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DIELECTRIC FUNCTION OF A METAL NANOSPHERE COVERED WITH A LAYER OF ADSORBED MOLECULES

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Due to the presence of an adsorbate layer on a nanoparticle, electron scattering will be anisotropic, and the diagonal components of the dielectric tensor of such a composite nanoparticle will have the form (1), where $\beta_c = (R_c/R)^3$ is the volume content of the metal in the composite particle (R_c is the radius of the metal core, R is the radius of the entire composite particle), ϵ_s is the dielectric constant of the adsorbate, and the components of the tensor of the dielectric constant of the metal core within the framework of the Drude model have the form (2). Here ϵ^{∞} is the contribution of the crystal lattice to the

dielectric constant; ω_p – frequency of volume plasmons; wis the frequency of the incident electromagnetic wave, and the expression for the effective relaxation rate has the form (3). In the ratio (3) γ_{bulk} is the rate of bulk relaxation, which for each metal it is fashionable to consider as a constant value; sgand γ_{rad} – rates of surface relaxation and radiation attenuation. Note that for relatively small particles, the value γ_{rad} can be neglected. The rate of surface relaxation can be written as (4).

Where $v_{\rm F}$ is the Fermi speed of electrons, (5) is an effective parameter that describes the degree of loss of coherence during scattering of electrons on the surface of a nanoparticle, $v_{\rm s} = v_{\rm F}/2R_{\rm c}$ is the frequency of individual electron oscillations.

The last term in formula (3) describes the relaxation processes caused by the presence of



the "metal - adsorbed layer" interface (6) where the frequency dependences of the coefficient $\mathscr{A}_{(0)}^{\text{interface}}$ are determined by formulas (7,8).

In formulas (7) and (8): $\sigma_0 = 64\omega_F Q/3\pi n_e v_F (n_e - \text{concentration of electrons}, Q - a \text{ number that depends on the symmetry of the adsorbed resonance state, } Q = 0,2 \text{ for } s\text{- and } p_z\text{-states}, Q \approx 0,33 - \text{ for } p_x\text{- and } p_y\text{-states}); \omega_F = \varepsilon_F/\hbar (\varepsilon_F - \text{Fermi energy}); n_a - \text{ surface density of adsorbed atoms; } \omega_{sp} - \text{ frequency of SPR, a } (9 - 11) \text{ is the local density of states around the adsorbed atom (molecule); } \varepsilon_a \text{ and } \Gamma_a - \text{ amplitude and width of spectral lines, respectively; } d \text{ is the distance between the center of the adsorbed molecule and the image plane.}$

$$\mathscr{I}_{\parallel}^{\text{merrac}} = \frac{\pi}{8} n_a \sigma_0 \left(\frac{m}{\epsilon^{\infty} + 2\epsilon_{\text{m}}} \right) \mathscr{I}(\omega)$$

$$(8)$$

$$\mathscr{I}(\hbar\omega) = \frac{\pi}{4\epsilon_{\text{F}} \hbar\omega} \int_{\epsilon_{\text{F}} \omega h}^{\epsilon_{\text{F}}} dE \left[E \Gamma_a \varrho_a \left(E + \hbar\omega \right) + \left(E + \hbar\omega \right) \Gamma_a \varrho_a \left(E \right) \right]$$

$$(9)$$

$$\mathscr{I}_{\perp}(\hbar\omega) = \frac{1}{2\pi^2 \epsilon_0} \left(ed \right)^2 \int_{\epsilon_{\text{F}} \omega h}^{\epsilon_{\text{F}}} dE \varrho_a \left(E \right) \varrho_a \left(E + \hbar\omega \right)$$

$$(10)$$

$$\varrho_a \left(\epsilon \right) = \frac{1}{\pi} \frac{\Gamma_a / 2}{\left(\epsilon - \epsilon_a \right)^2 + \left(\Gamma_a / 2 \right)^2}$$

$$(11)$$

In fig. 1 shows the frequency dependences of the real parts of the diagonal components of the dielectric tensor of a spherical Au particle covered with a layer of oleylamine. At the same time, the dependences $\operatorname{Re}\epsilon_{@}^{\parallel}(\hbar\omega)$ are qualitatively similar to similar dependences for metallic spherical nanoparticles covered with a layer of a conventio nal dielectric. This similarity consists in the presence of two extremes and small-scale oscillations in the infrared part of the spectrum due to the manifestation of kinetic effects, as well as in the same nature of the maximum shifts with increasing particle radius and outer layer thickness. Regarding the dependence $\operatorname{Re}\epsilon_{@}^{\perp}(\hbar\omega)$, we note that in the visible part of the spectrum, this value slightly decreases with increasing frequency, while in the infrared region of the spectrum, these dependences have several minima and maxima.

The frequency dependence curves of the imaginary parts of the diagonal components of the dielectric tensor of the particle are Au@OAm shown in Fig.2. As in the case of dependency dependencies $\text{Im}\epsilon_{@}^{\parallel}(\hbar\omega)$ are qualitatively similar to similar dependences for metal-dielectric nanoparticles. Thus, an increase in the size of the metal core results in an increase in the magnitude $\max(\text{Im}\epsilon_{@}^{\parallel})$ and their shift to lower frequencies. As for dependencies $\text{Im}\epsilon_{@}^{\perp}(\hbar\omega)$, it is necessary to note a weak dependence on frequency in the visible part of the spectrum and a complex dependence (the presence of oscillations) in the infrared region.





Fig. 2.