STARK EFFECT IN NUCLEAR QUADRUPOLE SPIN ECHO

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Submitted May 2, 1970

Zh. Eksp. Teor. Fiz. 59, 1884–1895 (December, 1970)

The Stark effect in multilevel spin systems was investigated experimentally and theoretically by a pulse method. An analytic expression is obtained for the frequency shifts of the nuclear quadrupole resonance (NQR) in the Stark effect in the case of an arbitrary nuclear spin and in the absence of axial symmetry of the electric field gradient of the crystal. It is shown that the "slow beats" of the envelopes of the induction and spin-echo signals carry useful information concerning the values of the components of the tensor R of the electric effect both in single crystals and in polycrystalline samples. The results of experiments on pulsed observation of the Stark effect in NQR on the nuclei Sb^{121} and Sb^{123} in $SbCl_3$ and $2SbCl_3 \cdot C_{10}H_8$ and also Bi^{209} in $BICl_3$ are in good agreement with the theory. The data obtained with Cl^{35} nuclei in a number of chlorine-substituted hydrocarbons agree with the results of stationary experiments by others.

THE Stark effect in nuclear quadrupole resonance (NQR), discovered 10 years ago by Bloembergen[1], was investigated mainly on halogen nuclei (chlorine, bromine, iodine) using a stationary procedure.

In the case of polycrystalline samples, the influence of the external electric field becomes manifest in a broadening of the absorption line, since the electrically induced shift of the NQR frequencies includes an appreciable angular dependence. The increase of the second moment of the NQR line is assumed to be proportional to the squares of the mean-squared frequency shift averaged over the powder. Such a procedure for estimating the R-tensors of the electric effect is quite crude, especially in those cases when the frequency shifts lie within the limits of the line width.

In the case of many-level spin systems (nuclear spin $J > 3/2$), there is no theory of the Stark effect for a nonaxial electric field gradient (EFG). The only exception is the rather cumbersome procedure proposed by Dixon and Bloembergen[2] for estimating the NQR frequency shifts and realized by them for the particular case of the I^{127} nuclei ($J = 5/2$) in HIO_3.

It was shown in[3,4] that a pulsed NQR method makes it possible to study the Stark effect in polycrystalline samples. Electrically induced shifts of NQR frequencies become manifest in the form of "slow beats" of the envelopes of the induction and spin-echo signals.

We present in this paper the theory and the results of an experimental investigation of the Stark effect for many-level quadrupole spin systems on the nuclei Sb^{121} ($J = 5/2$), Sb^{123} ($J = 7/2$), and Bi^{209} ($J = 9/2$). In addition, the pulse procedure was applied to chlorine compounds already investigated by the stationary method[5,6].

1. THEORY OF THE STARK EFFECT FOR MANY-LEVEL SPIN SYSTEMS

When an external homogeneous electric field is applied, the Stark effect in NQR can be described by a total Hamiltonian in the form[2]

$$\mathcal{H} = \sum_{jk} Q_{jk}\left(q_{jk} + \sum_i R_{ijk}E_i\right), \qquad (1)$$

where

$$Q_{jk} = \frac{eQ}{6J(2J-1)}\left[\frac{3}{2}(I_jI_k + I_kI_j) - \delta_{jk}J(J+1)\right]$$

is the tensor of the quadrupole moment of a nucleus with spin J; I_j and I_k are the components of the spin angular momentum I of a nucleus with quadrupole moment Q; q_{jk} is the tensor of the unperturbed electric field gradient of the crystal.

A weak perturbation is described by the tensor $\Delta q_{jk} = \sum_i R_{ijk}E_i$, which contains the components of the electric field E_i relative to the principal axes of the EFG (x, y, z) and the third-rank tensor R_{ijk}, which can be assumed equal to $\partial q_{jk}/\partial E_i$ if polarization and piezoelectric effects are neglected[1)]. However, to describe the Stark effect in many-level spin systems in the absence of axial symmetry of the EFG, it is more convenient to use another form of the Hamiltonian (1), namely

$$\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_E = \frac{eQq_{zz}}{4J(2J-1)}[3I_z^2 + I^2 + \eta(I_x^2 - I_y^2)] + \sum_{m=-2}^{2} Q_m \Delta q_{-m}, \qquad (2)$$

where eQq_{zz} is the quadrupole-coupling constant and η is the EFG asymmetry parameter.

By regarding each term of the perturbation in (2) with respect to the magnetic quantum number m from the point of view of first-order perturbation theory, we can readily show[2] that $\mathcal{H}$ reduces to the form

$$\mathcal{H} = \frac{eQ}{4J(2J-1)}\left\{[3I_z^2 - J(J+1)]\left(q + \sum_i E_iR_{i33}\right)\right. \qquad (3)$$

$$\left. + \frac{1}{2}(I_+^2 + I_-^2)\left[q\eta + \sum_i E_i(R_{i11} - R_{i22})\right]\right\} = \mathcal{H}(q + \Delta q, \alpha + \Delta\alpha).$$

Here $\alpha = q\eta$, and indices 1, 2, and 3 are equivalent to the indices x, y, and z. The energy levels, and consequently also the NQR frequencies, become functions not only of $q = q_{zz}$ and of $\alpha = q_{xx} - q_{yy}$, but also of the

[1)] Only 15 out of the 27 components of the third-rank tensor R are linearly independent in the general case [2]. Symmetry in the location of the investigated nucleus in the crystal can lead to a further reduction in their number.

parameters Δq and $\Delta\alpha$, which are of the order of 10^{-4}–10^{-5} relative to the former.

It is known that for any spin J and for an arbitrary transition, the NQR frequency can be represented by the expansion[7]

$$\nu_{m,\,m-1} = eQq\sum_{n=0}^{\infty} C_n(m)\eta^{2n}. \tag{4}$$

Confining ourselves to terms of first order in Δq and $\Delta\alpha$ and making the substitutions $\nu \to \nu + \Delta\nu$, $q \to q + \Delta q$, $\alpha \to \alpha + \Delta\alpha$, we obtain an analytic expression for the NQR frequency shifts under the influence of an external electric field:

$$\Delta\nu_i = \left(\nu_i - \eta\frac{\partial\nu_i}{\partial\eta}\right)\frac{\Delta q}{q} + \left(\frac{\partial\nu_i}{\partial\eta}\right)\frac{\Delta\alpha}{q}, \tag{5}$$

where ν_i is the frequency of an arbitrary quadrupole transition.

It is easy to verify that in the case $J = 3/2$, when the there is only one transition $\pm 1/2 \to \pm 3/2$ with frequency $\nu = (eQq/2h)\sqrt{1+\eta^2/3}$, we obtain from (5) the Dixon-Bloembergen formula[2]

$$\Delta\nu = \frac{\nu_0}{1+\eta^2/3}\left(\frac{\Delta q}{q} + \frac{\eta}{3}\frac{\Delta\alpha}{q}\right). \tag{6}$$

Analogously for J = 1, when there are frequencies $\nu_\pm = (eQq/4h)(1 \pm \eta/3)$, it follows from (5) that[2]

$$\nu_\pm(E) - \nu_\pm(0) = \frac{3eQq}{4h}\left(\frac{\Delta q}{q} \pm \frac{1}{3}\frac{\Delta\alpha}{q}\right). \tag{7}$$

With the aid of the obtained expression (5) we can easily estimate the Stark shifts also for an arbitrary transition in the case $J > 3/2$, when the analytic expressions for ν cannot be obtained at an arbitrary value of the EFG asymmetry parameter η. However, since expansions of the type (4) for $\nu(\eta)$ (up to η^8) are known[8] for the spins $J = 5/2$, $7/2$, and $9/2$, it follows that for small values of η ($\eta < 0.5$) it is easy to calculate $\partial\nu_i/\partial\eta$. On the other hand, if the asymmetry parameter η has an arbitrary value (from 0 to 1), then we can calculate $\partial\nu_i/\partial\eta$ by the procedure described below.

Any scalar equation of n-th order (n = 2J + 1, where J is the spin of the nucleus) can be represented by two equivalent forms:

$$\sum_{k=0}^{n} a_k\lambda^{n-k} = 0 \tag{8}$$

and

$$\prod_{i=1}^{n}(\lambda - \lambda_i) = 0, \tag{9}$$

where λ_j are the roots of the secular equation (8). Taking the derivative of (9) with respect to the asymmetry parameter at $\lambda = \lambda_i$, we get

$$\frac{\partial\lambda_i}{\partial\eta}\prod_{\substack{k=1\\ j\neq i}}^{n}(\lambda_i - \lambda_j) = \sum_{k=2}^{n}\lambda_i^{n-k}\frac{\partial a_k}{\partial\eta}, \tag{10}$$

where we took into account the condition $\sum_i \lambda_i = 0$. Using (10), we readily obtain the sought $\partial\nu_i/\partial\eta$:

$$\frac{\partial\nu_i}{\partial\eta} = \frac{\partial\lambda_{i+1}}{\partial\eta} - \frac{\partial\lambda_i}{\partial\eta}. \tag{11}$$

In the case $J = 5/2$ we have the following connection between λ_i and ν_i:

$$\lambda_1 = 1/3(-2\nu_1 - \nu_2), \quad \lambda_2 = 1/3(\nu_1 - \nu_2), \quad \lambda_3 = 1/3(\nu_1 + 2\nu_2). \tag{12}$$

The secular equation in this case is[7]

$$\lambda^3 - 7(3+\eta^2)\lambda - 20(1-\eta^2) = 0 \tag{13}$$

(λ is in units of eQq/20). Expression (10) for a spin $J = 5/2$ leads to the following results:

$$\frac{\partial\nu_1}{\partial\eta} = \frac{2}{3}\eta\frac{14\nu_2^2 + 14\nu_1\nu_2 - 7\nu_1^2 + 120\nu_2 + 60\nu_1}{\nu_1\nu_2(\nu_1+\nu_2)}, \tag{14}$$

$$\frac{\partial\nu_2}{\partial\eta} = \frac{2}{3}\eta\frac{14\nu_1^2 + 14\nu_1\nu_2 - 7\nu_2^2 - 120\nu_1 - 60\nu_2}{\nu_1\nu_2(\nu_1+\nu_2)}. \tag{15}$$

Here ν_1 and ν_2 (in the same units as λ) are the experimentally measured NQR frequencies of the transitions $\pm 1/2 \to \pm 3/2$ and $\pm 3/2 \to \pm 5/2$, respectively.

A similar procedure, which we did not describe here, can be readily applied also for spins $J = 7/2$ and $9/2$. The calculated values of the $\Delta\nu_i$ of the substances experimentally investigated in the present work are listed in Table I.

2. CALCULATION OF THE INDUCTION AND SPIN-ECHO AMPLITUDES FOR THE STARK EFFECT IN NQR

When a homogeneous constant electric field and a radio-frequency magnetic field are applied simultaneously, the total Hamiltonian of the quadrupole spin system can be written in the form of the sum $\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_E + \mathcal{H}_1$, where $\mathcal{H}_1 = -\gamma\hbar H_X(t) I_X = -2\gamma\hbar I_X H_1 \cos\omega t$ is the Hamiltonian of the interaction of the magnetic moment of the nucleus with a radio-frequency magnetic field linearly polarized along the axis perpendicular to the field **E**; H_1 and ω are the amplitude and frequency of the radio-frequency field.

The density matrix of the quadrupole spin system is a solution of the Neumann equation. The evolution of the density matrix $\rho(t)$, with the aid of which $\bar{I}_X$, which is proportional to the induction and echo amplitude, is calculated, is specified by the unitary transformation $\rho(t) = S(t)\rho(0)S^{-1}(t)$, where $\rho(0)$ is the initial or equilibrium density matrix.

In the calculation of the induction amplitude, the unitary matrix is $S_1(t) = D_1R_1$, where the matrices R and D determine respectively the behavior of the spin system during the period and after the termination of the action of the radio-frequency field. $\rho(t)$ was calculated by a method similar to that described in[9,10] with account taken of the Hamiltonian $\mathcal{H}$, i.e., under constant action of the electric field that leads to an NQR frequency shift relative to the unperturbed frequency $\omega_0 = \omega$. The expression for the induction amplitude after a 90° pulse is obtained in the following form:

$$T = T_0\cos(\Delta\omega t) = T_0\cos(2\pi\Delta\nu t), \tag{16}$$

where T_0 is the induction amplitude in the absence of an electric field[9,10].

To calculate the amplitude of the spin-echo signal, which appears at $t = 2\tau$ after the action of a pair of 90°–180° pulses with a time interval τ between them, it is necessary to calculate the unitary matrix $S(t) = S_2S_1 = D_2R_2D_1R_1$, where the indices 1 and 2 pertain to the first and second pulses. It is clear from physical considerations[11] that to obtain the effect, i.e., to obtain beats on the envelope of the echo signals, it is

Table I. Theoretical and experimental data on the Stark effect in polycrystals. Values of the constants c and d in the NQR frequency shifts calculated from formula (5). R-tensor components calculated from (27)

Isotope, spin	Transition	ν, MHz (T = 77°K)	$c/10^6\ q^{-1}$, Hz	$d/10^6\ q^{-1}$, Hz	$10^{12}\ x_i/q^2$ $(kV/cm)^{-2}$
			$SbCl_3$		
Sb^{121}, $J = 5/2$	$1/2 \longleftrightarrow 3/2$	59.685	55.4	22.7	$x_1 = 7.9 \pm 0.8$
	$3/2 \longrightarrow 5/2$	114.246	115.8	−8.32	
Sb^{123}, $J = 7/2$	$1/2 \longrightarrow 3/2$	39.096	31.2	41.9	$x_2 = 16.2 \pm 1.6$
	$3/2 \longrightarrow 5/2$	68.622	70.9	−11.9	
	$5/2 \longrightarrow 7/2$	104.460	105.2	−4.0	$x_3 = 17.1 \pm 10$
			$BiCl_3$		
Bi^{209}, $J = 9/2$	$1/2 \longrightarrow 3/2$	33.78	9.45	41.7	
	$3/2 \longrightarrow 5/2$	25.93	20.1	10.0	$x_1 = 176 \pm 20$
	$5/2 \longrightarrow 7/2$	37.85	43.4	−9.50	$x_2 = 399 \pm 40$
	$7/2 \longrightarrow 9/2$	52.74	55.8	−5.30	$x_3 = 836 \pm 80$
			$2SbCl_3 \cdot C_{10}H_8$		
Sb^{121}, $J = 5/2$	$1/2 \longrightarrow 3/2$	59.427	59.4		$R_{333}/q = (4.5 \pm 0.5) \cdot 10^{-6}$, $(kV/cm)^{-2}$
	$3/2 \longrightarrow 5/2$	118.903	119		
Sb^{123}, $J = 7/2$	$1/2 \longrightarrow 3/2$	36.058	36.1	0	
	$3/2 \longrightarrow 5/2$	72.151	72.2		
	$5/2 \longrightarrow 7/2$	108.2	108.2		

Note. The x_i are expressed in units of q^2, since the EFG component $q \equiv q_{ZZ}$ cannot be calculated from a known quadrupole-coupling constant eQq, owing to the lack of exact data on the quadrupole moments Q of the antimony and bismuth nuclei.

necessary to have an electric field either between the pulses, or between the second pulse and the echo signal, i.e., E should be superimposed on the sample in the form of the pulses whose sequences are described in[4,11]. This follows at least from the fact that in a constant electric field the phase differences of individual spin packets (in a coordinate system rotating with a frequency ω) accumulating in the interval τ cancel out, owing to the NQR frequency shift $2\pi\Delta\nu\tau$, during the second time interval τ, and the echo signal remains insensitive to the NQR frequency shift.

The effect is obtained mathematically if the matrices D_1 and D_2, which are proportional to $\exp(i\omega t)$ and $\exp[i\omega(t-\tau)]$, contain different frequencies ω: with a shift $\Delta\omega$ (in the presence of E) and without a shift (E = 0). We present here an expression for the envelope of the quadrupole-echo signals at $t = 2\tau$, when the electric field is turned on in pulse fashion in one of the intervals τ:

$$A = A_0 \cos(2\pi\Delta\nu\tau); \tag{17}$$

A_0 is the amplitude of the echo in the absence of an electric field E. A similar formula was obtained by Mims[11] for the envelopes of electron paramagnetic echo signals.

It is seen from (16) and (17) that the amplitude of the induction and the amplitude of the echo-signal envelope experience "slow beats" with a frequency that is equal, on the one hand, to the NQR frequency shifts described by formula (5), and is determined, on the other hand, from

$$\Delta\nu = 1/2\Delta t_n \tag{18}$$

or

$$\Delta\nu = 1/2\Delta\tau_n, \tag{19}$$

since the period of the cosine is equal to π; Δt_n and $\Delta\tau_n$ are the periods of the beats of the induction and spin-echo envelope amplitudes, respectively.

Everything stated so far pertains to single crystals. In polycrystalline samples, the general expression for the electrically induced NQR frequency shifts, which can be written in the form $\Delta\nu_i = c_i\Delta q + d_i\Delta\alpha$ (c_i and d_i are numerical coefficients), should be averaged over a sphere of unit radius:

$$\begin{gathered}\nu_i = \nu_i^0 + \Delta\nu_i,\\ \langle\Delta\nu_i\rangle = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\Delta\nu_i \sin\vartheta\, d\vartheta\, d\varphi = 0,\\ \langle\Delta\nu_i^2\rangle = c_i^2\langle\Delta q^2\rangle + 2c_id_i\langle\Delta q\Delta\alpha\rangle + d_i^2\langle\Delta\alpha^2\rangle.\end{gathered} \tag{20}$$

Let us consider the information that can be obtained from the induction and spin-echo signals, determined in the case of the single crystal by (16) and (17), but averaged over a polycrystal. The induction signal T_0 is the Fourier transform of the NQR line form function $g(\omega - \omega_0)$, i.e.,

$$T_0 = \int_{-\infty}^{\infty} g(\omega - \omega_0)\bar{I}_x(t)\, d\omega = G(t).$$

When an electric field is applied, we can write for a polycrystalline sample $\langle T\rangle = G(t)\Phi(t)$, where

$$\Phi(t) = \langle\cos(\Delta\omega t)\rangle = \langle\cos[2\pi t(c\Delta q + d\Delta\alpha)]\rangle. \tag{21}$$

To average (21) it is necessary to integrate, over a sphere of unit radius, a cosine whose argument is a complicated function of ϑ and φ of the vector **E** in the system of the principal axes of the EFG:

$$\begin{gathered}c\Delta q + d\Delta\alpha = c\Sigma E_iR_{i33} + d\Sigma E_i(R_{i11} - R_{i22})\\ = [cR_{133} + d(R_{111} - R_{122})]E_0\sin\vartheta\cos\varphi\\ + [cR_{233} + d(R_{211} - R_{222})]E_0\sin\vartheta\sin\varphi\\ + [cR_{333} + d(R_{311} - R_{322})]E_0\cos\vartheta = a_1E_1 + a_2E_2 + a_3E_3.\end{gathered} \tag{22}$$

It is obvious from (22) that the Stark shift $\Delta\nu$ of the NQR frequency can be represented as the scalar product $\mathbf{a}\cdot\mathbf{n}$, where **n** is the unit vector and **a** is a certain vector with components E_0a_1, E_0a_2, and E_0a_3. The scalar product $\mathbf{a}\cdot\mathbf{n}$ is written in turn in the form

$$\Delta\nu = \mathbf{an} = E_0\sqrt{a_1^2 + a_2^2 + a_3^2}\cos\vartheta'.$$

Thus, Eq. (21) reduces to the integral

$$\frac{1}{2}\int_0^{\pi}\cos(2\pi tE_0\sqrt{a_1^2+a_2^2+a_3^2}\cos\vartheta')\sin\vartheta'\,d\vartheta' = \frac{\sin(2\pi tE_0\sqrt{a_1^2+a_2^2+a_3^2})}{2\pi tE_0\sqrt{a_1^2+a_2^2+a_3^2}} \tag{23}$$

where a_1, a_2, and a_3 are determined by (22).

Using (20) and (22), we can easily see, averaging over the sphere[2)], that

$$E_0\sqrt{a_1^2+a_2^2+a_3^2} = \gamma\sqrt{3\langle\Delta\nu^2\rangle}. \tag{24}$$

Consequently, the beat frequency of the induction signal described by a function of the type $\sin x/x$, is proportional to the root-mean-square NQR frequency shift. A similar averaging procedure can easily be carried out also in the case of the spin-echo signal envelope (for A).

In analogy with (18) and (19), we have for the induction

$$E_0\sqrt{a_1^2+a_2^2+a_3^2} = 1/2\Delta t_n \tag{25}$$

and for the echo

$$E_0\sqrt{a_1^2+a_2^2+a_3^2} = 1/2\Delta\tau_n. \tag{26}$$

Replacing, for example in (26), the a_i by their expressions from (22) and introducing the notation

$$x_1 = \sum_i R_{i33}^2, \quad x_2 = \sum_i R_{i33}(R_{i11}-R_{i22}), \quad x_3 = \sum_i (R_{i11}-R_{i22})^2,$$
$$A_1 = c^2, \quad A_2 = 2cd, \quad A_3 = d^2, \quad B = (2\Delta\tau_n E_0)^{-2}, \tag{27}$$

we obtain for the Stark effect at a definite NQR frequency the equation

$$A_1x_1 + A_2x_2 + A_3x_3 = B. \tag{28}$$

To determine the sought constants x_i, which are connected with the average values $\langle\Delta q^2\rangle$, $\langle\Delta q\Delta\alpha\rangle$, and $\langle\Delta\alpha^2\rangle$ from (20) by the relations

$$\langle\Delta q^2\rangle = {}^1/_3E_0^2x_1, \quad \langle\Delta q\Delta\alpha\rangle = {}^1/_3E_0^2x_2, \quad \langle\Delta\alpha^2\rangle = {}^1/_3E_0^2x_3, \tag{29}$$

it is necessary to have experimentally-measured values of B for at least three NQR transitions for the same isotope ($J \geq {}^7/_2$) or for different isotopes ($J_1 > {}^3/_2$, $J_2 > {}^3/_2$, $J_1 \neq J_2$) of the same element in the given substance. In this case it is easy to set up the system

$$\sum_{j=1}^{3} A_{ij}x_j = B_i. \tag{30}$$

A solution of this system of linear inhomogeneous equations yields all the sought quantities defined by expressions (27) and (29). In the opposite case, i.e., when the measurements of the Stark effect in polycrystalline samples are possible only at one or two NQR frequencies of a certain nucleus, it is possible to obtain only the quantity $\sqrt{\langle\Delta\nu^2\rangle}$ and to determine the relations between $\langle\Delta q^2\rangle$, $\langle\Delta q\Delta\alpha\rangle$ and $\langle\Delta\alpha^2\rangle$.

We note finally, that in the particular case when the EFG has axial symmetry, when $d_i = 0$ (see (14)) and $R_{133} = R_{233} = 0$ (owing to the axial symmetry), the electrically-induced shifts are described by a single parameter R_{333}. In this case $a_1 = a_2 = 0$, $a_3 = cR_{333}$ and formula (5) reduces to the simple expressions

$$\Delta\nu_i = \nu_i\Delta q/q, \quad \Delta q = R_{333}E_0\cos\vartheta \tag{31}$$

or

$$\Delta\nu_i = \Delta\nu_i^{max}\cos\vartheta, \quad \Delta\nu_i^{max} = \nu_iE_0q^{-1}R_{333}, \tag{32}$$

which are equivalent to expression (13) in the paper of Dixon and Bloembergen[2]. It is then possible to determine the parameter R_{333} in a polycrystal, from experiments on the Stark effect at one NQR frequency, by determining the beat frequency of the induction or spin echo envelopes, described by the expression $\sin(2\pi\Delta\nu^{max}t)/2\pi\Delta\nu^{max}t$ (see (23)).

We note also that in the case of a spin $J = {}^3/_2$, even at a nonzero symmetry parameter, up to $\eta = 0.3$, it is possible to replace (5) with sufficient accuracy by expressions (31) and (32) in order to obtain the parameter R_{333}[4].

3. SAMPLES AND EXPERIMENTAL PROCEDURE

The main objects of the experimental investigation of many-level quadrupole spin systems were antimony trichloride ($SbCl_3$), bismuth trichloride ($BiCl_3$) and the molecular complex antimony trichloride–naphthalene ($2SbCl_3 \cdot C_{10}H_8$). The samples were purified by double distillation in vacuum. In addition, to compare the capabilities of the pulsed and stationary procedures, we investigated the Stark effect (by the pulsed method) in a number of chlorine-substituted hydrocarbons: $CHCl_3$, CCl_4, $C_2H_4Cl_2$, C_6H_5Cl, Cl_2 (which were investigated by the stationary method by Bloembergen and co-workers[5,6]) and C_2Cl_6 (not investigated by the stationary method). The sample thickness ranged from 2 to 4 mm. The electric field, directed perpendicular to the magnetic radio-frequency field, ranged from 0 to 50 kV/cm. The experiment was performed at T = 77°K.

The spin-echo signal was observed with the universal spin-echo apparatus[12] supplemented with a source of adjustable voltage pulses, controlled by the programming unit of the spectrometer. The echo-signal envelope was observed on an oscilloscope or registered with an automatic recorder using the program unit and an integrator[13]. A block diagram of the setup is shown in Fig. 1. Electric-field pulses were applied to the sample in accordance with the programs described in[4]. A typical record of the spin-echo signal envelope is shown in Fig. 2 of[4]. The total error in

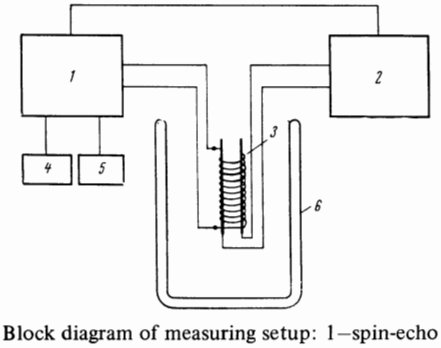

FIG. 1. Block diagram of measuring setup: 1–spin-echo spectrometer, 2–electric-voltage pulse source, 3–measuring cell, 4–oscilloscope, automatic recorder, 6–Dewar with liquid nitrogen.

[2)]The averaging of $\langle\Delta\nu^2\rangle$ with allowance for the intensity of the stationary NQR signals, carried out by Dixon and Bloembergen [2], leads to the same result, but 5/2 is obtained in place of 3.

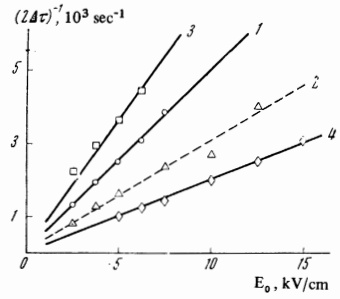

FIG. 2. Reciprocal periods of the "slow beats" of the spin-signal envelope in $SbCl_3$ vs. external electric field, T = 77°K: 1–Sb^{121}, transition 1/2 → 3/2; 2–Sb^{121}, 3/2 → 5/2; 3–Sb^{123}, 1/2 → 3/2, 4–Sb^{123}, 3/2 → 5/2.

the experimental data consisted of the error in the measurement of the beat periods and the error in the determination of the electric field intensity. This total error made the accuracy of the calculated R-tensor component approximately 10%.

4. DISCUSSION OF RESULTS

As shown in Sec. 2, to determine all the x_i (i = 1, 2, 3) it is necessary to observe the Stark effect at not less than three independent frequencies. Out of the five possible NQR transitions in $SbCl_3$[14], we observed "slow beats" of the echo signal envelope by application of a pulsed electric field for four transitions, namely the transitions $\pm 1/2 \rightarrow \pm 3/2$ and $\pm 3/2 \rightarrow \pm 5/2$ of Sb^{121} and the transitions $\pm 1/2 \rightarrow \pm 3/2$ and $\pm 3/2 \rightarrow \pm 5/2$ of Sb^{123}. The most distinct beats were observed in the first, third, and fourth transition, while only the first minimum of the spin-echo envelope was registered for the second transition. A plot of the reciprocal period $(2\Delta\tau)^{-1}$ against the intensity of the external electric field is shown in Fig. 2.

Using Table I, which lists the values of the coefficients c_i and d_i in the relations $\Delta\nu_i = c_i\Delta q + d_i\Delta\alpha$ for the corresponding transitions, we can easily set up the system of Equations (30) for the three indicated transitions. To calculate $B = (2\Delta\tau E_0)^{-2}$, we chose the values 340, 225, and 700 μsec for $2\Delta\tau$ in a field E_0 = 7.5 kV/cm.

The solution of the system

$$3.07\,x_1 + 2.52\,x_2 + 0.52\,x_3 = 0.154,$$
$$0.97\,x_1 + 2.61\,x_2 + 1.76\,x_3 = 0.351,$$
$$5.03\,x_1 - 1.69\,x_2 + 0.14\,x_3 = 0.0363$$

yields $x_1 = 0.00790$, $x_2 = 0.0162$, $x_3 = 0.171$, which are listed in appropriate units in Table I. Using these values and formulas (29), we get $\langle\Delta q^2\rangle/q^2 = 1.48\cdot10^{-10}$, $\langle\Delta q\Delta\alpha\rangle/q^2 = 3.04\cdot10^{-10}$, $\langle\Delta\alpha^2\rangle/q^2 = 32.1\cdot10^{-10}$. The root-mean-square NQR frequency shifts $\sqrt{3\langle\Delta\nu_i^2\rangle}$, calculated with the aid of the latter, are exactly equal to the slow-beat frequencies $(2\Delta\tau)^{-1}$ in the same field E_0 = 7.5 kV/cm, namely 2.96, 4.44, and 1.43 kHz. The value of $\sqrt{3\langle\Delta\nu_2^2}$ calculated in the same manner for $\nu_2(Sb^{121})$ is 2.20 kHz, which is in very good agreement with the experimental $(2\Delta\tau)^{-1}$ = 2.22 kHz ($2\Delta\tau$ is the distance to the first minimum of the spin-echo signal envelope and equals 450 μsec).

The asymmetry parameter in $SbCl_3$ at 77°K is equal to $\eta = 0.1875$. As predicted by the theory, such a value of the asymmetry parameter causes the beat frequencies to be 1.5 times larger for the lower transition of Sb^{123} than for the lower transition of Sb^{121}, although the NQR frequencies are 39.1 and 59.7 MHz, respectively. The excellent agreement between theory and experiment is due to the much larger contribution made to the electrically induced NQR frequency shifts by $\Delta\alpha$ (the so-called induced asymmetry parameter), than by Δq (change of q_{zz}). Indeed, $\sqrt{\langle\Delta\alpha^2\rangle}/\sqrt{\langle\Delta q^2\rangle}$ = 4.6. We note that in the presence of axial symmetry of the EFG, the ratio of the frequencies of the "slow beats" should, as seen from (31), be equal to the ratio of the NQR frequencies of the corresponding transitions, and consequently it should be 59.7/39.1 = 1.53 for $SbCl_3$, i.e., the inverse of that observed.

In the molecular complex $2SbCl_3\cdot C_{10}H_8$, the asymmetry parameter is $\eta = 0$[14]. The observed beat frequencies for the transitions given in Table I (Fig. 3) agree with formula (31). According to the discussion at the end of Sec. 2, this enables us to estimate the R-tensor component: $R_{333} = 4.5\times10^{-6}\,q[\text{kV/cm}]^{-1}$.

Of the four possible transitions of the Bi^{209} nucleus ($J = 9/2$) in polycrystalline $BiCl_3$, distinct beats were observed for the transition $\pm 7/2 \rightarrow \pm 9/2$ with a period $2\Delta\tau$ = 330 μsec (E_0 = 7.5 kV/cm; see Fig. 4). Less distinct beats were observed for the transitions $\pm 5/2 \rightarrow \pm 7/2$ and $\pm 1/2 \rightarrow \pm 3/2$ with respective periods 480 (E_0 = 7.5 kV/cm) and 150 μsec (E_0 = 5 kV/cm) (Fig. 4). For the transition $\pm 3/2 \rightarrow \pm 5/2$ we were able to observe only the appearance of the first minimum of the spin-echo envelope, at a distance 2τ = 320 μsec (E_0 = 5 kV/cm). Therefore the system of equations (30) was set up for the three transitions with frequencies ν_1, ν_3, and ν_4 (see Table I), with allowance for the asymmetry parameter η = 0.584 at 77°K. The obtained values of x_i are listed in Table I.

The corresponding mean values are $\langle\Delta q^2\rangle/q^2 = 33\cdot10^{-10}$, $\langle\Delta q\Delta\alpha\rangle/q^2 = 74.8\cdot10^{-10}$, $\langle\Delta\alpha^2\rangle/q^2$

Table II. Start effect on Cl^{35} nuclei. Comparison of the values of R_{333} obtained by the pulsed and stationary methods

Substance	ν, MHz (77°K)	R_{333}, 10^9 cm^{-1}	
		from (36)	from [5,6]
$CHCl_3$	38.3081	5.2±0.5	6.7±0,3
	38.2537		
CCl_4	40.6083	5.1±0.5	5.5±1,0
C_6H_5Cl	34.6219	5.9±0.5	6.5±0.5
$C_2H_4Cl_2$	34.361	5.4±0.5	6.02
C_2Cl_6	40.688	4.4±0.4	—
Cl_2	54.248	6.8±0.7	7.8±1.0

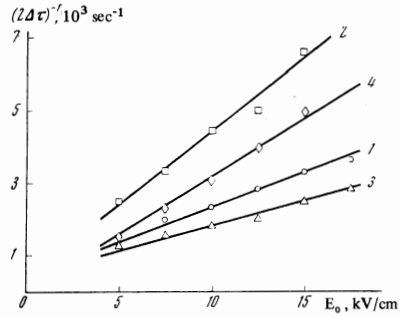

FIG. 3. Plot of $(2\Delta\tau)^{-1}$ against E_0 in $2SbCl_3\cdot C_{10}H_8$, T = 77°K: 1–Sb^{121}, transition 1/2 → 3/2, 2–Sb^{121}, 3/2 → 5/2, 3–Sb^{123}, 1/2 → 3/2, 4–Sb^{123}, 3/2 → 5/2.

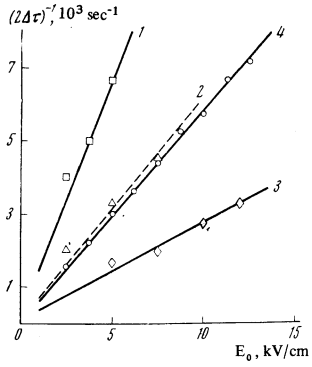

FIG. 4. Dependence of $(2\Delta\tau)^{-1}$ on E_0 for the nuclei Bi^{209} in $BiCl_3$, T = 77°K: 1–transition $1/2 \rightarrow 3/2$, $2–3/2 \rightarrow 5/2$, $3–5/2 \rightarrow 7/2$, $4–7/2 \rightarrow 9/2$.

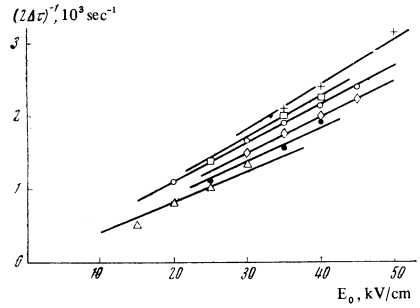

FIG. 5. Dependence of $(2\Delta\tau)^{-1}$ on E_0 for the nucleus C^{35}, T = 77°K: +–Cl_2, □–C_6H_5Cl, ○–$C_2H_4Cl_2$, ◇–$CHCl_3$, ●–CCl_4, △–C_2Cl_6.

$= 157.10^{-10}$. Hence for the transition $\pm 3/2 \rightarrow \pm 5/2$ we have $\sqrt{3\langle \Delta\nu_2^2 \rangle} = 4.20$ kHz ($E_0 = 7.5$ kV/cm), corresponding to the experimental value $(2\Delta\tau)^{-1} = 3.1$ kHz ($E_0 = 5$ kV/cm).

Figure 5 shows the results of pulse measurements of the Stark effect on Cl^{35} nuclei ($J = 3/2$) in a number of chlorine-substituted hydrocarbons. Since the asymmetry parameters in these compounds are small ($\eta < 0.2$), the beat frequency of the echo-signal envelopes is determined in the given electric field by only one parameter R_{333}, which can easily be calculated from (32). The values of R_{333} obtained in this manner and those determined by the stationary method for measurements of the second moment of the NQR absorption line[5,6] are compared in Table II. Satisfactory agreement within the limits of experimental error is obtained for almost all the substances. Some discrepancy in the values of R_{333} for Cl_2 and $CHCl_3$ can be explained, on the one hand, as being due to the fact that our measurements were performed in weaker fields E_0 (where the beat periods were still large enough to be observable), and on the other hand, to the lower accuracy, from our point of view, of the stationary measurements for these substances, since splitting of the NQR lines takes place in them.

A complete theoretical interpretation (the determination of all the components of the R tensor) is possible only in the case of single crystals. For polycrystalline samples, it is possible to determine three constants (the functions of these components) only if the Stark effect is observed for not less than three quadrupole transitions. We succeeded in showing that agreement between the calculated and measured frequency shifts for one or several additional transitions is a good control of the correctness of the theoretical conclusions (relations (5), (23), (25), and (26) and of the interpretation of the experimental data.

Thus, the pulse procedure for observing the Stark effect in NQR offers the following advantages over the stationary procedure:

1) The interpretation of the experimental data is much simpler in the pulse procedure[4,11].

2) There is no need for accurate measurements of the NQR frequencies or of their absolute shifts[3,4,11].

3) In the method proposed here we can measure the root-mean-square NQR frequency shifts in polycrystals in the case of weak electric fields, when these shifts lie within the limits of the line width, something very difficult to do in the stationary case.

4) Frequently, visual observation on the oscilloscope screen is sufficient, something impossible in the stationary method[3,4,11].

The authors thank V. S. Grechishkin for interest in the work, and A. N. Osipenko and B. F. Amirkhanov for a discussion of the results of averaging over the polycrystal.

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Translated by J. G. Adashko
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