The influence of electric field on rotational part of nuclear spin-lattice relaxation times in in polar liquids

The Influence of Electric Field on Rotational Part of Nuclear Spin-lattice Relaxation Times in Polar Liquids

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Résumé. — La communication présente les résultats de la théorie de l'influence d'un champ électrique périodique sur les temps de relaxation spin-milieu dans des liquides polaires. On a considéré deux modèles de cette influence, dont l'un implique l'effet qui pourrait être détecté expérimentalement dans les liquides polaires suffisamment visqueux.

Let us consider a polar liquid containing the molecules of two nuclear spins $I = \frac{1}{2}$. Relaxation caused by rotation is caused by interaction of the spin of the same molecules. According to BPP $\left(\frac{1}{T_1}\right)_{\text{rot}}$ $((T_1)_{\text{rot}}$ — rotational part of spin-lattice relaxation time) is proportional to the spectral densities of correlation functions of some random functions of time $(\sin \theta \cos \theta e^{i\varphi}, \sin^2 \theta e^{2i\varphi})$ the densities taken for proper frequencies. The angles θ, φ which determine the position of straight line connecting the spins of the molecule in external magnetic field change with time at random due to the rotational Brownian motion. In the paper of BPP [1] this motion is described by the diffusion equation.

The question may be asked if the placing of a sample containing a polar liquid in harmonic electric field of proper frequency will change and to what extent the relaxation time due to the molecular rotation.

The effect of an electric field on rotational motion of polar molecules can be taken into account on two ways.

1. By description of this motion by the generalised diffusion equation:

$$\frac{\delta \Psi}{\delta t} = D \, \Delta_\varepsilon \, \Psi + \frac{D}{k\mathrm{T}} \, \mathrm{div} \, (\Psi \, \mathrm{grad} \, V) \, ,$$

where

V = dipol potential in electric field;

$\psi\,(\theta,\,\varphi,\,t)$ = the density of probability of finding the spin-spin axis in the direction $(\theta,\,\varphi)$;

Δ_s = Laplace operator on the surface of the sphere;

D = diffusion constant acc. to Stokes' equation $D = \dfrac{k\,T}{8\,\pi\,a^3\,\eta}$.

2. By independent (to certain extent) treating of the motion in the external field and the rotational diffusion, e.g. assuming the existence of very strong local electric fields ($\mu F \gg kT$) which are caused by the molecules of the next surroundings and polarize the molecule completely. In this case we assume that the change of direction of local field caused by the surrounding molecules can be described by the equation:

$$\frac{\delta\Psi}{\delta t} = D\,\Delta_s\,\Psi$$

and the effect of the external field will be given by the change of the direction of the total field in given point, due to periodic oscillations of the external field.
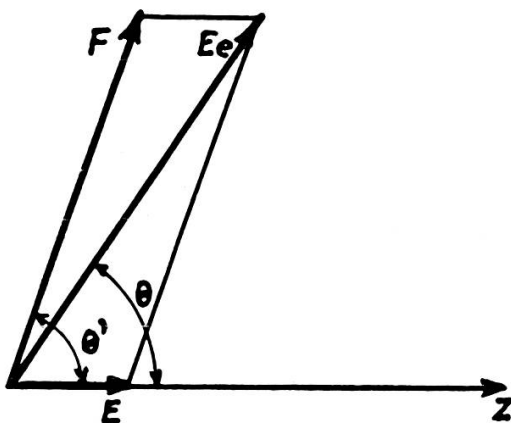

Fig. 1.

The electric field $E = E_0 \sin \omega_0\,t$ is directed towards Z. F is the field due to the molecules of the next surroundings and E_e is the total local field.

In both cases the calculated correlation functions are not stationary; they depend not only on the time differences but also on the initial moment (by the phase of the external field). Then the probability of transition of spin between two Zeeman levels in a time unit is a function of time (in this case a harmonic function). As for measurement of relaxation time

the time of observation must be of the same order as the relaxation time and is always very long in comparison to the alteration period of probability, the average value of this probability may be taken.

The first description leads to the following results:

$$\left(\frac{1}{T_1}\right)_{rot} \sim J_1(\omega) \approx \frac{4}{15}\frac{1}{r^6}\frac{\tau_2}{1+\omega^2\tau_2^2} + \frac{1}{60\,r^6}\left(\frac{\mu\,E_0}{k\,T}\right)^2\frac{\tau_2^2}{9\,\omega^4\,\tau_2^4 + 10\,\omega^2\,\tau_2^2 + 1}$$

$$\frac{1-3\,\omega^2\,\tau_2^2}{3\,\tau_2^2}\qquad\frac{\tau_2}{1+\frac{1}{4}(\omega-\omega_0)^2\,\tau_2^2} + \frac{4}{15\,r^6}\left(\frac{\mu\,E_0}{k\,T}\right)^2\frac{\tau^2}{18\,\omega^4\,\tau_2^4 + 10\,\omega^2\,\tau_2^2 + 1}$$

$$\frac{1+9\,\omega^2\,\tau_2^2}{9\,\tau_2^2}\qquad\frac{\tau_2}{1+9(\omega-\omega_0)^2\,\tau_2^2}$$

$$\tau_2 = \frac{1}{3}\,\tau_1$$

where τ_1 is Debye correlation time. It is seen from this equation that as the change of relaxation introduced by the external field is of the order of $\left(\frac{\mu\,E_0}{k\,T}\right)^2$ and almost independent on τ_2 it is practically not measurable.

In the second case we have:

$$J_1(\omega) = \frac{4}{15}\frac{1}{r^6}\frac{\tau_2}{1+\omega^2\tau_2^2} + \left(\frac{E_0}{F}\right)^2\frac{1}{r^6}\left(\frac{3\cdot10^{-2}\,\tau_2}{1+\frac{1}{4}(\omega-\omega_0)^2\,\tau_2^2} + \right.$$
$$\left. + \frac{3,6\cdot10\,\tau_2}{1+9(\omega-\omega_0)^2\,\tau_2^2}\right)\cdot$$

For $\omega\tau_2 \gg 1$ we can write:

$$J_1(\omega) = \frac{4}{15}\frac{1}{r^6}\frac{1}{\omega^2\,\tau_2} + \frac{6}{15\,r^6}\left(\frac{E_0^2}{F}\right)^2\tau_2 = \frac{2}{15\,r^6}\frac{1}{\omega^2\,\tau_2}\left[2 + 3\left(\frac{E_0}{F}\right)^2\omega^2\,\tau_2^2\right]\cdot$$

It is seen that in this case, the main term and the term due to the field depend in a different way on τ_2.

Theoretically τ_2 can be chosen in such a way that both terms will be of the same order.

REFERENCE

1. BLOEMBERGEN, N., E. M. PURCELL, R. V. POUND, *Phys. Rev.*, 73, 679 (1948).