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CONTRIBUTION TO THE THEORY OF THE MOSSBAUER EFFECT ON BROWNIAN PARTICLES

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We consider recoilless resonant absorption of quanta by nuclei contained in Brownian particles suspended in a liquid. Besides the translational motion of the Mossbauer atom together with the particle, account is taken of its rotational motion. For spherical particles in the classical approximation, the absorption spectrum is determined and is found to differ greatly from the Lorentz spectrum, which takes into account only the translational motion. The broadening of the absorption line is considered with allowance for rotation of the suspended particle. The results are compared with experiments on the Mossbauer effect on Brownian particles containing absorbing atoms.

RESONANT recoilless absorption of quanta has been used in a number of investigations to study the properties of liquid systems containing Mossbauer atoms. These atoms may be either a component part of a system[1-3], or imbedded in relatively large impurity particles suspended in the investigated liquid[4-6].

The connection between the cross section for resonant absorption of γ quanta and the dynamics of molecular or Brownian motion in a liquid was considered in[7-9]. Usually the rotational motion of the suspended particle is neglected, and the translational motion is described by a simple diffusion equation. In this case the absorption line has a Lorentz shape. The solution of the Langevin equation for Brownian motion yields a spectrum that coincides in practice with the Lorentz spectrum for small particles. Only for very large particles does such a spectrum differ from the Lorentz spectrum.

In this paper we investigate the influence of rotational Brownian motion on the Mossbauer spectrum of particles suspended in a liquid and containing absorbing atoms. It is shown that allowance for the rotational motion greatly changes the form of the absorption line of the γ quanta, and the experimental results are well described by this curve. The experimental data on the line broadening of resonant absorption with allowance for the rotational motion of the Brownian particles, lead to larger effective dimensions of these particles than without allowance for their rotation.

The results of the present paper are applicable to solutions, provided sufficiently large molecules or molecular complexes, containing the Mossbauer atoms, are considered.

1. The effective cross section of resonant absorption of γ quanta is determined by the van Hove autocorrelation function, which gives complete information on the dynamics of the atoms of the absorbing system[7]:

$$\sigma(\omega)=\frac{\sigma_0\Gamma}{4\hbar}\int\limits_{-\infty}^{\infty}dt\exp\left[-i\omega t-\frac{\Gamma}{2\hbar}|t|\right]G_s(\varkappa,t). \tag{1}$$

Here σ_0 is the cross section of recoilless resonant scattering, $\hbar\omega = E - E_0$, E is the energy of the incident γ quanta, $h\kappa = p$ is their momentum, E_0 is the resonant energy, Γ is the natural width of the excited level of the nucleus, and $G_s(\kappa, t)$ is the Fourier transform of the van Hove function:

$$G_s(\varkappa,t)=\langle\exp[-i\varkappa\mathbf{X}(0)]\exp[i\varkappa\mathbf{X}(t)]\rangle, \tag{2}$$

where **X** is the position of the absorbing atom, and the angle brackets denote quantum-mechanical and statistical averaging.

The motion of the Mossbauer atom contained in the Brownian particles suspended in the liquid can be represented by the sum of the motion of the particle mass center and the rotation of the atom together with the particle about the mass center. If we neglect the correlation between the translational and rotational motions of the Brownian particle, then (2) can be rewritten in the form

$$G_s(\varkappa,t)=G_s{}^t(\varkappa,t)G_s{}^r(\varkappa,t)=\langle e^{-i\varkappa\mathbf{R}(0)}e^{i\varkappa\mathbf{R}(t)}\rangle\langle e^{-i\varkappa\mathbf{r}(0)}e^{i\varkappa\mathbf{r}(t)}\rangle, \tag{3}$$

where **R** is the coordinate of the mass center of the Brownian particle in the immobile coordinate system, and **r** is the radius vector of the atom in the moving coordinate system with origin at the mass center of the Brownian particle. The translational diffusion motion of a spherical particle will be described, just as in[7], by the simple diffusion equation. In this case

$$G_s{}^t(\varkappa,t)=\exp(-2W_a-\varkappa^2Dt), \tag{4}$$

where D is the diffusion coefficient, $2W_a = (\hbar\kappa)^2/8MkT$ is the analog of the Debye-Waller factor, M is the mass of the Brownian particle, and T is the temperature.

Allowance for the influence of the rotational Brownian motion of the spherical particle on the Mossbauer spectrum will be carried out in the classical approximation with the aid of the probability density $W(\mathbf{\Omega}, \mathbf{\Omega}_0, t)$, which determines the probability that the orientation of the particle will change within a time t from $\mathbf{\Omega}_0$ to $\mathbf{\Omega}$:

$$G_s{}^r(\varkappa,t)=\frac{1}{8\pi^2}\int d\Omega\,d\Omega_0\,W(\Omega,\Omega_0,t)\exp[i\varkappa(\mathbf{r}(t)-\mathbf{r}(0))]. \tag{5}$$

The function $W(\mathbf{\Omega}, \mathbf{\Omega}_0, t)$. satisfying the equation of rotational diffusion $\partial W/\partial t = \Theta\Delta W$ and the initial condition $W(\mathbf{\Omega}, \mathbf{\Omega}_0, 0) = \delta(\mathbf{\Omega} - \mathbf{\Omega}_0)$, is of the form[10,11]

$$W(\Omega,\Omega_0,t)=\sum_{l,m,n}\frac{2l+1}{8\pi^2}D_{mn}^{(l)}(\Omega)D_{mn}^{(l)*}(\Omega_0)\exp[-l(l+1)\Theta t]. \tag{6}$$

Here Θ is the coefficient of rotational diffusion and $D_{mn}(l)$ are generalized spherical functions orthogonal with respect to all the indices and normalized in such a way that (see[12])

$$\int d\Omega \, |D_{mn}^{(l)}(\Omega)|^2 = 8\pi^2/(2l+1).$$

After substituting (6) in (5), we readily get (see, for example,[13])

$$G_s^r(\varkappa, t) = \frac{\pi}{\varkappa r} \sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) J_{l+1/2}^2(\varkappa r) \exp[-l(l+1)\Theta t], \tag{7}$$

where $J_{l+1/2}(x)$ are Bessel functions. The absorption cross section (1) assumes, when (3), (4), and (7) are taken into account, the form

$$\sigma(\omega) = \sigma_0 \Gamma (2\hbar\Theta\varkappa^2 r^2)^{-1} \exp(-2W_a) \operatorname{Re} \varphi(\varkappa r, \omega), \tag{8}$$

where

$$\varphi(z, \omega) = \pi \sum_{l=0}^{\infty} \left(l + \frac{1}{2}\right) z J_{l+1/2}^2(z) [l(l+1) + b]^{-1}, \tag{9}$$

and

$$b = \frac{\varkappa^2 D}{\Theta} \left[1 + \frac{\Gamma/2 + i\hbar\omega}{\hbar\varkappa^2 D}\right] = \frac{4}{3}(\varkappa a)^2 \left[1 + \frac{\Gamma/2 + i\hbar\omega}{\hbar\varkappa^2 D}\right]. \tag{10}$$

In the last equation, we used the Stokes values of the coefficients of translational and rotational diffusion for a spherical particle of radius a, equal to $kT/6\pi a\eta$ and $kT/8\pi a^3\eta$, where η is the viscosity of the surrounding medium[10,11].

The square of the Bessel function can be represented in the following integral form[14]:

$$J_{l+1/2}^2(z) = \frac{2}{\pi} \int_0^1 \frac{dx}{\sqrt{1-x^2}} J_{2l+1}(2zx),$$

and for (9) we have

$$\varphi(z, \omega) = 2z \int_0^1 \frac{dx}{\sqrt{1-x^2}} \sum_{l=0}^{\infty} \frac{2(2l+1) J_{2l+1}(2zx)}{(2l+1)^2 - \nu^2},$$

where we have introduced the notation $\nu^2 = 1 - 4b$. The series under the integral sign is the Neumann series for the Lommel function $s_{0,\nu}(2zx)$[14]. Expanding the Lommel function in powers of zx and integrating term by term, we obtain the generalized hypergeometric series

$$\varphi(z, \omega) = z^2 b^{-1} {}_2F_3\left(1, 1;\ \frac{3}{2}, \frac{3+\nu}{2}, \frac{3-\nu}{2};\ -z^2\right), \tag{11}$$

which converges at all values of z for complex ν[14].

2. An investigation of the behavior of the function $\varphi(z, \omega)$ in the form (9) or (11) is difficult, but it turns out that for experiments on Mossbauer absorption it is sufficient to investigate its asymptotic form at large values of $|b|$. Indeed, it follows from (10) that $|b| > (\kappa a)^2$, and $\kappa \gtrsim 10$ Å^{-1} for all the known resonant recoilless transitions[15], so that $|b| \gtrsim 10^2$ all the way to atomic particle dimensions.

It can be shown that the principal term of the asymptotic expansion (11) at large values of $|b|$ (or $|\nu|$) is given by

$$\begin{aligned} \varphi(z, \omega) &= z^2 b^{-1} {}_2F_1(1, 1; 3/2; -z^2 b^{-1}) + O(1/b) \\ &= (1 + b/z^2)^{-1/2} \operatorname{Ar\,sh}(z/\sqrt{b}) + O(1/b), \quad \operatorname{Re}\sqrt{b} > 0, \end{aligned} \tag{12}$$

where we have used the value of the function ${}_2F_1$[14].

Thus, the γ-quantum absorption spectrum takes the form

$$\sigma(\omega) = \sigma_0 \Gamma (2\hbar\Theta\varkappa^2 r^2)^{-1} e^{-2W_a} \left\{\operatorname{Re}\left(1 + \frac{b}{(\varkappa r)^2}\right)^{-1/2} \operatorname{Arsh}\frac{\varkappa r}{\sqrt{b}} + O\left(\frac{1}{b}\right)\right\} \tag{13}$$

and differs from the Lorentz spectrum. In the limit as $r \to 0$, when the absorbing atom does not take part in the rotational motion of the Brownian particle (it is located exactly at the center), we obtain from (13) a well known result[7], in which account is taken of only of the translational motion of the absorbing atom:

$$\lim_{r\to 0} \sigma(\omega) = \sigma_L(\omega) = \frac{1}{4} \sigma_0 \Gamma \exp(-2W_a) \frac{\Gamma + 2\hbar\varkappa^2 D}{1/4(\Gamma + 2\hbar\varkappa^2 D)^2 + (\hbar\omega)^2}. \tag{14}$$

For very low temperatures, when the diffusion coefficient decreases sharply, so that $\kappa r/\sqrt{b} \ll 1$, expression (13) has again a simple Lorentz form (the rotational motion of the Brownian particle "freezes"). In (13) it is assumed that the absorbing atom is located inside the Brownian particle at a distance r from its mass center. Since the position of the absorbing atom inside the Brownian particle is not exactly known, the spectrum (13) must be averaged over all the possible positions. For a homogeneous distribution of the absorbing atoms inside the Brownian particles, we obtain from (13)

$$\bar{\sigma}(\omega) = \frac{1}{V} \int_{(V)} d\mathbf{r}\, \sigma(\omega) = \sigma_0 \Gamma \exp(-2W_a) (2\hbar\varkappa^2 D)^{-1} \bar{\varphi}(\omega), \tag{15}$$

where V is the volume of the Brownian particle and

$$\bar{\varphi}(\omega) = 4\operatorname{Re}[\sqrt{1 + b/(\varkappa a)^2} \operatorname{Ar\,sh}(\varkappa a/\sqrt{b}) - 1] + O(1/b). \tag{16}$$

Figure 1 shows a plot of $\bar{\varphi}$ (curve 1) as a function of $x = \omega/D\kappa^2$. The figure shows for comparison the dependence on x for a Lorentz spectrum (curve 2).

It is easy to verify that in the case $|b| \gg 1$, which leads to the asymptotic estimate (13), the main contribution to the rotational effects is made by small-angle rotations of the Brownian particle. We note that in this connection, as indicated by Podgoretskii (private communication), the result (13) can be approximately obtained from simpler kinematic considerations. For arbitrary b, however, the general result (8) and (11) cannot be significantly simplified.

3. In experiments on resonant absorption of γ quanta, one usually investigates the dependence of the absorption on the relative velocity v of the source and the absorber. For thin absorbers, the experimentally measured spectrum can then be written in the form[7,16]

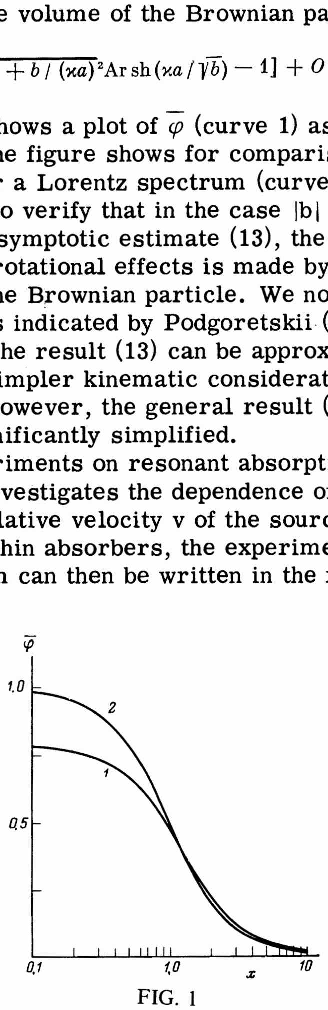

FIG. 1

$$\varepsilon(s)=\alpha\exp(-2W_e)\frac{\Gamma\hbar}{2\pi}\int_{-\infty}^{\infty}d\omega\sigma(\omega)\left[\left(\frac{\Gamma}{2}\right)^2+(\hbar\omega+s)^2\right]^{-1},$$

where $\exp(-2W_l)$ is the probability of emitting γ quanta without recoil, α is the relative fraction of the resonant quanta in the emission spectrum, and $s = E_0v/c$. In the case of homogeneous distribution of the absorbing atoms inside the Brownian particles, the velocity absorption spectrum, in accordance with (15), (16), and (10), takes the form

$$\varepsilon(s)=2\alpha\Gamma\sigma_0(\hbar\varkappa^2D)^{-1}\exp(-2W_e-2W_a)\cdot$$
$$\times\operatorname{Re}\left[\sqrt{1+\frac{4}{3}\left(1+\frac{\Gamma+is}{\hbar\varkappa^2D}\right)}\operatorname{Arsh}\sqrt{\frac{3}{4}\left(1+\frac{\Gamma+is}{\hbar\varkappa^2D}\right)^{-1}}-1\right].\quad(17)$$

From this we can readily obtain the value of the absorption maximum $\bar{\epsilon}(0)$, which makes it possible to determine the width of the absorption line[16]:

$$\Gamma+\Gamma'=\frac{1}{\pi\varepsilon(0)}\int_{-\infty}^{\infty}ds\varepsilon(s)$$
$$=\frac{1}{4}\hbar\varkappa^2D\left[\sqrt{1+\frac{4(\Gamma+\hbar\varkappa^2D)}{3\hbar\varkappa^2D}}\operatorname{Arsh}\sqrt{\frac{3\hbar\varkappa^2D}{4(\Gamma+\hbar\varkappa^2D)}}-1\right]^{-1},\quad(18)$$

where Γ' is the broadening due to the Brownian motion. The corresponding expression without allowance for the rotational motion of the Brownian particle is[7]

$$\Gamma+\Gamma_L'=\Gamma+\hbar\varkappa^2D,\qquad(19)$$

so that the functional dependence of (18) on the quantity $\hbar\kappa^2D/\Gamma$ is different then in (19). The ratio of the width (18) to (19) varies linearly from 1 at $\hbar\kappa^2D/\Gamma = 0$ to 1.272 at $\hbar\kappa^2D/\Gamma > 70$. However, this nonlinearity which is manifest in (18), is too negligible compared with the general linear growth, similar to (19), although in estimating the dimensions of the diffusing objects from a comparison of the theoretical widths with the experimental ones, calculation by means of (19) yields values that are always lower than those obtained from (18). Thus, allowance for the rotational Brownian motion is essential in order to refine the dimensions of the diffusing objects.

There are known experiments on the temperature dependence of the resonance line width[5,6], in which this width was found to be nonlinearly dependent on T/η, and by the same token also on D. The slight nonlinearity of (18) does not explain this effect. However, as shown by the calculations of Kordyuk et al.[9], the agreement with the experimental line-broadening data, for relatively large particles can in such cases be described satisfactorily by describing more accurately the translational Brownian motion in accordance with the Langevin theory. It is possible that additional allowance of the rotational motion, even in accordance with the scheme described above, would improve the results of[9].

4. Let us compare our results with the experimental data. In[4-6] they investigated the Mossbauer effect on suspensions of SnO_2 particles in different liquids. The experimental data point to a strong dependence of the absorption spectrum on the technology of preparation of the suspension. Figure 2 shows a comparison of the results of calculations of the Mossbauer spectrum by means of formula (17), with the experiment of Lisichenko[4], performed on a suspension of tin oxide in glycerine. The solid curves represent the results of calculations of the relative change of the intensity, $\alpha(v) = [I(v) - I(0)]/I(0) \sim [\bar{\epsilon}(v) - \bar{\epsilon}(0)]$ of the radiation passing through the absorber, as a function of v. Curve 1 corresponds to the parameters α = 7.3% and $s/\hbar\kappa^2Dv = 1.1$, and curve 2 to α = 4.9% and $s/\hbar\kappa^2Dv = 1.5$. The experimental points on the curves correspond to 300 (curve 1) and 336°K (curve 2). The radii of the suspended particles, calculated from the parameters of the curves, are 4.6 and 40 Å for the series of experiments at the first and second temperatures, respectively. Such a difference in the particle dimensions is possibly due to their settling. As shown by measurements[4,6], after the lapse of a certain time, the resonance lines changes their shape and intensity.

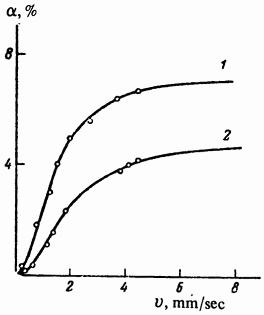

FIG. 2

Bonchev and co-workers[6] investigated the dependence of the line width on T/η when the viscosity of a glycerine suspension is varied by diluting it with water at a constant temperature. A linear dependence of these quantities was obtained. A similar result was observed also for a suspension of SnO_2 in silicone oil following a change of viscosity with increasing temperature. To reconcile these results with Eq. (18), it is necessary to assume that the radii of the suspended particles are 530 and 380 Å, respectively. Allowance for only the translational diffusion yields in this case values of radii that are smaller by approximately 20%.

In[2,3] they investigated solutions of iron salts in glycerine. The foregoing approach, strictly speaking, does not apply to such objects. However, Craig and Sutin described the experimental broadening of the resonance line of $Co^{57}Cl_2$ in glycerine by using a simple diffusion model[7], and estimated the dimensions of the diffusing object. These estimates give for the radius of the object a value of 0.65 Å, which is comparable with the dimensions of the iron ions in crystals, but is smaller than the expected value. Similar calculations, carried out with the aid of (18), give approximately 0.90 Å. For molecules of hemoglobin dissolved in glycerine, the same authors obtained for the radius a value 7.4 Å. Estimates on the basis of (18) yield 10 Å, which is still smaller than that obtained by other methods[2,7].

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58