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NANOPARTICLES AND GIANT RAMAN SCATTERING

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Abstract

The field for linear aggregates of metallic nanospheres is calculated. This field is analogous to that of the surface TM_0 wave of a metallic cylinder with a negative dielectric permittivity. The spontaneous emission of an atom into a surface wave is shown to be greatly enhanced. This enhancement is as great as 10^{14} times for a two-photon process (Raman scattering). The TM_0 wave is concentrated in the vicinity of the nanocylinder surface instead of extending in space to infinity. Being restricted in its length, the nanocylinder radiates efficiently into free space in contrast to the case of an infinite (plane or cylindrical) surface. The duration of the atomic dipole radiation is about 1 fs under the conditions discussed. The situation considered can be realized readily in actual experiments. It can explain the pronounced increase in the Raman intensity in the experiments described by Nie and Emory in 1997.

Keywords: nanocylinder, surface-enhanced Raman scattering, surface TM_0 wave.

1. Introduction

We consider below the surface TM_0 wave of a metallic cylinder. The zero critical frequency sets off this wave from other surface waves of the cylinder [1]. This means that the TM_0 wave exists at an arbitrarily small radius a of the cylinder.

The surface waves, so-called surface plasmons (in metals) and surface polaritons (in ionic crystals), exist in the frequency range where the dielectric permittivity of the material is negative and greater (in absolute value) than that of the material adjoining the metal or ionic crystal. In what follows we shall consider a surface plasmon on a small silver cylinder.

The following problems are considered sequentially. First we describe a surface TM_0 wave and calculate the wave numbers and propagation losses. We then normalize this wave similarly to the field oscillators in quantum radiation theory. Thereafter the probability of spontaneous radiation of an excited atom (molecule) in the field of the surface TM_0 wave is calculated and compared with that for spontaneous radiation of an atom (molecule) in the empty space. Hereinafter we use the term "atom" to mean both atom and molecule. We have found a pronounced increase in the probability of spontaneous emission of an atom in the vicinity of the surface of the cylinder section of length $L_c = \pi/h$ and of small radius $a \ll \lambda_0$. Here, $h > \omega/c$ is the wave number of the surface wave, $\lambda_0 = 2\pi c/\omega$, and ω is

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the frequency of the atomic transition. We show next that the surface wave on the restricted cylinder section radiates into ambient space in contrast to the same wave on the infinite cylinder and calculate the radiating power. The excitation efficiency of the surface wave is then determined by the reciprocity theorem. The consideration performed is then used to interpret the experimental data on the observation of surface-enhanced (giant) Raman scattering (SERS) by molecules on so-called hot colloidal particles of silver and other metals [2].

2. Results and Discussion

In our previous paper [3] we have presented the investigation technique for the problem of atomic radiation in the vicinity of small bodies. The atomic radiation in the vicinity of a small metal sphere and of the apex of a metal needle supported by a plane (bicone) has also been considered. In this paper, we continue our studies of various bodies. We have found such bodies that produce the pronounced amplification effect of radiative processes.

The electromagnetic field in the space without charges and currents is described by the wave equation

$$\nabla\nabla\cdot\vec{A}-\nabla\times\nabla\times\vec{A}+k^2\vec{A}=0,\ k^2=\varepsilon\mu(\omega/c)^2 \tag{1}$$

with the subsidiary condition

$$\mathrm{div}\vec{A}=0. \tag{2}$$

A TM_0 wave is one of the eigenwaves of the vector wave equation. The solutions of Eq. (1) in the form of surface waves can be found using the general expression for the eigensolutions of Eq. (1) from [4]. These general formulas are in the form of the following functions:

$$\vec{M}_\lambda=\nabla\times\vec{a}\psi_\lambda,\ \vec{N}_\lambda=\frac{1}{\sqrt{k^2}}\nabla\times\vec{M}_\lambda,\ \vec{M}_\lambda=\frac{1}{\sqrt{k^2}}\nabla\times\vec{N}_\lambda. \tag{3}$$

The vector $\vec{a}$ in (3) is a fixed arbitrary unit vector whose choice depends on the selection of the frame of reference and ψ_λ is the eigensolution of the equation

$$\nabla^2\psi+k^2\psi=0. \tag{4}$$

In cylindrical coordinates (r,θ,z) the unit vector $\vec{i}_z$ of the z axis has to be chosen as $\vec{a}$.

The eigensolutions of Eq. (4) have the form

$$\psi_\lambda=\psi_{{}^{e}_{0}n\lambda}=Z_n(\lambda r)\begin{matrix}\cos\\ \sin\end{matrix}n\theta e^{ihz},\ k^2=h^2+\lambda^2. \tag{5}$$

On the left-hand side of (5), λ serves as the collective subscript and then denotes the transverse wave number. $Z_n(\lambda r)$ designates Bessel functions of the integer index. In the case of surface waves, the transverse wave number λ is the imaginary quantity (or complex quantity with a small real part). Therefore, the real quantity $\gamma=-i\lambda$ is conveniently entered instead of λ, while the Bessel functions of the pure imaginary argument $Z_n(\lambda r)=J_n(\lambda r)$, $Y_n(\lambda r)$, $H_n^{(1,2)}(\lambda r)$ are conveniently replaced with the modified Bessel functions $I_n(\gamma,r)$ and $K_n(\gamma,r)$. In what follows we need the formulas for the derivatives with respect to the argument for modified Bessel functions of zero index ($n=0$). They have the following form:

$$\frac{d}{dx}I_0(x)=I_1(x),\ \frac{d}{dx}K_0(x)=-K_1(x). \tag{6}$$

The description of the Bessel functions can be found in [5]. We obtain after the necessary rearrangements that the eigenwaves in cylindrical coordinates have the form

$$\begin{gathered}
\vec{M}_\lambda = \nabla \times \vec{i}_z \cdot \psi_{{}^{e}_{0}n\gamma} = \vec{m}_{{}^{e}_{0}n\gamma} e^{ihz}, \\
\vec{N}_\lambda = \frac{1}{\sqrt{k^2}} \nabla \times \vec{M}_\lambda = \vec{n}_{{}^{e}_{0}n\gamma} e^{ihz}, \\
\vec{m}_{{}^{e}_{0}n\gamma} = \mp \frac{n}{r} Z_n(\gamma r) \begin{matrix}\cos \\ \sin\end{matrix} n\theta \cdot \vec{i}_r - \frac{d}{dr} Z_n(\gamma r) \begin{matrix}\cos \\ \sin\end{matrix} n\theta \cdot \vec{i}_\theta, \\
\vec{n}_{{}^{e}_{0}n\gamma} = \frac{ih}{\sqrt{k^2}} \frac{d}{dr} Z_n(\gamma r) \begin{matrix}\cos \\ \sin\end{matrix} n\theta \cdot \vec{i}_r \mp \frac{ihn}{\sqrt{k^2} r} Z_n(\gamma r) \begin{matrix}\cos \\ \sin\end{matrix} n\theta \cdot \vec{i}_\theta - \frac{\gamma^2}{\sqrt{k^2}} Z_n(\gamma r) \begin{matrix}\cos \\ \sin\end{matrix} n\theta \cdot \vec{i}_z, \\
Z_n(\gamma r) = I_n(\gamma r),\ K_n(\gamma r), \\
\gamma = \sqrt{h^2 - k^2}.
\end{gathered} \tag{7}$$

Formulas (7) are written in an easy-to-use form for considering the surface waves. Since k^2 can be both positive and negative quantity (see below), we write $\sqrt{k^2}$. With $k^2 > 0$ we have $\sqrt{k^2} = k$, while for $k^2 < 0$, $\sqrt{k^2} = i|k|$.

We shall consider a metallic cylinder with radius a. The parameters of the medium and space inside the cylinder will be designated by the subscript $i = 1$, while those characterizing the space outside the cylinder will be supplied with the subscript $i = 2$. At $n = 0$ formulas (7) take the form

$$\begin{gathered}
\vec{M}_{0\gamma i} = \nabla \times \vec{i}_z \cdot \psi_{0\gamma i} = \vec{m}_{0\gamma i} e^{ihz},\ \vec{m}_{0\gamma i} = -\frac{d}{dr} Z_0(\gamma_i r) \cdot \vec{i}_\theta, \\
\vec{N}_{0\gamma i} = \frac{1}{\sqrt{k_i^2}} \nabla \times \vec{M}_{0\gamma i} = \vec{n}_{0\gamma i} e^{ihz},
\end{gathered} \tag{8}$$

$$[-3mm]\vec{n}_{0\gamma i} = \frac{ih}{\sqrt{k_i^2}} \frac{d}{dr} Z_0(\gamma_i r) \cdot \vec{i}_r - \frac{\gamma_i^2}{\sqrt{k_i^2}} Z_0(\gamma_i r) \cdot \vec{i}_z, \tag{9}$$

$$Z_0(\gamma_1 r) = I_0(\gamma_1 r),\ Z_0(\gamma_2 r) = K_0(\gamma_2 r),\ \gamma_i = \sqrt{h^2 - k_i^2}.$$

The parameters of the problem should be chosen, since further investigation will be carried out numerically. The cylinder will be considered to be made of silver. We take the permittivity ε_1 of silver at the wavelength $\lambda_0 = 633$ nm from [6] ($\varepsilon_1' + i\varepsilon'' = -19 + i0.53$). The space denoted by the subscript $i = 2$ will be considered as the free space, $\varepsilon_2 = 1$.

The admissible values h are determined from the characteristic equation. The latter arises when equating the tangential field components $\vec{E}$ and $\vec{H}$ at the interface of two media. The $\vec{E}$ and $\vec{H}$ fields can be obtained using the vector-potential $\vec{A}$. It can be chosen for the TM_0 wave in the following form:

$$\vec{A}_i = A_i \vec{N}_{0\gamma i} e^{-i\omega t},\ \vec{E}_i = -\frac{1}{c} \frac{\partial \vec{A}_i}{\partial t} = i \frac{\omega}{c} \vec{A}_i,\ \vec{H}_i = \frac{1}{\mu_i} \mathrm{rot} \vec{A}_i,\ i = 1, 2. \tag{10}$$

A standing wave on the cylinder section of the resonance length ($\lambda/2 = \pi/h$) is considered. The reference point for z is placed in the cylinder mid-length. Such a choice of the reference point for z along with the boundary conditions implies a distinct choice of the arguments φ_{A_1} and φ_{A_2} in the expressions

$A_1 = |A_1|e^{i\varphi_{A_1}}$ and $A_2 = |A_2|e^{i\varphi_{A_2}}$. We put $\varphi_{A_1} = \pi/2$ and $\varphi_{A_2} = 0$. By this is also meant (as will be seen from further consideration) that $\mathcal{E}_{iz}^{\rm st}(z = \pm\pi/2h) = 0$ and $\mathcal{E}_{ir}^{\rm st}(z = 0) = 0$. The vector-potentials of fields $\vec{\mathcal{A}}_i^{\rm st}$ in the corresponding spaces $i = 1$ and $i = 2$ written in the real-valued form can be presented as follows:

$$\begin{aligned}\vec{\mathcal{A}}_1^{st} &= 2|A_1|\left\{-\frac{h\gamma_1}{\kappa_1}I_1(\gamma_1 r)\sin hz\cdot\vec{i}_r - \frac{\gamma_1^2}{\kappa_1}I_0(\gamma_1 r)\cos hz\cdot\vec{i}_z\right\}\cos\omega t,\\ \vec{\mathcal{A}}_2^{st} &= 2|A_1|\mathcal{R}_A\left\{\frac{h\gamma_2}{k_2}K_1(\gamma_2 r)\sin hz\cdot\vec{i}_r - \frac{\gamma_2^2}{k_2}K_0(\gamma_2 r)\cos hz\cdot\vec{i}_z\right\}\cos\omega t.\end{aligned} \tag{10}$$

Formulas (10) are written with consideration for the boundary conditions that consist in the equality of the tangential field components $\vec{\mathcal{E}}_{1t}^{st} = \vec{\mathcal{E}}_{2t}^{st}$, $\vec{\mathcal{H}}_{1t}^{st} = \vec{\mathcal{H}}_{2t}^{st}$ at $r = a$ (a is the cylinder radius). The electric field written in the real-valued form ($\kappa_1^2 = -k_1^2$) is given by

$$\begin{aligned}\vec{\mathcal{E}}_1^{st} &= 2\frac{\omega}{c}|A_1|\left\{-\frac{h\gamma_1}{\kappa_1}I_1(\gamma_1 r)\sin hz\cdot\vec{i}_r - \frac{\gamma_1^2}{\kappa_1}I_0(\gamma_1 r)\cos hz\cdot\vec{i}_z\right\}\sin\omega t,\\ \vec{\mathcal{E}}_2^{st} &= 2\frac{\omega}{c}|A_1|\mathcal{R}_A\left\{\frac{h\gamma_2}{k_2}K_1(\gamma_2 r)\sin hz\cdot\vec{i}_r - \frac{\gamma_2^2}{k_2}K_0(\gamma_2 r)\cos hz\cdot\vec{i}_z\right\}\sin\omega t.\end{aligned} \tag{11}$$

The magnetic field (also in the real-valued form) is written as

$$\begin{aligned}\vec{\mathcal{H}}_1^{st} &= 2|A_1|\frac{\kappa_1\gamma_1}{\mu_1}I_1(\gamma_1 r)\cos hz\cos\omega t\cdot\vec{i}_\theta,\\ \vec{\mathcal{H}}_2^{st} &= 2|A_1|\mathcal{R}_A\frac{k_2\gamma_2}{\mu_2}K_1(\gamma_2 r)\cos hz\cos\omega t\cdot\vec{i}_\theta.\end{aligned} \tag{12}$$

One can see from (11) that the z-components of the electric fields on each side of the interface of two media are in phase, while their r-components are out of phase.

The ratio $|A_1|/|A_2|$ and the characteristic equation have been found equating the z-components of $\vec{\mathcal{E}}_1^{\rm st}$ and $\vec{\mathcal{E}}_2^{\rm st}$ and the θ-components of $\vec{\mathcal{H}}_1^{\rm st}$ and $\vec{\mathcal{H}}_2^{\rm st}$ with $r = a$. The amplitude ratio is

$$\mathcal{R}_A = \frac{|A_2|}{|A_1|} = \left(\frac{\gamma_1}{\gamma_2}\right)^2\frac{k_2}{\kappa_1}\frac{I_0(\gamma_1 a)}{K_0(\gamma_2 a)} = \frac{\mu_2}{\mu_1}\frac{\gamma_1}{\gamma_2}\frac{\kappa_1}{k_2}\frac{I_1(\gamma_1 a)}{K_1(\gamma_2 a)}\,. \tag{13}$$

The characteristic equation has the form

$$\frac{\gamma_1}{\gamma_2}\frac{I_0(\gamma_1 a)}{K_0(\gamma_2 a)} = \frac{\mu_2}{\mu_1}\frac{\kappa_1^2}{k_2^2}\frac{I_1(\gamma_1 a)}{K_1(\gamma_2 a)}\,. \tag{14}$$

The electric field pattern close to the surface of a nanocylinder with radius $a = a_0/k_0 = 10$ nm at wavelength $\lambda_0 = 633$ nm ($k_0 = 0.993\cdot 10^5$ cm^{-1}) is presented in Fig. 1. The parameter $\lambda = 2\pi/h$ appearing in the variable along the abscissa axis is the wavelength and h is the longitudinal wave number of the surface wave along the cylinder of radius a. In Fig. 2, the dependence of the longitudinal wave number h on the nanocylinder radius a is presented. The longitudinal wave number of a surface wave is always greater than ω/c. For the flat surface it is expressed as

$$h = \frac{\omega}{c}\left(\frac{\varepsilon}{\varepsilon+1}\right)^{1/2},$$

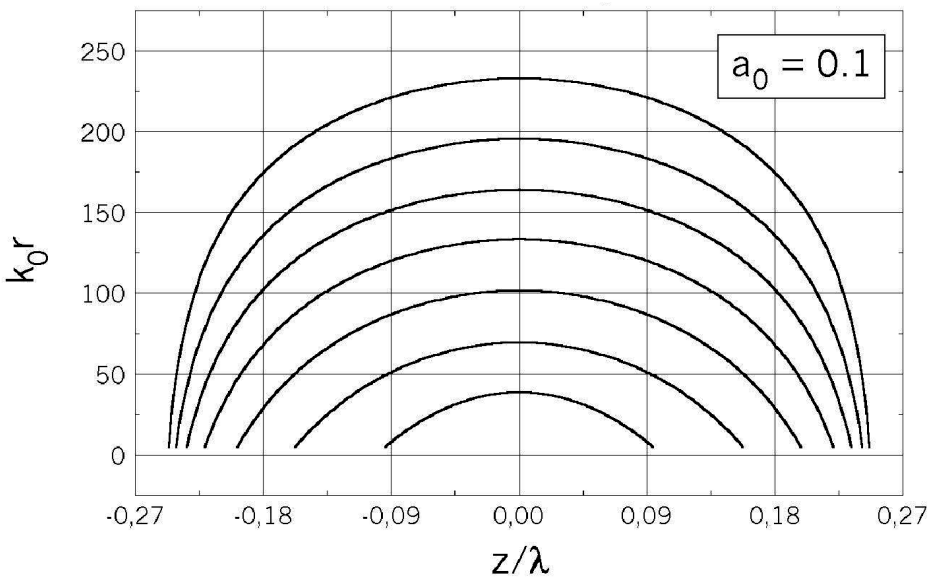

Fig. 1. An electric field pattern for a TM_0 wave close to the surface of a nanocylinder with radius $a = a_0/k_0 =$ 10 nm at wavelength $\lambda_0 = 633$ nm. The nanocylinder axis coincides with the abscissa axis.

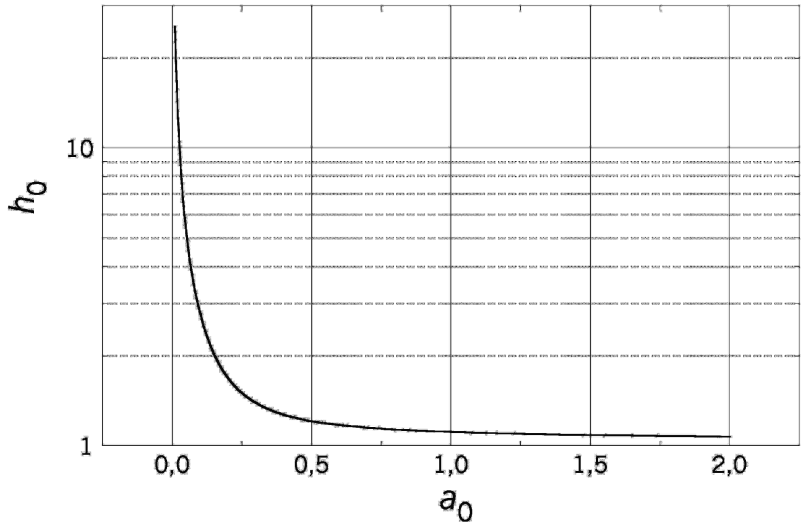

Fig. 2. Longitudinal wave number $h = h_0 k_0$ of the surface TM_0 wave on the silver cylinder of radius $a = a_0/k_0$ ($k_0 = 0.993 \cdot 10^5$ cm^{-1}).

where ε is the dielectric permittivity of the metal with $\varepsilon < 0$ and $|\varepsilon| \gg 1$. The value of h increases drastically at small a and, correspondingly, the TM_0 wave is significantly retarded.

Let us normalize the TM_0 wave according to the condition

$$\int\limits_V [\vec{\mathcal{A}}^{st}(\vec{r})]^2 d\tau = 4\pi c^2, \tag{15}$$

which is usually used to normalize the eigenoscillations of a field (field oscillators) in the quantum theory of radiation [7]. In Eq. (14), $\vec{\mathcal{A}}^{st}(\vec{r})$ is the coordinate part of the vector-potential of the eigenwave of Eq. (1). With such a normalization, the energy of the field oscillator is found to be a multiple of the integer number of quanta.

The specific feature of our consideration is that the integral in (15) contains two parts that describe the space $i = 1$ and the space $i = 2$. The form of the potential $\vec{\mathcal{A}}^{st}(\vec{r})$ is varied when passing from the inner space $i = 1$ to the outer one $i = 2$:

$$\int\limits_V [\vec{\mathcal{A}}^{st}(\vec{r})]^2 d\tau = \int\limits_{i=1} [\vec{\mathcal{A}}_1^{st}(\vec{r})]^2 d\tau + \int\limits_{i=2} [\vec{\mathcal{A}}_2^{st}(\vec{r})]^2 d\tau = \frac{4\pi^2 |A_1^2|}{k_0 h_0}(C_1 + C_2) = 4\pi c^2,$$

$$C_1 = \left(\frac{h_0}{\kappa_{01}}\right)^2 \mathrm{Int}I_1 + \left(\frac{\gamma_{01}}{\kappa_{01}}\right)^2 \mathrm{Int}I_0,$$

$$C_2 = \mathcal{R}_A^2 \left[\left(\frac{h_0}{k_{02}}\right)^2 \mathrm{Int}K_1 + \left(\frac{\gamma_{02}}{k_{02}}\right)^2 \mathrm{Int}K_0\right], \tag{16}$$

$$\mathrm{Int}I_n = \int\limits_0^{\gamma_{01} a_0} x[I_n(x)]^2 dx,\ \mathrm{Int}K_n = \int\limits_{\gamma_{02} a_0}^{\infty} x[K_n(x)]^2 dx,\ n = 0, 1,$$

$$k_0 = \omega/c,\ \kappa_{01}^2 = -k_{01}^2,\ h_0 = h/k_0,\ \gamma_{01} = \gamma_1/k_0,\ \gamma_{02} = \gamma_2/k_0,\ k_{02} = k_2/k_0.$$

The expression for the factor $|A_1|^2$ ($|A_1|$ is the normalizing constant for the field eigenmode) has the following form:

$$|A_1|^2 = \frac{c^2}{\pi} \frac{h_0 k_0}{C_1 + C_2}\ . \tag{17}$$

The dependence of $|A_1|$ on the cylinder radius a is presented in Fig. 3.

We now have all that is necessary to calculate the probability of spontaneous transition in an atom with photon emission into the surface TM_0 wave of a metallic nanocylinder. We shall follow the theory of spontaneous emission from [7] in our calculations.

The probability of the one-photon transition in a quantum system, which is formed by the atom and field, is described by the formula

$$w_{n|0} = \frac{2\pi}{\hbar} |H_{n|0}|^2 \rho_E, \tag{18}$$

where $H_{n|0}$ is the matrix element of the interaction operator H_{int} of the atom with the field and ρ_E is the number density of radiation oscillators in the energy scale. On optical frequencies, the interaction operator is described by the formula

$$H_{\mathrm{int}} = -\frac{e}{mc}(\vec{p}\vec{A}), \tag{19}$$

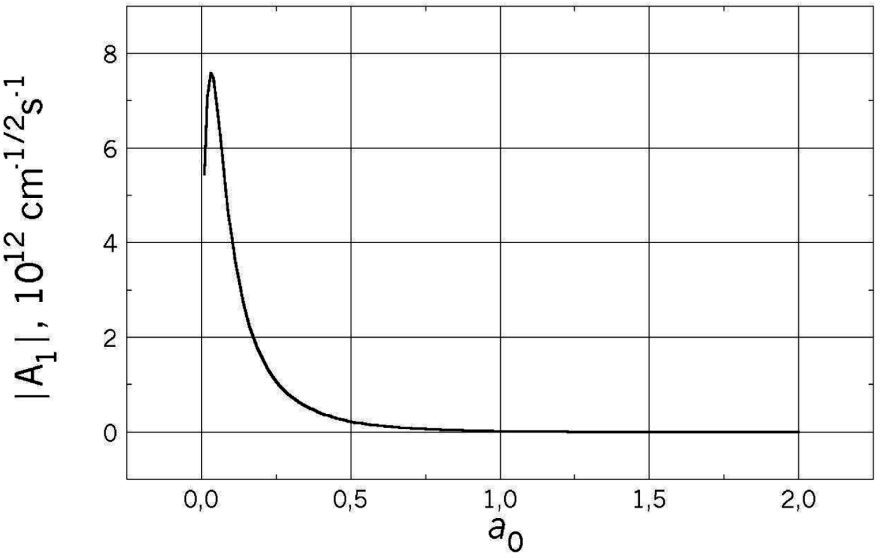

Fig. 3. Normalized constant $|A_1|$ for the vector-potential of the surface TM_0 wave on the cylinder of radius $a = a_0/k_0$ and length π/h.

where $\vec{p}$, e, and m are the mechanical momentum, charge, and mass of the atomic electron, respectively, while $\vec{A}$ is the vector-potential of the free radiation field. In our case, $\vec{A} \equiv \vec{A}(\vec{r}, t)$ is expressed as

$$\vec{A}(\vec{r}, t) = (a_\lambda + a_\lambda^{\dagger})\vec{A}_\lambda(\vec{r}) = (a_\lambda + a_\lambda^{\dagger})\vec{\mathcal{A}}_2^{st}(\vec{r}). \tag{20}$$

The matrix element $H_{n|0}$ is calculated by the following formula:

$$H_{n|0} \equiv H_{an'_\lambda=1|bn_\lambda=0} = -\frac{e}{mc}\int \psi_a^* \Psi_{n_\lambda}^* \left[\vec{p}(a_\lambda + a_\lambda^{\dagger})\vec{\mathcal{A}}_\lambda(\vec{r})\right] \psi_b \Psi_{n'_\lambda} d\tau. \tag{21}$$

Here, Ψ_{n_λ} and $\Psi_{n'_\lambda}$ are the eigenfunctions of the Hamiltonian of the free radiation field, ψ_a and ψ_b are the eigenfunctions of the free atom, a_λ and $a_\lambda^{\dagger}$ are the annihilation and creation operators of a photon, respectively, and $d\tau = d\tau_{ab} \cdot d\tau_U$ is the phase-space volume element of variables of the atom (τ_{ab}) and the field (τ_U). In the case of transition with photon emission, the contribution to the $H_{n|0}$ is provided only by the integral $\int \Psi_{n_\lambda}^* a_\lambda^{\dagger} \Psi_{n'_\lambda} d\tau_U$. This integral is equal to

$$a_{n_\lambda+1|n_\lambda}^{\dagger} = \sqrt{\frac{\hbar}{2\omega_\lambda}(n_\lambda + 1)}.$$

For spontaneous radiation, $n_\lambda = 0$.

We have to calculate the integral over the atomic coordinates τ_{ab} in (20). In what follows we shall restrict our consideration to the assumption that $\vec{\mathcal{A}}_2^{st}(\vec{r})$ varies only slightly in the space portion where ψ_a and ψ_b are different from zero. In this case, we can remove the factor $\vec{\mathcal{A}}_2^{st}(\vec{r})$ out of the integral sign. This undoubtedly restricts the generality of consideration. Recall that the standing wave is considered

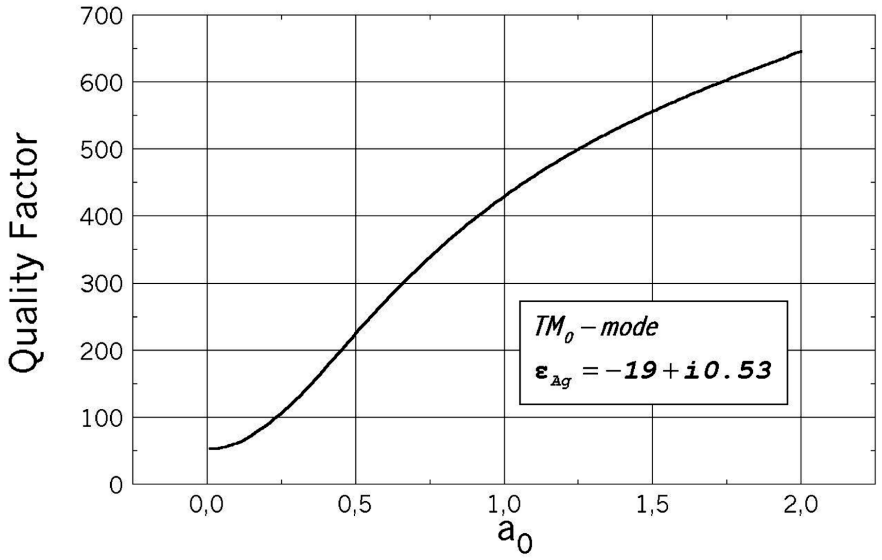

Fig. 4. Q-factor of a standing surface TM_0 wave on a silver cylinder of radius $a = a_0/k_0$ and length π/h.

on a section of the nanocylinder of length π/h. The vector-potential of a TM_0 mode has two components, $\vec{\mathcal{A}}^{st}_{2r}(\vec{r})$ and $\vec{\mathcal{A}}^{st}_{2z}(\vec{r})$. The product $\vec{p}\vec{\mathcal{A}}^{st}_{2}$ peaks at $z = \pm\pi/(2h)$ and $z = 0$. In the first case, the dipole should be oriented along (towards) $\vec{i}_r$, while in the second case it is aligned along $\vec{i}_z$.

We replace the integral $\int \psi^*_a|\vec{p}|\psi_b d\tau_{ab}$ with the value $-i\omega m x_{ab}$, where x_{ab} is the matrix element of the x coordinate operator of an electron in the oscillating external field. We obtain as a result the following expressions for the square of the modulus of the matrix element $|H_{an'_\lambda=1|bn_\lambda=0}|^2$:

$$|H_{an'_\lambda=1|bn_\lambda=0}|^2 = \frac{2\hbar\omega^3 e^2}{c^4}|A_1|^2\mathcal{R}^2_A|x_{ab}|^2\left(\frac{h_0\gamma_{02}}{k_{02}}\right)^2 K^2_1(\gamma_{02}a_0),$$
$$|H_{an'_\lambda=1|bn_\lambda=0}|^2 = \frac{2\hbar\omega^3 e^2}{c^4}|A_1|^2\mathcal{R}^2_A|x_{ab}|^2\left(\frac{\gamma^2_{02}}{k_{02}}\right)^2 K^2_0(\gamma_{02}a_0). \qquad (22)$$

These expressions were obtained for the first and second cases, respectively (we set $r = a$).

We seek the value of ρ_E, i.e., the number density of field oscillators in the energy scale. In this case, we follow the recommendations from [8]. They imply that $\rho_E = 1/(\hbar\omega/Q)$ for a resonator, which supports only a single mode. The parameter Q is the resonator Q-factor. So far it has been assumed that h is the real quantity. We intend now to consider the imaginary part of h. The dependence of the ratio $Q = \mathrm{Re}h/\mathrm{Im}h$ on a is shown in Fig. 4.

We are capable now of calculating the probability of spontaneous transition. We shall perform calculations for the first case:

$$w^{(TM_0)}_{an'_\lambda=1|bn_\lambda=0} = F_1 \cdot F_2,$$
$$F_1 = \frac{4}{3}\frac{e^2\omega^3}{\hbar c^3}|x_{ab}|^2,\ F_2 = \frac{3h_0}{C_1 + C_2}\mathcal{R}^2_A\left(\frac{h_0\gamma_{02}}{k_{02}}\right)^2 K^2_1(\gamma_{02}a_0)\frac{\mathrm{Re}h}{\mathrm{Im}h}\ . \qquad (23)$$

The factor F_1 coincides exactly with the expression for the probability of spontaneous emission of a photon in the free space. The factor F_2 shows the changes that occur in the nanocylinder in space.

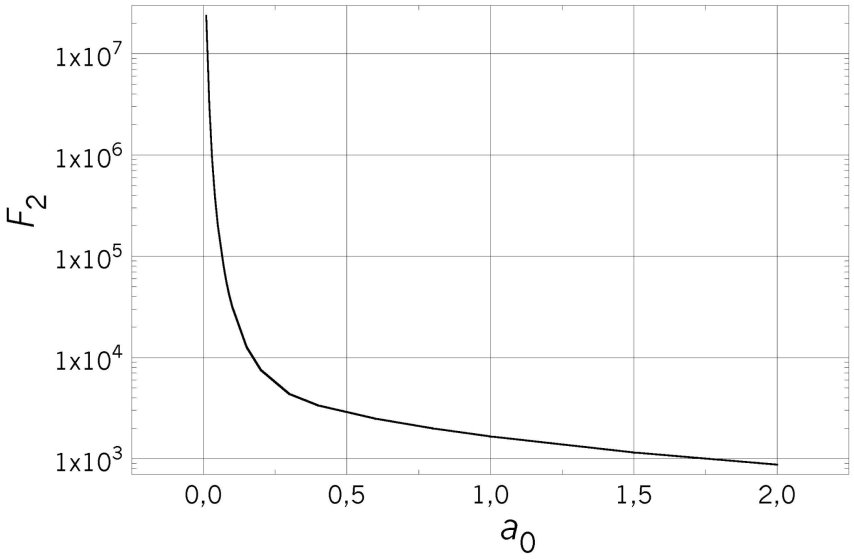

Fig. 5. Factor F_2 showing the factor of increase of $w_{n|0}$ for an atom that emits into the surface TM_0 wave of a cylinder of radius $a = a_0/k_0$.

Figure 5 shows the dependence of F_2 on the nanocylinder radius a. Note that we are dealing with dipole allowed transition rather than with forbidden (in the dipole approximation) magnetic-dipole or quadrupole transitions. With $a_0 = 0.01$ (the cylinder diameter is ~ 2 nm) the probability $w_{n|0}$ increases by more than $\sim 10^7$ times. This means that the dipole transition in these conditions is accomplished for the time 10^{-15} s. In this case, the atom emits femtosecond pulses of virtually white light.

The nanocylinder section having oscillating charges of opposite sign at its ends emits into free space. An infinite cylinder with a surface TM_0 wave does not emit since constructive interference is impossible for sources arranged so densely that the distance between them is less than the wavelength in free space.

We have to know the value of the induced dipole moment to find the radiating power. This value can be obtained by summing up the induced polarization $\vec{\mathcal{P}}_1^{st}$ in the nanocylinder volume. According to the definition of the polarization [4] we have

$$\vec{\mathcal{P}}_1^{st} = \frac{\varepsilon_1 - 1}{4\pi} \vec{\mathcal{E}}_1^{st}(\vec{r}). \tag{24}$$

We obtain the total dipole moment $\vec{d}$ of the nanocylinder by integrating the z-component of the polarization $\vec{\mathcal{P}}_1^{st}$ with respect to r and z. The value obtained should be additionally multiplied by $(\hbar/2\omega)^{1/2}$ to take into account the normalization of a TM_0 mode of the field:

$$\vec{d} = (\hbar/2\omega)^{1/2} \int\limits_{-\pi/(2h)}^{\pi/(2h)} dz \int\limits_0^a \vec{\mathcal{P}}_{1z}^{st} 2\pi r dr. \tag{25}$$

The $\vec{\mathcal{P}}_{1r}^{st}$ component does not produce any contribution to $\vec{d}$.

We calculate the mean radiating power P by the formula for an elementary oscillating dipole [4] (d_0

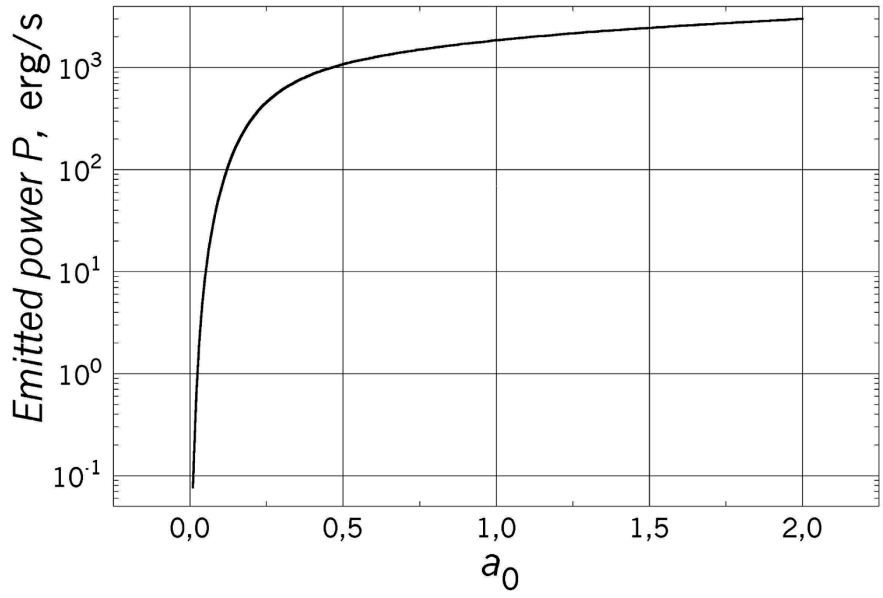

Fig. 6. Power emitted by a cylinder section of length π/h, on which a surface TM_0 wave is excited.

is the amplitude of the dipole vibrations)

$$P = (1/3)cd_0^2k_0^4. \tag{26}$$

In Fig. 6, the dependence of P on the cylinder radius $a = a_0/k_0$ is shown. The curve was calculated without regard for the radiation losses in the resonator Q-factor.

The formulas obtained are also applicable to the Raman scattering process of a photon [6] provided that the matrix element in formula (18) is replaced by the so-called composite matrix element

$$H_{n|0} \to K_{n|0} = \sum_{n'} \frac{H_{n|n'}H_{n|0}}{E_0 - E_{n'}} \,. \tag{27}$$

Since the Raman scattering is the two-photon process, the effect of increasing the field strength will enter into the transition probability to the fourth power rather than to the second one.

3. Conclusions

To summarize, an excited atom (molecule) in the vicinity of a linear aggregate of metallic nanoparticles was shown to emit spontaneously into a surface TM_0 wave of the aggregate. The emission rate exceeds that of the spontaneous emission of an atom in free space by many (~ 7) orders of magnitude. The surface TM_0 wave of an aggregate of finite length emits effectively into outer space as distinct from that of a cylinder or an infinitely long plane. Because of this, the enhancement effect for the atomic transition becomes the radiative one. This effect is distinguished from the process described in [9] where the atomic excitation is transferred to the nonradiating surface wave. We believe that the calculations performed explain well the effect of the pronounced increase in the Raman intensity (SERS effect) in the experiments described in [2].

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