Effect of collective motions in a fluid on the microscopic magnetic spin parameters

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It is shown that orientation interaction between nonspherical molecules and shear-stress fluctuations play an important role in spin-lattice relaxation in a fluid. It is found that the NMR spectrum in a fluid flowing with a velocity gradient may differ significantly (with respect to resonance-line frequencies and numbers) from the NMR spectrum in a fluid at rest.

1. INTRODUCTION

A large number of papers are now available (see the reviews of[1,2]) on the study of nuclear (NMR) and electron (EPR) magnetic resonances and the rates of spin-lattice relaxation in fluids. As a rule, the dynamics of individual molecules are considered in the theoretical description of these experiments, and collective motions in the fluid are almost never taken into account. For example, it is always assumed[3] that the NMR spectrum in a flowing fluid is the same as in the same fluid at rest. In the calculation of the important contribution of the internal molecular fields to the spin-lattice relaxation in fluids, usually only rotational diffusion of the individual molecules is considered. At the same time, it is well known that the distribution of the orientations of nonspherical molecules becomes an isotropic in a fluid with shear stresses. This leads to double refraction of light in a fluid flowing with a velocity gradient (the Maxwell effect[4]).

It is shown below that this orientation interaction of nonspherical molecules with shear stresses, and also spin-rotational interaction, lead to a change in the NMR spectrum (with respect to the resonance line frequencies and numbers) in the flowing fluid in comparison with the fluid at rest, and are very important in the calculation of the rate of spin-lattice relaxation in a fluid. We have succeeded in connecting data on the times of rotational and shear relaxations obtained by the light-scattering method with the time of rotational relaxation τ_{mr} found by reduction of measurements of spin-lattice relaxation in fluids.

The static effect of fluid flow on the NMR spectrum is found to have the same relation to the dynamic effect of formation of narrow acoustic paramagnetic resonance lines in a fluid[5] as the effect of deformation has on NMR and EPR spectra and acoustic paramagnetic resonance in solids[2].

2. THE HAMILTONIAN OF THE PROBLEM

For simplicity, we limit ourselves to a fluid consisting of uniaxial molecules, the orientation of which is described by the symmetric tensor

$$\varphi_{\alpha\beta}=n_\alpha n_\beta-{}^1/_3\delta_{\alpha\beta},\quad \mathrm{Sp}\,\varphi=0, \tag{1}$$

n is a unit vector parallel to the axis of the molecule. The Hamiltonian H_S of the spins pertaining to a single molecule (the contribution of the intermolecular interactions to H_S will not be considered here) is the sum of the Zeeman H_Z, quadrupole H_Q, dipole-dipole H_{DD} and scalar H_{SC} spin-spin, and spin-rotational H_{SR} interactions:

$$H_S=H_Z+H_Q+H_{DD}+H_{SC}+H_{SR},\quad H_Z=\sum_j\beta_j(g_j{}^iH_\alpha, S_{\alpha,j}+g_j{}^aH_\alpha\varphi_{\alpha\gamma}S_{\gamma,j}),$$

$$H_Q=\sum_j D_{Q,j}S_{\alpha,j}\varphi_{\alpha\gamma}S_{\gamma,j},\quad H_{DD}=\sum_{j<k}\beta_j\beta_k r_{jk}{}^{-3}A(j,k)S_{\alpha,j}\varphi_{\alpha\gamma}S_{\gamma,k},$$

$$H_{SC}=\sum_{j<k}(W(r_{jk})+\beta_j\beta_k r_{jk}{}^{-3}B(j,k))S_{\alpha,j}S_{\alpha,k},$$

$$H_{SR}=\sum_j J_\alpha C_{\alpha\gamma}{}^jS_{\gamma,j};$$

$$g_j{}^i=g_{\perp,j}+{}^1/_3(g_{\parallel,j}-g_{\perp,j}),\quad g_j{}^a=g_{\parallel,j}-g_{\perp,j},$$

$$A(j,k)=-(g_j{}^i+g_j{}^a)(g_k{}^i+g_k{}^a)-2g_j{}^ig_k{}^i,$$

$$B(j,k)=-{}^2/_3(g_j{}^ig_k{}^a+g_j{}^ag_k{}^i)-{}^2/_9g_j{}^ag_k{}^a.$$

Here g_j^i, g_j^α are the isotropic and anisotropic parts of the g factors, $S_{\alpha,j}$ the α projection, $D_{Q,j}C^j_{\alpha,\gamma}$ the constants of the quadrupole and spin-rotational interactions, B_j the nuclear (Bohr) magneton of the nuclear (electronic) j-th spin, $W(r_{jk})$ the scalar, in particular, the exchange- and hyperfine-interaction constant of the j-th and k-th spins, situated at a distance r_{jk} from one another, and J the total momentum of the molecule. The repeated indices imply summation from 1 to 3. It is assumed that the spins are on the axis of the molecule. A Hamiltonian like (2) is also obtained in the case when the spins are not on the axis of the molecule. The frequencies and integrated intensities of the NMR and EPR lines in the fluid are usually described by the Hamiltonian $\overline{H}_S$ obtained by averaging $H_S(2)$ over the orientations **n** and directions of rotation **J** of the molecules:

$$\overline{H}_S=\sum_j\beta_jg_j{}^iH_\alpha S_{\alpha,j}+H_{SC} \tag{3}$$

The Hamiltonian of the spin-lattice interaction H_{SL} is

$$H_{SL}=H_{SR}+H_{SL}{}'+H_{SL}{}''; \tag{4}$$

$$H_{SL}{}'=\sum_j\beta_jg_j{}^aH_\alpha\varphi_{\alpha\gamma}S_{\gamma,j}+D_{Q,j}S_{\alpha,j}\varphi_{\alpha\gamma}S_{\gamma,j}\;\cdot$$

$$+\sum_{j<k}\beta_j\beta_k r_{jk}{}^{-3}A(j,k)S_{\alpha,j}\varphi_{\alpha\gamma}S_{\gamma,k}\equiv R_{\alpha\beta}{}^\varphi\varphi_{\alpha\beta}, \tag{5}$$

$$H_{SL}{}''=\sum_{j<k}\left(\frac{\partial W(r_{jk})}{\partial r_{jk}}\frac{r_{jk}}{3}-\beta_j\beta_k\frac{B(j,k)}{r_{jk}{}^3}\right)S_{\gamma,j}S_{\gamma,k}\varepsilon u_{\alpha\alpha}$$

$$+\left(\frac{\partial W(r_{jk})}{\partial T}+\beta_j\beta_k\frac{\partial}{\partial T}\frac{B(j,k)}{r_{jk}{}^3}\right)S_{\gamma,j}S_{\gamma,k}\Theta\equiv R^uu_{\alpha\alpha}+R^T\Theta. \tag{6}$$

The Hamiltonian H'_{SL} is connected with the reorientation of the molecule, H''_{SL} with the modulation of the scalar interaction on changes in the density ρ_0 by an amount $-u_{\alpha\alpha}$ and in the temperature T by Θ; ϵ^{-1} is a constant which indicates how many times move slowly the intramolecular distances change than the intermolecular distances under hydrostatic compression.

For the description of the fluid, we use the theory of Leontovich with two relaxation times—τ_1 for rotation and τ_2' for shear, in the form suggested by Volterra.[6] A more general theory has been constructed by Rytov;[7]

however, it is simpler to make the necessary estimates in the model of Volterra, even though it is more limited in application. At each point x, the fluid is described by the tensor φ_{ik}, the displacement vector d, and the tensors of the displacements u_{ik}, the shear displacements u_{ik}', the instantaneous equilibrium displacement H_{ik}, the effective shear s_{ik}' and the shear stresses σ_{ik}':

$$u_{ik}=\frac{1}{2}\left(\frac{\partial d_i}{\partial x_k}+\frac{\partial d_k}{\partial x_i}\right),\quad u_{ik}'=u_{ik}-\frac{1}{3}\delta_{ik}u_{\alpha\alpha},\quad s_{ik}'=u_{ik}'-H_{ik}. \tag{7}$$

The "instantaneous" shear gives a contribution $F^{[6]}$ to the free energy density:

$$F=\mu s_{ik}'s_{ik}'+{}^1/_2 a\varphi_{ik}^2+bs_{ik}'\varphi_{ik}, \tag{8}$$

where μ is the high-frequency shear modulus, a and b are constants corresponding to the contribution to F of the anisotropy of orientation of the molecules and the interaction of the orientation of the molecules with the shear.

The equations of motion of the fluid have the form

$$\begin{gathered}\dot\varphi_{ik}+\Gamma_1\varphi_{ik}=-Db^{-1}\Gamma_1\sigma_{ik}',\quad \rho_0c_V\dot\Theta=\lambda\Delta\Theta-K\alpha\dot u_{\beta\beta},\\ \dot\sigma_k'+\Gamma_2\sigma_{ik}=2\mu\dot u_{ik}'+b\dot\varphi_{ik},\quad \rho_0\dot v_i=\frac{\partial\sigma_{ik}'}{\partial x_k}+K\frac{\partial u_{\beta\beta}}{\partial x_i}-K\alpha\frac{\partial\Theta}{\partial x_i},\\ \dot u_{\beta\beta}=\frac{\partial v_\beta}{\partial x_\beta},\quad c=a-\frac{b^2}{2\mu},\quad D=\frac{b^2}{2\mu c},\quad \Gamma_1=\frac{1}{\tau_1},\quad \Gamma_2=\frac{1}{\tau_2},\end{gathered} \tag{9}$$

v is the velocity, K the modulus of compression, c_V the specific heat at constant volume, α, λ the coefficients of thermal expansion and thermal conductivity. Usually,[7] $\Gamma_1 \gg \Gamma_2$, i.e., the rotational relaxation takes place more rapidly than the shear relaxation.

3. RATE OF SPIN-LATTICE RELAXATION IN A FLUID

We calculate the rate of spin-lattice relaxation as a consequence of the interaction (see (4))

$$H_{SL}-H_{SR}=H_{SL}'+H_{SL}'',\quad H_{SL}'+H_{SL}''=\sum_r F^rA^r, \tag{10}$$

where F^r, A^r are operators acting on the variables of the fluid and of the spin system, respectively. Let $\sigma^*(t)$, $\sigma_0(t)$ be the nonequilibrium and equilibrium density matrices, and ω_p^r the frequencies of the spin system in the interaction representation

$$A^r(t)=\sum_p A_p^r\exp(i\omega_p^r t). \tag{11}$$

The rate of change of the mean value of the physical quantity Q of the spin system is

$$\frac{d}{dt}\mathrm{Sp}(\sigma^*Q)=-(a^*-a_0),\quad a^*=\mathrm{Sp}(E\sigma^*(t)),\quad a_0=\mathrm{Sp}(E\sigma_0(t)), \tag{12}$$

$$E={}^1/_2\sum_{r,r',p,p'}\delta(\omega_p^r-\omega_{p'}^{r'})\int_{-\infty}^{+\infty}\exp(i\omega_p^r\tau)\langle F^r(\tau)F^{r'}(0)\rangle d\tau[A_{p'}^{r'},[A_p^r,Q]_-]_-,$$

$\langle\ \rangle$ denotes the thermodynamic mean over the "lattice" variables of the fluid:

$$E=\frac{1}{2}\sum_{r,r',p,p'}\delta(\omega_p^r-\omega_{p'}^{r'})(\langle\tilde F^r(-i\omega_p^r)F^{r'}(0)\rangle$$
$$+\langle\tilde F^{r'}(i\omega_p^r)F^r(0)\rangle)[A_{p'}^{r'},[A_p^r,Q]_-]_-,\quad \tilde F^r(s)=\int_0^\infty e^{-s\tau}F^r(\tau)d\tau. \tag{13}$$

We carry out the Laplace transformation (13) in time in Eqs. (9) and the Fourier transformation over the coordinates. For simplicity, we consider only the practically most important case in which the frequencies of the spins are small in comparison with the rate of the relaxation processes in the fluid, i.e., $|\omega_p^r| \ll \Gamma_1, \Gamma_2$. We also take into account the slowness of the latter in comparison with the frequencies of short (with momentum q_m) sound waves, i.e., $\mu q_m^2 \gg \Gamma_1|\omega_p^r|$, $\mu q_m^2 \gg \Gamma_2|\omega_p^r|$. Noting that the short-wavelength excitations in a fluid in spin-lattice relaxation are the most important because of the large phase volume, we get for the Fourier components (with momentum q) after cumbersome transformations

$$\begin{aligned}\tilde\varphi_{ik}(\mathbf{q},s)={}&(\tau_1+D\tau_2)\varphi_{ik}(\mathbf{q},0)-\frac{D}{b}\tau_2\sigma_{ik}'(\mathbf{q},0)\\ &+\frac{D\tau_2}{q^2}\left(q_i\varphi_{k\gamma}(\mathbf{q},0)q_\gamma+q_k\varphi_{i\gamma}(\mathbf{q},0)q_\gamma-\frac{2}{3}\delta_{ik}q_\gamma\varphi_{\gamma\delta}(\mathbf{q},0)q_\delta\right)\\ &-\frac{D\tau_2}{bq^2}\left(q_i\sigma_{k\gamma}'(\mathbf{q},0)q_\gamma+q_k\sigma_{i\gamma}'(\mathbf{q},0)q_\gamma-\frac{2}{3}\delta_{ik}q_\gamma\sigma_{\gamma\delta}'(\mathbf{q},0)q_\delta\right)\\ &+\left(q_iq_k+q_kq_i-\frac{2}{3}\delta_{ik}q^2\right)\left[\frac{D\tau_2}{q^4}q_\gamma\varphi_{\gamma\delta}(\mathbf{q},0)q_\delta\right.\\ &\left.+\frac{D\tau_2}{bq^4}q_\gamma\sigma_{\gamma\delta}'(\mathbf{q},0)q_\delta+\frac{D\mu\tau_2}{bq^2}u_{\gamma\gamma}(\mathbf{q},0)\right];\\ \tilde u_{\gamma\gamma}(\mathbf{q},s)={}&\frac{\tau_2}{Kq^2}(bq_i\varphi_{ik}(\mathbf{q},0)q_k-q_i\sigma_{ik}'(\mathbf{q},0)q_k)+\frac{4}{3}\frac{\mu}{K}\tau_2u_{\gamma\gamma}(\mathbf{q},0).\end{aligned} \tag{14}$$

Substituting (14) in (12), and (13) and averaging over the directions of the momenta q, we get

$$\begin{aligned}E=&-\left(\tau_1+\frac{3}{5}D\tau_2\right)\sum_{\mathbf{q}}\langle\varphi_{ik}(\mathbf{q},0)\varphi_{i'k'}(-\mathbf{q},0)\rangle[R_{i'k'}^\varphi,[R_{ik}^\varphi,Q]_-]_-\\ &-\frac{4}{3}\frac{\mu}{K}\tau_2\langle u_{\alpha\alpha}(\mathbf{q},0)u_{\gamma\gamma}(-\mathbf{q},0)\rangle[R^u,[R^u,Q]_-]_-.\end{aligned} \tag{15}$$

The estimate shows that temperature fluctuations do not make an appreciable contribution to the spin-lattice relaxation.

Frequently (see[6,7]) $D \gtrsim 1$, $\tau_2 \sim 10\ \tau_1$ and in such cases the spin-lattice relaxation is determined not by the "pure" rotational relaxation of the molecules (the term $\sim\tau_1$ in (15)), but by the slower shear relaxation (the term $\sim\tau_2$ in (15)). Therefore the time of rotational relaxation of the molecules τ_{mr}, obtained from the usual (see, for example,[1]) treatment of the spin-lattice relaxation, should be closer to τ_2 rather than to τ_1. This is evidently in agreement with the experimental values of τ_1, τ_2 determined from Rayleigh light scattering, and with the τ_{mr} found from the proton spin-lattice relaxation as a consequence of the intramolecular dipole-dipole interactions.[8] Thus, in bromobenzene, $\tau_1 = 0.31$, $\tau_2 = 11$, $\tau_{mr} = 5$, in toluene, $\tau_1 = 0.19$, $\tau_2 = 5.2$, $\tau_{mr} = 1.9$; in fluorobenzene, $\tau_1 = 0.2$, $\tau_2 = 4.5$, $\tau_{mr} = 9$; in benzene, $\tau_1 = 0.24$, $\tau_2 = 2.6$, $\tau_{mr} = 1.4$; in chlorobenzene,[9] $\tau_1 = 0.77$, $\tau_2 = 9.3$, $\tau_{mr} = 4$ (τ_1, τ_2, τ_{mr} are in units of 10^{-12} sec).

As an example, we consider the spin-lattice relaxation in the case of two, in general different, spins located on the axis of the molecule. The equations of motion of the longitudinal components of the spins have the form

$$\frac{dS_{z,i}}{dt}=-\sum_j\frac{S_{z,j}-\langle S_{z,j}\rangle}{T_{ij}},\quad i,j=1,2. \tag{16}$$

From (15), (13), (12), and (8), we get, after cumbersome calculations of the traces and thermodynamic averaging $\langle\ \rangle$.

$$\begin{aligned}\frac{1}{T_{11}}={}&\left(\tau_1+\frac{3}{5}D\tau_2\right)\frac{TN}{c}\left[(\beta_1g_1^aH)^2+4D_{Q,1}^2\left(\frac{9\langle S_{z,1}^4\rangle}{S_1(S_1+1)}-S_1(S_1+1)\right)\right.\\ &\left.+(\beta_1\beta_2r_{12}^{-3}A(1,2))^2\frac{10}{9}S_2(S_2+1)\right]+\frac{8}{9}\frac{TN\mu}{K^2}\tau_2\varepsilon^2\\ &\times(2S_1+1)(2S_2+1)S_2(S_2+1)\left(\frac{\partial W(r_{12})}{\partial r_{12}}\frac{r_{12}}{3}-\beta_1\beta_2\frac{B(1,2)}{r_{12}^3}\right)^2,\end{aligned} \tag{17}$$

$$\frac{1}{T_{12}}=\left(\tau_1+\frac{3}{5}D\tau_2\right)\frac{TN}{c}\left(\frac{\beta_1\beta_2A(1,2)}{r_{12}{}^3}\right)^2\frac{5}{9}S_1(S_1+1)$$
$$-\frac{8}{9}\frac{TN\mu}{K^2}\tau_2\varepsilon^2(2S_1+1)(2S_2+1)S_1(S_1+1)\left(\frac{\partial W(r_{12})}{\partial r_{12}}\frac{r_{12}}{3}-\beta_1\beta_2\frac{B(1,2)}{r_{12}{}^3}\right)^2, \tag{18}$$

N is the number of molecules per unit volume; T_{22}^{-1} and T_{21}^{-1} are obtained by permutation of the numbers 1 and 2 in (17) and (18).

What has been said above allows us to understand why τ_2 and τ_{mr} do not exactly agree: Eqs. (15), (17), and (18) contain the factor ~DTN/c, which characterizes the interaction of the molecule with the shear stresses. On the other hand, comparison of τ_2 and τ_{mr} makes it possible in principle to determine such an important parameter as D/c. For example, for bromobenzene, assuming approximately that the axis n (1) is perpendicular to the benzene ring (this is equivalent to the replacement of A(1,2) in (17) and (18) by A(1,2)/2, we obtain the time T_{1p} of the longitudinal relaxation of the protons as a consequence of the dipole-dipole interaction from Eqs. (15), (17) (18):

$$\frac{1}{T_{1p}}\approx\frac{5}{16}\left(\tau_1+\frac{3}{5}D\tau_2\right)\frac{TN}{c}\sum_j\left(\frac{\beta_1\beta_jA(1,j)}{r_{1j}{}^3}\right)^2.$$

For T ≈ 300°K, N ~ 0.6×10^{22} cm^{-1}, $\tau_1 = 0.3\times10^{-12}$ sec, $\tau_2 = 11\times10^{-12}$ sec, $\tau_{mr} = 5\times10^{-12}$ sec, and D ~ 1, comparing T_{1p}^{-1} with the experimental rate of spin-lattice relaxation[8] ~ $6.3\times10^9\,\tau_{mr}$ sec^{-1}, we obtain c ~ 6D × 10^8 erg-cm^{-3}.

4. THE SPIN HAMILTONIAN IN A FLOWING FLUID

The characteristic frequencies of hydrodynamic fluid flow are usually much smaller than $1/\tau_1$, $1/\tau_2$, $1/\tau_J$ (τ_J is the relaxation time of the angular momentum of the molecule). Therefore the spin Hamiltonian H_S^{FL} in the flowing fluid is obtained by substitution in (2):

$$\varphi_{\alpha\beta}=-\frac{D}{b}\mu\tau_2\left(\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}-\frac{2}{3}\delta_{\alpha\beta}\frac{\partial v_\gamma}{\partial x_\gamma}\right), \tag{19}$$

$$H_{SR}\approx\frac{1}{6}\sum_j\mathrm{Sp}(C^jI)S_{\alpha,j}\,\mathrm{rot}_\alpha\,\mathrm{v}, \tag{20}$$

$I_{\alpha\beta}$ is the moment of inertia tensor of the molecule.

As is shown below, the increment $H_S^{FL}-\overline{H}_S$ (3) to the Hamiltonian $\overline{H}_S$ leads to a change in the NMR resonance frequencies by a fraction of a Hertz. To observe this, the fluid must therefore be in constant and radio-frequency magnetic fields for times of the order of several seconds. At the necessary high flow velocities and without an unrealistic increase in the dimensions of the apparatus, this is possible only in fluid motion along closed paths, particular cases of which are considered below.

1. Fluid rotating as a solid with angular velocity Ω:

$$H_S{}^{FL}=\overline{H}_S+{}^1/_3\sum_j\mathrm{Sp}(C^jI)\Omega_\alpha S_{\alpha,j}\qquad\varphi_{\alpha\beta}=0, \tag{21}$$

This expression corresponds to a very small shift Δω in the NMR frequency. Thus, for F^{19} in the octahedral molecule SF_6,[10]

$$I_{\alpha\alpha}\approx9{,}45\cdot10^{-38}\mathrm{g.\ cm}^2, C_\parallel{}^j+2C_\perp{}^j\approx8{,}67\cdot10^4\,\mathrm{sec}^{-1},\quad|\Delta\omega|\approx5{,}4\cdot10^{-6}\cdot\Omega/2\pi$$

and even for $\Omega/2\pi = 10^4$ sec^{-1}, the shift $|\Delta\omega| \approx = 0.05$ sec^{-1}, while the rate of spin-lattice relaxation of F^{19} in SF_6[10] is ~0.6 sec^{-1} (T = 223°K).

2. Fluid located between two coaxial cylinders (Fig. 1).

The inner and outer cylinders, with radii R_1, R_2, rotate with angular velocities Ω_1, Ω_2 as in apparatus for study of the Maxwell effect,[11] $R_2 = R_1 + \delta$, $\delta \ll R_1$, R_2. For laminar flow (see[12]) at the point $r = (x_1^2 + x_2^2)^{1/2}$,

$$\mathrm{rot}_3\,\mathrm{v}\approx(\Omega_2-\Omega_1)\frac{R_1}{\delta},\qquad\mathrm{rot}_1\,\mathrm{v}=\mathrm{rot}_2\,\mathrm{v}=0,$$
$$\varphi_{\alpha\beta}\approx\frac{D\mu\tau_2}{bR_1\delta}(\Omega_1-\Omega_2)(e_{\alpha3\gamma}x_\beta x_\gamma+e_{\beta3\gamma}x_\alpha x_\gamma). \tag{22}$$

In this equation, $\varphi_{\alpha\beta}$ corresponds to a given point in the fluid, while in (2) it corresponds to the position of a given spin moving with velocity v. Since we are interested in H_S^{FL} in a change in the NMR frequency $|\Delta\omega| \ll |\Omega_2 - \Omega_1|$, to calculate Δω in (2) we need to replace $\varphi_{\alpha\beta}$, curl v by $\overline{\varphi}_{\alpha\beta}$, when curl v—the average of $\varphi_{\alpha\beta}$, curl v over the circular trajectory of given spin. From (22), we get $\overline{\varphi}_{\alpha\beta} = 0$ and

$$H_S{}^{FL}\approx\overline{H}_S+\frac{1}{6}\sum_j\mathrm{Sp}(C^jI)\frac{R_1}{\delta}|\Omega_2-\Omega_1|S_{3,j}. \tag{23}$$

In liquid SF_6[10] for $R_1/\delta = 200$, $|\Omega_2 - \Omega_1| = 2\pi\times10^3$ sec^{-1} (this corresponds to the velocity gradient ~10^6 sec^{-1}) in a magnetic field parallel to the axis of the cylinders, the shift in the NMR frequency of F^{19} $|\Delta\omega| \approx 0.5$ sec^{-1}, i.e., it is quite noticeable. Measurement of Δω makes it possible to determine Sp (C^jI) directly in the fluid and to compare it with data obtained on individual molecules by the molecular-beam method. At the present time, the constants of spin-rotation interaction in a fluid are determined very inaccurately from the rate of spin-lattice interaction because of our lack of knowledge of the relaxation time τ_J.

3. Fluid placed between two belts passed around cylinders and moving with the velocities Ω_1R_1, Ω_2R_2; $R_2 = R_1 + \delta$; $\delta \ll R_1$, R_2; $R_1 \ll L$ (Fig. 2).

For laminar flow, averaged over the trajectory of the fluid particle,

$$\overline{\mathrm{rot}_3\,\mathrm{v}}\approx(\Omega_2-\Omega_1)R_1/\delta,\qquad\overline{\mathrm{rot}_1\,\mathrm{v}}=\overline{\mathrm{rot}_2\,\mathrm{v}}=0,$$
$$\varphi_{12}\approx\frac{D\mu\tau_2R_1}{2b\delta}(\Omega_2-\Omega_1),\qquad\varphi_{11}=\overline{\varphi}_{22}=\overline{\varphi}_{33}=\overline{\varphi}_{13}=\overline{\varphi}_{23}=0. \tag{24}$$

We transform to the set of coordinates x_1', x_2', x_3' obtained by rotation of x_1, x_2, x_3 through the angle Φ about the x_3 axis and subsequent rotation about the new x_1 axis through the angle ϑ. Let the magnetic field be directed along x_3'. Substituting (24) in (2), and keeping only the secular terms in H_S^{FL}, we obtain

$$H_S{}^{FL}\approx\overline{H}_S+\frac{1}{6}\frac{R_1}{\delta}(\Omega_2-\Omega_1)\sum_j\mathrm{Sp}(C^jI)\cos\vartheta S_{3',j}$$
$$+\frac{DR_1}{2b\delta}(\Omega_2-\Omega_1)\mu\tau_2\sin^2\vartheta\sin2\Phi\left[\sum_j\beta_jg_j{}^aHS_{3',j}+D_{Q,j}S_{3',j}^2\right. \tag{25}$$
$$\left.-\sum_{j<k}\beta_j\beta_k\frac{A(j,k)}{2r_{jk}{}^3}(S_{\alpha',j}S_{\alpha',k}-3S_{3',j}S_{3',k})\right].$$

The first term in the square brackets leads to a shift in the NMR frequency as a consequence of the anisotropic part of the g factor, the second to quadrupole splitting of the NMR lines, the third, to the appearance of dipole-dipole interaction in the NMR spectrum, i.e.,

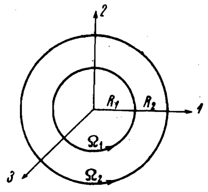

FIG. 1

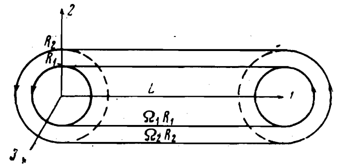

FIG. 2

to a change in the number and frequencies of the NMR lines. For example, in the case of two identical spins S = ½, in place of a single NMR resonance line there appear two lines with frequency separation

$$0.75\beta_1^2 A\,(1.2)\,r_{12}^{-3}\sin^2\vartheta\sin 2\Phi\,\frac{D\mu\tau_2 R_1}{b\delta}(\Omega_2-\Omega_1)$$

None of these effects are observed in ordinary NMR spectra of fluids. They may appear on freezing, but then not only intramolecular interactions such as in (25) are important, but also intermolecular spin-spin interactions. The anisotropic orientation of the molecules due to shear stresses is important in (25) as in the Maxwell effect. However, in contrast to the Maxwell effect, not only the integrated properties of the molecule as a whole (shape, the constants D, b, μ, τ_2) are important, but also its microstructure. We note that the shift and splitting $\Delta\omega_j$ (25) of the NMR lines of the j-th spin in the flowing fluid due to dipole-dipole interaction of the j-th and k-th spins will occur only when $|\Delta\omega_j| > T_{1k}^{-1}, T_{ck}^{-1}, T_{cj}^{-1}$($T_{1i}^{-1}$, T_{ci}^{-1} are the rates of spin-lattice relaxation and chemical exchange of the i-th spin). If $|\Delta\omega_j| \ll T_{1k}^{-1}$ or $|\Delta\omega_j| \ll \max(T_{cj}^{-1}, T_{ck}^{-1})$, then, as a consequence of the kinematic narrowing, $|\Delta\omega_j|$ becomes very small and (25) is inapplicable.

We proceed to the numerical estimate. In bromobenzene, the dipole-dipole interaction creates (25) a complicated proton NMR spectrum the components of which are separated from one another by an amount of the order of

$$\Delta_1\omega=\beta_1^2 A\,(1.2)\,r_{12}^{-3}\sin^2\vartheta\sin 2\Phi\,\frac{D\mu\tau_2 R_1}{b\delta}|\Omega_2-\Omega_1|.$$

At $\mu \sim 10^{10}$ erg-cm^{-3}, $\vartheta = \pi/2$, $\Phi = \pi/4$, $R_1/\delta = 200$, $|\Omega_2 - \Omega_1| = 2\pi \times 10^2$ sec^{-1}, $c \approx 6D \times 10^8$ erg-cm^{-3} (Sec. 3), the rate of spin-lattice relaxation is ~0.05 sec^{-1} and $\Delta_1\omega \approx 0.2$ sec^{-1}, i.e., $\Delta\omega$ is evidently detectable.

To increase $H_S^{FL} - \overline{H}_S$, it is desirable to increase the velocity gradient of the fluid, but then the flow will become turbulent.[12] In the general case, it is not known how the expressions (22)—(25) change in this case. However, in developed turbulence, the intense mixing across the flow may possibly lead to a situation in which the velocity gradient averaged over the trajectory of each given particle, will be equal to the velocity gradient averaged over the volume of the fluid, i.e., $(\Omega_2 - \Omega_1)R_1/\delta$. In this case, the results (22)—(25) will again be applicable. The turbulent mixing is small in the viscous laminar sublayer of fluid at the wall[12], but the latter is so thin in the given case that even molecular diffusion can evidently guarantee the necessary mixing inside it.

The results of Secs. 1—4 are applicable both for NMR and for EPR. However, it is difficult to observe a change (Sec. 4) in the EPR spectrum in the fluid at the attainable flow velocities because of the shorter times of longitudinal and transverse relaxations in EPR in comparison with NMR.

In conclusion, we note that definite interest would attach to a study of spin resonance in flowing liquid crystals, which have oriented (and also translational in the smectic phase) long-range order, even in the absence of shear stresses.

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