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Optical absorption of the composite with the nanoparticles, which are covered with the surfactant layer

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The optical properties of the nanocomposite with two-layer spherical inclusions "metallic core – surfactant layer" have been studied in the work. The question connected with an influence of the processes at the interface "metal – adsorbate" on the excitation of the surface plasmonic resonances in the nanoparticle has been studied. The fact of splitting of the surface plasmonic resonance due to the influence of the absorption bond near the surface of the metallic nanoparticles and due to the emergence of the additional energy states has been established. The relations for the effective parameters which describe the losses of coherence under the scattering at the chemical interface have been obtained. The calculations for the frequency dependencies of the diagonal components of the dielectric permittivity tensor of two-layer nanoparticle and for the absorption coefficient of the nanocomposite have been performed. It has been shown that the frequency dependencies for the real and imaginary parts of the longitudinal component of the dielectric tensor are close to the similar dependencies for the real and imaginary parts of the dielectric function for the spherical metallic nanoparticle. At the same time the real and imaginary parts of the transverse component weakly depend on the frequency in the visible spectrum and oscillate in the infrared range. It has been established that the absorption coefficient of the composite can have one or two maximums depending on the sizes and on the material of the particles-inclusions.

Keywords: dielectric tensor, absorption coefficient, adsorbate, surface plasmonic resonance, nanocomposite, size dependence, effective relaxation rate.

Introduction

Metallic nanoparticles play the significant role in electronic, optoelectronic, thermal and biomedical applications and, precisely for this reason, they attract an attention of the researchers for a long time (see, e.g., [1,2] and references therein). The new trend in optics of metallic nanostructures – nanoplasmonics has appeared due to this fact. One of the important problems of this trend is the study of an optical absorption in the external electromagnetic field [3, 4] and the setting of an optical response which is very useful for the practical applications [5]. An optical absorption of the metallic nanoparticles is induced by the surface plasmonic resonances (SPR), which are the collective oscillations of conduction electrons, excited by the electromagnetic wave [6].

Localized SPR in the metallic nanoparticles of the simplest geometry (spheres, ellipsoids, cylinders) are fundamental for the understanding of the properties of surface plasmons and they have been researched for several decades (see, e.g., [7] and references therein). However, the available in the literature data, connected with the size dependencies for the frequencies of SPR and for the widths of resonance lines, are rather controversial and the dominant physical mechanism, which determines these size dependencies, is the subject of serious debate (see, e.g., [8] and references therein).

The width of the resonance line is directly proportional to the relaxation rate (plasmon decay rate) and the additive contribution into the relaxation rate is given by the different mechanisms, in particular: volumetric damping, scattering on the surface of the

nanoparticle and the radiation damping [9]. The volumetric damping is determined by the processes of electron-electron scattering, electron-photon scattering and also by the scattering of electrons on the impurity atoms and on the defects of the crystal structure [10]. The contribution of the scattering of electrons on the surface of the nanoparticles increases with the decrease in their size [11], while the radiation damping plays an important role for the relatively big particles [12].

It was considered in the majority of experimental [13–15] and theoretical works [11, 12, 16–19] that the width of SPR line varies smoothly with the variation of the dielectric permittivity of the environment. It was established in the work [20] in the frameworks of the finite equations method that the width of SPR line oscillates as the dielectric permittivity function of the environment. The expressions for the surface plasmons lifetime was obtained in the works [11, 12] using the same method and taking into account the surface and radiation relaxation channels. The work [21] contains the numerical studies, based on the independent of time approximation of the local density, which indicate the existence of the size oscillations of the width of SPR line.

The presence of the surfactant (molecules, adsorbed on the surface of the nanoparticles), which is used for the stabilization of the metallic nanoparticles [22], is one more important factor of the shift and the widening of SPR peaks. It is connected with the fact that the additional energy states appear as the result of the adsorption bonding near the surface of metallic nanoparticles. These states contribute into the decay of the surface plasmons, excited in the particle. That is why the presence of the chemically modified surface results in the decrease in amplitude and increase in thickness of SPR peaks in metallic nanoparticles, which was confirmed with the help of two-photon emission spectroscopy [23]. The extension value for SPR line is considered to be one of the main parameters in such applications as sensorics [24], surface-enhanced Romanov scattering [25], field concentration on the ends of nanowires [26], plasmonic nanolithography [27], nanooptics [28] ets.

The study of the optic characteristics of the composites with two-layer nanoparticles-inclusions of the different morphology is of great practical interest from the viewpoint of the production of the materials with the predetermined properties. In previous works [29–31] the absorption by the composites with two-layer spherical nanoparticles, namely: metal-oxide nanoparticles [29], bimetallic nanoparticles [30], shell nanoparticles [31] was studied. In particular, it was established in [29] that the numerical results in the frameworks of the model of the particle with oxide shell are in good agreement with the experimental results as for the absorption spectrum. Moreover, it is known that the optical properties of both metallic nanoparticles and adsorbates, with the help of which these particles are functionalized, are very different from the properties of the composite particle. It should be pointed out that the question connected with the influence of the layer of the surfactant on the absorption properties of nanocomposite with the inclusions of type "metal-adsorbate" is unexplored. That is why the study of the influence of chemical interaction on the interface "metallic core – adsorbate layer" on the adsorption

spectrum of nanocomposite with such layered particles is actual.

I. Basic relations

Let us consider the composite that consists of the dielectric medium with permittivity ϵ_m and the spherical nanoparticles coated in the layer of adsorbed molecules immersed in this medium (fig. 1).
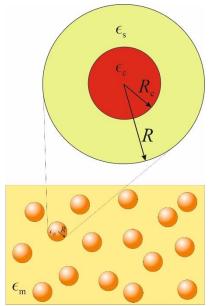

Fig. 1. Geometry of the problem.

The scattering of electrons is anisotropic due to the presence of the adsorbate layer on the nanoparticle, and the absorption coefficient of such composite is equal to [32]

$$\eta(\omega) = \frac{1}{3}\Big(2\eta_\perp(\omega) + \eta_\parallel(\omega)\Big), \qquad (1)$$

Where

$$\eta_{\perp(\parallel)}(\omega) = \frac{9\omega}{c}\beta\epsilon_m^{3/2}\frac{\mathrm{Im}\epsilon_@^{\perp(\parallel)}(\omega)}{\left[\mathrm{Re}\epsilon_@^{\perp(\parallel)}(\omega)+2\epsilon_m\right]^2+\left[\mathrm{Im}\epsilon_@^{\perp(\parallel)}(\omega)\right]^2}. \quad (2)$$

Here ω is the frequency of the incident electromagnetic wave, and c – its velocity; β – the volumetric content of metallic fraction in the dielectric matrix; $\epsilon_@^{\perp(\parallel)}$ – the diagonal components of the dielectric tensor of the composite nanoparticle "metallic core – adsorbed layer of molecules", which are determined by the relation [33]

$$\epsilon_@^{\perp(\parallel)} = \epsilon_s\frac{\epsilon_c^{\perp(\parallel)}+2\epsilon_s+2\beta_c\big(\epsilon_c^{\perp(\parallel)}-\epsilon_s\big)}{\epsilon_c^{\perp(\parallel)}+2\epsilon_s-\beta_c\big(\epsilon_c^{\perp(\parallel)}-\epsilon_s\big)}. \qquad (3)$$

In formula (3) $\beta_c = (R_c/R)^3$ is the volumetric content of metal in the composite nanoparticle (R_c is the radius of metallic core, R is the total radius of the composite particle), ϵ_s is the dielectric permittivity of adsorbate, and the components of the tensor of the dielectric permittivity

of metal core in the frameworks of Drude model have the form

$$\epsilon_c^{\perp(\parallel)} = \epsilon^\infty - \frac{\omega_p^2}{\omega\left(\omega + i\gamma_{eff}^{\perp(\parallel)}\right)}, \qquad (4)$$

where ϵ^∞ is the contribution of the crystal lattice into the dielectric permittivity; ω_p is the frequency of bulk plasmons, and the expression for the effective relaxation rate has the form

$$\gamma_{eff}^{\perp(\parallel)} = \gamma_{bulk} + \gamma_s + \gamma_{rad} + \gamma_{chem}^{\perp(\parallel)}. \qquad (5)$$

In relation (5) γ_{bulk} is the bulk relaxation rate, which is considered to be constant for each metal; γ_s and γ_{rad} are the surface relaxation rate and radiation decay rate. Let us point out that the value γ_{rad} can be neglected for the relatively small particles.

The surface relaxation rate can be written in the form

$$\gamma_s = \mathscr{A}_{size}\frac{v_F}{R_c}, \qquad (6)$$

where v_F is Fermi electron velocity; R_c is the radius of the nanoparticle,

$$\mathscr{A}_{size} = \frac{1}{4}\left(\frac{\omega_p}{\omega}\right)^2\left[1 - \frac{2v_s}{\omega}\sin\frac{\omega}{v_s} + \frac{2v_s^2}{\omega^2}\left(1 - \cos\frac{\omega}{v_s}\right)\right] \quad (7)$$

is an effective parameter which describes the degree of coherence loss under the scattering of electrons on the surface of the nanoparticle [11], $v_s = v_F/2R_c$ is the frequency of the individual oscillations of electrons.

The last addend in formula (5) describes the process of relaxation, caused by the presence of the interface "metal – adsorbed layer" [34,35]

$$\gamma_{chem}^{\perp(\parallel)} = \mathscr{A}_{\perp(\parallel)}^{interface}\frac{v_F}{R_c}. \qquad (8)$$

In order to calculate parameters $\mathscr{A}_{\perp(\parallel)}^{interface}$ let us use the approach, proposed in [34]. In the frameworks of this approach the local density of the states around adsorbed atom (molecule) can be described with the help of Lorentz formula

$$\varrho_a(\varepsilon) = \frac{1}{\pi}\frac{\Gamma_a/2}{(\varepsilon-\varepsilon_a)^2+(\Gamma_a/2)^2}, \qquad (9)$$

where ε_a and Γ_a are an amplitude and the width of the spectral line, correspondingly.

Thus, the frequency dependencies for the coefficients $\mathscr{A}_{\perp(\parallel)}^{interface}$ are determined by formulas

$$\mathscr{A}_{\perp}^{interface} = 4n_a\frac{\omega_{sp}}{v_F}\frac{\epsilon_s}{\epsilon^\infty+2\epsilon_s}\mathscr{F}_\perp(\omega); \qquad (10)$$

$$\mathscr{A}_{\parallel}^{interface} = \frac{3}{8}n_a\sigma_0\left(\frac{1+2\epsilon_s}{\epsilon^\infty+2\epsilon_s}\right)\mathscr{F}(\omega). \qquad (11)$$

In formulae (10) and (11): $\sigma_0 = 64\omega_F Q/3\pi n_e v_F$ (n_e is the concentration of electrons, Q is the number, which depends on the symmetry of the adsorbed resonance state, $Q = 0,2$ for s - and p_z -states, $Q \approx 0,33$ – for p_x - and p_y -states); $\omega_F = \varepsilon_F/\hbar$ (ε_F is Fermi energy); n_a is the surface density of adsorbed atoms; ω_{sp} is the frequency of SPR, and

$$\mathscr{F}(\hbar\omega) = \frac{\pi}{4\varepsilon_F\hbar\omega}\int_{\varepsilon_F-\hbar\omega}^{\varepsilon_F}d\varepsilon[\varepsilon\Gamma_a\varrho_a(\varepsilon+\hbar\omega)(\varepsilon+\hbar\omega)\Gamma_a\varrho_a(\varepsilon)]; \qquad (12)$$

$$\mathscr{F}_\perp(\hbar\omega) = \frac{1}{2\pi^2\epsilon_0}(ed)^2\int_{\varepsilon_F-\hbar\omega}^{\varepsilon_F}d\varepsilon\varrho_a(\varepsilon)\varrho_a(\varepsilon+\hbar\omega) \qquad (13)$$

Where d is the distance between the center of adsorbed molecule and the image plane.
Calculating the integrals in (12) and (13) and taking into account the expression (9), we obtain

$$\mathscr{A}_{\parallel}^{interface} = \frac{3\Gamma_a}{16\varepsilon_F}n_a\sigma_0\left(\frac{1+2\epsilon_s}{\epsilon^\infty+2\epsilon_s}\right)^2\left\{\text{arctg}\frac{2(\varepsilon_F-\varepsilon_a)}{\Gamma_a} + \frac{\Gamma_a}{8\hbar\omega}ln\frac{(\varepsilon_F+\hbar\omega-\varepsilon_a)^2+\left(\frac{\Gamma_a}{2}\right)^2}{(\varepsilon_F-\hbar\omega-\varepsilon_a)^2+\left(\frac{\Gamma_a}{2}\right)^2} - \frac{1}{2\hbar\omega}\left[(\hbar\omega + \right.\right.$$
$$+\varepsilon_a)\text{arctg}\frac{2(\varepsilon_F-\hbar\omega-\varepsilon_a)}{\Gamma_a} + (\hbar\omega -$$
$$\left.\left.\varepsilon_a)\text{arctg}\frac{2(\varepsilon_F+\hbar\omega-\varepsilon_a)}{\Gamma_a}\right]\right\} \qquad (14)$$

$$\mathscr{A}_{\perp}^{interface} = \frac{(ed)^2}{2\pi^2\epsilon_0}n_a\frac{\omega_{sp}}{v_F}\frac{\epsilon_s}{\epsilon^\infty+2\epsilon_s}\frac{\Gamma_a^2}{\hbar^2\omega^2+\Gamma_a^2}\times\left\{\frac{2}{\Gamma_a}\left(\text{arctg}\frac{2(\varepsilon_F+\hbar\omega-\varepsilon_a)}{\Gamma_a} - \text{arctg}\frac{2(\varepsilon_F-\hbar\omega-\varepsilon_a)}{\Gamma_a}\right) + \right.$$
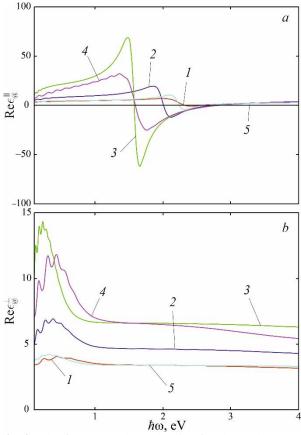$$\left.\frac{1}{\hbar\omega}ln\frac{[(\varepsilon_F+\hbar\omega-\varepsilon_a)^2+(\Gamma_a/2)^2][(\varepsilon_F-\hbar\omega-\varepsilon_a)^2+(\Gamma_a/2)^2]}{[(\varepsilon_F-\varepsilon_a)^2+(\Gamma_a/2)^2]^2}\right\} \quad (15)$$

The relations (1) – (3) taking into account formulae (4) – (8) and (14), (15) are going to be used further in order to obtain the numerical results.

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II. Results of the calculations and their discussion

The calculations have been performed for the composites with the particles of the different content and size, covered with the layer of oleylamine of the different thickness, situated in different matrices. The parameters of metals and dielectric permittivities of the matrices are given in Tables 1 and 2, and the parameters of oleylamine – in Table 3, correspondingly.

Figure 2 shows the frequency dependencies for the real parts of the diagonal components of the dielectric tensor for the spherical particle Au, covered with the layer of oleylamine. It should be pointed out that the nature of dependencies $Re\epsilon_@^\parallel(\hbar\omega)$ and $Re\epsilon_@^\perp(\hbar\omega)$ is significantly different. The frequency dependencies for the real part of the longitudinal component of dielectric tensor (Fig. 2, a) are qualitatively similar to the similar dependencies for the metallic spherical nanoparticles, covered with the layer of an ordinary dielectric [36]. This similarity means the presence of two extrema (maximum and minimum) and the small-scale oscillations in the infrared part of the spectrum due to the manifestation of the kinetic effects, and also means the same character of the shifts of maximums under the increase in radius of the particle (sequence of the curves $1 \to 2 \to 3$) and in the thickness of the external layer (sequence of the curves $4 \to 2 \to 5$). As for the dependence $Re\epsilon_@^\perp(\hbar\omega)$, let us point out that this value decreases insignificantly with the increase in frequency in the visible part of the spectrum. At the same time, these dependencies have several minimums and maximums in the infrared part of the spectrum (Fig. 2, b). Such behavior can be explained by the significant influence of the local density of the states, generated by adsorbed molecules of oleylamine on $Re\epsilon_@^\perp$, whereas the similar influence on $Re\epsilon_@^\parallel$ is almost absent.

Fig. 2. The frequency dependencies for the real parts of the longitudinal (*a*) and transverse (*b*) components of the dielectric tensor for the particles of different sizes with the core Au: $1 - R_c = 10$ nm; $t = 5$ nm;
$2 - R_c = 20$ nm; $t = 5$ nm; $3 - R_c = 50$ nm; $t = 5$ nm;
$4 - R_c = 20$ nm; $t = 2$ nm;
$5 - R_c = 20$ nm; $t = 10$ nm.

Figure 3 shows the curves of the frequency dependencies for the imaginary parts of the diagonal components of the dielectric tensor for particle

Table 1.

The parameters of metals (see, e.g., [36, 37] and the references there)

Metals Parameters	Au	Ag	Cu	Pd	Pt	Al
$n_e, 10^{22}\ cm^{-3}$	5.91	5.85	17.2	2.53	9.1	18.2
ϵ^∞	9.84	3.70	12.03	2.52	4.42	0.7
$\hbar\omega_p, eV$	9.07	9.17	12.6	9.7	15.2	15.4
$\hbar\gamma_{bulk}, eV$	0.023	0.016	0.024	0.091	0.069	0.082
ε_F, eV	5.59	5.72	7.56	8.49	13.6	11.03
$v_F, 10^6\ m/s$	1.41	1.49	1.34	2.84	2.98	1.91

Table 2.

Dielectric permittivities of the matrices [35]

Substance	Air	CaF_2	Teflon	Al_2O_3	TiO_2	C_{60}
T_m	1	1.54	2.3	3.13	4.0	6.0

Table 3.

Parameters of oleylamine [38]

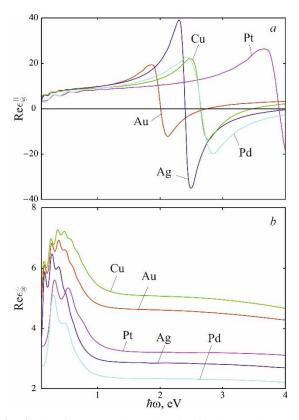| d, nm	n_a, cm^{-2}	ε_a, eV	Γ_a, eV	ϵ_s
10	$1.27 \cdot 10^{12}$	1	1	2.13

Au@OAm. Let us point out that, as in the case of the dependencies $Re\epsilon_@^\parallel(\hbar\omega)$, the dependencies $Im\epsilon_@^\parallel(\hbar\omega)$ (Fig. 3, a) are qualitatively similar to the similar dependencies for metal-dielectric nanoparticles. The increase in sizes of the metallic core (the increase in content of metal in the nanoparticle) results in the increase in the value of $max(Im\epsilon_@^\parallel)$ and in their shift into the range of smaller frequencies ("red" shift) – sequence of the curves $1 \to 2 \to 3$. The increase in the thickness of the adsorbed layer results in the "blue" shift along with the decrease in the value of maximum (sequence of the curves $4 \to 2 \to 5$). As for the dependence $Im\epsilon_@^\perp(\hbar\omega)$, it should be pointed out the weak dependence on the frequency in the visible part of the spectrum and the complicated dependence (the presence of the oscillations) in the infrared region (Fig. 3, b). Such behavior of the imaginary part of the transverse component of the dielectric tensor also can be explained by the influence of the local density of the states, induced by the adsorbed molecules.

Fig 3. The frequency dependencies for the imaginary parts of the longitudinal (a) and transverse (b) components of the dielectric tensor for the particles of different sizes with the core Au under the same values of the parameters as in Figure 2.
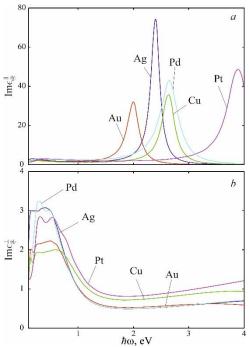
The Figures 4 and 5 show the curves of the frequency dependencies for the real and imaginary parts of the diagonal components of the dielectric tensor for the particles of the fixed size with the cores of different metals. It should be pointed out that the curves $Re\epsilon_@^\parallel(\hbar\omega)$ and $Im\,\epsilon_@^\parallel(\hbar\omega)$ (Fig 4, a i 5, a) for the particles with the cores of different metals are qualitatively similar (the presence of two maximums and minimums for $Re\epsilon_@^\parallel$ and maximums for $Im\,\epsilon_@^\parallel$). However, these curves are

quantitatively different in both magnitude and location of extrema. Such quantitative differences result from the significant difference between the contributions of the crystal lattice into the dielectric permittivity and the frequencies of bulk plasmons for different metals. The curves $Re\epsilon_@^\perp(\hbar\omega)$ and $Im\,\epsilon_@^\perp(\hbar\omega)$ for the particles with the cores of different metals are also qualitatively similar (Fig. 4, b and 5, b). They depend insignificantly on the frequency in the visible part of the spectrum, and oscillate in the infrared part of the spectrum, and moreover, both the values $Re\epsilon_@^\perp$ and $Im\,\epsilon_@^\perp$ have the same order for all particles through all frequency region which is under the investigation.

Fig. 4. The frequency dependencies for the real parts of the longitudinal (a) and transverse (b) components of the dielectric tensor for the particles with the cores of different metals ($R_c = 20\,nm; t = 5$ nm).

Figure 6, a shows the frequency dependencies for the transverse, longitudinal and integral coefficients of the absorption for the composite with nanoparticles Au@OAm ($R_c = 20\,nm$, $t = 5\,nm$). Due to the fact that $\eta_\perp$ has the maximum in the infrared domain of the spectrum, and $\eta_\parallel$ - in the visible domain, an integral coefficient of the absorption η_Σ has two maximums, which correspond to the maximums $\eta_{\perp(\parallel)}$. Let us point out that $max\,\eta_\parallel$ is reached at the frequency of the surface plasmonic resonance $\omega_{sp}^\parallel$, which is close to the frequency ω_{sp} for the spherical metal-dielectric particle (in the case $\gamma_{chem}^\perp = \gamma_{chem}^\parallel = 0$ the splitting of the frequencies disappears and $\omega_{sp}^\parallel = \omega_{sp}^\perp = \omega_{sp}$).

Fig. 5. The frequency dependencies for the imaginary parts of the longitudinal (*a*) and transverse (*b*) components of the dielectric tensor for the particles with the cores of different metals ($R_c = 20\ nm$; $t = 5$ nm).

Now let us determine the frequency of the longitudinal surface plasmonic resonance. As is known, the condition of the excitation of SPR is

$$\eta_\parallel(\omega) \rightarrow max,$$
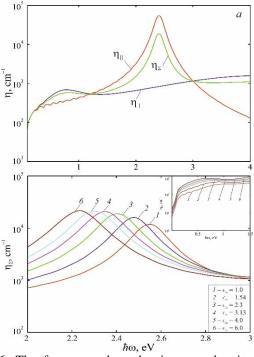
Or

$$Re\epsilon_@^\parallel + 2\epsilon_m = 0. \tag{16}$$

Using the expressions (3) and (4) and taking into account the fact that in an optical range of frequencies $\omega \gg \gamma_{eff}^\parallel$, we obtain the relation for the frequency of SPR

$$\omega_{sp}^\parallel = \frac{\omega_p}{\sqrt{\epsilon^\infty + 2\epsilon_S \frac{(1-\beta_C)\epsilon_S + (2+\beta_C)\epsilon_m}{(1+2\beta_C)\epsilon_S + 2(1-\beta_C)\epsilon_m}}}. \tag{17}$$

Table 4 gives the calculations for the frequencies of the longitudinal SPR using formula (17) for the particles in teflon and C_{60} with the different metallic cores under the different content of metal. Let us point out that the increase in the dielectric permittivity of the matrix dielectric and in the volumetric content of metallic fraction (decrease in the thickness of the adsorbate layer) results in the decrease in the frequency of SPR. At the same time the frequency of SPR increases, speaking about the sequence of metals $Au \rightarrow Ag \rightarrow Cu \rightarrow Pt$, due to the fact that $\omega_p^{Au} < \omega_p^{Ag} < \omega_p^{Cu} < \omega_p^{Pt}$.

As for $max\ \eta_\perp$ in the infrared part of the spectrum, it should be pointed out that it can be associated both with SPR at the frequency $\omega_{sp}^\perp$, and with the kinetic effects in this domain of the frequencies. The authors plan to deal with the detailed study of this issue and with the development of the corresponding theory in the next work. The results of the calculations of the influence of the dielectric properties of the matrix on the integral

absorption coefficient of the composite with the particles Au@OAm (Fig. 6, *b*) indicate the presence of the red shift and small increase in value of the maximum of the integral absorption coefficient with the increase in the dielectric permittivity of the matrix medium.
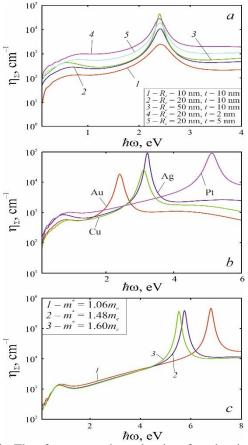

Fig. 6. The frequency dependencies: *a* – longitudinal, transverse and integral absorption coefficients of the composite with the particles Au@OAm in teflon ($\beta = 0.15$); *b* – integral absorption coefficient of the composite with the particles Au@OAm ($\beta = 0.15$) in the different matrices ($R_c = 20\ nm$; $t = 5$ nm).

The results of the calculations of the frequency dependence of the integral absorption coefficient for the composite with the nanoparticles Au@OAm of the different sizes indicate the fact that the location of the maximum of the integral absorption coefficient (in the visible part of the spectrum) is practically independent on the radius of the metallic core of the particle and on the thickness of the adsorbed molecules layer (Fig 7, *a*). At the same time, the increase in the content of metal in the nanoparticle results in the increase in the value of this maximum, and also the other maximum appears in the infrared part of the spectrum. Apart from this, the maximums $\eta_\Sigma(\hbar\omega)$ shift towards "blue" side, and their value increases in the sequence of materials of the cores of the particles-inclusions $Au \rightarrow Cu \rightarrow Ag \rightarrow Pt$ (Fig 7, *b*), due to the fact that the frequencies of the surface plasmonic resonance increase exactly in this order. The second maximum of the integral absorption coefficient (in the infrared part of the spectrum) is noticeable only for the particles-inclusions with the cores Au, Cu, Ag. Also let us point out that $max\ \eta_\Sigma$ for the composite with the particles Al@OAm shifts towards "blue" side with the decrease in effective electron mass (Fig 7, *c*), because in this case the frequency of bulk plasmons increases and the frequency of the surface plasmonic resonance increases correspondingly.

The frequencies of SPR for the nanoparticles with the cores of different metals with the different volumetric content of metal

| β_c | $\epsilon_m = 2.3$ | | | | $\epsilon_m = 6.0$ | | | |
| | $\omega_{sp}^{\parallel}, eV$ | | | | $\omega_{sp}^{\parallel}, eV$ | | | |
	Au	Ag	Cu	Pt	Au	Ag	Cu	Pt
0.1	2.413	3.242	3.118	5.159	2.385	3.176	3.086	5.062
0.2	2.410	3.235	3.115	5.150	2.351	3.099	3.049	4.950
0.3	2.407	3.229	3.112	5.140	2.315	3.019	3.007	4.831
0.4	2.404	3.222	3.109	5.130	2.275	2.935	2.963	4.706
0.5	2.402	3.215	3.106	5.120	2.232	2.846	2.913	4.573
0.6	2.399	3.209	3.102	5.110	2.185	2.753	2.859	4.432
0.7	2.396	3.202	3.099	5.100	2.134	2.653	2.799	4.281
0.8	2.393	3.195	3.096	5.091	2.076	2.548	2.731	4.120
0.9	2.390	3.188	3.093	5.081	2.013	2.435	2.656	3.946
1.0	2.387	3.181	3.089	5.070	1.941	2.313	2.570	3.758

Fig. 7. The frequency dependencies for the integral absorption coefficient of the composite with the particles in teflon ($\beta = 0.15$): a – Au@OAmof the different sizes; b – of the fixed size ($R_c = 20\,nm$; $t = 5$ nm) with the cores of the different metals; c – Al@OAm of the fixed size ($R_c = 20\,nm$; $t = 5$ nm) under the different values of the effective mass.

The contribution of all mechanisms, in particular, the mechanism connected with the presence of the interface "metal – adsorbed layer" into the widening of the lines of the surface plasmonic resonance has been analyzed.

It has been established that the behavior of the frequency dependencies of the real and imaginary parts of the longitudinal component of the dielectric tensor for the composite spherical nanoparticles is the same as for the frequency dependencies of the real and imaginary parts of the dielectric function of the spherical metallic nanoparticle, namely, the same quantity of the extremums of the real and imaginary parts, the presence of the small-scale oscillations in the infrared part of the spectrum, caused by the kinetic phenomena, and also the red shift of the maximums under the increase in the radius of the particle.

It has been shown that the influence of the local density of the states, formed by molecules of adsorbate, is significant for the real and imaginary parts of the transverse component of the dielectric tensor for two-layer nanoparticle.

It has been demonstrated the presence of two maximums in the frequency dependencies of the integral absorption coefficient of the composite with the spherical layered nanoparticles "metallic core – adsorbate layer", which are located in the different parts of the spectrum. These maximums correspond to the maximums of the transverse and longitudinal absorption coefficients. Moreover, the maximums of the longitudinal absorption coefficient are reached at the frequencies of the surface plasmonic resonance, which are close to the similar values for the spherical metal-dielectric nanoparticles.

The evolution of the size dependencies of the frequency of the longitudinal SPR for two-layer nanoparticles "metal – adsorbate layer" under the increase in content of metallic fraction for the different dielectric matrices and the cores of different metals has been studied in non-dissipative approximation.

Conclusions

The theory of the light wave absorption by the composite with the spherical two-layer nanoparticles of the type "metallic core - surfactant" has been constructed.

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Оптичне поглинання композиту з наночастинками, вкритими шаром поверхнево-активної речовини

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В роботі досліджено оптичні властивості нанокомпозиту з двошаровими сферичними включеннями «металеве ядро – шар поверхнево активної речовини». Розглянуто питання про вплив процесів на інтерфейсі «метал – адсорбат» на збудження поверхневих плазмонних резонансів у наночастинці. Встановлено факт розщеплення поверхневого плазмонного резонансу внаслідок впливу адсорбційних зв'язків поблизу поверхні металевих наночастинок і виникнення додаткових енергетичних станів. Отримано співвідношення для ефективних параметрів, що описують втрати когерентності при розсіюванні на хімічному інтерфейсі. Проведено розрахунки частотних залежностей діагональних компонент тензора діелектричної проникності двошарової наночастинки та коефіцієнта поглинання нанокомпозиту. Показано, що частотні залежності дійсної й уявної частин поздовжньої компоненти діелектричного тензора близькі до аналогічних залежностей дійсної й уявної частин діелектричної функції сферичної металевої наночастинки, в той час як дійсна й уявна частини поперечної компоненти слабко залежать від частоти у видимій області спектра й осцилюють в інфрачервоній області. Встановлено, що коефіцієнт поглинання нанокомпозиту може мати один або два максимуми в залежності від розмірів і матеріалу частинок-включень.

Ключові слова: діелектричний тензор, коефіцієнт поглинання, адсорбат, поверхневий плазмонний резонанс, нанокомпозит, розмірна залежність, ефективна швидкість релаксації.