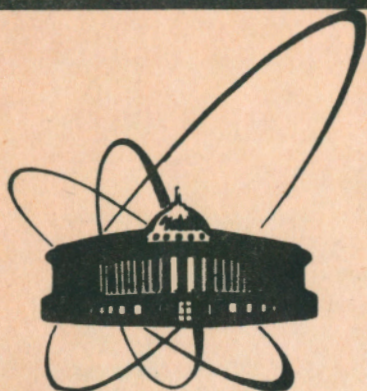


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DEPOLARIZED LIGHT SCATTERING
IN A MODEL OF GLOBULAR MACROMOLECULES
WITH INTERNAL DYNAMICS

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In many cases, the heat motion of macromolecules in a solution is influenced by their internal dynamics. This, in its turn, has an effect on the scattering or absorption spectra of the electromagnetic radiation. Unlike such experimental methods as Mössbauer spectroscopy that allows one to study details of the thermal internal motion of atoms in macromolecules, the Rayleigh light scattering spectra of macromolecules are first of all determined by their diffusion motion¹⁻³⁾. Doppler shifts that are reliably and fast measured using the light beating spectroscopy, enable us to find the translational diffusion coefficients of the scatterers. Under the experimental condition $qR \gg 1$ (R is the size of the macromolecule, $q = (4\pi/\lambda)\sin(\theta/2)$ is the difference between the wave vectors of the incident and scattered light, λ is the wavelength and θ is the scattering angle), the effects of the internal macromolecular motion are very small against a background of the diffusion motion. Nevertheless, using special computational procedures, it is possible to separate the mode corresponding to the internal dynamics⁴⁾ (the experiments⁴⁾ have been carried out to find the possibilities of the correlation spectroscopy of scattered light in the study of the internal dynamics of polymer coils). In^{5,6)}, the deviations of the half-widths of the spectra from the pure diffusion-like ones for the translational motion have been observed. The character of the relaxation differed from the one-exponential law. This allowed one to register the contribution of the fluctuations of the DNA coil form. However, quantitative results corresponding to the DNA internal dynamics have not been obtained.

The depolarized Rayleigh light scattering from the solution of optically anisotropic macromolecules is now used mainly for the determination of rotational diffusion coefficients⁷⁾. The anisotropy of the polarizability of

macromolecules performing Brownian motion exhibits itself in the depolarized scattering also if $qR \neq 0$. For small θ , the influence of the translational diffusion on the spectra is suppressed. The intensity of the scattered light with the polarization normal to that of the incident light is determined by the correlation function of the polarizability tensors a_{ij} in the laboratory frame ⁷⁾. For dilute solution of anisotropic macromolecules, the normalized intensity of the scattered light is defined as

$$I(t) = \langle a_{xz}(t)a_{xz}(0) \rangle / \langle a_{xz}^2 \rangle. \quad (1)$$

Here, the angle brackets denote the statistical averaging. It is assumed that the light beam moves along the axis y and the polarization of the incident and observed light is parallel to the axes z and x , respectively.

The dynamics of rigid anisotropic particles is determined by their orientational motion and in the diffusion approximation is well investigated ^{2,3)}. For deformable particles, the conception of the orientational dynamics loses its sense. It has to be replaced by the concept of the conformational dynamics determined by internal degrees of freedom. The essential peculiarity of all types of motion (including short-range one) realized in the protein structure consists in the fact that they are of highly collective, correlated character. Even very localized changes in the conformational state of the protein lead to cooperative excitations of the considerable part of the macromolecule ^{8,9)}.

In our previous paper ¹⁰⁾, the low-frequency vibrational excitations of globular protein macromolecules have been studied. These excitations effectively took into account displacements and turns of the molecular groups and fragments and their conformational transitions. The collective excitations have been taken into account by introducing some dynamical variables describing the rotation of the

macromolecule and the deformation and asymmetry of its surface form. The results of such a modelling have been used to study the resonance absorption of gamma quanta by Mössbauer marks connected with the macromolecule ^{11,12}. In the present paper, we consider the effects of internal collective excitations of globular macromolecules in the depolarized light scattering.

We will proceed with the model of collective excitations of protein molecules that was proposed in ¹¹. In the most simple case, taking into account the excitations leading to quadrupole deviations of the macromolecule surface from the equilibrium spherical one, the Einstein-Smoluchowski equation has been derived in ¹⁰. This equation describes the probability density for the state of the macromolecule to change during the time t from the initial to the final state. The quadrupole dynamic deformation is the average of the true deformation over the internal motion of atoms. To describe this deformation, it is convenient to use a set of five collective variables: three Euler angles $\Omega(\omega_1, \omega_2, \omega_3)$ giving the orientation of the orthogonal molecule-fixed axes with respect to the laboratory frame and two parameters $0 \leq \beta < \infty$ and $0 \leq \gamma \leq \pi/3$ characterizing the form of the macromolecule in its own coordinate system. The detailed discussion of the meaning of these parameters is given in ¹³. The Einstein-Smoluchowski equation in the space of the variables β, γ and Ω ¹⁰ is difficult to solve. Here, we will use its more simple variant describing rotational-vibrational excitations with four variables β and Ω . The parameter γ will be fixed by some γ_{eff} . Such excitations are known from the collective model of the atomic nuclei as the so-called longitudinal-rotational excitations (see ¹³). The kinetic equation with $\gamma = \gamma_{\text{eff}}$ is

$$\frac{\partial P}{\partial t} = \lambda(4 + \beta \frac{\partial}{\partial \beta})P + (\beta^{-3} \frac{\partial}{\partial \beta} \beta^3 \frac{\partial}{\partial \beta} - \frac{1}{4} \beta^{-2} \sum_{\sigma=1}^3 c_{\sigma} I_{\sigma}^2)P. \quad (2)$$

Here, $c_{\sigma} = \sin^{-2}(\gamma - 2\pi\sigma/3)$ and I_{σ} are the projections of the

quantum-mechanical angular momentum onto the molecule-fixed axes ($\hbar=1$). The nondimensional time $\tau=kTt/Z$ and the elasticity parameter $\lambda=C/kT$ are introduced. The coefficients C and Z determine the potential energy of the deformation and the dissipative function, respectively^{10,11}). The initial condition for equation (2) and the volume element in our 4-dimensional space are as follows:

$$P(\tau=0) = \delta(\beta-\beta(0))\delta(\Omega-\Omega(0))\beta^{-3}, \quad dV = \beta^3 d\beta d\Omega. \quad (3)$$

The solution of (2) can be searched for as a linear combination of the particular solutions

$$P(\beta, \Omega, \tau) \sim e^{4\lambda\tau - E\tau} F(\beta)\Phi(\Omega). \quad (4)$$

Substituting this into (2), we obtain two equations

$$[(1/2)\sum_{\sigma=1}^3 c_{\sigma} I_{\sigma}^2 - \epsilon]\Phi(\Omega) = 0, \quad (5)$$

$$[\lambda\beta \frac{d}{d\beta} + \beta^{-3} \frac{d}{d\beta} \beta^3 \frac{d}{d\beta} - \frac{\epsilon}{2} \beta^{-2} + E] F(\beta) = 0, \quad (6)$$

with ϵ and E being the parameters of separation. Eq.(6) after some substitutions becomes the equation defining the Laguerre polynomials so that

$$F_{ns}(\beta) = y^n e^{-y} L_n^{2n+1}(y), \quad y = \lambda\beta^2/2, \quad (7)$$

$$E_{ns} = 2\lambda(n+s+2), \quad n=0,1,\dots,$$

where s depends also on the proper values of (5), ϵ , because

$$s = \frac{1}{2}(\sqrt{1+\epsilon/2} - 1). \quad (8)$$

Now, let us introduce the probability density of the deformed particle to transfer from the initial state $\beta(0)=\beta_0$ to the

final state $\beta(\tau) \equiv \beta$:

$$\Pi_s(y, y_0, \tau) = \frac{\lambda^2}{2} (y y_0 z)^s e^{-y} \sum_{n=0}^{\infty} \frac{z^n n!}{\Gamma(n+2s+2)} L_n^{2s+1}(y) L_n^{2s+1}(y_0),$$

$$y = \lambda \beta^2 / 2, \quad y_0 = \lambda \beta_0^2 / 2, \quad z = \exp(-2\lambda\tau). \quad (9)$$

The series in (9) can be summed by using the properties of the Laguerre polynomials, but we will not write down this result. Note that independently of the magnitude of s , Π_s satisfies the condition $\Pi_s(y, y_0, 0) = \beta^{-3} \delta(\beta - \beta_0)$.

Consider now eq.(5) for the function $\Phi(\Omega)$. The differential operator in this equation (if c_{σ}^{-1} are replaced by the principal values of the inertia tensor J_{σ}) is the quantum-mechanical operator of the asymmetrical rotator⁽¹³⁾. So its proper functions and values can be written immediately using the well-known results⁽¹⁴⁾. The orthogonal proper functions are linear combinations of the Wigner functions,

$$\Phi_{IK\nu}(\Omega) = \sum_K A_{IK\nu} D_{MK}^I(\Omega), \quad (10)$$

where M and K run from $-I$ to I . Let us explain the appearance of one more index ν . Substituting $\Phi_{IK\nu}$ into (5), multiplying it from the left by D_{MK}^{I*} , and integrating over Ω with the use of orthogonality properties of the Wigner functions, we obtain $2I+1$ algebraic equations to determine $A_{IK\nu}$. From the condition of nontrivial solvability of this algebraic system, we obtain the secular equation of the degree $2I+1$ that has to be solved with respect to $\varepsilon_{I\nu}$. The roots of this equation are denoted by the subscript $\nu=1, 2, \dots, 2I+1$. Thus, we have $2I+1$ proper values $\varepsilon_{I\nu}$ for all I and every value of ν corresponds to own set of real coefficients $A_{IK\nu}$, e.g., for $I=2$ we have five values $\varepsilon_{2\nu}$, $\nu=1, \dots, 5$, and 25 coefficients $A_{2\nu IK}$ (some of them are identical). Now, one can easily write down the Green function of the initial equation (2). It is of the form

$$P(\beta, \Omega, \beta_0, \Omega_0, \tau) = \sum_s \Pi_s(y, y_0, \tau) \Phi_s(\Omega) \Phi_s^*(\Omega_0), \quad \Omega_0 = \Omega(0), \quad (11)$$

where the summation over s means the summation over all I, M and ν . Thus, the rotational-vibrational excitations of deformable particles, which are used to model internal motions of globular protein macromolecules, are fully described by the function (11). This is the probability density of the state change of the globule. The stationary probability distribution is the Boltzmann distribution in β vibrations and equiprobable one in possible orientations given by the angles Ω :

$$P(\tau \rightarrow \infty) = \lambda^2 \exp(-\lambda \beta^2 / 2) / 16\pi^2. \quad (12)$$

Let us return to the intensity density of the depolarized light scattering (1). By using the formulae ³⁾

$$a_0 = [2a_{xx} - a_{yy}] / \sqrt{6}, \quad a_{\pm 1} = \mp a_{xz} - i a_{yz}, \quad (13)$$

$$a_{\pm 2} = [a_{xx} - a_{yy}] / 2 \pm i a_{xy},$$

we express the Cartesian components of the polarizability tensor in the laboratory frame through the components of the spherical tensor of the second rank, a_μ ($\mu=0, \pm 1, \pm 2$). The rules of the transformation of a_μ from the laboratory frame to the molecule-fixed system are as follows ³⁾:

$$a_\mu = \sum_\eta \alpha_\eta D_{\mu\eta}^2(\Omega), \quad \alpha_\mu = \sum_\eta a_\eta D_{\mu\eta}^{2*}(\Omega), \quad (14)$$

where α_μ are the spherical components of the tensor in the molecule-fixed system. From (13) and (14) we obtain

$$a_{xz} = \frac{1}{2} \sum_\mu \alpha_\mu [D_{-1\mu}^2(\Omega) - D_{1\mu}^2(\Omega)]. \quad (15)$$

As usually, the statistical averaging in (1) must be

performed in two stages. Firstly, the averaging over the final states has to be carried out by using (11), and then the obtained result must be averaged over the initial states with the help of (12). The averaged value of $\langle a_{xz}(t)a_{xz}(0) \rangle$ will be calculated in the following way. The components a_{xz} contain only the Wigner functions with $I=2$. So due to their orthogonality properties, the terms with $I \neq 2$ in (11) will give no contribution to the final result. Due to the same reasons, all terms containing products of the Wigner functions with nonequal M vanish. The functions with $M=1$ and -1 give the same contributions. Thus, we will average with the following incomplete function from (11):

$$P \rightarrow \sum_{\nu\kappa\kappa'} \Pi_{2\nu}(Y, Y_0, \tau) A_{2\nu\kappa} A_{2\nu\kappa'} D_{1\kappa}^2(\Omega) D_{1\kappa'}^{2*}(\Omega_0). \quad (16)$$

The averaging over the Euler angles can now be easily carried out to give

$$\langle a_{xz}(t)a_{xz}(0) \rangle = \frac{4\pi^2}{25} \sum_{\mu\mu'\nu} [\alpha_{\mu}^*(t)\alpha_{\mu'}(0)]_{\beta\beta_0} A_{2\nu\mu} A_{2\nu\mu'}, \quad (17)$$

where

$$[\dots]_{\beta\beta_0} = \frac{\lambda^2}{2} \int_0^{\infty} d\beta_0 \beta_0^3 e^{-\lambda\beta_0^2/2} \int_0^{\infty} d\beta \beta^3 \Pi_{2\nu}(Y, Y_0, \tau) (\dots). \quad (18)$$

Analogously,

$$\langle a_{xz}^2(0) \rangle = \frac{1}{10} \sum_{\mu} [|\alpha_{\mu}(0)|^2]_{\beta_0}, \quad [\dots]_{\beta_0} = \frac{\lambda^2}{2} \int_0^{\infty} d\beta_0 \beta_0^3 e^{-\lambda\beta_0^2/2} (\dots). \quad (19)$$

Formulae (17)-(19) are the main results of the paper. By using the β -dependence of the polarizability tensor $\alpha_{1\kappa}$ in the molecule-fixed system they fully determine the intensity of the depolarized scattering (1). We will consider here two special simple cases.

At the beginning, we consider the components $\alpha_{1\kappa}$ to be some constants that characterize the macromolecule. In this case, it follows from (19) that

$$\langle a_{xz}^2(0) \rangle = g_\alpha^2/15, \quad (20)$$

$$g_\alpha^2 = (1/2) \{ (\alpha_{11} - \alpha_{22})^2 + (\alpha_{11} - \alpha_{33})^2 + (\alpha_{22} - \alpha_{33})^2 + 6(\alpha_{12}^2 + \alpha_{13}^2 + \alpha_{23}^2) \}.$$

The nonzero values of $\epsilon_{2\nu}$ and $A_{2\nu k}$ are as follows:

$$\epsilon_{21} = (c_1 + c_2 + 4c_3)/2, \quad \epsilon_{22} = (c_1 + 4c_2 + c_3)/2, \quad (21)$$

$$\epsilon_{23} = (4c_1 + c_2 + c_3)/2, \quad \epsilon_{2\sigma} = c_1 + c_2 + c_3 \pm g,$$

$$A_{212} = A_{221} = A_{231} = A_{23-1} = -A_{21-2} = -A_{22-1} = \sqrt{5}/4\pi,$$

$$A_{200} = \mp\sqrt{5}(g_\pm/g)^{1/2}/\sqrt{4\pi}, \quad A_{2\sigma 2} = A_{2\sigma-2} = \sqrt{5}(g_\pm/2g)^{1/2}/4\pi,$$

where

$$\sigma=4,5, \quad g^2=(c_1+c_2+c_3)^2-3(c_1c_2+c_1c_3+c_2c_3), \quad g_\pm=g\pm(2c_3-c_1-c_2)/2.$$

After integration in (18) and summation in (17) with the use of (21) and (20), the final result for the intensity function will be

$$I(t) = \sum_{\nu=1}^5 N_\nu i_\nu(\tau), \quad (22)$$

$$N_1 = 3\alpha_{12}^2/g_\alpha^2, \quad N_2 = 3\alpha_{13}^2/g_\alpha^2, \quad N_3 = 3\alpha_{23}^2/g_\alpha^2,$$

$$N_{4,5} = \frac{3}{8g_\alpha^2} \{ \sqrt{g_\pm}(\alpha_{11} - \alpha_{22}) \mp \sqrt{g_\mp/3}(2\alpha_{33} - \alpha_{11} - \alpha_{22}) \}^2,$$

$$i_\nu(\tau) = z^\nu {}_2F_1(s, s; 2s+2; z) / {}_2F_1(s, s; 2s+2; 1).$$

The weight multipliers obey the condition $\sum N_\nu=1$, z is defined in (9), and s , that depends on $\epsilon_{2\nu}$ from (21), is given in (8). The result becomes much simpler if the principal axes of the polarizability tensor coincide with the principal axes of the inertia tensor. If, in addition, $\alpha_{11}=\alpha_{22}$, we have instead of (22)

$$I(\tau) = [i_4(\tau)g_- + i_5(\tau)g_+]/2g. \quad (23)$$

Now, consider the components α_{ik} being dependent on the variable β . This is possible due to the internal motion. Particularly, the following natural assumption can be made. We assume that the polarizability tensor is proportional to the inertia tensor J_{ik} . The tensor J_{ik} is given, e.g., in ¹³⁾. So

$$\alpha_{ik} = \delta_{ik} \alpha_{11}, \quad \alpha_{11} \sim \beta^2 (1/c_1, 1/c_2, 1/c_3). \quad (24)$$

Acting as in the above consideration but with the additional integration over β and β_0 in (18) and (19), we obtain the result of the same structure as in (22) with $N_4 + N_5 = 1$, $N_{1,2,3} = 0$,

$$N_{4,5} = \frac{3}{8g_0c^2} (\sqrt{g_{\pm}}(1/c_1 - 1/c_2) + \sqrt{g_{\mp}/3}(2/c_3 - 1/c_1 - 1/c_2))^2, \quad (25)$$

$$G_c^2 = [(1/c_1 - 1/c_2)^2 + (1/c_1 - 1/c_3)^2 + (1/c_2 - 1/c_3)^2]/2,$$

$$i_{\nu}(\tau) = z^s {}_2F_1(s-1, s-1; 2s+2; z) / {}_2F_1(s-1, s-1; 2s+2; 1).$$

Thus, the correlation function of the intensity of the light scattered from the macromolecules with internal motion considerably differs from the known result for rigid ellipsoidal particles ³⁾. First of all, in the case of rigid ellipsoids, the time dependence is determined by the linear superposition of five exponents. Their relaxation times are constructed from the principal values of the tensor of rotational diffusion. In our model, the essential contribution in (22) or (25) is also exponential. It strongly depends on the values $\epsilon_{2\nu}$, connected with the particle form. Furthermore, this exponential contribution is modulated by the hypergeometric functions depending on time and the form parameter. If the polarizability of the macromolecule is

known, the time dependence of the intensity of the scattering is given only by the ratio of the elasticity constant and the friction coefficient, C/Z , and by the parameter γ . It seems to be possible to determine these phenomenological quantities experimentally and to compare them with the results on the temperature dependence of the Mössbauer effect ^{11,12)}.

References

1. Pusey P.N.- in: Photon correlation and light beating spectroscopy.- H.Z.Cummins and E.R.Pike, eds., Mir, Moscow, 1978, p.386.
2. Pecora R.- J.Chem.Phys., 1968, 49, p.1038.
3. Valiev K.A., Ivanov E.N.-Uspekhi fiz.nauk,1973,109, p.31.
4. Balabonov S.M., et al.- Biofizika, 1987, 32, p.933.
5. Schmidt R.L., Boyle J.A., Mayo J.A.- Biopolymers, 1977, 16, p.317.
6. Schmidt R.L., Whitehorn M.A., Mayo J.A.- Biopolymers, 1977, 16, p.327.
7. Cummins H.Z.- see ref.1, p.287.
8. Karplus M., McCammon J.A.- CRC Crit.Rev.Biochem., 1981, 9, p.293.
9. McCammon J.A.- Rep.Progr.Phys., 1984, 47, p.1.
10. Zatovsky A.V., Lisy V.- Physica A, 1983, 119, p.369.
11. Zatovsky A.V., Lisy V.- Biofizika, 1984, 29, p.35.
12. Zatovsky A.V., Klishko V.Yu.- Mol.biol.(Moscow), 1989, 23, p.1091.
13. Davydov A.S.- Excited states of atomic nuclei, Atomizdat, Moscow, 1967 (in Russian).
14. Davydov A.S.- Quantum mechanics, Nauka, Moscow, 1973 (in Russian).

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