PECULIARITIES OF THE ABSORPTION OF ULTRASHORT LASER PULSES BY ASYMMETRIC METALLIC NANOPARTICLES

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The theory allowing the calculations of the energy absorbed by the particles of a non-spherical shape subjected to the irradiation by laser pulses of various durations in the region of surface plasmon excitation is developed. For the particles of the oblate or prolate spheroidal shape, the dependence of the absorbed energy on a number of variables, including a particle volume, a degree of the shape deviation from a spherical one, a pulse duration, and the value of a shift of the carrier frequency of a laser ray from the frequency of the surface plasmon excitation in a spherical particle, is found.

1. Introduction

Metallic nanoparticles (MNs) are interesting objects from the viewpoints of physics of condensed state and practical applications. An increase in the local electric fields in the close vicinity of nanoparticles allows the utilization of MNs as markers in biological systems [1]. The modern optical investigations make it possible to test the optical response of a separate nanoparticle and, thus, to study the properties of separate nanoobjects [2]. This opens the new opportunities for the direct probing of the many-electron dynamics in confined systems. The remarkable results were obtained recently in works [3–5]. In recent years, the ultrafast dynamics of electrons in MNs attracts the permanent attention of experimenters. Nanostructures have been widely used in modern devices of high-speed electronics and optoelectronics. Owing to the recent achievements in the ultrafast spectroscopy technique, it has become possible to monitor the femtosecond dynamics of the electron gas confined in MNs [6]. The use of short-duration pulses makes it feasible to study the dynamics of fast processes occurring in atoms, molecules, and solids. Pico- and femtosecond resolutions allow to study of vibrational and rotational intramolecular motions, the dynamics of carriers in semiconductors (and semiconductor nanostructures), the phase transitions in solids, the processes of formation and breakdown of chemical bonds, etc. [7,8]. The capability to generate powerful femtosecond pulses has lead to the appearance of a new, rapidly developing branch – the desk-mounted high-energy physics.

When a MN is placed in the field of a monochromatic electromagnetic (EM) wave and the wavelength is far greater than the particle size, both the individual and collective kinds of absorption are observed. The collective absorption is associated with the excitation of the so-called surface resonances (plasmons). There are three such resonances in an ellipsoidal particle and one in a spherical particle. In the case of a monochromatic wave, the collective contribution becomes dominant provided that the wave frequency is close to one of the frequencies of plasma resonances. Numerous applications in decorative painting [9] and optical devices [10] are based just on the resonances of surface plasmons. However, in spite of the appreciable theoretical efforts [11], a body of problems has remained unsolved hitherto.

An interesting situation is observed in the case of ultrashort pulses. The shorter the pulse, the greater is its set of harmonics. Thus, the ultrashort pulses can excite all the plasma resonances. This is associated with the fact that, in such an ultrashort pulse, one can always find the harmonics which correspond to the resonance frequencies of surface plasmons. This feature of the absorption of ultrashort pulses by MNs we study in this work. One more feature influencing the absorption is associated with the shape of a particle. Earlier, we showed that, in the case of asymmetric MNs, the optical conductivity, which determines both the electric absorption and the half-width of plasma resonances, becomes the tensor quantity [12]. As far as we know, such a feature of the absorption of ultrashort optical pulses by asymmetric MNs is first taken into account.

In this paper we study for the first time, the peculiar features of the absorption of ultrashort pulses by the MNs, whose dimensions are far less than the electron

free path. Such investigations have attracted a lot of interest of experimenters in recent years. In particular, we will find: (i) the energy of short- and long-duration laser pulses spent on the collective excitements in MNs; (ii) its dependence on the particle shape, wave frequency, pulse duration, and particle sizes; (iii) the shift of the resonance frequency of the absorption with respect to the plasmon frequency in a spherical MN.

2. Model and Starting Positions

Consider a case where an MN is irradiated by a laser pulse, whose electric field is given as

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0\exp\left[-\Gamma^2\left(t-\frac{\mathbf{k_0 r}}{\omega_\mathbf{0}}\right)^2\right]\cos\left[\omega_0\left(t-\frac{\mathbf{k_0 r}}{\omega_\mathbf{0}}\right)\right], \tag{1}$$

where Γ is the quantity reciprocal to the pulse duration, ω_0 is the carrier frequency of an EM wave, $|\mathbf{k_0}|=\omega_0/c$, and $\mathbf{E}_0$ is the maximal value of electric field in a pulse. In addition to the electric component, the field of a laser pulse contains also the magnetic one which is associated with the former through the corresponding Maxwell equation

$$\mathrm{rot}\mathbf{E}(\mathbf{r},t)=-\frac{1}{c}\frac{\partial}{\partial t}\mathbf{H}(\mathbf{r},t). \tag{2}$$

We set $\mathbf{E}(\mathbf{r},t)$ in the form (1) and will find the magnetic component of a pulse, by using Eq. (2). Relation (2) takes the simplest form if one operates with the Fourier components of the above quantities. Actually, we obtain from (1):

$$\mathbf{E}(\mathbf{r},\omega)=\int\limits_{-\infty}^{\infty}\mathbf{E}(\mathbf{r},t)e^{i\,\omega\,t}dt=\mathbf{E_0}\frac{\sqrt{\pi}}{2\,\Gamma}e^{i\,\mathbf{k_0 r}}\ \ {}^{\frac{\omega}{\omega_0}}\ \times$$

$$\times\left[\exp\left(-\frac{(\omega-\omega_0)^2}{4\Gamma^2}\right)+\exp\left(-\frac{(\omega+\omega_0)^2}{4\Gamma^2}\right)\right]. \tag{3}$$

Using Eq. (3) in explicit form and carrying out the Fourier transformation in Eq. (2), we find

$$\mathbf{H}(\mathbf{r},\omega)=\mathbf{m}\times\mathbf{E}(\mathbf{r},\omega), \tag{4}$$

where $\mathbf{m}=\mathbf{k_0}/k_0$ is the unit vector.

The Fourier component of the electric field amplitude takes the simplest form in the limit $\Gamma\to 0$:

$$\mathbf{E}(\mathbf{r},\omega)_{\Gamma\to 0}=\pi\mathbf{E_0}e^{i\mathbf{k_0 r}\omega/\omega_0}[\delta(\omega-\omega_0)+\delta(\omega+\omega_0)]. \tag{5}$$

Whereas the electric field of a laser pulse creates the potential electric field $\mathbf{E}_{\rm in}(\mathbf{r},t)$ inside an MN, the magnetic field induces the eddy current field $\mathbf{E}_{\rm ed}(\mathbf{r},t)$. To calculate the energy absorbed by an MN, we should know the inner fields $\mathbf{E}_{\rm in}(\mathbf{r},t)$ and $\mathbf{E}_{\rm ed}(\mathbf{r},t)$. To find these quantities, we pay attention to the following feature of the coordinate dependence of the Fourier components (3) and (4): when the characteristic dimension R of a nanoparticle is such that

$$k_0R\ll 1, \tag{6}$$

i.e. the wavelength of the carrying wave is far greater than the MN dimension, the coordinate dependence of the Fourier components $\mathbf{E}(\mathbf{r},\omega)$ and $\mathbf{H}(\mathbf{r},\omega)$ can be neglected inside the particle. This means that, in order to determine the inner fields inside an MN, provided that inequality (6) is satisfied, we can set the Fourier components of these fields such as they would be in the spatially uniform fields:

$$\mathbf{E}(\mathbf{r},\omega)\to\mathbf{E}(0,\omega)\ \ \text{and}\ \ \mathbf{H}(\mathbf{r},\omega)\to\mathbf{H}(0,\omega). \tag{7}$$

In the case of an asymmetric MN which has, for example, the form of an ellipsoid, this allows us to write the components of the inner electric field as

$$(E_{\rm in}(\omega))_j\approx\frac{E_j^{(0)}(0,\omega)}{1+L_j[\varepsilon(\omega)-1]}, \tag{8}$$

and the magnetic eddy current field as

$$(E_{\rm ed}(\mathbf{r},\omega))_x\approx$$

$$\approx i\frac{\omega}{c}\left(\frac{z}{R_z^2+R_x^2}H_y^{(0)}(0,\omega)-\frac{y}{R_x^2+R_y^2}H_x^{(0)}(0,\omega)\right)R_x^2 \tag{9}$$

by analogy with the procedure described in [13]. The other components of the eddy current field can be obtained from Eq. (9) by means of a cyclic permutation of indices. The notations in formulas (8) and (9) are as follows: L_j $(j=x,y,z)$ – the geometrical factors, also known as the depolarization factors [14], $\varepsilon(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$ – the frequency-dependent complex permittivity of the particle, R_x, R_y, R_z – the ellipsoid semiaxes in the x, y, and z directions, respectively.

It is seen from expressions (8) and (9) that the uniform external electric field induces also the uniform electric potential field inside the ellipsoidal MN, whereas the uniform external magnetic field generates the

coordinate-dependent eddy current field. The inner fields $\mathbf{E}_{\rm in}(\mathbf{r},t)$ and $\mathbf{E}_{\rm ed}(\mathbf{r},t)$ induce the currents inside the MN with the corresponding densities $\mathbf{j}_{\rm in}(\mathbf{r},t)$ and $\mathbf{j}_{\rm ed}(\mathbf{r},t)$. As a result, the particle absorbs the energy of the EM field of an incident laser wave. The total absorbed energy can be presented as (see [14])

$$w=\int\limits_{-\infty}^{\infty} dt\; W(t)=w_e+w_m=\frac{1}{2}{\rm Re}\int\limits_{-\infty}^{\infty} dt\int\limits_{V} d\mathbf{r}\times$$

$$\times[\mathbf{j}_e(\mathbf{r},t)\;\mathbf{E}^*_{\rm in}(\mathbf{r},t)+\mathbf{j}_{\rm ed}(\mathbf{r},t)\;\mathbf{E}^*_{\rm ed}(\mathbf{r},t)], \qquad (10)$$

where the integration should be carried out over the whole particle volume. Here, $W(t)$ is the absorbed power. Depending on whether the absorption is brought about by $\mathbf{E}_{\rm in}(\mathbf{r},t)$ or $\mathbf{E}_{\rm ed}(\mathbf{r},t)$, it is called electric or magnetic absorption, respectively. In view of the equality

$$\int\limits_{-\infty}^{\infty}\mathbf{j}_e(\mathbf{r},t)\;\mathbf{E}^*_{\rm in}(\mathbf{r},t)\;dt=\int\limits_{-\infty}^{\infty}\mathbf{j}_e(\mathbf{r},\omega)\;\mathbf{E}^*_{\rm in}(\mathbf{r},\omega)\;\frac{d\omega}{2\pi}$$

which follows, in particular, from the Parseval relation for the Fourier integral [15], expression (10) can be rewritten as

$$w=\frac{1}{4\pi}\int\limits_{-\infty}^{\infty} d\omega\;{\rm Re}\int\limits_{V} d\mathbf{r}\times$$

$$\times[\mathbf{j}_e(\mathbf{r},\omega)\;\mathbf{E}^*_{\rm in}(\mathbf{r},\omega)+\mathbf{j}_{\rm ed}(\mathbf{r},\omega)\;\mathbf{E}^*_{\rm ed}(\mathbf{r},\omega)]. \qquad (11)$$

The values of $\mathbf{E}_{\rm in}(\omega)$ and $\mathbf{E}_{\rm ed}(\mathbf{r},\omega)$ can be calculated from formulas (8) and (9), respectively. Thus, the problem remaining to be done is to find the Fourier components of the current densities $\mathbf{j}_{\rm in}(\mathbf{r},\omega)$ and $\mathbf{j}_{\rm ed}(\mathbf{r},\omega)$. In the general case, the current produced by the inner fields $\mathbf{E}_{\rm in}(\omega)$ and $\mathbf{E}_{\rm ed}(\mathbf{r},\omega)$ at a point $\mathbf{r}$ of the particle can be expressed as the integral over all values of electron velocities:

$$\mathbf{j}(\mathbf{r},\omega)=2e\left(\frac{m}{2\pi\hbar}\right)^3\int\limits_{-\infty}^{\infty} d^3v\;\mathbf{v}\;f_1(\mathbf{r},\mathbf{v},\omega). \qquad (12)$$

Here, $f_1(\mathbf{r},\mathbf{v},\omega)$ is the Fourier component of the nonequilibrium distribution function usually considered as an addition to the equilibrium Fermi distribution function $f_0(\varepsilon)$ which depends only on the electron kinetic energy ε. Usually, the way to calculate the function $f_1(\mathbf{r},\mathbf{v},\omega)$ consists in the solution of the corresponding linearized Boltzmann kinetic equation. As a rule, this equation is written for the time-dependent distribution function (see, for example, [13]). Performing the Fourier transformation of this equation with the use of expression (3) and

$$f_1(\mathbf{r},\mathbf{v},\omega)=\int\limits_{-\infty}^{\infty} f_1(\mathbf{r},\mathbf{v},t)\;e^{i\,\omega\,t}\,dt,$$

we obtain the equation for f_1:

$$(\nu-i\omega)\;f_1(\mathbf{r},\mathbf{v},\omega)+\mathbf{v}\frac{\partial}{\partial\mathbf{r}}f_1(\mathbf{r},\mathbf{v},\omega)+$$

$$+e\;\mathbf{v}\;[\mathbf{E}_{\rm in}(\omega)+\mathbf{E}_{\rm ed}(\mathbf{r},\omega)]\;\frac{\partial}{\partial\varepsilon}f_0(\varepsilon)=0, \qquad (13)$$

where ν is the collision frequency in the particles bulk. To move further, we should add the corresponding boundary conditions to Eq. (13). We take assumption of the diffuse reflection of electrons from the inner surface of a particle

$$f_1(\mathbf{r},\mathbf{v},\omega)|_S=0, \qquad \upsilon_n<0 \qquad (14)$$

as the boundary conditions. Here, υ_n is the velocity component normal to the surface S. The substantiation of such boundary conditions and the solution of (13) are presented, in particular, in [12].

3. Plasmon Resonances

To this point, we have considered the general approach which includes both electric and magnetic absorptions. It was stressed above that the absorption can be either individual or collective. When an MN is in the field of a monochromatic EM wave and the wave frequency is far from the plasmon resonance, the individual mechanism of absorption prevails. In this case, as was shown in [12], the electric or magnetic absorption can be dominant depending on a number of factors, namely on the wave frequency, its polarization, the MN size and shape. The present work concentrates, however, on the features of the absorption of ultrashort laser pulses. In this case, the main contribution to the absorption results from the plasma resonances, i.e. from the collective mechanism which is a constituent part of electric absorption. For this reason, in Eq. (10), we will further take into consideration only to the absorption caused by the electric component of the EM field. To find the total energy of electric absorption,

we will start from expressions (11) and (12), and determine the form of the function $f_1(\mathbf{r}, \mathbf{v}, t)$, by solving Eq. (13) with the corresponding boundary conditions. Then, we will substitute the obtained function into Eq. (12) and calculate the Fourier components of the current density. Finally, by taking into account that the Fourier components of the inner field are described by expression (8), we will substitute the obtained Fourier components of the current density into Eq. (11). The similar procedure was described in detail in [12] and, thus, we won't repeat it. We only note that the kinetic equation (13) almost completely coincides with Eq. (27) of work [12] with the only difference: $\mathbf{E}_{\rm in}(\omega)$ should be substituted by $\mathbf{E}_{\rm loc}(\omega)$. What is more, the integrand of the integral over frequencies in Eq. (11) formally coincides with the initial expression in our work [12]. Thus, we can use the results in [12], in particular formula (75), and write the total energy of electric absorption in the form

$$w_e = \frac{V}{4\pi}\sum_{j=1}^{3}\int\limits_{-\infty}^{\infty}\omega^4\frac{\sigma_{jj}(\omega)\,|E_j^{(0)}(0,\omega)|^2}{\left(\omega^2-\omega_j^2\right)^2+[2\gamma_j(\omega)]^2\omega^2}d\omega, \qquad (15)$$

where the frequency dependence of $E_j^{(0)}(0,\omega)$ is given by expression (3). Here,

$$\gamma_j(\omega) = 2\pi\, L_j\sigma_{jj}(\omega) \qquad (16)$$

is the half-width of a plasmon resonance which strongly depends on the geometrical shape of a particle and is defined in terms of diagonal components of the optical conductivity tensor. For the different directions j, it is governed by the aforementioned factor L_j. For a spheroidal particle ($R_x = R_y \equiv R_\perp$), these components, for example, are reciprocal to the square of the frequency at high frequencies and have the form

$$\sigma_{(\perp)}(\omega) = \frac{9}{32\,\pi}\frac{\upsilon_{\rm F}}{R_\perp}\left(\frac{\omega_p}{\omega}\right)^2\binom{\eta(e_s)}{\rho(e_s)}, \qquad (17)$$

where $\upsilon_{\rm F}$ is the electron velocity on the Fermi sphere, ω_p is the frequency of plasma oscillations of electrons in a metal, and $\eta(e_s)$ and $\rho(e_s)$ are some functions depending on the spheroid eccentricity e_s (see their analytical form in [12]). Figure 1 shows the dependence of these functions on the ratio between the spheroid semiaxes, $R_\perp/R_\parallel$. Such a character of the functions η and ρ ensures the analogous behavior of components of the conductivity tensor as functions of $R_\perp/R_\parallel$. For a spherical particle, $\eta = \rho = 2/3$.

The half-widths of plasmon resonances are an important characteristic, since it contains the information about the character of interactions in the system. Through the interaction between surface plasmons and single-particle excitations, the electron scattering gives rise to the decay of surface plasmons, which reveals itself in the broadening of lines of the differential transmission spectra. The surface plasmon decay can occur in different ways, depending on the particle size. Often, the contribution of the Landau decay [16] to the linewidth, which is dominant in the case of a small particle radius a of the order of 5–20 Å [17], is calculated. At greater particle sizes, the Landau decay competes with the decays caused by other interactions. Recently, we studied [18] how the relation between the transverse $\gamma_\perp$ and longitudinal $\gamma_\parallel$ components of the plasmon resonance half-width depends on the degree of ellipsoid's oblateness or prolateness for the frequencies that are higher or lower than the characteristic frequency of electron reflection from the particle walls.

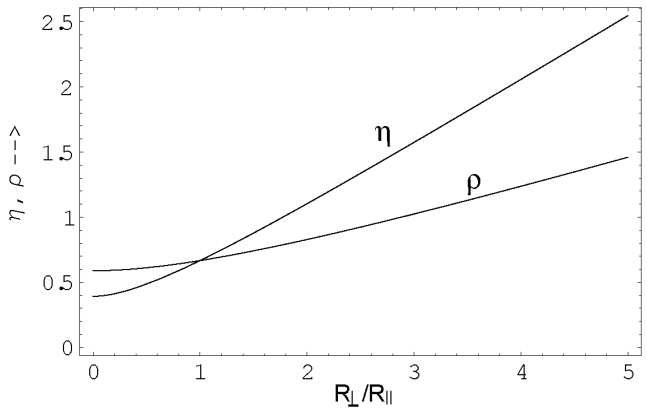

Fig. 1. Dependence of the functions η and ρ on a ratio between the spheroid semiaxes, $R_\perp/R_\parallel$

In the case where the plasmon decay is not significant, we can represent δ-function in expression (15) as (see [19])

$$\delta(x) = \frac{1}{\pi}\lim_{\alpha\to 0}\frac{\alpha}{\alpha^2+x^2}.$$

Then, the expression for the absorbed energy takes the form

$$w_e|_{L\to 0} = \frac{V}{64}\frac{\omega_p^2}{\Gamma^2}\sum_{j=1}^{3}\left|\mathbf{E}_{0j}\times\right.$$

$$\left.\times\left(\exp\left[-\frac{(\omega_j-\omega_0)^2}{4\Gamma^2}\right]+\exp\left[-\frac{(\omega_j+\omega_0)^2}{4\Gamma^2}\right]\right)\right|^2, \qquad (18)$$

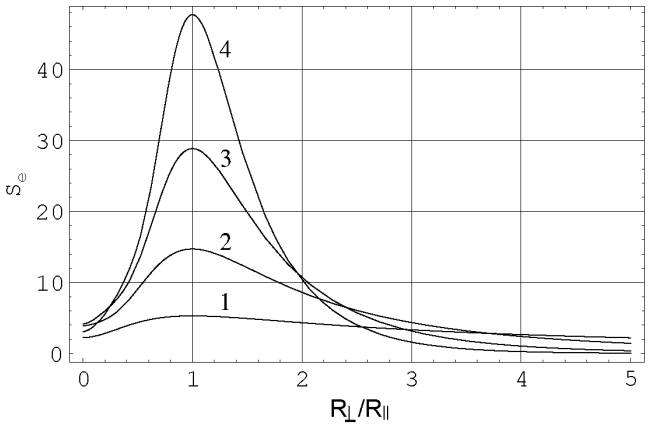

Fig. 2. Dependence of the energy absorbed by a spheroidal MN at the plasmon resonance frequency on the ratio between the spheroid semiaxes for different values of Γ,s^{-1}: 1.085×10^{15} (*1*), 0.651×10^{15} (*2*), 0.465×10^{15} (*3*), and 0.362×10^{15} (*4*)

where

$$\omega_j = \sqrt{L_j}\omega_p. \tag{19}$$

We limit the analysis of Eq. (18) to the case of a spheroidal MN and choose, for convenience, such a polarization of the electric field which makes it possible to excite the plasmon oscillations of electrons both along and across the spheroid rotation axis. If the field components $\mathbf{E}_{0\|}$ and $\mathbf{E}_{0\perp}$ are directed along and across the rotation axis, respectively, then such a polarization is, in the general case,

$$E_{0\|} \equiv |\mathbf{E}_0|\cos\theta; \quad E_{0\perp} = |\mathbf{E}_0|\sin\theta, \tag{20}$$

where θ is the angle between the spheroid rotation axis and the vector of the incident electric field strength $\mathbf{E}_0$. Then, frequencies (19) can be rewritten as the frequencies of electron oscillations along and across the axis of rotation:

$$\omega_{\|,\perp} = \sqrt{L_{\|,\perp}}\omega_p, \tag{21}$$

which, for the given $L_{\|,\perp}$ will be the frequencies of the corresponding plasmon resonances.

In what follows, for the sake of illustration, we will calculate the quantity

$$S_e = \frac{w_e}{V|\mathbf{E}_0|^2/(4\pi)} \tag{22}$$

which is the ratio of the energy absorbed by a unit of the MN volume to the incident wave energy.

Figure 2 shows the dependence of S_e on the degree of ellipsoid's oblateness or prolateness in the case where $\theta = \pi/4$ and the frequency equals that of surface plasmons of a spherical particle $\omega_0 = \omega_p/\sqrt{3} \equiv \Omega$. Here and below, the calculations are carried out with the use of formulas (18) and (20) – (22), given the concentration of electrons in a particle 10^{22} cm^{-3} and $\omega_p \approx 5.6\times10^{15}$ s^{-1}. As follows from curves *1–4*, the laser pulses of longer duration are absorbed more effectively. As for the shape dependence of the absorption, the maximum of absorption is achieved at $R_\perp/R_\| = 1$, i.e. when the particles have the spherical shape.

It is convenient to measure Γ in the fractions of the carrier frequency ω_0. Then, the duration of a laser pulse can be set in the carring wave periods or wavelengths, that is $\frac{1}{\Gamma} = n\frac{2\pi}{\omega_0} = \frac{n\lambda_0}{c}$, where n is an arbitrary quantity, and c is the light velocity. Thus, for the region of plasmon resonances, each wavelength which is a multiple of λ_0 can be brought into correspondence with a certain pulse duration (see table), given $\omega_0 \equiv \Omega$.

The calculation of S_e was also carried out by means of the numerical integration in formula (15) for the various particle radii R within the range $R = 50 \div 400$ Å (here, $R = (R_\| R_\perp^2)^{1/3}$). On the whole, it turned out that the value of S_e, calculated numerically, is (i) slightly smaller than the values obtained on the basis of formula (18) and (ii) depends on R very weakly for various Γ [1]. At the same time, the latter dependence is more pronounced at smaller Γ provided that R is not great ($R = 50 \div 150$ Å). For example, for a particle with $R = 100$ Å at $\Gamma = 0.36\times10^{15}$ s^{-1}, the highest possible values of S_e calculated analytically with the use of Eq. (18) exceed those numerically determined from formula (15) by about 7%. For greater R and Γ, this percentage decreases. For this reason, we will rest in the further calculations of S_e on the evaluations performed according to formula (18).

A correspondence between the value inverse to the pulse duration and the wavelength of a carrier wave in the region of plasmon resonances

$\Gamma\times10^{15}$, s^{-1}	$\lambda/2\pi$
3.256	λ_0
1.085	$3\lambda_0$
0.6512	$5\lambda_0$
0.4652	$7\lambda_0$
0.3618	$9\lambda_0$
0.3256	$10\lambda_0$

[1] This dependence appears in Eq. (15) from γ which depends on R due to the conductivity tensor (17).

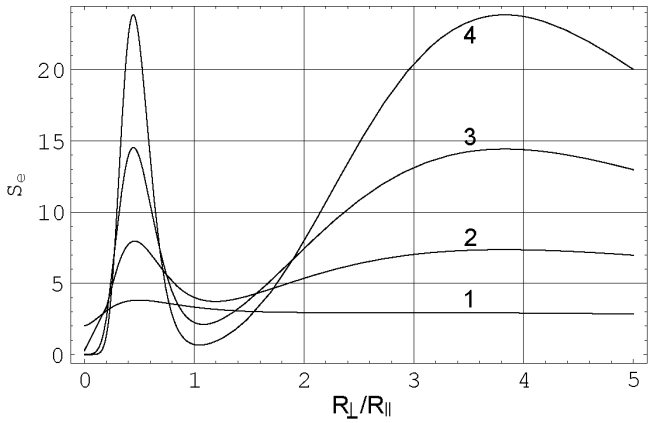

Fig. 3. The same as in Fig. 2, for the frequency $\omega_0 = 2.20626 \times 10^{15}$ s^{-1}

As soon as the carrier frequency deviates from that of the surface plasmon in a spherical particle, the peak of absorbed energy depending on the ratio $R_\perp/R_\parallel$ splits into two ones: the first maximum corresponds to the prolate particles ($R_\perp/R_\parallel < 1$), whereas the second – to the oblate particles ($R_\perp/R_\parallel > 1$). This fact is illustrated in Fig. 3 for the frequency $\omega_0 = 2.21 \times 10^{15}$ s^{-1} and various values of the incident pulse duration.

If the pulse duration is fixed, then, changing the frequency of a carrier wave, we can trace the evolution of the dependence of the maximum of absorbed energy on the MN shape. Figures 4,*a* and 4,*b* illustrate such dependences. For comparison, the absorption curve at a frequency $\omega_0 = \Omega$, where Ω is the resonance frequency of a spherical MN, is shown (curve *1* in each part of the figure). For the frequencies exceeding Ω (see Fig. 4,*a*), the absorption maximum first shifts towards the side of more oblate particles with increase in ω_0 and then splits into two peaks: the first one is observed at $R_\perp/R_\parallel > 1$, whereas the second one – at $R_\perp/R_\parallel < 1$. Figure 4,*b* demonstrates the data calculated for the frequencies lower than Ω, with the calculations carried out for the same values of the incident pulse duration. As the frequency gets lower, the absorption maximum shifts towards the side of more prolate particles and, afterwards, splits into two, as in the former case. As ω_0 deviates from the resonance frequency, the peak of the absorbed energy first decreases in absolute value, then splits and finally, as the carrier frequency strongly differs from Ω, the values of both emerged peaks stabilize.

These results are in compliance with the correlation, established by us earlier [18], between the geometrical

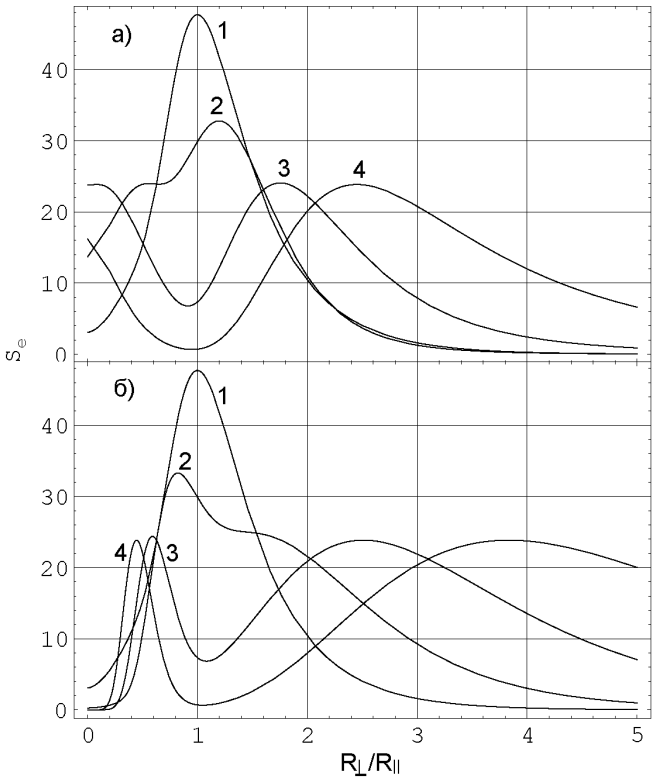

Fig. 4. Dependences of the energy absorbed by a spheroidal MN on the degree of its oblateness or prolateness for $\Gamma \approx 0.362 \times 10^{15}$ s^{-1}, at the frequencies ω_0 higher than that of the plasmon resonance Ω of a spherical MN (*a*): $\omega_0 = 3.606 \times 10^{15}$ s^{-1} (*2*), 3.956×10^{15} s^{-1} (*3*), and 4.306×10^{15} s^{-1} (*4*) and lower than Ω (*b*): $\omega_0 = 2.906 \times 10^{15}$ s^{-1} (*2*), 2.556×10^{15} s^{-1} (*3*), and 2.206×10^{15} s^{-1} (*4*). Curves *1* in both parts of the figure correspond to the case $\omega_0 = \Omega$

shape of a nanoparticle and the frequency of the light absorption, depending on which a rapid growth in the strength of light pressure on a particle is observed.

Let us choose the prolateness or oblateness of a nanoparticle fixed and trace how the absorption changes as a function of the carrier frequency. In the case of a prolate MN, with increase in the duration of the incident laser pulse, one observes not only the growth of the peak of absorbed energy, but also its splitting (as Γ becomes higher than a certain critical value) into two peaks (a doublet) located on the opposite sides of the line $\omega_0/\Omega = 1$, where Ω corresponds to the resonance frequency of a spherical particle (Fig. 5). It is worth to note that the peaks at $\omega_0 < \Omega$ and $\omega_0 > \Omega$ correspond to the plasmon resonance frequencies $\omega_\parallel$ and $\omega_\perp$(see (21)), respectively, whereas the inverse situation is characteristic of oblate particles: the former peak corresponds to $\omega_\perp$ and the latter – to $\omega_\parallel$.

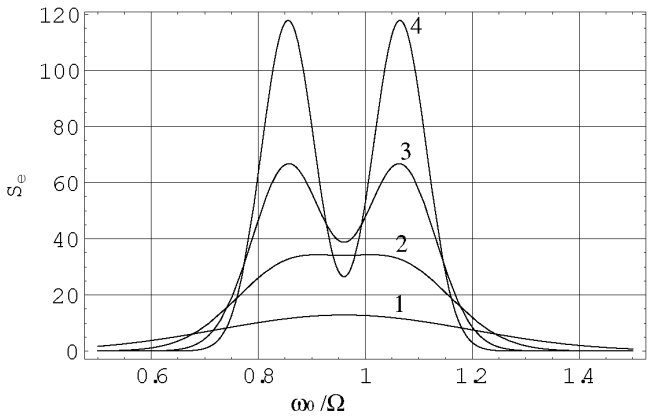

Fig. 5. Dependence of the energy absorbed by a prolate ($R_\perp/R_\parallel = 0.7$) spheroidal MN on the frequency of a carrier wave for different values of Γ, s^{-1}: 0.651×10^{15} (*1*), 0.326×10^{15} (*2*), 0.217×10^{15} (*3*), and 0.163×10^{15} (*4*)

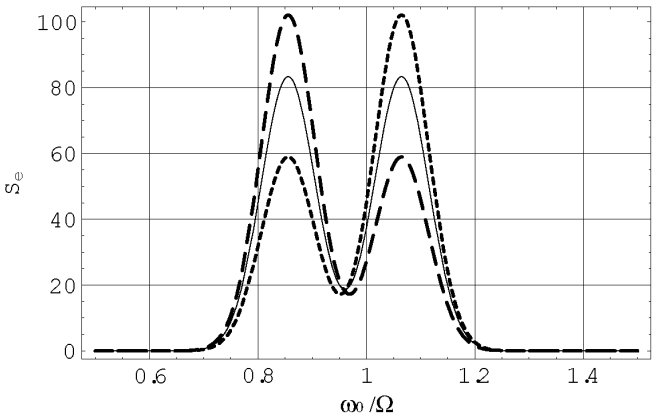

Fig. 6. Dependence of the energy absorbed by a prolate ($R_\perp/R_\parallel = 0.7$) spheroidal MN on the frequency of a carrier wave for $\Gamma = 0.163 \times 10^{15}$, s^{-1} and different angles of the laser pulse incidence: $\theta = \pi/4$ – solid line, $\theta = \pi/3$ – dotted line, and $\theta = \pi/6$ – dashed line

Thus, contrary to the case of spherical particles, the spheroidal MNs, either prolate or oblate, exhibit a doublet in the spectrum of absorption provided that Γ is sufficiently small. The doublet originates from two plasmon resonances excited in particles by ultrashort laser pulses. At $\theta = \pi/4$, both the peaks of the doublet have the same height, which, being practically independent of a degree of the particle prolateness or oblateness, strongly depends on the pulse duration. In the case of prolate MNs, a minimum of the dip between the absorption peaks is achieved at frequencies lower than Ω and shifts towards the longer waves with increase in the prolateness degree. The other tendency is characteristic of oblate MNs: the minimum is observed at frequencies higher than Ω and, as the oblateness degree increases, it first shifts towards the shorter waves and then, at sufficiently high oblateness degrees, the movement changes its direction.

The absorption peaks display the similar behavior. As the degree of MN prolateness increases, the distance between the peaks of the doublet grows due to the more drastic shift of the peak, caused by the plasmon resonance at the frequency $\omega_\parallel$, towards the longer waves. At the same time, the height of the peaks remains constant provided that the degree of prolateness is small enough. Quite similar behavior is also characteristic of oblate MNs: the distance between the peaks of the doublet grows with increase in the degree of MN oblateness. The reason for this is either the more drastic shift of the peak, caused by the plasmon resonance at $\omega_\parallel$, towards the high frequency side of the spectrum (at sufficiently small degrees of oblateness) or the reverse movement of the peak, caused by the plasmon resonance at $\omega_\perp$ (at higher degrees of oblateness). The height of the peaks remains constant as the degree of oblateness keeps small enough.

Under various experimental conditions, a small shift, either blue or red, with respect to the value $\omega_0 = \Omega$ has been observed. A number of microscopic approaches has been developed to explain such a shift (see, for example, [20]). The most successful approaches are thought to be those built on the basis of a jelly model with the use of the theory of linear response in the limits of time-dependent local density [21]. However, these approaches don't account for the shift caused by a change in the particle shape. It is the most important feature of our approach that results in the facts that the shape of MNs specifies the frequency, at which the resonance absorption occurs, and the shift of the plasmon absorption peak is associated with a change in the particle shape.

The relative height of the peaks in the doublet can be tuned by means of changing the angle of the laser pulse incidence. Figure 6 allows one to trace how the plasmon absorption along and across the spheroid rotation axis changes as the angle of incidence θ is reduced from $\pi/3$ to $\pi/6$. For convenience, we consider the prolate particle with $R_\perp/R_\parallel = 0.7$, as in Fig. 5. As is seen from Fig. 6, the peak intensities are the same at $\theta = \pi/4$, but they become different as θ deviates from this value. So, for example, at $\theta = \pi/3$, the peak associated with the resonance at $\omega_\parallel$ is characterized by a reduced intensity, contrary to the peak associated with $\omega_\perp$, which is characterized by an increased intensity. At $\theta = \pi/6$,

however, the inverse situation is observed. These data suggest that, whereas the intensity of the peak at $\omega_\perp$ reaches a maximum at $\theta = 0$ and turns into zero at $\theta = \pi/2$, the peak at $\omega_\parallel$ has maximum intensity at $\theta = \pi/2$ and minimum one – at $\theta = 0$.

At the end, we consider the qualitatively different limit transition when the width of an incident laser pulse is sufficiently large. To do this, we represent δ-function as (see [19])

$$\delta(x) = \frac{1}{\sqrt{\pi}} \lim_{\alpha \to 0} \frac{1}{\alpha} \exp(-x^2/\alpha^2),$$

and calculate, according to Eq. (3), the value of $(\mathbf{E}(0,\omega))^2$ which is included in Eq. (15):

$$(\mathbf{E}(0,\omega))^2 \approx \mathbf{E}_0^2 \left(\frac{\pi}{2}\right)^{3/2} \frac{1}{\Gamma}\{\delta(\omega-\omega_0)+\delta(\omega+\omega_0)\}. \tag{23}$$

Now relations (15) and (23) yield

$$w_e|_{\Gamma\to 0} = \frac{V}{2\pi} \left(\frac{\pi}{2}\right)^{3/2} \frac{1}{\Gamma} \sum_j \frac{\omega_0^4\, \sigma_{jj}(\omega_0)\, E_{0j}^2}{(\omega_0^2-\omega_j^2)^2 + (2\gamma(\omega_0))^2\omega_0^2}. \tag{24}$$

As is seen from Eq. (24), the absorbed energy is proportional to the pulse duration $1/\Gamma$. Expression (24) divided by the pulse duration gives us the value of the energy which is absorbed by a nanoparticle on average in a unit of time at its irradiation by long-duration pulses. This quantity differs by the multiplier $\frac{1}{2}\sqrt{\pi/2}$ from the analogous quantity obtained for the absorption of a monochromatic wave. The multiplier $1/2$ appears as a result of different choices of the expressions for the EM wave field: in work [12], we set it as $\mathbf{E}_0 \exp[i(\omega t - \mathbf{kr})]$; but, here at $\Gamma \to 0$, we have $\mathbf{E}_0 \cos(\omega_0 t - \mathbf{k}_0\mathbf{r})$ according to formula (1). The additional multiplier $\sqrt{\pi/2}$ results from the fact that we deal with the Gaussian-like, rather than rectangular pulse.

4. Conclusions

We have developed the theory which describes the features of the absorption of ultrashort EM pulses by metallic nanoparticles, depending on the particle shape and the pulse duration. The simple analytic expressions are obtained, which make it possible to study the absorption of these pulses by surface plasmons, i.e. by the high-energy excitation of the electron gas in such nanoparticles. The analysis of the dependence of the energy absorbed by a spheroidal MN on the degree of its prolateness or oblateness is carried out for the different values of pulse duration and frequencies higher, lower, or identical to the plasmon resonance frequency.

At the frequency of a carrier wave which coincides with that of the surface plasmon, the maximum absorption is observed for spherical MNs. As soon as the carrier frequency deviates from that of the surface plasmon in a spherical particle, two maxima appear in the dependence of the absorbed energy on the ratio of spheroid semiaxes: one of them corresponds to the prolate particles, while the other – to the oblate particles. As the frequency deviates from the resonance one, the peak of the absorbed energy first decreases in absolute value, then splits and finally stabilizes for the more and more prolate or oblate particles.

For the case of spheroidal NPs subjected to the laser irradiation, with increase in the pulse duration, the peak in the dependence of the absorption on the frequency of a carrier wave also splits into two peaks located on the opposite sides of the value corresponding to the resonance frequency of a spherical particle. The peaks of the doublet originate from the resonances excited by ultrashort laser pulses at the frequencies of plasmon oscillations along or across the spheroid rotation axis. A distance from the minimum in a dip between the doublet peaks to the frequency of the plasmon resonance for a spherical particle provides the information about the degree of prolateness or oblateness of a nanoparticle.

As the degree of prolateness or oblateness increases, the distance between the doublet components grows. At the fixed incident angle of a laser pulse, the peak height keeps constant, with its value being dependent only on the pulse duration. The features of the change of the relative absorption intensity of a pulse along and across the spheroid rotation axis with change in the angle of incidence are traced.

The peculiarities of the absorption of long-duration laser pulses by nanoparticles are discussed.

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ОСОБЛИВОСТІ ПОГЛИНАННЯ УЛЬТРАКОРОТКИХ ЛАЗЕРНИХ ІМПУЛЬСІВ АСИМЕТРИЧНИМИ МЕТАЛЕВИМИ НАНОЧАСТИНКАМИ

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Р е з ю м е

Для наночастинок несферичної форми розроблено теорію, яка дозволяє обчислити енергію, що ними поглинається при опроміненні ультракороткими лазерними імпульсами різної тривалості в області збудження поверхневих плазмонів. Для частинок, що мають форму сплюснутого чи витягнутого сфероїда, знайдено залежність цієї енергії від об'єму наночастинки, міри відхилення частинки від сферичної форми, тривалості імпульсу та величини зміщення несучої частоти лазерного променя відносно частоти поверхневого плазмона у сферичній частинці.