

ROTATIONAL STRUCTURE OF HYPER-RAYLEIGH SCATTERING BY LINEAR MOLECULES

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Abstract. The effect of rotational motion of linear molecules on their hyper-Rayleigh scattering spectra is calculated from angular momentum theory. The expressions derived for the intensities of the hyper-Raman rotational lines are used to calculate the rotational structure of the hyper-Rayleigh line of gaseous CO.

1. Introduction

Recently, numerous papers on nonlinear light scattering have appeared. Kielich [1] and Li [2] predicted theoretically that second harmonic scattering should be exhibited by fluids consisting of molecules without a centre of symmetry; first observations of these effects by laser techniques are due to Terhune and co-workers [3].

In the elastic case, the scattered frequency is an exact multiple of the incident frequency. In the inelastic case, it is modulated by the eigen-frequencies of the micro-system. The two cases correspond to hyper-Rayleigh and hyper-Raman scattering, respectively. With molecules, the eigen-frequencies are defined essentially by the atomic vibrations. The quantum-mechanical basis of these new effects has been discussed by Kielich [4], and Cyvin *et al.* [5] have investigated the selection rules for vibrational hyper-Raman transitions.

Studies of linear light scattering have revealed the influence of molecular rotations on the band envelope of the scattered spectrum. The relevant theory discussing this was proposed by Placzek and Teller [6]; for a review of the experimental data, we refer to the monograph of Herzberg [7], and to the articles by Stoicheff [8] and Edwards [9]. Available measuring techniques permit the observation of rotational structure in nonlinear scattering and this has been confirmed by the results of Maker [10] for methane molecules, where the relevant theory is also presented.

In this paper, we calculate the rotational line intensities, in the approximation of hyperpolarizability theory, for molecules having the symmetry $C_{\infty v}$. The conditions for this approach have been discussed by Long and Stanton [11]. Numerical calculations of the intensities of the various lines in the pure rotational hyper-Raman have been made for the carbon monoxide molecule.

2. Elastic Second Harmonic Scattering by Linear Molecules

We consider a system of N noninteracting molecules, scattering light independently of one another. Let us first deal with elastic nonlinear scattering at the frequency 2ω , the

intensity of which is given by the following second-rank tensor [1, 4] (our calculations are performed in the system of Gauss' units):

$$I_{ij}^{2\omega} = \frac{N}{2} \frac{\pi (2\omega)^4}{c^5} \langle b_{ikm}^{2\omega} b_{jln}^{2\omega} \rangle I_{kl} I_{mn}, \quad (1)$$

where I_{kl} is the intensity tensor of incident light, and the symbol $\langle \rangle$ denotes classical, or quantal, averaging.

The third-rank tensor $b_{ikm}^{2\omega}$ defines that part of the second-order nonlinear molecular polarizability (i.e. the first order hyperpolarizability) which depends on the doubled frequency of the incident light wave [1]. In the ground state of the molecule, $b_{ikm}^{2\omega}$ is symmetric in the indices k and m , whereas in the absence of electronic dispersion and absorption it can be dealt with as totally symmetric [4].

The tensor $b_{ijk}^{2\omega}$, which is given in the laboratory coordinates X, Y, Z , denoted by Latin indices i, j, k, \dots , is now transformed to molecular coordinates 1, 2, 3, denoted by Greek indices $\alpha, \beta, \gamma, \dots$ according to the well-known transformation formula:

$$b_{ijk}^{2\omega} = c_{i\alpha} c_{j\beta} c_{k\gamma} b_{\alpha\beta\gamma}^{2\omega}, \quad (2)$$

where the transformation coefficients $c_{i\alpha}$ are direction cosines between the axes i and α of the two Cartesian coordinate systems.

Let us consider, within the class of linear molecules, those having the point group symmetry $C_{\infty v}$ e.g. HCl, CO, OCS, for which the symmetric hyperpolarizability tensor is given as follows [1]:

$$b_{\alpha\beta\gamma}^{2\omega} = b_{113}^{2\omega} (\delta_{\alpha\beta} S_\gamma + \delta_{\beta\gamma} S_\alpha + \delta_{\gamma\alpha} S_\beta) + (b_{333}^{2\omega} - 3b_{113}^{2\omega}) S_\alpha S_\beta S_\gamma. \quad (3)$$

S_α denoting the α -component of the unit vector \mathbf{S} in the direction of the 3-axis of molecular coordinates which coincides with the C_∞ symmetry axis of the molecule, and $\delta_{\alpha\beta}$ - Kronecker's unit tensor.

With the incident light wave propagating along Y , and its electric vector vibrating along Z , we assume for simplicity that the scattered light is observed at 90° i.e. along X . On assuming this geometry of observation the intensity tensor of scattered light [1] exhibits but two mutually perpendicular symmetric components, namely:

$$I_{YY}^{2\omega} = \frac{N}{2} \frac{\pi (2\omega)^4}{c^5} \langle (b_{YZZ}^{2\omega})^2 \rangle I_{ZZ}^2, \quad (4a)$$

$$I_{ZZ}^{2\omega} = \frac{N}{2} \frac{\pi (2\omega)^4}{c^5} \langle (b_{ZZZ}^{2\omega})^2 \rangle I_{ZZ}^2, \quad (4b)$$

where with regard to the transformations (2) and (3) we have:

$$b_{YZZ}^{2\omega} = \frac{1}{5} \{ \alpha_{2\omega} + \beta_{2\omega} (5c_{Z3}^2 - 1) \} c_{Y3}, \quad (5a)$$

$$b_{ZZZ}^{2\omega} = \frac{1}{5} \{ 3\alpha_{2\omega} + \beta_{2\omega} (5c_{Z3}^2 - 3) \} c_{Z3}, \quad (5b)$$

with the notation:

$$\alpha_{2\omega} = b_{333}^{2\omega} + 2b_{113}^{2\omega}, \quad \beta_{2\omega} = b_{333}^{2\omega} - 3b_{113}^{2\omega}. \quad (6)$$

In the absence of external fields, the scattering molecule takes all orientations with respect to the axes X, Y, Z of laboratory coordinates with equal probability, so that a classical isotropic averaging over the direction cosines can be performed on the right hand terms of Equations (4a) and (4b):

$$\begin{aligned} \langle c_{Y3}^2 \rangle &= \langle c_{Z3}^2 \rangle = \frac{1}{3}, & \langle c_{Z3}^4 \rangle &= \frac{1}{5}, \\ \langle c_{Y3}^2 c_{Z3}^2 \rangle &= \frac{1}{15}, \quad \langle c_{Z3}^6 \rangle = \frac{1}{7}, & \langle c_{Y3}^2 c_{Z3}^4 \rangle &= \frac{1}{35}. \end{aligned} \quad (7)$$

Finally, we obtain for the intensity components of incoherent second-harmonic scattering by linear molecules:

$$I_{YY}^{2\omega} = \frac{N\pi(2\omega)^4}{1050c^5} (7\alpha_{2\omega}^2 + 8\beta_{2\omega}^2) I_{ZZ}^2, \quad (8a)$$

$$I_{ZZ}^{2\omega} = \frac{N\pi(2\omega)^4}{350c^5} (21\alpha_{2\omega}^2 + 4\beta_{2\omega}^2) I_{ZZ}^2. \quad (8b)$$

The expressions (8a) and (8b) are particular cases of earlier results [1]. We have here components related to the mean hyperpolarizability of the molecule $b^{2\omega} = (b_{333}^{2\omega} + 2b_{113}^{2\omega})/3 = \alpha_{2\omega}/3$ and components related to an anisotropy of hyperpolarizability, defined as $\beta_{2\omega} = b_{333}^{2\omega} - 3b_{113}^{2\omega}$. Defining the depolarisation ratio as $D_v^{2\omega} = I_{YY}^{2\omega}/I_{ZZ}^{2\omega}$, we obtain:

$$D_v^{2\omega} = \frac{7\alpha_{2\omega}^2 + 8\beta_{2\omega}^2}{63\alpha_{2\omega}^2 + 12\beta_{2\omega}^2}. \quad (9)$$

On neglecting the anisotropy of hyperpolarizability ($\beta_{2\omega} = 0$), we have $D_v^{2\omega} \approx \frac{1}{9}$.

3. Semi-Classical Theory of the Rotational Structure of Nonlinearly Scattered Light

Quantum-mechanical calculations enable us to take into consideration the influence of molecular rotation on the spectrum of scattered light. In solving this problem, we resort to an idea due to Placzek [6] and methods based on the theory of angular momentum.

The intensity of a line of the scattered light spectrum is proportional to the squared matrix element of the dipole moment operator between the initial state $|n v J \tau M\rangle$ and final state $|n' v' J' \tau' M'\rangle$ of the molecule, where n and v are sets of quantum numbers describing respectively the electronic vibrational state, whereas the quantum numbers $J \tau M$ describe molecular rotation.

We restrict our considerations to processes accounted for by the hyperpolarizability tensor $b_{\alpha\beta\gamma}$ containing information on scattering of the types 2ω and $2\omega \pm \omega_m$, where ω_m is a frequency related to the change in state of the molecule. In usual scattering conditions, molecules do not undergo a change of their electronic state, so that the

tensor $b_{\alpha\beta\gamma}$ may be averaged with regard to this state and is now a function of the normal coordinates Q [4, 11]:

$$b_{\alpha\beta\gamma}(Q) = b_{\alpha\beta\gamma}(0) + \sum_i \left(\frac{\partial b_{\alpha\beta\gamma}}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 b_{\alpha\beta\gamma}}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j + \dots \quad (10)$$

The first term of this expansion accounts for the hyper-Rayleigh scattering discussed in Section 2, whereas the second term describes vibrational hyper-Raman scattering [5]. Molecular rotation contributes to both. The intensity of light scattered with the frequency $2\omega \pm \omega_m$ into the unit solid angle in the X -direction is:

$$I^{2\omega \pm \omega_m} = I_{YY}^{2\omega \pm \omega_m} + I_{ZZ}^{2\omega \pm \omega_m} \quad (11a)$$

with

$$I_{YY}^{2\omega \pm \omega_m} = \frac{2\pi(2\omega \pm \omega_m)^4}{c^5} g_I N_{vJ\tau} \frac{1}{2J+1} \sum_{MM'} \left| (b_{YYZ}^{2\omega})_{v'J'\tau'M'} \right|^2 I_{ZZ}^2 \quad (11b)$$

$$I_{ZZ}^{2\omega \pm \omega_m} = \frac{2\pi(2\omega \pm \omega_m)^4}{c^5} g_I N_{vJ\tau} \frac{1}{2J+1} \sum_{MM'} \left| (b_{ZZZ}^{2\omega})_{v'J'\tau'M'} \right|^2 I_{ZZ}^2 \quad (11c)$$

where g_I is the nuclear statistical weighting factor, and $N_{vJ\tau}$ the number of molecules in the initial state.

In order to calculate the intensity distribution in the purely rotational hyper-Raman spectrum for which $v = v'$, which we shall be referring to as the rotational structure of hyper-Rayleigh scattering, the first term of the expansion (10) of $b_{\alpha\beta\gamma}$ has to be inserted into (11). The second term permits the calculation of the rotational structure of the vibrational hyper-Raman lines.

With the aim of calculating the matrix elements of $b_{\alpha\beta\gamma}$, it is convenient to perform a linear transformation by resorting to the spherical tensor A_m^l :

$$b_{\alpha\beta\gamma} = \sum_{klm} c_{\alpha\beta\gamma}^{klm} A_m^{l,k}, \quad (12)$$

where l, m denote respectively the rank and element of the spherical tensor, and the index k serves for distinguishing various tensors of the same rank occurring in the sum (12). The coefficients $c_{\alpha\beta\gamma}^{klm}$ have been tabulated by Maker [12].

In quantal calculations, the transition from laboratory to molecular coordinates is greatly facilitated by the use of spherical tensors. The latter behave according to the following simple transformation law:

$$A_m^l = \sum_{m'} D_{m'm}^l(\alpha, \beta, \gamma) \tilde{A}_{m'}^l, \quad (13)$$

where the transformation coefficients $D_{m'm}^l(\alpha, \beta, \gamma)$ are Wigner functions depending on the Euler angles α, β, γ defining the orientation of the molecular reference system with respect to the laboratory system. The tilde denotes a tensor characterizing the molecule in coordinates attached to the latter.

As mentioned in Section 2, outside regions of electronic dispersion and absorption the tensor $b_{\alpha\beta\gamma}$ can be assumed to be symmetric in all its indices. The tensor elements b_{YZZ} and b_{ZZZ} are expressed in terms of the spherical tensors by the following relations:

$$\begin{aligned} b_{YZZ} &= \frac{1}{\sqrt{30}}(A_1^1 + A_{-1}^1) - \sqrt{\frac{2}{15}}(A_1^3 + A_{-1}^3), \\ b_{ZZZ} &= -i\sqrt{\frac{3}{5}}A_0^1 + i\sqrt{\frac{2}{5}}A_0^3. \end{aligned} \quad (14)$$

The rotational wave functions can be represented as linear combinations of Wigner functions; for the case of symmetric top-like molecules they are of a simple form, since $\tau = K$,

$$|JKM\rangle = i^{J-K} \sqrt{\frac{2J+1}{8\pi^2}} D_{KM}^J(\alpha, \beta, \gamma), \quad (15)$$

whereas for linear molecules, for which $K=0$, the Wigner functions reduce to spherical harmonics $Y_M^J(\beta, \alpha)$.

When calculating the matrix elements we resort to the formula:

$$\begin{aligned} \frac{1}{8\pi^2} \iiint D_{K_1 M_1}^{J_1}(\alpha, \beta, \gamma) D_{K_2 M_2}^{J_2}(\alpha, \beta, \gamma) D_{K_3 M_3}^{J_3}(\alpha, \beta, \gamma) \times \\ \times \sin \beta \, d\alpha \, d\beta \, d\gamma = \begin{pmatrix} J_1 & J_2 & J_3 \\ K_1 & K_2 & K_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}, \end{aligned} \quad (16)$$

where the

$$\begin{pmatrix} J_1 & J_2 & J_3 \\ K_1 & K_2 & K_3 \end{pmatrix}$$

are the Wigner coefficients.

By the above proposed method, we calculated the intensities of the various rotational lines of the hyper-Rayleigh scattering spectrum of linear molecules. In the case of molecules possessing the symmetry $C_{\infty v}$, the hyperpolarizability tensor has two mutually independent elements $b_{333}^{2\omega}$ and $b_{113}^{2\omega} = b_{223}^{2\omega}$. We give the scattered intensities as functions of the parameters $\alpha_{2\omega}$ and $\beta_{2\omega}$ related by formulae (6) with the tensor elements $b_{\alpha\beta\gamma}^{2\omega}$.

For linear molecules, we have the selection rules $\Delta J = \pm 1$, $\Delta J = \pm 3$. The intensities of scattered light, polarized parallel to the Z -axis, are:

$$\begin{aligned} I_{ZZ}^{2\omega+\omega_R} &= \frac{2\pi(2\omega + \omega_R)^4}{c^5} \frac{N}{Z} e^{-E_J/kT} \left\{ \frac{3}{25} \alpha_{2\omega}^2 J + \right. \\ &\quad \left. + \frac{6}{175} \beta_{2\omega}^2 \frac{J(J-1)(J+1)}{(2J+3)(2J-3)} \right\} I_{ZZ}^2, \quad \Delta J = -1, \end{aligned} \quad (17a)$$

$$\begin{aligned} I_{ZZ}^{2\omega-\omega_R} &= \frac{2\pi(2\omega - \omega_R)^4}{c^5} \frac{N}{Z} e^{-E_J/kT} \left\{ \frac{3}{25} \alpha_{2\omega}^2 (J+1) + \right. \\ &\quad \left. + \frac{6}{175} \beta_{2\omega}^2 \frac{J(J+1)(J+2)}{(2J-1)(2J+5)} \right\} I_{ZZ}^2, \quad \Delta J = +1, \end{aligned} \quad (17b)$$

$$I_{ZZ}^{2\omega+\omega_R} = \frac{2\pi(2\omega+\omega_R)^4}{c^5} \frac{N}{Z} e^{-E_J/kT} \times \left\{ \frac{2}{35} \beta_{2\omega}^2 \frac{J(J-1)(J-2)}{(2J-1)(2J-3)} \right\} I_{ZZ}^2, \quad \Delta J = -3, \quad (17c)$$

$$I_{ZZ}^{2\omega-\omega_R} = \frac{2\pi(2\omega-\omega_R)^4}{c^5} \frac{N}{Z} e^{-E_J/kT} \times \left\{ \frac{2}{35} \beta_{2\omega}^2 \frac{(J+1)(J+2)(J+3)}{(2J+3)(2J+5)} \right\} I_{ZZ}^2, \quad \Delta J = +3. \quad (17d)$$

Above, N is the number of molecules in the sample, Z the sum of states or the rotational partition function, E_J the energy of the molecule in the state J , and

$$\omega_R = \frac{1}{\hbar} |E(J') - E(J)|.$$

It is worth noting that, for $\Delta J = \pm 1$, formulae (17) yield both isotropic and anisotropic scattering, as in the classical case (8). However, for $\Delta J = \pm 3$, we obtain nonlinear scattering of a purely anisotropic nature.

For the component $I_{YY}^{2\omega \pm \omega_R}$, the J -dependence is the same but the coefficients are different. The numerical coefficient of the isotropic part $\alpha_{2\omega}^2$ has to be multiplied by a factor of $\frac{1}{5}$, and that of the anisotropic part $\beta_{2\omega}^2$ by $\frac{2}{3}$. Thus, on the branch $\Delta J = \pm 3$, the depolarisation ratio $D_2^{2\omega}$ is independent of J and amounts to $\frac{2}{3}$. For the branch $\Delta J = \pm 1$, one has the following expressions for the J -dependence of the depolarisation ratio:

$$D_v^{2\omega} = \frac{7\alpha_{2\omega}^2(4J^2 - 9) + 12\beta_{2\omega}^2(J^2 - 1)}{63\alpha_{2\omega}^2(4J^2 - 9) + 18\beta_{2\omega}^2(J^2 - 1)}, \quad \Delta J = -1, \quad (18a)$$

$$D_v^{2\omega} = \frac{7\alpha_{2\omega}^2(4J^2 + 8J - 5) + 12\beta_{2\omega}^2 J(J+2)}{63\alpha_{2\omega}^2(4J^2 + 8J - 5) + 18\beta_{2\omega}^2 J(J+2)}, \quad \Delta J = +1, \quad (18b)$$

For the case $\beta_{2\omega} < \alpha_{2\omega}$, the depolarisation ratio for the branch $\Delta J = \pm 1$ is approximately $\frac{1}{5}$, in agreement with the classical result (9).

The sum over all J and all permitted transitions divided by 4 yields the total line intensity as defined by the formulae (8a) and (8b), derived by classical averaging over all possible orientations of the molecule [1, 4].

From formulae (17), we calculated the line intensities of carbon monoxide. Since in the case of molecules like CO the rotational energy is [7]:

$$E(J) = BJ(J+1) - DJ^2(J+1)^2, \quad (19)$$

where $B = h/8\pi^2 Ic \text{ cm}^{-1}$ with I the inertia moment of the molecule, and D a perturbation constant related with centrifugal forces, the separation in wave numbers between

the lines of the rotational spectrum and the purely hyper-Rayleigh lines is of the form:

$$\Delta\nu = 2(BJ - 2DJ^3), \quad \Delta J = -1 \quad (20a)$$

$$\Delta\nu = -2B(J+1) + 4D(J+1)^3, \quad \Delta J = +1 \quad (20b)$$

$$\Delta\nu = (6B - 24D)(J-1) - 12D(J-1)^3, \quad \Delta J = -3 \quad (20c)$$

$$\Delta\nu = -(6B - 24D)(J+2) + 12D(J+2)^3, \quad \Delta J = +3. \quad (20d)$$

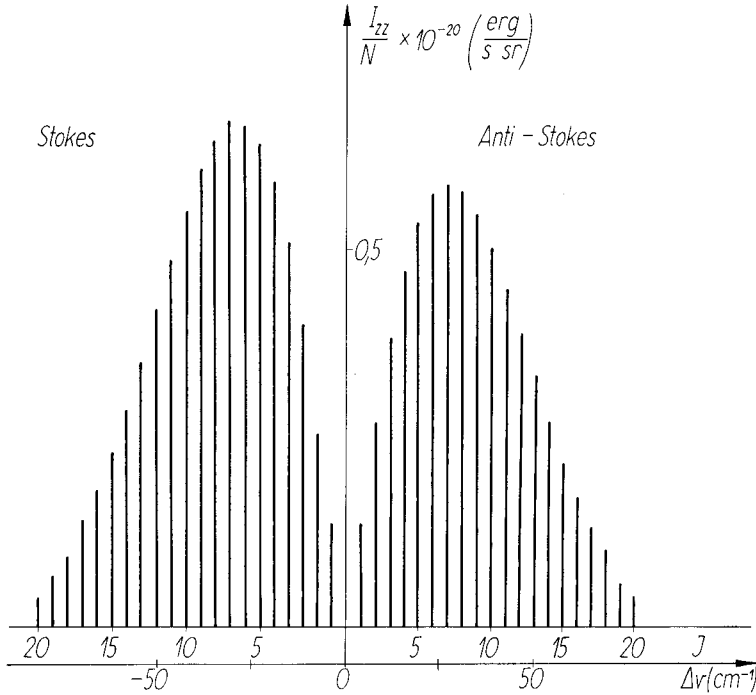


Fig. 1. Calculated intensity distribution in the rotational spectrum of CO (branches for the selection rules $\Delta J = \pm 1$).

Since $D \ll B$, we have neglected D in our calculations. For the CO molecule, B amounts to 1.931 cm^{-1} [13] and the hyperpolarizability tensor elements are:

$$b_{333} = -98.28 \times 10^{-32} \text{ cm}^5/\text{esu}, \quad b_{113} = -15.16 \times 10^{-32} \text{ cm}^5/\text{esu}.$$

[14]. The sample was assumed to be illuminated with a neodymium laser, emitting a beam intensity of $I = 0.4 \times 10^{16} \text{ erg cm}^{-2} \text{ s}^{-1}$. The intensity distribution calculated for $I_{ZZ}^{2\omega \pm \omega_R}$ is shown in Figures 1 and 2.

Since for CO the anisotropic parameter $\beta_{2\omega}^2$ is nearly one order of magnitude smaller than the isotropic parameter $\alpha_{2\omega}^2$, the shape of the spectrum is determined essentially by the branches $\Delta J = \pm 1$ only. In the case of the molecules LiH and BF the

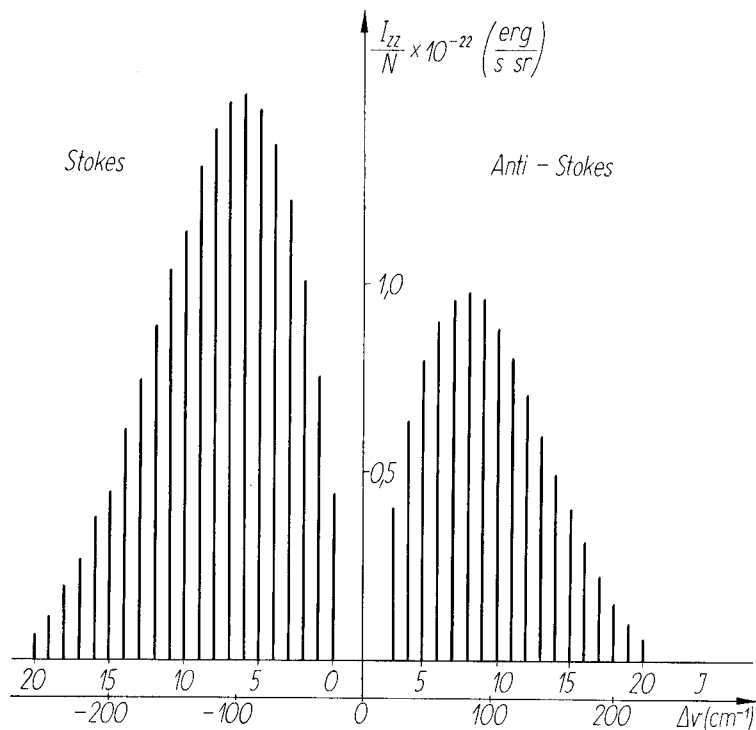


Fig. 2. Calculated intensity distribution in the rotational spectrum of CO (branches for the selection rules $\Delta J = \pm 3$).

parameters $\alpha_{2\omega}$ and $\beta_{2\omega}$ are numerically comparable [14] and the shape of the spectrum depends appreciably on the anisotropic part also.

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