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On a plasmon resonance in ellipsoidal nanoparticles

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***Abstract*. The dependence of the plasmon resonance frequency of metal ellipsoids of revolution on their eccentricity is calculated. The plasmon resonance shifts to the red with increasing eccentricity and its intensity increases. The resonance intensity increases with decreasing the imaginary part of the dielectric constant of a metal. The plasmon resonance frequency in a suspension of randomly oriented prolate nanoparticles (with a large eccentricity) almost exactly coincides with that in a suspension of oriented particles. These features permit the efficient improvement of the sensitivity and resolving power of optoacoustic tomography by introducing prolate metal nanoparticles into the region of an object under study. The possibility of plasmon resonance narrowing by introducing metal nanoparticles into an amplifying medium is pointed out.**

Keywords: *plasmon resonance, eccentricity, nanoparticles.*

1. Introduction

Much attention paid by researchers to the study of physical properties and methods of preparation of nanoparticles is related to their experimental and technological applications [1 – 6]. One of the promising applications of nanoparticles in biomedical technology is their use as optoacoustic contrast agents for imaging of biological tissues, as well as photoactivated therapeutic agents [7, 8]. In optoacoustic tomography of cancer tumours located inside tissues, near-IR lasers are used [9, 10] because their radiation can penetrate sufficiently deep inside biological tissues.

Among these lasers, yttrium aluminium garnet and alexandrite lasers are most popular. To enhance the contrast of a tumour image relative to normal biological tissues, the absorption resonance of the introduced nanoparticles should coincide with the wavelength of a laser used for illumination of biological tissues. However, the resonance absorption of a nanosphere, whose size is much smaller than the wavelength of light, is caused by the so-called plasmon resonance [11]. The plasmon resonance wavelength of most metals lies in the visible or shorter-wavelength region.

It was pointed out in papers [4, 5] that the absorption spectrum of metal nanoparticles can be shifted by varying the thickness of a metal layer deposited on the surface of a quartz nanosphere. In this paper, we study the possibility of controlling the resonance frequency and the intensity of absorption of light by metal ellipsoids by varying their eccentricity.

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2. Plasmon resonance in ellipsoids of revolution

To calculate the intensity and resonance absorption frequency of an ellipsoid, it is necessary to know the amplitude of an electromagnetic field inside it. If the wavelength is noticeably smaller than the linear size of the ellipsoid, then the field components E_k inside the ellipsoid are expressed in terms of the external (exciting) field components E_{0k} as [12]

$$E_k = \frac{2\varepsilon_0}{(\varepsilon - \varepsilon_0)A_k + 2\varepsilon_0} E_{0k}\,, \tag{1}$$

where $\varepsilon = \varepsilon' + \mathrm{i}\varepsilon''$ is the dielectric constant of the metal from which the nanoellipsoid is fabricated; ε_0 is the dielectric constant of the medium in which nonoellipsoids are immersed. It is assumed in expression (1) that the axes x, y, and z of the coordinate system are directed along the ellipsoid axes, and the subscript takes the values x, y, z. The quantity A_k is determined by the integral

$$A_k = \int_0^\infty \frac{abc}{(s + d_k^2)[(s + a^2)(s + b^2)(s + c^2)]^{1/2}}\,\mathrm{d}s, \tag{2}$$

where $d_x \equiv a$; $d_y \equiv b$, $d_z \equiv c$; a, b, and c are the ellipsoid axes. The conditions of the validity of expression (1) are discussed in section 4.

For a sphere ($a = b = c$), we have $A_k = 2/3$, and expression (1) takes the form

$$E_k = \frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_{0k}. \tag{3}$$

In this case, we deal with a 'classic' plasmon resonance, whose frequency is determined by the condition $\varepsilon' + 2\varepsilon_0 = 0$. The calculation shows that the resonance of a gold nanosphere placed in water lies at $\lambda = 520$ nm and that of a silver nanosphere at $\lambda = 390$ nm.

For an ellipsoid of revolution ($b = c$) with the z axis directed along the field, we have

$$A_z(\xi) = \int_0^\infty \frac{\xi}{(s+\xi^2)(s+1)[(s+\eta)]^{1/2}}\,\mathrm{d}s, \qquad \xi = \frac{a}{b}. \quad (4)$$

For the field is oriented perpendicular to the rotation axis of the ellipsoid,

$$A_\perp(\xi) = \int_0^\infty \frac{\xi}{(s+1)^2(s+\xi^2)^{1/2}}\,\mathrm{d}s. \quad (5)$$

In the approximation considered here, when the linear size of a nanoparticle is small compared to the wavelength, the field inside the particle is homogeneous, so that the radiation power absorbed in its unit volume is

$$P(\lambda,\xi) =$$

$$= \frac{\varepsilon''}{\lambda}\sum_k \frac{\varepsilon_0^2}{[\varepsilon'(\lambda)A_k(\xi)+(2-A_k)\varepsilon_0]^2+[\varepsilon''(\lambda)A_k(\xi)]^2}|E_{0k}|^2. \quad (6)$$

Expression (6) shows that the effect of the ellipsoid shape and of its orientation with respect to the field is determined by coefficients A_k, which depend, according to (4) and (5), only on one parameter, namely, the ellipsoid eccentricity ξ.

We will perform further calculations for a suspension of gold nanoparticles in water. The wavelength dependences of complex dielectric constants for some metals are presented in handbook [13]. These dependences for gold, silver, and platinum in the visible range are presented in Fig. 1. We assume that water is transparent over the entire visible range, so that its dielectric constant ε_0 is real and equal to 1.77. Figs 2, 4, and 5 show the wavelength dependences of the power absorbed by ellipsoids of revolution with different eccentricities.

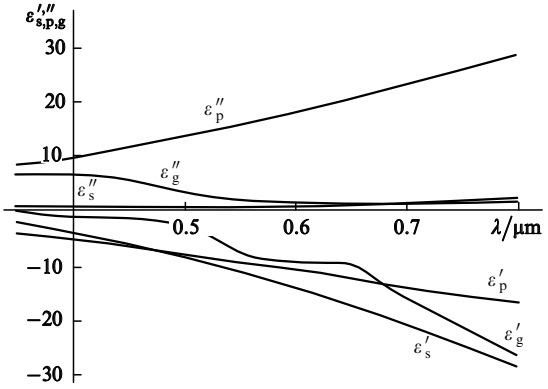

Figure 1. Real and imaginary parts of the dielectric constant for gold (ε'_g, ε''_g), silver (ε'_s, ε''_s), and platinum (ε'_p, ε''_p) [13].

One can see from Fig. 2 that, if the field is directed along the ellipsoid axis, the resonance absorption peak increases and strongly shifts to the red with increasing eccentricity. If the external field is directed perpendicular to the ellipsoid axis, the resonance slightly shifts to the blue with increasing eccentricity. In this case, the resonance peak is weaker than the plasmon resonance peak in a sphere. These properties can be explained by analysing expression (6). At the resonance, we have $\partial P(\lambda,\xi)/\partial\lambda = 0$ by definition. If the values of ε'' and $\mathrm{d}\varepsilon''/\mathrm{d}\lambda$ are small compared to $\mathrm{d}\varepsilon'/\mathrm{d}\lambda$ near the resonance (which is, for example, the case for gold and silver, Fig. 1), then the resonance wavelength is quite accurately determined by the equation

$$\varepsilon'(\lambda)A_k(\xi) + [2 - A_k(\xi)]\varepsilon_0 \approx 0. \quad (7)$$

This gives

$$P(\lambda_{\mathrm{res}},\xi) = \frac{1}{\lambda_{\mathrm{res}}}\frac{\varepsilon_0^2}{\varepsilon''(\lambda_{\mathrm{res}})[A_k(\xi)]^2}|E_{0z}|^2. \quad (8)$$

The value of $A_z(\xi)$ decreases with increasing ξ (Fig. 3), resulting, according to (8), in the enhancement of the resonance peak. The real part of the dielectric constant of gold, being negative, increases in modulus with increasing wavelength (Fig. 1). This property in the visible range is also inherent in other metals, for example, silver or platinum, so that the resonance wavelength shifts to the red with decreasing $A_z(\xi)$. Note that, according to (8), the power absorbed at the resonance increases (rather than decreases!) with decreasing ε''. This is explained by the fact that, although the absorption of light by the material decreases linearly with decreasing ε'', the field inside the ellipsoid increases simultaneously inversely proportional to $(\varepsilon'')^2$.

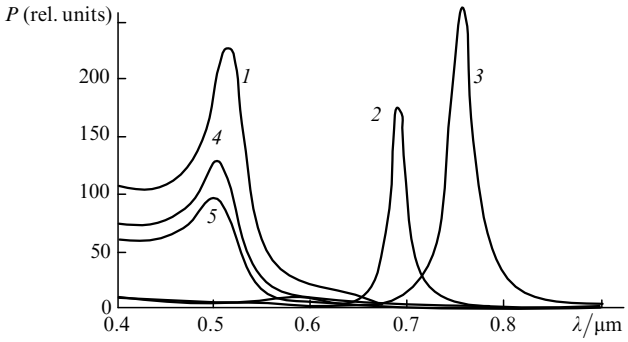

Figure 2. Dependences $P(\lambda,\xi)$ for a sphere ($\xi = 1$) (*1*) and a prolate ellipsoid of revolution for $\xi = 3$ (*2*, *4*) and $\xi = 4$ (*3*, *5*) when the external field is directed along the ellipsoid axis (*2*, *3*) and perpendicular to it (*4*, *5*). The scale of curves *1*, *4*, and *5* over the ordinate is magnified by a factor of twenty.

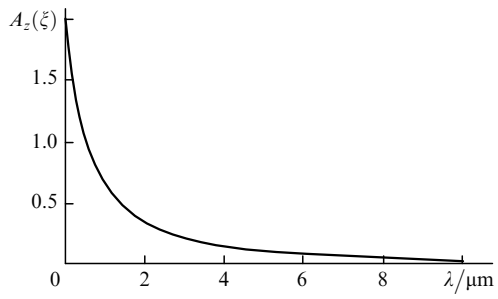

Figure 3. Function $A_z(\xi)$.

The values of ε'' and $\mathrm{d}\varepsilon''/\mathrm{d}\lambda$ for platinum are comparable with $\mathrm{d}\varepsilon'/\mathrm{d}\lambda$ (Fig. 1), so that the resonance frequency for platinum ellipsoids is not determined by

equation (7). For this reason, the dependence of the resonance absorption on ε'' for platinum nanoparticles is more complicated.

Let us compare the characteristics of the plasmon resonance in a prolate ellipsoid of revolution and a spheroid. The power absorbed by a spheroid is shown in Fig. 4. When the field is oriented perpendicular to the spheroid axis, the resonance frequency noticeably shifts to the red, as in the case of a prolate ellipsoid whose rotation axis is directed along the field. However, the resonance intensity for the spheroid is much lower. When the field is directed along the spheroid axis, the resonance slightly shifts to the blue and its intensity noticeably decreases compared to that for a sphere. Both these facts can be explained by expressions (7) and (8).

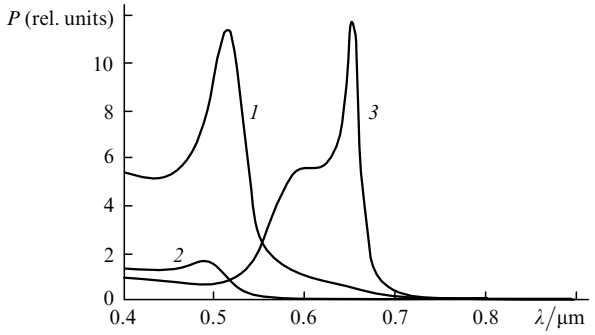

Figure 4. Dependences $P(\lambda, \xi)$ for a sphere with $\xi = 1$ (*1*) and a spheroid with $\xi = 0.25$ (*2*, *3*) for the external field directed along (*2*) and perpendicular (*3*) to the spheroid axis.

In the experiment, radiation can be nonpolarised and ellipsoids can be randomly oriented. In this case, the integration of expression (5) over the orientation angles results in the expression

$$P(\lambda, \xi) = \frac{|E_0|^2}{3}\frac{\varepsilon''}{\lambda}\varepsilon_0^2\left\{\frac{1}{|[\varepsilon(\lambda)-\varepsilon_0]A_z(\xi)+2\varepsilon_0|^2} + \frac{2}{|[\varepsilon(\lambda)-\varepsilon_0]A_\perp(\varepsilon)+2\varepsilon_0|^2}\right\}. \quad (9)$$

The second term in (9) corresponds to the contribution to absorption from ellipsoids with the rotation axis directed perpendicular to the field. This contribution is very small compared to that from longitudinally oriented particles (Fig. 2). Therefore, the resonance frequency in a suspension of randomly oriented particles will almost coincide with that in the case of a regular longitudinal orientation of particles, whereas the intensity of the absorption peak will be three times weaker. The coincidence of absorption resonance frequencies for oriented and randomly oriented prolate ellipsoids makes it possible to control the resonance frequency by varying the ellipsoid eccentricity because in this case the ellipsoids introduced to the object under study should not be oriented.

Table 1 presents eccentricity for gold, silver, and platinum ellipsoids and the relative intensity of absorption resonances of nanoparticles in water. The data are presented for the emission wavelength 755 nm of an alexandrite laser. It is obvious that for nanoparticles immersed in another medium the eccentricity of nanoellipsoids should be changed.

Table 1.

Material	Wavelength/nm	Eccentricity	Resonance intensity (rel. units.)
Gold	755	3.98	265
Silver	755	4.34	360
Platinum	755	6.25	27

One can see from Table 1 that the parameters of gold and silver are approximately equivalent and strongly differ from those of platinum. Especially, the intensity of the resonance peak for platinum is much weaker. Our calculation shows that absorption resonances in gold and silver are much narrower than in platinum. The half-width of the 755-nm resonance peak in Fig. 2 for gold nanoparticles is of about 15 nm. The resonance absorption peak for silver nanoparticles has approximately the same half-width, whereas the resonance for platinum nanoparticles is very broad, as shown in Fig. 5.

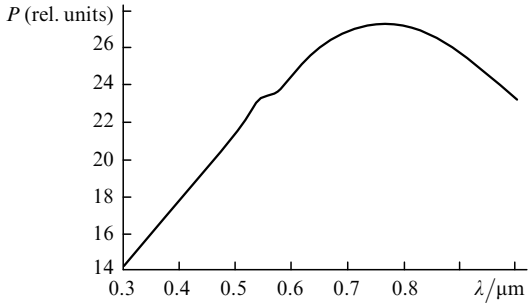

Figure 5. Dependence $P(\lambda)$ for a platinum ellipsoids of revolution with the eccentricity $\xi = 6.25$.

Let us also point out the following fact. If a metal ellipsoid is placed in an amplifying medium ($\varepsilon_0 = \varepsilon_0' - i\varepsilon_0''$, $\varepsilon_0'' > 0$), the expression (8) can be written in the form

$$P(\lambda_{\rm res}, \xi) = \frac{\varepsilon''}{\lambda_{\rm res}}\frac{\varepsilon_0^2}{[A_k\varepsilon'' - (2-A_k)\varepsilon_0'']^2}|E_{0z}|^2. \quad (10)$$

One can see that, by appropriately choosing the gain in the medium, the plasmon resonance can be made very narrow and intense. Therefore, if the gain resonance of the active medium is comparatively narrow, it should be made coincident with the plasmon resonance. The choice of the active medium is favoured by the fact that the parameter $A_k(\xi) \ll 1$ for strongly prolate ellipsoids. This means that the gain should compensate not for ε'' but for a much smaller value $A_k\varepsilon''$. Nevertheless, to observe this effect in a suspension of gold or silver particles, an active medium with a very high gain, of the order of 10^2 cm^{-1}, is required, even for the eccentricity $\xi \approx 10$.

3. Applicability of approximations used

Our calculations were based on expression (1) for the field inside of an ellipsoid. This expression is in essence the first term in the expansion of field in a series in the parameter $(2\pi/\lambda)d_k[|\varepsilon(\lambda)|]^{1/2}$, and, therefore, is valid for $(2\pi/\lambda) \times a[|\varepsilon(\lambda)|]^{1/2} < 1$ [11], or for

$$a < d_{\max}(\lambda) \equiv \frac{\lambda}{2\pi[|\varepsilon(\lambda)|]^{1/2}}, \qquad (11)$$

where a is the maximum linear size of the ellipsoid. The value of $d_{\max}(\lambda)$ depends on the wavelength range and the material used. For gold ellipsoids in the wavelength range from 0.4 to 1 μm, we have $d_{\max}(\lambda) \leqslant 38$ nm (Fig. 6).

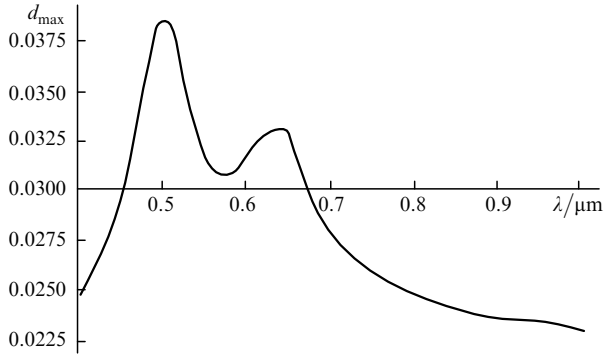

Figure 6. Wavelength dependence of $d_{\max}$ for a gold ellipsoid.

The restriction imposed on the ellipsoid size is not the only one. The expansion coefficient in the parameter $(2\pi/\lambda)d_k[|\varepsilon(\lambda)|]^{1/2}$ is proportional to the quantity $[\varepsilon(\lambda)A_k + (2 - A_k)\varepsilon_0]^{-1}$. Because $\varepsilon(\lambda)A_k + (2 - A_k)\varepsilon_0 \approx \mathrm{i}A_k\varepsilon''(\lambda)$ at the resonance, the omitted terms are small at the resonance if [10]

$$\frac{2\pi}{\lambda_{\text{res}}}\, a\, \frac{|\varepsilon(\lambda_{\text{res}})|^{1/2}}{A_z\varepsilon''(\lambda_{\text{res}})} < 1. \qquad (12)$$

The condition (12) is more stringent than (11) because of the smallness of A_z for large ξ. Estimates show that the condition (12) restricts the size of gold nanoparticles by the values 10–15 nm.

Inequalities (11) and (12) restrict the applicability of expression (1) for large nanoparticles. However, the restriction also exists for small nanoparticles. In the case of very small nanoparticles, the so-called size quantisation is manifested, when the motion of electrons inside a body can no longer be considered as quasi-free. The size quantisation becomes substantial if the coherence length l_{coh} of the electron wave function exceeds the minimum size of the nanoellipsoid. It has been found experimentally [14] that the size quantisation in metals is manifested in nanoparticles of size one nanometre and lower.

Therefore, expression (1) is valid in the interval of sizes of nanobodies determined by the expression

$$l_{\text{coh}} < a < d_{\max}(\lambda). \qquad (13)$$

However, this does not mean that the effects described above will disappear in large ellipsoids - they will only change quantitatively. When $a > d_{\max}(\lambda)$, the field inside the ellipsoid should be calculated by solving an electrodynamic problem, similarly to the Mie problem on excitation of a sphere by a plane wave [12]. Such attempts have been made (see, for example, paper [15] and references therein); however, no comparatively simple practical calculations for large ellipsoids have been proposed so far.

4. Conclusions

The directional transport (for example, in the bloodstream) of prolate metal nanoparticles to the organ under study can substantially improve the sensitivity of various methods of optical and optoacoustic tomography because absorption of light by metal nanoparticles at the plasmon resonance frequency substantially exceeds absorption of light by biological tissues in the near-IR region. It is clear intuitively that the nanoparticles should not be strictly ellipsoidal. These can be nanocylinders or particles consisting of several coaxial (or almost coaxial) nanospheres in contact.

Our preliminary calculations show that the frequency of the reflection resonance can be controlled in the same wave as that of the absorption resonance of a nanoparticle. This can be useful both for the development of scattering tomography of biological tissues [16] and for the fabrication of materials with a controlled refractive index [6].

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