

# Nuclear magnetic relaxation in a doubly rotating coordinate system as a method for investigating slow molecular motion

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A method for investigating slow molecular motion in solids was developed and implemented experimentally. The method is based on the measurement of the longitudinal nuclear spin relaxation time  $T_{1\rho\rho}$  in an effective field  $H'_e$  acting in a doubly rotating coordinate system (DRCS). The method involves locking of the nuclear magnetization by the field  $H'_e$  ("spin locking" in the DRCS) and subsequent direct recording of the continuous relaxation curve at the NMR frequency in a rotating coordinate system (RCS). Experiments were carried out under conditions when the nuclear dipole interactions were suppressed by the "magic angle" method in the RCS. A report is given of a study of the temperature dependence of the relaxation time  $T_{1\rho\rho}$  of protons in solid benzene. Additional minima of the relaxation time are reported at molecular rotation and self-diffusion rates of the order of  $10^2$ – $10^3$  sec $^{-1}$ , corresponding to the NMR frequency in the field  $H'_e$ . These rates are one or two orders of magnitude less than those that can be investigated by the familiar methods using a minimum of the relaxation time  $T_{1\rho}$  in the RCS.

It is known that nuclear spin relaxation is a valuable source of information on molecular motion in solids. This information is usually derived from the temperature dependence of the longitudinal relaxation time. The most important task is to determine the position of the relevant curve, which gives directly the correlation time  $\tau_c$  of molecular motion. For example, the minimum of the longitudinal relaxation time  $T_1$  in a static magnetic field  $H_0$  corresponds to fast motion at rates

$$\tau_c^{-1} \approx \omega_0 \approx \gamma H_0 \sim 10^8 \text{ sec}^{-1},$$

where  $\gamma$  is the nuclear gyromagnetic ratio; a minimum of the longitudinal relaxation time  $T_{1\rho}$  in an effective field  $H_e \ll H_0$  acting in a rotating coordinate system (RCS) corresponds to a slower motion characterized by  $\tau_c^{-1} \approx \omega_e \approx \gamma H_e \sim 10^5$  sec $^{-1}$  (Ref. 1). However, studies of even slower motion by this method are difficult because a further lowering of  $H_e$  is limited by the local field  $H_L$ , which is due to the nuclear dipole-dipole interactions. In typical homonuclear systems containing protons or the  $^{19}\text{F}$  nuclei this limit is of the order of  $\omega_L \approx \gamma H_L \sim 10^4$ – $10^5$  sec $^{-1}$ .

A way out of these difficulties was suggested in Refs. 2 and 3. The idea was to reduce deliberately the local field by a strong rf interaction with the spin system and then to create a new relatively weaker effective field  $H'_e \ll H_e$  and use it to determine the parameters of the longitudinal spin relaxation.<sup>1)</sup>

It was specifically proposed in Refs. 2 and 3 that homonuclear dipole interactions should be suppressed (in the first order) by the application of a strong continuous rf field  $2H_1 \cos \omega t$  with a half-amplitude  $H_1 \gg H_L$  and of frequency  $\omega = \omega_0 - \Delta$ , ensuring the condition of the "magic angle" between the directions  $\mathbf{H}_e$  and  $\mathbf{H}_0$  is satisfied<sup>5</sup>:

$$\theta \approx \arccos(\Delta/\omega_e) = \arccos(1/\sqrt{3}) \approx \theta_m$$

where  $\omega_e = [\Delta^2 + (\gamma H_1)^2]^{1/2}$ . Then the component of the dipole interactions in the RCS secular relative to the  $Z \parallel \mathbf{H}_e$  axis is governed only by a correction obtained from the second order of perturbation theory<sup>5</sup>:

$$\hat{\mathcal{H}}_{dp}^{00} = \frac{1}{\omega_e} [\hat{\mathcal{H}}_{dp}^{(1)}, \hat{\mathcal{H}}_{dp}^{(-1)}] + \frac{1}{2\omega_e} [\hat{\mathcal{H}}_{dp}^{(2)}, \hat{\mathcal{H}}_{dp}^{(-2)}], \quad (1)$$

where  $\hat{\mathcal{H}}_{dp}^{(m)}$  represents the usual terms of the dipole Hamiltonian in the RCS which are nonsecular relative to the  $Z$  axis. The field  $H_{L\rho}$  local in the RCS, described by the Hamiltonian (1), usually amounts to  $(10^{-1}$ – $10^{-2})H_L$ .

Under these conditions a new effective field  $H'_e \ll H_e$  can be created by harmonic modulation of the frequency  $\omega$  of an rf field; the modulation frequency is  $\Omega = \omega_e - \Delta'$  and the depth of modulation is  $\delta\omega$ . Consequently an alternating linearly polarized effective magnetic field appears in the RCS and it has a component  $2H_2 \cos \Omega t$ , perpendicular to the field  $\mathbf{H}_e$  and it obeys  $2\gamma H_2 = \delta\omega \sin \theta$  (Ref. 2). This means that in a doubly rotating coordinate system (DRCS) (with the second rotation about the direction of  $\mathbf{H}_e$  at a frequency  $\Omega$ ) there is a static effective field

$$H'_e = [(\Delta'/\gamma)^2 + H_2^2]^{1/2},$$

directed at an angle  $\theta' = \arccos(\Delta'/\gamma H'_e)$  to the field  $\mathbf{H}_e$  (Fig. 1). As expected,<sup>3</sup> if  $H_{L\rho} < H'_e \ll H_e$ , the longitudinal nuclear relaxation time  $T_{1\rho\rho}$  in the field  $\mathbf{H}'_e$  should carry information on the spectral density of molecular motion at a frequency  $\gamma H'_e$  and this frequency can be considerably less than  $\omega_L$ . This gives us grounds for assuming that the determination of the time  $T_{1\rho\rho}$  should help to study slower molecular motion. Experimental implementation of this method is described below.

Experiments were carried out on protons in samples of polycrystalline benzene of about 0.1 cm $^3$  volume in the tem-

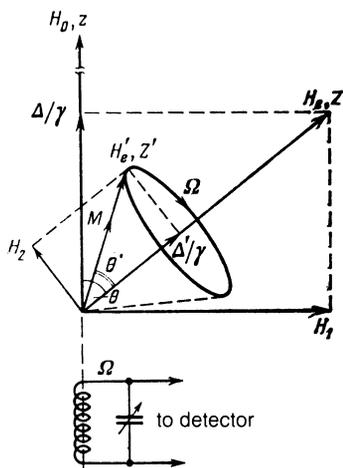


FIG. 1. Diagram showing the effective fields in the rotating and doubly rotating coordinate systems.

perature range  $T$  from 77 to 276 K in a field  $H_0 = 0.33\text{T}$ ;  $\omega_e / 2\pi = 100\text{ kHz}$ ;  $\theta = \theta_m$ . The modulation frequency  $\Omega$  was selected to be exactly equal to  $\omega_e$  (i.e.,  $\Delta' = 0$ ), so that  $H'_e = H_2$  and  $\theta' = 90^\circ$ . The relaxation time  $T_{1\rho\rho}$  was determined by locking the nuclear magnetization  $\mathbf{M}$  by the field  $\mathbf{H}_2$  ("spin locking" in the DRCS), described in Ref. 2. In our experiments this was achieved by adiabatic application of a frequency-modulated rf field, which automatically ensured adiabatic application of the field  $H_2$ . During adiabatic application the depth of modulation  $\delta\omega$  was  $2\pi$  (16.7 kHz), which in the case of  $\theta = \theta_m$  corresponded to  $\gamma H_2 = 2\pi$  (6.8 kHz). Next, at the end of the spin locking procedure, the field  $H_2$  was reduced to the required value.

After spin locking in the DRCS the vector  $\mathbf{M}$  was directed along the field  $\mathbf{H}_2$  and rotated together with this field around  $\mathbf{H}_e$  at a frequency  $\omega_e$  inducing a corresponding signal in a low-frequency detection coil<sup>2,6</sup> (see Fig. 1). This signal decayed exponentially with a characteristic time  $T_{1\rho\rho}$ ; an example of a relaxation curve obtained in the course of amplitude detection is shown in Fig. 2. It should be stressed that the whole of this curve was recorded continuously during one experiment. A high sensitivity was favored by a spectrally narrow received band governed by the relatively long

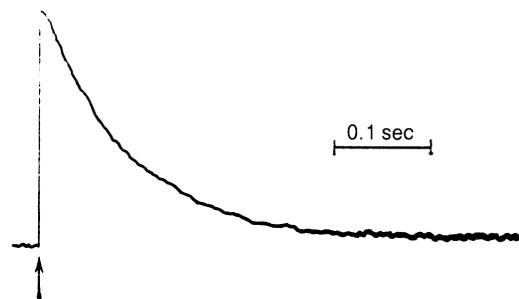


FIG. 2. Typical relaxation curve used to determine the relaxation time  $T_{1\rho\rho}$ . The arrow identifies the onset of spin-locking in the doubly rotating coordinate system. Solid benzene,  $T = 194\text{ K}$ ,  $\gamma H_2 / 2\pi = 6.8\text{ kHz}$ .

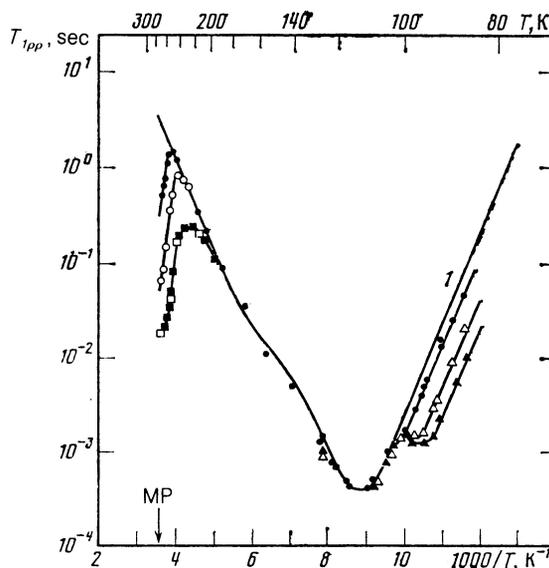


FIG. 3. Temperature dependences of  $T_{1\rho\rho}$  for solid benzene obtained for  $\gamma H_2 / 2\pi = 6.88\text{ kHz}$  ( $\bullet$ ),  $2.1\text{ kHz}$  ( $\Delta$ ),  $1.3\text{ kHz}$  ( $\blacktriangle$ ),  $815\text{ Hz}$  ( $\circ$ ),  $210\text{ Hz}$  ( $\blacksquare$ ), and  $170\text{ Hz}$  ( $\square$ ): 1) contribution to the relaxation corresponding to Eq. (3). Here, MP is the melting point of benzene.

time  $T_{1\rho\rho}$  (it should be noted that in the usual pulse methods this band is governed by the short time  $T_2$ ).

The temperature dependence of  $T_{1\rho\rho}$  is shown in Fig. 3. Curve 1 was obtained for the highest value  $\gamma H_2 / 2\pi = 6.8\text{ kHz}$ , resembling closely the known temperature dependence of the time  $T_{1\rho}$ : a deep minimum was clearly due to rotation of the benzene molecules about the sixfold axis and the fall near the melting point was due to self-diffusion between vacancies.<sup>7</sup> However, on reduction of  $\gamma H_2$ , there were new singularities: an additional minimum appeared in the low-temperature part and the fall in the self-diffusion region became much stronger.

In interpreting these results we shall bear in mind that the effective dipole Hamiltonian acting in the inclined RCS with the  $Z \parallel H_e$  axis under the "magic angle" conditions is<sup>3</sup>

$$\hat{\mathcal{H}}_{dp}^e = \sum_{m=\pm 1, \pm 2} \hat{\mathcal{H}}_{dp}^{(m)} + \hat{\mathcal{H}}_{dp}^{00}, \quad (2)$$

where the first term on the right-hand side represents the usual nonsecular first-order interaction and the second is the secular second-order correction described by Eq. (1). After transformation to the DRCS with the  $Z' \parallel H'_e$  axis, directed in our case perpendicular to the  $Z$  axis, and for  $H_{L\rho} \ll H_2$  these two terms become nonsecular, so that their random modulation by molecular motion makes the contributions  $1/T_{1\rho\rho}^{(1)}$  and  $1/T_{1\rho\rho}^{(0)}$  respectively to the total longitudinal relaxation rate  $T_{1\rho\rho}^{-1}$  in the DRCS.

In the case of the spin  $I = 1/2$  the first of these contributions is

$$\frac{1}{T_{1\rho\rho}^{(1)}} = \frac{\gamma^4 \hbar^3}{64} [10J_0(\omega_e) + 2J_0(2\omega_e) + 144J_1(\omega_0) + 45J_2(2\omega_0)]. \quad (3)$$

where  $J_i(\omega)$  are the spectral densities of the corresponding correlation functions (see, for example, Ref. 7). [Strictly speaking, Eq. (3) contains the frequencies  $k\omega_0 \pm m\omega_e \pm n\gamma H_2$  and  $m\omega_e \pm n\gamma H_2$ , where  $k, m = 1, 2$  and  $n = 1, 2, 3$ , but if  $\gamma H_2 \ll \omega_e \ll \omega_0$ , we can ignore the difference between the "side" and central frequencies.] Equation (3) differs from the corresponding expression for  $T_{1\rho}$  (Ref. 7) only in respect of its coefficients. It represents a deep minimum of the relaxation time  $T_{1\rho\rho}^{(1)}$  at  $\tau_c^{-1} \approx \omega_e$ .

Another most interesting contribution to  $T_{1\rho\rho}^{-1}$  is due to the second term on the right-hand side of Eq. (1). In the simplest case of a two-spin rigid molecule with isotropic rotation and  $I = 1/2$ , it amounts to<sup>3</sup>

$$\frac{1}{T_{1\rho\rho}^{(0)}} = \gamma^2 H_{L\rho}^2 \frac{\tau_c}{1 + (\gamma H_2 \tau_c)^2}. \quad (4)$$

This formula predicts a minimum of the relaxation time  $T_{1\rho\rho}$  at much lower molecular motion rates,  $\tau_c^{-1} = \gamma H_2$ , but its depth against the background of the contribution described by Eq. (3) is small because of the smallness of the factor  $H_{L\rho}^2$  in Eq. (4). It is shown in Ref. 3 that this makes it difficult to detect a minimum of Eq. (4) at relatively high values of  $\gamma H_2 \gtrsim \omega_L$ , but if  $\gamma H_2 \ll \omega_L$  this minimum should be clearly observed.

Curve 1 in Fig. 3 is calculated from Eq. (3) using the actual values of the correlation functions and the parameters of molecular motion in benzene given in Ref. 7 [correlation time  $\tau_c = (7.82 \times 10^{-15} \text{sec}) \times \exp(E_a/RT)$ , where  $E_a = 4.36 \text{ kcal/mole}$ ]. We can see that in the molecular rotation region it agrees well with the experimental results obtained for  $\gamma H_2/2\pi = 6.8 \text{ kHz}$ ; in particular, a minimum of  $T_{1\rho\rho}$  is observed at  $\tau_c^{-1} = 2\pi \times 10^5 \text{ sec}^{-1}$ . It should be noted that  $\gamma H_2 \approx \omega_L = 2\pi(7.7 \text{ kHz})$  applies here on the basis of Ref. 8, so that the additional minimum due to the contribution (4) should not appear.

Minima of this kind are however observed on reduction of  $\gamma H_2$ . They are located at  $\tau_c^{-1} = \gamma H_2 \sim 2\pi \times 10^3 \text{ sec}^{-1}$ , i.e., they correspond to molecular rotation which is two orders of magnitude slower.

The relaxation time  $T_{1\rho\rho}$  falls steeply in the temperature range  $T > 200 \text{ K}$ , which is associated with the self-diffusion of molecules between vacancies.<sup>7</sup> Measurements were made in this range only down to  $+3^\circ \text{C}$ , in order to avoid accidental melting of a sample (the melting point of benzene is  $+5.5^\circ \text{C}$ ). The results obtained for the highest value of  $\gamma H_2$  again agree qualitatively with the data on  $T_{1\rho}$  (Ref. 7); in particular, we used them to find the activation energy for this type of motion,  $E_a = 19 \text{ kcal/mole}$ , which is intermediate between the estimates given in Refs. 7 and 9.

Figure 4 shows the experimental dependences of  $T_{1\rho\rho}$  on the value of  $\gamma H_2$  in the self-diffusion region (after subtraction of the contribution due to rotation). Three regions can be distinguished in these curves. At the highest values of  $\gamma H_2/2\pi \sim 5 \times 10^3 \text{ Hz}$  the dependence of  $T_{1\rho\rho}$  on  $\gamma H_2$  disappears, indicating predominance of the contribution described by Eq. (3) (in this range of temperatures the local field  $\omega_L/2\pi$  is partly averaged by fast molecular rotation and is now  $3.1 \text{ kHz}$ —see Ref. 8). The law  $T_{1\rho\rho} \propto (\gamma H_2)^2$  is

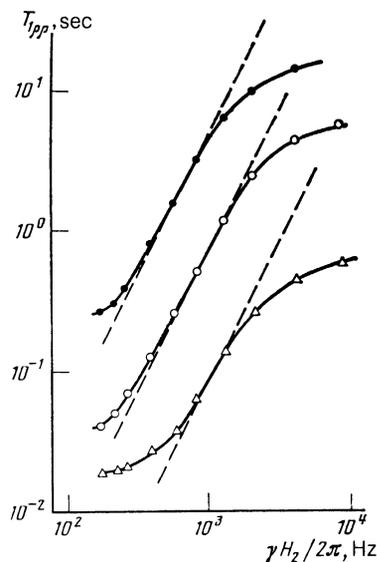


FIG. 4. Dependences of the relaxation time  $T_{1\rho\rho}$  on the field  $\gamma H_2$  in the range of diffusion of benzene molecules at  $T = -23.5^\circ \text{C}$  (●),  $-11.5^\circ \text{C}$  (○),  $+2.0^\circ \text{C}$  (Δ). The dashed lines represent the dependence  $T_{1\rho\rho} \propto H_2^2$ .

obeyed in the intermediate region, which is in agreement with Eq. (4) if  $\gamma H_2 \tau_c \gg 1$ . It should be pointed out that for  $\gamma H_2/2\pi \lesssim 800 \text{ Hz}$  the initial part of the relaxation curve exhibits damped oscillations associated with the oscillatory exchange of energy between the Zeeman and nonsecular dipole-dipole subsystems in the DRCS. Similar effects have been observed earlier in the laboratory coordinate system and in the RCS (Refs. 10–12).

Finally, at the minimum values of  $\gamma H_2/2\pi \approx 200 \text{ Hz}$  the curves of Fig. 4 show "bending" associated with the approach of  $\gamma H_2$  to the value  $\gamma H_{L\rho} = 2\pi \times 150 \text{ sec}^{-1}$ . In this case we are measuring not so much  $T_{1\rho\rho}$  as  $T_{1d\rho}$ , which is the spin-lattice relaxation time of the reservoir of the dipole interactions in the RCS, represented by the second-order Hamiltonian of Eq. (1); the existence of such a quasiequilibrium reservoir at  $\theta = \theta_m$  has been demonstrated experimentally.<sup>6</sup> We can expect a minimum in the temperature dependence of  $T_{1d\rho}$  to occur at  $\tau_c^{-1} \approx \gamma H_{L\rho}$ . The approach to this minimum at the maximum investigated temperatures (Figs. 3 and 4) has made it possible to estimate directly the correlation time for self-diffusion:  $\tau_c \approx 1 \text{ msec}$  at  $2^\circ \text{C}$ . Its order of magnitude is in agreement with an estimate (1.5 msec) obtained from measurements of  $T_{1\rho}$  employing model representations<sup>7</sup> and also with our estimates based on the observation of the "cascade" narrowing of the NMR line in the RCS (Ref. 4).

The general expression for  $T_{1\rho\rho}^{(0)}$  is more complex than the simple formula (4) and it includes spectral densities of two- and three-spin autocorrelation and cross-correlation functions at frequencies  $\gamma H_2$  and  $3\gamma H_2$ . This complicates somewhat a quantitative analysis of the data on  $T_{1\rho\rho}$  in the range of slow motion, but provides an opportunity to obtain in principle valuable information of greater variety, including data on the nature of molecular motion.<sup>3</sup>

It therefore follows that determination of a parameter (relaxation time  $T_{1\rho\rho}$ ) new to magnetic resonance spectroscopy should facilitate considerable progress in the study of slow molecular motion in solids, extending the range of the correlation times which can be determined directly by one or two orders of magnitude. This method essentially represents the next step after transformation from the laboratory to the rotating coordinate system (from  $T_1$  to  $T_{1\rho}$ ), and it may be particularly useful in studies of the molecular dynamics of macromolecules, vitrification processes, diffusion in crystals, etc.

<sup>1)</sup>Another approach to the study of slow motion proposed in Ref. 3 and realized in Ref. 4 involves determination of the transverse relaxation time  $T_{2\rho}$  in a field  $H_z$  under conditions of rf suppression of the dipole interactions (cascade narrowing effect).

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