in the magnetic field induction B were determined by V. L. Ginzburg in his theory of magnetized plasma [Ginzburg et al. (1975)]

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp} = 1 - \frac{\omega_p^2(\omega + i\gamma)}{\omega[(\omega + i\gamma)^2 - \Omega_L^2]}, \quad \varepsilon_{zz} = \varepsilon_{\parallel} = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}. \quad (3)$$

The gyration vector $g(\omega|B)$, which determines the off-diagonal elements of the tensor $\bar{\varepsilon}(\omega|B)$: $\varepsilon_{xy} = -\varepsilon_{yx} = ig$, has the form

$$g(\omega|B) = \frac{\omega_p^2 \Omega_L}{\omega[(\omega + i\gamma)^2 - \Omega_L^2]}. \quad (4)$$

The parameters $\omega_p = \sqrt{4\pi e^2 n_e / m}$ and $\Omega_L = eB / (mc)$ in (3)-(4) is plasma (Langmuir) and Larmor frequencies of electrons, respectively; γ is the electron collision frequency (dissipation coefficient).

Dipole dynamic polarizability of the spherical metal nanoparticle placed in a magnetic field is a magnetodependent second rank tensor, as well as a metal permittivity,

$$\bar{\alpha}(\omega|\mathbf{B}) = [\bar{\varepsilon}(\omega|\mathbf{B}) - \varepsilon_m \mathbf{I}] [\bar{\varepsilon}(\omega|\mathbf{B}) + 2\varepsilon_m \mathbf{I}]^{-1} R^3. \quad (5)$$

Through $[\bar{\varepsilon}(\omega|\mathbf{B}) + 2\varepsilon_m \mathbf{I}]^{-1}$ in (5) is denoted a tensor, the inverse of the tensor $[\bar{\varepsilon}(\omega|\mathbf{B}) + 2\varepsilon_m \mathbf{I}]$. Then for the polarizability tensor $\bar{\alpha}(\omega|\mathbf{B})$ of a spherical particle in a magnetic field of induction B on the basis of (3-5), we obtain

$$\bar{\alpha}(\omega|\mathbf{B}) = R^3 \begin{pmatrix} \frac{(\varepsilon_{\perp} - \varepsilon_{ex})(\varepsilon_{\perp} + 2\varepsilon_{ex}) - g^2}{(\varepsilon_{\perp} + 2\varepsilon_{ex})^2 - g^2} & \frac{ig3\varepsilon_{ex}}{(\varepsilon_{\perp} + 2\varepsilon_{ex})^2 - g^2} & 0 \\ \frac{-ig3\varepsilon_{ex}}{(\varepsilon_{\perp} + 2\varepsilon_{ex})^2 - g^2} & \frac{(\varepsilon_{\perp} - \varepsilon_{ex})(\varepsilon_{\perp} + 2\varepsilon_{ex}) - g^2}{(\varepsilon_{\perp} + 2\varepsilon_{ex})^2 - g^2} & 0 \\ 0 & 0 & \frac{(\varepsilon_{\parallel} - \varepsilon_{ex})}{(\varepsilon_{\parallel} + 2\varepsilon_{ex})} \end{pmatrix}. \quad (6)$$

Thus, from the conditions of minimization (and if $\gamma = 0$ - conversion to zero) of the denominators ($\varepsilon_{\parallel} + 2\varepsilon_{ex}$) and ($\varepsilon_{\perp}^2 - g^2 + 4\varepsilon_{\perp}\varepsilon_{ex} + 4\varepsilon_{ex}^2$) the matrix elements (6) are formed of *plasmon resonances*. In the case of vacuum $\varepsilon_{ex} = 1$ from the first resonance is obtained the Mie frequency Ω_{Me} . From the condition

$$\varepsilon_{\perp}^2 - g^2 + 4\varepsilon_{\perp}\varepsilon_{ex} + 4\varepsilon_{ex}^2 = 0 \tag{7}$$

get two other resonant frequencies. Indeed, substituting (3) and (4) to (7), we obtain

$$\varepsilon_{\perp}(\omega_{\pm}) = -2 \pm g \text{ or } \frac{\omega^2 - \Omega_L^2}{\omega \pm \Omega_L} = \frac{\Omega_{Me}^2}{\omega}.$$

From these equations it follows immediately $\omega_{\pm} \approx \Omega_{Me} \pm \Omega_L / 2$, that is, the fundamental frequency of the plasmon resonance splits into two components, the distance between which is equal to the Larmor frequency: $\Delta\omega_{\pm} \approx \Omega_L$. With increasing of the magnetic field the interval of the divergence component is proportional to the field. Tensor (6) with (3) and (4) can be written in the form of representing the explicit dependence on frequency ω

$$\tilde{\alpha}(\omega) = R^3 \omega_p^2 \begin{pmatrix} \frac{F(\omega)}{D^{(+)}(\omega)D^{(-)}(\omega)} & \frac{3i\Omega\omega}{D^{(+)}(\omega)D^{(-)}(\omega)} & 0 \\ -\frac{3i\Omega\omega}{D^{(+)}(\omega)D^{(-)}(\omega)} & \frac{F(\omega)}{D^{(+)}(\omega)D^{(-)}(\omega)} & 0 \\ 0 & 0 & \frac{1}{F(\omega)} \end{pmatrix}, \tag{8}$$

where $D^{(\pm)}(\omega) = 3\omega(\omega \pm \Omega_L + i\gamma) - \omega_p^2$, $F(\omega) = \omega_p^2 - 3\omega(\omega + i\gamma)$. Accordingly three plasmon resonances occurs at frequencies that are the roots of the equations $D^{(\pm)}(\omega) = 0$ and $F(\omega) = 0$, wherein one of the resonances, namely $\omega_p^2 / F(\Omega_{Me})$, a nonmagnetic sensitive. Two magnetically resonant frequencies ω_{\pm} are the roots of the quadratic equation $D^{(\pm)}(\omega_{\pm}) = 0$: $\omega_{\pm} = (\Omega_{Me}^2 + \Omega_L^2 / 4)^{1/2} \pm \Omega_L / 2$.

In Fig. 2 shows a graph of the light absorption rate by the molecule derived from expressions (1) to (5). The graph constructed for the orientation of the dipole moment vector \mathbf{p} at angle $\pi/4$ to the vectors \mathbf{B} and \mathbf{r} , and in Fig. 3 - the same relationship, but for the direction \mathbf{p} of the angle $\pi/2$ with vectors \mathbf{B} and \mathbf{r} .

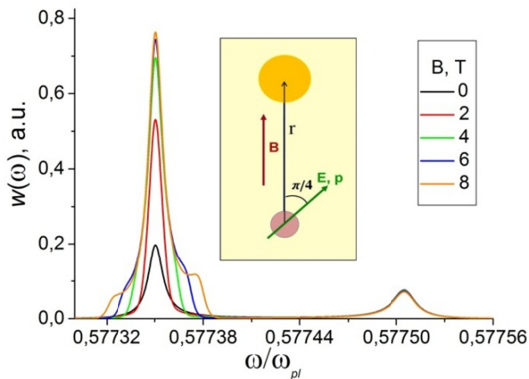


Fig. 2. Transformation of the photon absorption spectrum by the cluster in the increasing magnetic field from 0 to 10 T for the angle $t = \pi / 4$.

$$R = 7, r = 12 \text{ nm}, \omega_{pl} = 13.87 \times 10^{15} \text{ sec}^{-1}, \theta = 0$$

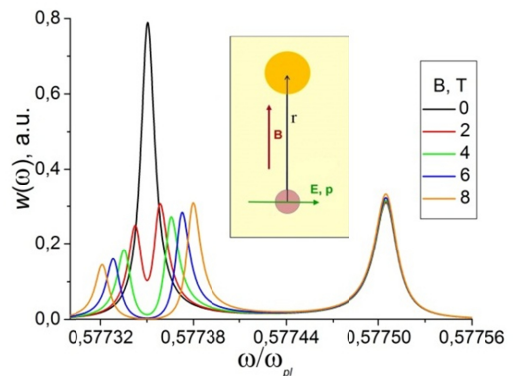


Fig. 3. Transformation of the photon absorption spectrum by the cluster in the increasing magnetic field from 0 to 10 T for the angle $t = \pi / 2$.

$$R = 7, r = 12 \text{ nm}, \omega_{pl} = 13.87 \times 10^{15} \text{ sec}^{-1}, \theta = 0$$

In the absence of a magnetic field ($B = 0$), the absorption spectrum of the system has two peaks, one of which corresponds to the conditionally NP plasmon resonance (it lies in the low-frequency region), and the second peak - is mainly determined by the light absorption of the molecule.

With the inclusion of a magnetic field the absorption spectra of the system are transformed in various ways, depending on the orientation of the vectors \mathbf{p} , \mathbf{E} and \mathbf{B} . In the case of the orientation $\pi/4$ (Fig. 2) in the low-frequency spectral band of the absorption rate begins to increase with increasing induction B field from 0 to 8 T. Thus there is a splitting of the plasmon resonance peak position onto three spectral components. For orientation $\pi/2$ (Fig. 3) with increasing magnetic field the absorption rate gradually decreases, and the spectral peak in the low frequency region is broken down into two components. In addition, it can be seen that the peak corresponding to the conditional molecule, on the contrary, there has been a slight increase, i.e. absorption rate on the "molecular" frequency increases with increasing magnetic field. Thus, depending on how directed vector dipole moment of the molecule, the photonic absorption rate by the composite system in the magnetic field can both increase and decrease.

3. Spontaneous emission of light by molecule

For spontaneous emission of the dipole type, the rate of the corresponding transitions in the free molecule is determined by the expression [Landau, Lifshitz (1989)]

$$w_{sp}(\omega) = \frac{4}{3} \frac{\omega^3}{\hbar c^3} |\mathbf{p}_{if}|^2. \quad (9)$$

In the presence of NP the field $\mathbf{E}_p(\omega)$ of the molecular dipole \mathbf{p} induces in metal NP a dipole moment $\mathbf{P} = \tilde{\alpha}(\omega|\mathbf{B})\mathbf{E}_p(\omega)$, then the expression (9) takes the form

$$w_{sp}(\omega) = \frac{4}{3} \frac{\omega^3}{\hbar c^3} \left[\left[\tilde{\mathbf{I}} + \tilde{\mathbf{G}}(\mathbf{r})\tilde{\alpha}(\omega|\mathbf{B}) \right] \mathbf{p} \right]^2. \quad (10)$$

Expanding the brackets in (10) we obtain the final expression

$$w_{sp}(\omega) = \frac{4}{3} \frac{\omega^3}{\hbar c^3} \left[p_{if}^2 + \mathbf{p} \left[\tilde{\mathbf{G}}(\mathbf{r})\tilde{\alpha}(\omega|\mathbf{B}) \right]^2 \mathbf{p} + 2 \operatorname{Re} \mathbf{p} \left(\tilde{\mathbf{G}}(\mathbf{r})\tilde{\alpha}(\omega|\mathbf{B}) \right) \mathbf{p} \right]. \quad (11)$$

The last term in the right part of (11) is the interference term, and it can be both positive and negative -

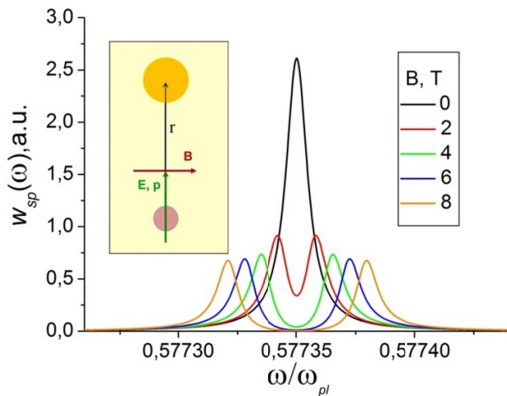


Fig. 4. Changes of the spontaneous emission rate of the cluster in the spectral range, corresponding to the plasmon resonance of the nanoparticle when exposed to an external magnetic field induction \mathbf{B}
 $R = 7$, $r = 12$ nm, $\omega_{pl} = 13.87 \times 10^{15} \text{ sec}^{-1}$, $t = \pi/2$, $\theta = \pi/2$

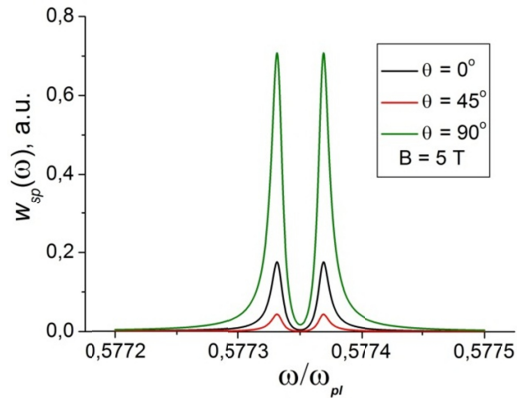


Fig. 5. Changes in the rate of spontaneous emission in the plasmon resonance spectral band at different orientations cluster axis with respect to the vector \mathbf{B}
 $R = 7$, $r = 12$ nm, $\omega_{pl} = 13.87 \times 10^{15} \text{ sec}^{-1}$, $t = \pi/4$, $B = 5$ T

depending on the mutual orientations of the vector \mathbf{p} and tensors $\vec{\mathbf{G}}(\mathbf{r})$, $\vec{\alpha}(\omega|\mathbf{B})$. Therefore, for different geometric configurations of the system may experience different responses to the external magnetic field.

In Fig. 4 shows the change in the spectrum of the spontaneous rate of deactivation of the "molecule-NP" in a magnetic field of varying induction B value. If $B = 0$, the rate value $w_{sp}(\omega)$ has the largest amplitude.

At inclusion of a magnetic field the spectral peak is split into two components which "diverge" on frequency with increase of induction B. Amplitude values of $w_{sp}(\omega)$ change when moving NP concerning a molecule on angles $\theta = 0, \pi/4, \pi/2$. In Fig. 4 shows a graph when the direction vector of the dipole moment of the molecule corresponds to the angle $t = \pi/4$. The following dependence is established clearly: if the angle between vectors of \mathbf{p} and \mathbf{B} is large, then the rate of the spontaneous radiating deactivation of the molecule located near NP will be larger.

As a result of the calculation it is found that absorption rate of photons by a "molecule-NP" system can be increased almost 4 times. This can be done by impacting the system by the external magnetic field with induction of about 10 T, when the vectors \mathbf{B} and \mathbf{r} are collinear, and the angle between them and the vector \mathbf{p} is 45 degrees.

In a case when the vector \mathbf{B} is orthogonal to vectors \mathbf{r} and \mathbf{p} , the spontaneous rate deactivation of a molecule decreases with increase of the magnetic field induction. The radiative deactivation rate of the cluster in a constant magnetic field increases with a location change of NP relative to the molecules to the angles $\theta = 0, \pi/4, \pi/2$. It should be noted that we do not considered the channel of nonradiative deactivation of the system, by the energy transfer from the excited molecule to the NP, and Lenz-Joule heat dissipation after that. This process, in turn, will depend on the external magnetic field, since its effectiveness is determined by the imaginary part of the polarizability of the metal particle.

So, the probability in unit time (rate) $w_{ri}(\omega)$ of nonradiative energy transfer from the molecule to the anisotropic nanoparticle with polarizability $\vec{\alpha}(\omega|\mathbf{B})$ can be presented through characteristics of field and cluster in the following form

$$w_{ri}(\omega) = \frac{1}{2\hbar} V \operatorname{Im} \left[\mathbf{E}^*(\omega) \vec{\alpha}(\omega|\mathbf{B}) \mathbf{E}(\omega) \right] = \frac{1}{2\hbar} V \operatorname{Im} \left[\mathbf{p} \vec{\mathbf{G}}(\mathbf{r}) \vec{\alpha}(\omega|\mathbf{B}) \vec{\mathbf{G}}(\mathbf{r}) \mathbf{p} \right],$$

where V is the volume of the nanoparticle.

As shown in [Kucherenko et al. (2015)], at the experimental measurement of a luminescent intensity of the molecules adjacent to the metal nanoparticles, it is necessary to take into account the contribution of the metal component of the system in its quantum yield of luminescence. The results of studies of molecular systems with metal NP in a magnetic field, where will be defined precisely these characteristics of luminescence, is scheduled to be published in the near future.

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