

Three-frequency thermal light scattering in electrolyte solutions

N.F.Bunkin, V.N.Strel'tsov

Abstract. Frequency-shifted scattering of a monochromatic electromagnetic wave is considered in the electrolyte solution upon intermediate absorption (emission) of a quantum of a longitudinal fluctuation thermal field. The spectrum of scattered emission is obtained depending on the plasma parameters of the medium.

Keywords: thermal scattering, electrolyte solutions, Rayleigh scattering.

The study of physical mechanisms of formation of the Rayleigh scattering line wing has remained a classical problem of molecular optics for several decades. Even the compilation of a bibliography on this subject is not a simple problem. The theoretical and experimental aspects of this problem are discussed in detail in papers [1–5].

In recent papers [6, 7] of one of the authors of this work, a new noise mechanism of scattering was proposed and studied. The mechanism is based on the nonlinear multiphoton interaction of the electromagnetic field of an incident wave with the fluctuation thermal longitudinal and transverse components of the field generated in an ion subsystem. The parameters of the field of scattered radiation are determined by the plasma parameters of the ion component and by the spatial symmetry of the system.

All the fourth-order nonlinear optical susceptibilities of usual isotropic media vanish in the dipole approximation. For this reason, the fluctuation part of the scattering tensor appears in the lowest order when the four-photon interaction of the incident, scattered, and thermal fields is taken into account in the Lagrangian of the system, which corresponds, in the case of small frequency shifts, to the Kerr (in the thermal field) nonlinearity in the system. This physical situation was considered in papers [6, 7].

In this paper, we study scattering of a plane monochromatic wave in the electrolyte solution taking into account the quadrupole cubic interaction of the incident and scattered fields with the fluctuation thermal field of a sample, which results in real or virtual Raman transitions in a molecular system (Fig. 1).

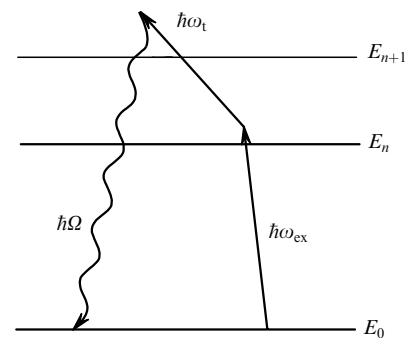


Figure 1. Three-photon up-conversion scattering (ω_{ex} is the incident-wave frequency, ω_t is the longitudinal thermal-field frequency, and Ω is scattered photon frequency).

Let us first determine the effective dipole moment corresponding to the third-order tensor of quadrupole scattering for an isolated molecule with a set of eigenstates $|n\rangle$ with energies E_n . We will consider only the longitudinal component of the thermal field, which is described by a random scalar potential $\varphi_t(\mathbf{r})$ in the Coulomb gauge used below. Under ordinary conditions, the correlation radius of the potential φ_t of the thermal field exceeds the size of scattering molecules, and the interaction of the thermal field with molecules can be treated in the dipole approximation.

In the nonrelativistic limit, the interaction of a scatterer with all the fields under study is described by the Lagrangian

$$L_{\text{int}} = - \sum_{\alpha} \frac{q_{\alpha} \mathbf{r}_{\alpha}}{c} [\mathbf{A}_{\text{ex}}(\mathbf{r}_{\alpha}) + \hat{\mathbf{A}}_{\text{qu}}(\mathbf{r}_{\alpha})] - \mathbf{d} \mathbf{E}_t, \quad (1)$$

where \mathbf{d} is the total dipole moment of a scattering molecule; \mathbf{r}_{α} are radius vectors of charges q_{α} in the molecule; α is the index of summation over all charges of a scattering molecule; $\mathbf{A}_{\text{ex}}(\mathbf{r}_{\alpha})$, $\hat{\mathbf{A}}_{\text{qu}}(\mathbf{r}_{\alpha})$ are the vector potentials of the incident plane wave and quantised transverse scattered field, respectively, taken at the positions of the corresponding charges; and $E_t = -\partial\varphi_t/\partial r$. Without changing the dynamics of the system, we can add the total derivative

$$\frac{d}{dt} \sum_{\alpha} \frac{q_{\alpha} \mathbf{r}_{\alpha}}{c} (\mathbf{A}_{\text{ex}} + \hat{\mathbf{A}}_{\text{qu}}).$$

to Lagrangian (1).

Then, Lagrangian (1) takes the form

$$L_{\text{int}} = \sum_{\alpha} \frac{q_{\alpha} \mathbf{r}_{\alpha}}{c} \left(\frac{d\mathbf{A}_{\text{ex}}}{dt} + \frac{d\hat{\mathbf{A}}_{\text{qu}}}{dt} \right) - \mathbf{d} \mathbf{E}_t.$$

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Received 3 July 2001

Kvantovaya Elektronika 32 (2) 135–139 (2002)

Translated by M.N.Sapozhnikov

The total derivative of the vector potential \mathbf{A} can be written in the form

$$\frac{d\mathbf{A}}{dt} = \frac{\partial\mathbf{A}}{\partial t} + \frac{\partial\mathbf{A}}{\partial\mathbf{r}_\alpha} \frac{\partial\mathbf{r}_\alpha}{\partial t}.$$

For $r = 0$, the first term in this expression describes the dipole interaction of a scatterer with the field, while the second term describes the quadrupole interaction. Below, we will consider the quadrupole interaction of a scatterer with the incident-radiation field \mathbf{A}_{ex} taking into account only the second term in the derivative $d\mathbf{A}/dt$.

Note that at a sufficiently high concentration of ions, the Debye shielding distance r_D determining the correlation radius for the longitudinal field E_l can be comparable to the wavelength c/ω_{ex} of the scattered optical field: $(\omega_{\text{ex}}/c) \times r_D \sim 1$. Under such conditions, the quadrupole term should be taken into account in the interaction of the molecular system with the fluctuation field. Finally, we have

$$L_{\text{int}} = -d_i E_{\text{qui}} - d_i E_{li} + \frac{1}{\omega_{\text{ex}} q_\alpha} d_i E_{\text{ex}i} k_j \dot{d}_{j\alpha}.$$

Here, \mathbf{k} is the wave vector of the incident wave; $\mathbf{k} \mathbf{E}_{\text{ex}} = 0$; i and j are the subscripts corresponding to the components in Cartesian coordinates (summation is performed over repeated subscripts). To avoid cumbersome expressions, we will assume that the system (1) contains one light (compared to others) charged particle, which makes a certain contribution to the electromagnetic interaction, and omit the number α of this charge. The return to the general case is obvious.

Consider the transition matrix element

$$M = \langle (\Omega, \lambda), 0 | U(\infty) | 0, 0 \rangle.$$

The initial state corresponds to a vacuum state of the quantised field and to the ground state of the scatterer. The final state corresponds to a scattered photon with the frequency Ω and polarisation λ ; $U(t)$ is the time evolution operator.

The required matrix element appears in the third order of smallness in the interaction potential

$$M_3 = \frac{i}{3! \omega_{\text{ex}} q_\alpha \hbar^3} \langle (\Omega, \lambda), 0 | \int \int \hat{P} [d_\alpha(t_1) E_{\text{qu}\alpha}(\Omega) e^{i\Omega t_1} \times d_j(t_2) E_{vj}(t_2) d_l(t_3) E_{\text{ex}l} e^{-i\omega_{\text{ex}} t_3} k_p \dot{d}_p(t_3)] dt_1 dt_2 dt_3 | 0, 0 \rangle. \quad (2)$$

Here, \hat{P} is the time-ordered operator in the interaction representation. The subscript α denotes now the components of vectors \mathbf{d} , \mathbf{E}_{qu} , the subscript l – the components of vectors \mathbf{d} , \mathbf{E}_{ex} , the subscript j – the components of vectors \mathbf{d} , \mathbf{E}_l , and the subscript p – the components of vectors \mathbf{k} , $\dot{\mathbf{d}}$.

Let us introduce the notation

$$\begin{aligned} & \langle r | d_l(t) E_{\text{ex}l} \exp(-i\omega_{\text{ex}} t) k_p \dot{d}_p(t) | n \rangle \\ &= \exp[-it(\omega_n - \omega_r + \omega_{\text{ex}})] k_p E_{\text{ex}l} \kappa_{pl}^{nr}, \end{aligned} \quad (3)$$

for the quadrupole-transition matrix element, where

$$\kappa_{pl}^{nr} = \sum_s i(\omega_s - \omega_n) d_p^{ns} d_l^{sr};$$

$d^{ns} = \langle n | \mathbf{d} | s \rangle$; ω_n is the eigenfrequency of the state $|n\rangle$. By expanding $\mathbf{E}_l(t)$ into the Fourier integral:

$$\mathbf{E}_l(t) = \int \mathbf{E}_l(\omega) e^{-i\omega t} d\omega, \quad (4)$$

substituting (3) and (4) into (2), and introducing in a standard way the intermediate unit operators $I = \sum |n\rangle \langle n|$, we find, after the integration,

$$\begin{aligned} M_3 &= -\frac{i}{3\hbar^3 \omega_{\text{ex}} q} E_{\text{qu}\alpha} E_{\text{ex}l} k_p E_{lj} (\Omega - \omega_{\text{ex}}) \\ &\times \sum_{n,r} \left[\frac{\kappa_{pl}^{on} d_j^{nr} d_\alpha^{ro}}{(\Omega - \omega_r + \omega_o)(\omega_{\text{ex}} + \omega_o - \omega_n)} \right. \\ &+ \frac{\kappa_{pl}^{on} d_\alpha^{nr} d_j^{ro}}{(\omega_{\text{ex}} + \omega_o - \omega_n)(\omega_{\text{ex}} - \Omega - \omega_r)} \\ &+ \frac{d_j^{on} \kappa_{pl}^{nr} d_\alpha^{ro}}{(\Omega - \omega_r)(\Omega - \omega_{\text{ex}} + \omega_o - \omega_n)} \\ &+ \frac{d_\alpha^{on} \kappa_{pl}^{nr} d_j^{ro}}{(\omega_o - \omega_n - \Omega)(\omega_{\text{ex}} - \Omega + \omega_o - \omega_r)} \\ &+ \frac{d_\alpha^{on} d_j^{nr} \kappa_{pl}^{ro}}{(\omega_o - \omega_n - \Omega)(\omega_o - \omega_r - \omega_{\text{ex}})} \\ &\left. + \frac{d_j^{on} d_\alpha^{nr} \kappa_{pl}^{ro}}{(\omega_o - \omega_n + \Omega - \omega_{\text{ex}})(\omega_o - \omega_r - \omega_{\text{ex}})} \right]. \end{aligned} \quad (5)$$

When resonance transitions exist in the system, we should introduce to the corresponding vanishing denominators the imaginary terms describing the decay of excited resonance levels. The matrix element (5) can be related to the effective dipole moment $\mathbf{d}(t)$ of the scattering system by considering the first-order transition with the Hamiltonian $H_{\text{eff}} = -\mathbf{d}(t) \mathbf{E}_{\text{qu}}(t)$.

Let us now calculate the intensity I of radiation scattered at the frequency Ω . The spectral component $I(\Omega)$ is determined by the expression

$$I(\Omega) \sim \int \mathbf{E}_l(t + t') \mathbf{E}_l^*(t) e^{i\Omega t} dt.$$

The random function \mathbf{E}_l is stationary, and the spectral components $\mathbf{E}_l(\omega)$ satisfy the equality $\langle E_{ij}(\Omega - \omega_{\text{ex}}, \mathbf{r}) \times E_{ij}^*(\omega' - \omega_{\text{ex}}, \mathbf{r}') \rangle = \psi_{ij}(\mathbf{r}, \mathbf{r}', \Omega) \delta(\Omega - \omega')$. Thus, $\langle I(\Omega) \rangle$ is determined by the correlator at the frequency $\Omega - \omega_{\text{ex}}$.

The Poynting vector \mathbf{W} of the scattered field in the wave region in the direction of the unit vector \mathbf{w} can be represented in the form

$$\mathbf{W} = \frac{c}{8\pi} [\mathbf{E} \mathbf{H}^*] = \frac{c}{8\pi} \mathbf{H}^2 \mathbf{w}.$$

In the Fraunhofer zone, we have

$$\begin{aligned} \mathbf{H}^2(\Omega) &= (\Omega/c)^2 (1/16\pi R^2) \int (\mathbf{d}(\Omega, \mathbf{r}) \mathbf{w}) (\mathbf{d}^*(\Omega, \mathbf{r}') \mathbf{w}) \\ &\times \exp[(-i\Omega/c)(\mathbf{r} - \mathbf{r}') \mathbf{w}] d\mathbf{r} d\mathbf{r}', \end{aligned}$$

where integration is performed over the scattering volume; R is the distance from the scatterer to the observation point. By neglecting edge effects in the case of sufficiently

large scattering volumes, it is convenient to use the Fourier representation

$$\mathbf{E}_t(\omega, \mathbf{r}) = \int \mathbf{E}_t(\omega, \mathbf{p}) e^{-i\mathbf{p}\mathbf{r}} d\mathbf{p}. \quad (6)$$

for the function $E_t(\omega)$. The fluctuation field $\mathbf{E}_t(\mathbf{r})$ can be considered homogeneous with good accuracy, and we have for the correlation function of Fourier transforms $\mathbf{E}_t(\mathbf{p})$

$$\langle \mathbf{E}_{ti}(\mathbf{p}, \omega) \mathbf{E}_{tj}(\mathbf{p}', \omega) \rangle = f_{ij}(\mathbf{p}, \omega) \delta(\mathbf{p} - \mathbf{p}').$$

Therefore, we obtain in the general case the density of the electromagnetic energy

$$\begin{aligned} \langle H^2 \rangle &= \left(\frac{\Omega^2}{4c\pi R} \right)^2 \iint e_{\beta\alpha\gamma} e_{\beta\tau\delta} n_\gamma n_\delta \chi_{\alpha ij} \chi_{lmqr}^* E_{\text{ex}j} E_{\text{ex}q} \\ &\times k_l k_r f_{im}(\Omega - \omega_{\text{ex}}, \mathbf{p}) \exp[i(\mathbf{k} - \mathbf{p} - (\Omega/c)\mathbf{n})\mathbf{r}] \\ &\times \exp[-i(\mathbf{k} - \mathbf{p} - (\Omega/c)\mathbf{n})\mathbf{r}'] \delta(\mathbf{p} - \mathbf{p}') d\mathbf{r} d\mathbf{r}' d\mathbf{p} d\mathbf{p}'. \quad (7) \end{aligned}$$

Here, χ are the nonlinear susceptibility tensors determining the dipole moment of the unit volume; e_{ijn} are the Levi-Civita symbols. In deriving (7), we neglected corrections for the acting field. We also assumed that the scattering medium is transparent for the incident light. The latter condition corresponds to the inequality $\omega_{\text{ex}} \gg \omega_p$, where ω_p is the plasma ion frequency. In weak electrolytes under usual conditions, this inequality is satisfied for the optical range with a great margin.

In an isotropic medium, the tensor of fourth rank has three independent base elements [8] $\chi_{xxxx}, \chi_{xyxy}, \chi_{xyyx}$. Other nondiagonal elements are obtained by a replacement of the corresponding coinciding subscripts in pairs. Diagonal elements are equal to the sum of the above elements.

We assume that the z axis of the chosen coordinate system coincides with the direction of the wave vector \mathbf{k} of the incident wave and the x axis is directed along the vector \mathbf{E}_{ex} . Then, the dipole moment \mathbf{d} contains only the components d_x, d_z , which are determined by the components E_{tz} and E_{tx} , respectively, of the thermal field. Consider radiation scattered in the direction of the incident wave. Such a configuration corresponds to the linear polarisation of radiation with the vector $\mathbf{H} = \{0, H, 0\}$.

For definiteness, we will perform calculations for a scattering sphere of radius ρ . After integration of (7) over spatial coordinates \mathbf{r}, \mathbf{r}' and \mathbf{p}' , we obtain

$$\begin{aligned} \langle H^2 \rangle &= \frac{\Omega^4}{c^2 R^2} |\chi_{xzxz}|^2 |E_{\text{ex}}|^2 k^2 \int f_{zz}(\Omega - \omega_{\text{ex}}, \mathbf{p}) \\ &\times \left[\frac{\sin(|\mathbf{k} - \mathbf{k}_p - \mathbf{p}|\rho)}{|\mathbf{k} - \mathbf{k}_p - \mathbf{p}|} - \rho \cos(|\mathbf{k} - \mathbf{k}_p - \mathbf{p}|\rho) \right]^2 d\mathbf{p} \\ &\times |\mathbf{k} - \mathbf{k}_p - \mathbf{p}|^{-4}. \quad (8) \end{aligned}$$

Here, $\mathbf{k}_p = (\Omega/c)\mathbf{w}$. One can easily see that the integrand in (8) has a removable singularity at $\mathbf{p} = \mathbf{k} - \mathbf{k}_p$.

The correlation function f_{zz} for the strength of the longitudinal component of an electric field has the form (see, for example, [9])

$$f_{zz}(\Omega - \omega_{\text{ex}}, \mathbf{p}) = i \frac{\theta(\Omega - \omega_{\text{ex}}, T)}{2\pi(\Omega - \omega_{\text{ex}})} \frac{1}{2\pi^2} \frac{p_z^2}{p^2} \left(\frac{1}{\varepsilon_L^*} - \frac{1}{\varepsilon_L} \right),$$

where

$$\theta(\omega, T) = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1}$$

is the mean energy of a Boson oscillator; T is temperature; ε_L is the longitudinal component of the permittivity of the scattering medium; $\mathbf{D}\mathbf{p} = \varepsilon_L \mathbf{E}\mathbf{p}$; \mathbf{D} is the electric induction vector.

We will employ, as usual [9], the hydrodynamic model for describing the ion component of the electrolyte solution. Such models, corresponding to the zero- and second-order moments of the velocity distribution function, adequately describe collective excitations (with wavelengths exceeding the Debye shielding distance) in systems of charged particles. Note that, under usual conditions, thermal excitations at the frequencies corresponding to such wavelengths, correspond to normal temperatures. We will further assume that the charged component contains light and heavy ions (as, for example, ions H^+ and OH^- in water). It is obvious that in this case the excitation in the system will be determined by the dynamics of light particles against the neutralising background of immobile heavy ions and neutral molecules of the solvent.

By specifying the deviation N of the density of light ions from the equilibrium density N_0 in terms of the gas-kinetic pressure $p_g = (N_0 + N)k_B T$, the coupled system of equations for fields and currents can be written in the usual form

$$N_0 m \frac{\partial \mathbf{v}}{\partial t} = -N_0 m \mathbf{v} + N_0 e \mathbf{E} - \nabla p_g,$$

$$\frac{\partial n}{\partial t} + N_0 \nabla \mathbf{v} = 0,$$

$$\text{rot } \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi \mathbf{j}}{c}, \quad (9)$$

$$\text{rot } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t},$$

$$\mathbf{j} = N_0 e \mathbf{v}.$$

Here, m is the mass of a light ion (which is assumed singly charged); $v = 1/\tau$; τ is the characteristic relaxation time of the distribution function; and the frequency ν determines the mobility $\mu = mv$ of ions. We can pass to the diffusion model by assuming formally in (9) that $\omega/\nu \ll 1$ and restricting ourselves to the zero-order terms in this parameter.

By performing the Fourier transform in (9) over spatial and time variables and solving the obtained algebraic equations for $\mathbf{j}(\omega, \mathbf{p})$, taking into account the definition of ε_L , we find

$$\varepsilon_L(\omega, \mathbf{p}) = 1 - \frac{\omega_p^2}{\omega^2} \frac{1}{1 + i\nu/\omega - Dp^2},$$

where $D = k_B T/m\omega^2$ determines the spatial dispersion.

By introducing a new variable $\mathbf{A} = \mathbf{p} + \mathbf{k}_p - \mathbf{k}$, passing to a spherical coordinate system with a polar axis coinciding with the z axis, integrating over the azimuthal angle φ , and substituting the obtained expression into the correlation function f_{zz} , we rewrite equation (8) in the form

$$\begin{aligned} \langle H^2 \rangle &= -2\pi A \int_{-1}^1 dx \int_0^\infty \frac{(Ax - \Delta k)^2}{A^2 + \Delta k^2 - 2A\Delta kx} \\ &\times \left\{ \frac{1 - \cos(2A\rho)}{2A^2} + \frac{1}{2}\rho^2[1 + \cos(2A\rho)] - \frac{\rho}{A}\sin(2A\rho) \right\} \\ &\times \left[\frac{1}{\Delta\omega^2 - \omega_p^2 - \alpha(A^2 + \Delta k^2 - 2A\Delta kx) + i\nu\Delta\omega} + \text{c.c.} \right] \frac{dA}{A^2}, \end{aligned} \quad (10)$$

where $A \sim (1/2)v\Delta\omega$; $\Delta k = \Delta\omega/c$; $\Delta\omega = \Omega - \omega_{\text{er}}$ is the detuning from the incident-wave frequency; $\alpha = k_B T/m$ is the square of the thermal velocity; $x = \cos\theta$; θ is the polar angle. The integral in (10) can be represented as a sum of two integrals according to the terms in the second factor in the integrand. Each of these integrals diverges at $A = 0$ [the point $A = 0$ in expression (10) is a removable singularity]. To overcome this difficulty, we can make the change of variables $A^2 \rightarrow A^2 + \varepsilon^2$ and pass to the limit $\varepsilon \rightarrow 0$ in final expressions. In this case, the contributions from poles $A = \pm i\varepsilon$ will be mutually compensated.

One can easily verify that the ordinary poles of the integrand in (10) corresponding to the roots $A_{1,2} = \Delta k[x \pm (x^2 - 1)^{1/2}]$ of the equation $A^2 - 2A\Delta kx + \Delta k^2 = 0$ make the contribution to the integral over x only in the region $x < 1$ [see below (11)]. Therefore, for frequency detunings $\Delta\omega\rho/c \gg 1$, which are of the main interest for real scattering macroscopic objects, the imaginary part of the coordinates of the poles will be $\sim \Delta k$, and oscillating terms in (10) can be neglected. Simultaneously, the condition $\rho^2 \gg A^{-2}$ will be fulfilled. In the above range of frequency detunings, the contribution from the ordinary poles to the required function $\langle H^2 \rangle$ has the form

$$\begin{aligned} \langle H^2 \rangle_1 &= \frac{4\pi^2 B \rho^2}{\Delta k[(\Delta\omega^2 - \omega_p^2)^2 + \nu^2 \Delta\omega^2]} \int_0^1 (1 - x^2)^{1/2} dx \\ &= \frac{\pi^3 B \rho^2}{\Delta k[(\Delta\omega^2 - \omega_p^2)^2 + \nu^2 \Delta\omega^2]}. \end{aligned} \quad (11)$$

For definiteness, the detunings $\Delta\omega$ in expression (11) are chosen positive $\Omega > \omega_{\text{ex}}$.

Consider now the contribution to the electromagnetic radiation from poles corresponding to the zeroes of the longitudinal component of the permittivity tensor of the medium. For $\Delta\omega > 0$, an ordinary pole at the point $1/\varepsilon_L$ lying in the upper half-plane of the complex plane A (recall that the subscript L corresponds in this case to the longitudinal component of the permittivity of the scattering medium) has the form

$$A_1 = \Delta kx + \left[\frac{1}{\alpha}(\Delta\omega^2 - \omega_p^2) - \Delta k^2(1 - x^2) + i \frac{\nu\Delta\omega}{\alpha} \right]^{1/2}.$$

Let us estimate the imaginary part of A_1 . For $\Delta\omega^2 - \omega_p^2 \gg \nu\Delta\omega$, we have $\text{Im} A_1 \sim \nu/\sqrt{\alpha}$. When $\Delta\omega \leq \omega_p$, we obtain $\text{Im} A_1 \sim (\nu\omega_p/\alpha)^{1/2}$. By repeating the previous reasoning, assuming that longitudinal thermal vibrations quite strongly decay over the characteristic size of the scattering volume, which is determined by the conditions

$$\rho \frac{\nu}{\sqrt{\alpha}} > 1, \quad \rho \left(\frac{\nu\omega_p}{\alpha} \right)^{1/2} > 1,$$

we can still neglect oscillating terms in (10). Note that these inequalities correspond obviously to the case when the correlation radius of the longitudinal thermal field is substantially lower than the scatterer size. The omitted oscillating terms determine, in the case of a weak decay, interference effects in the medium.

The thermal velocity of a hydrogen ion at normal temperatures is $\sqrt{\alpha} \sim 1.4 \times 10^5 \text{ cm s}^{-1}$, which is many orders of magnitude lower than the speed of light, and we have $\Delta\omega^2/\alpha \gg \Delta k^2$ for this ion. Away from the resonance, we have $(\Delta\omega^2 - \omega_p^2)/\alpha \gg \Delta k^2$, so that the term containing Δk^2 in the expression for A_1 under the root sign can be neglected. If $\nu c^2/\alpha > \omega_p$, the term with Δk^2 can be omitted near the resonance as well. We assume below that these conditions are fulfilled.

By choosing for the term $\sim 1/\varepsilon^*$ the integration contour passing in the lower half-plane A containing the pole $A_2 = A_1^*$, after calculation of residues and subsequent integration over x , we obtain finally

$$\langle H^2 \rangle_2 = \frac{\pi^2 B}{6\nu\Delta\omega} \frac{\rho^2 \sqrt{\alpha}}{\text{Re}[(\Delta\omega^2 - \omega_p^2) + i\nu\Delta\omega]^{3/2}}. \quad (12)$$

The ratio of contributions (12) and (11) to the total additive spectral emission line is

$$\frac{\langle H^2 \rangle_2}{\langle H^2 \rangle_1} \approx \frac{\{\alpha[(\Delta\omega^2 - \omega_p^2) + \nu\Delta\omega]\}^{1/2}}{6\pi c\nu}.$$

For small detunings and near the resonance, this ratio is $\sim (1/6\pi c)(\alpha\omega_p/\nu)^{1/2}$. Therefore, in the approximations used here, this ratio is smaller than unity, i.e., the contribution of $\langle H^2 \rangle_1$ dominates. The second contribution becomes comparable with the first one for $\Delta\omega \sim \nu c/\sqrt{\alpha}$. Under real conditions, $\langle H^2 \rangle_1$ covers virtually entire scattering spectrum.

It follows directly from the above discussion that the spectral distribution of scattered radiation does not depend on diffusion in the ion system, which determines the spatial dispersion of the thermal field. Note here that this is explained by the geometry of the process (scattered radiation is detected along the direction of propagation of the incident beam). For other observation angles corresponding to the contribution of $\langle H^2 \rangle_2$ comparable to that of $\langle H^2 \rangle_1$, the scattering spectrum can strongly depend on the rate of ion diffusion. The effect of thermal plasma oscillations on the shape of the scattering spectrum $I(\Delta\omega)$ (Fig. 2) strongly depends on the ratio of the plasma frequency ω_p to the width ν of the plasma oscillation line. When this line is broad ($\omega_p/\nu \leq 2$), the spectral density of scattered radiation monotonically decreases with increasing frequency shift $\Delta\omega$ of the scattered wave with respect to the incident wave. For sufficiently large detunings $\Delta\omega$, the intensity $I(\Delta\omega)$ of scattered radiation decreases as $\Delta\omega^{-5}$. In the case of a weak decay, the case $\omega_p/\nu > 2$ is realised, and the spectral curve $I(\Delta\omega)$ exhibits a minimum at the detuning

$$\Delta\omega_{\text{min}} = \left[\frac{3(2\omega_p^2 - \nu^2) - (16\omega_p^4 - 36\omega_p^2\nu^2 + 9\nu^4)^{1/2}}{10} \right]^{1/2},$$

and a maximum at the frequency

$$\Delta\omega_{\text{max}} = \left[\frac{3(2\omega_p^2 - \nu^2) + (16\omega_p^4 - 36\omega_p^2\nu^2 + 9\nu^4)^{1/2}}{10} \right]^{1/2}.$$

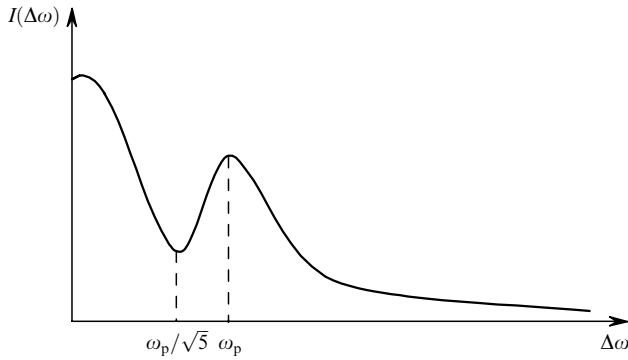


Figure 2. Spectral intensity of a scattered wave for $\omega_p/v > 2$.

As the ratio ω_p/v increases, the interval between frequencies $\Delta\omega_{\min}$ and $\Delta\omega_{\max}$ increases and the ratio of spectral intensities at these frequencies increases as well. When the plasma oscillation line is narrow ($\omega_p/v \gg 1$), the positions of the maximum and minimum of the spectral curve are determined by the expressions

$$\Delta\omega_{\min} \approx \omega_p/\sqrt{5}, \quad \Delta\omega_{\max} \approx \omega_p,$$

respectively, while the ratio of spectral intensities is $I(\omega_{\max})I^{-1}(\omega_{\min}) \sim \omega_p^2/3v^2$. Note that the absolute intensity of scattered radiation is determined by the cross section of the scatterer. In the diffusion model, the scattering spectrum has the shape $I(\Delta\omega) \sim [\Delta k(1 + \Delta\omega^2\tau_d^2)]^{-1}$, where $\tau_d = v/\omega_p^2$ is the time of dielectric relaxation in the medium. Therefore, the radiation intensity gradually decreases with increasing frequency shift. In this case, the width of the spectrum is $\sim 1/\tau_d$.

When the characteristic frequencies are close to the frequencies of resonance transitions in the scatterer, the scattering spectrum is determined by the one-photon absorption spectrum of the scatterer.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grants Nos 99-15-96023 and 01-02-17116).

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