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The Possibility of Studying Thermal Motion Correlation by Multiple Pulse NMR

V.E. Zobov and A.V. Ponomarenko*

L.V. Kirensky Institute of Physics, Academy of Science, Siberian Branch,
Krasnoyarsk 660036, USSR

SUMMARY

We present the results of a calculation of the spin-lattice and spin-spin relaxation for dipolar solid when it is irradiated by the WAHUHA and MREV-8 pulse sequences. The spin-spin relaxation rate which is determined by the second-order dipolar interaction term of the average Hamiltonian depends on thermal motion of four atoms. It has been shown that from the temperature dependence of this relaxation rate the degree of correlated atomic motion can be estimated.

INTRODUCTION

Since the development of multiple pulse NMR for high resolution in solids, considerable efforts have been made to study the spin-lattice relaxation in these experiments (HAEBERLEN and WAUGH, 1969, GRÜNDER, 1974, VEGA and VAUGHAN, 1978). The essential features of this relaxation are similar to spin-lattice relaxation in the rotating frame ($T_{1\rho}$-relaxation). However, for the pulse rf irradiation, the initial magnetization decays even in the rigid lattice case becouse of the spin-spin relaxation process, described by the high order terms of the average Hamiltonian (HAEBERLEN, 1976). In recent years, it has been demonstrated that here we have to deal with heating of spin system by quanta $\hbar\Omega n$ ($\Omega=2\pi/t_c$, t_c- the cycle time of the rf sequence), accomplished by simultaneous flip of two, three and more spins ("resonance processes") (IVANOV et al.,1978). If we have a train of rf pulses all pointing in the same direction in the rotating frame (a pulsed version of the spin locking experiment) the average Hamiltonian $\bar{H}_d^0$ is not equal to zero. In this case we have obtained that resonance processes are not sensitive to slow thermal motions (ZOBOV and PONOMARENKO, 1978). In this paper we analyse the line narrowing sequences with $\bar{H}_d^0=0$. Now the heating of spin system by resonance processes depends on thermal motions of the spins participated in the absorption of quanta $\hbar\Omega n$. Hence, it is possible, in principle, to study the degree of correlated motion of these spins.

THEORETICAL

The spin system in strong magnetic field $\vec{k}H_0$ we shall consider is irradiated by the WAHUHA sequence (see Figure 1) with a resonance offset $\Delta \ll 1/T_2$. In the toggling frame of referen-

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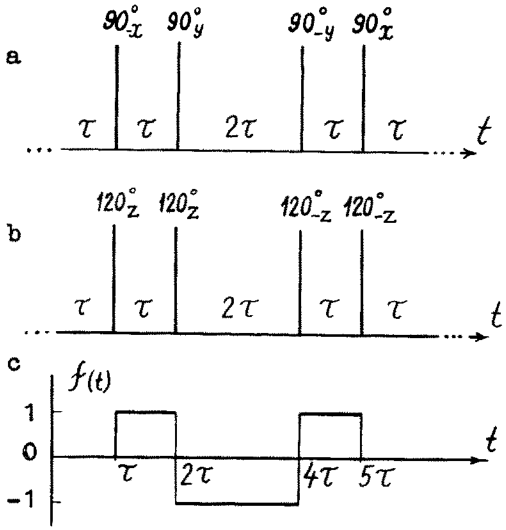

Fig. 1: Four-pulse sequence WAHUHA.

ce (HAEBERLEN, 1976) the Hamiltonian of the system becomes time dependent. In order to simplify the description of this dependence, it is convenient to replace the 90°-pulses along $\pm x, \pm y$ axes of the rotating frame by the train of 120°-pulses along the (111) and $(\overline{111})$ directions of this frame, and to go into a frame (tilted frame) with the Z axis along the (111) direction. Thus, in the tilted frame the Hamiltonian of the spin system under consideration is

$$\hbar\tilde{H}(t) = \hbar\tilde{H}_d(t) + \hbar\tilde{H}_\Delta(t) + \hbar\omega I_Z \quad , \tag{1}$$

where $\omega = \Delta/3^{1/2}$, $\tilde{H}_\Delta(t)$ is the time-dependent part of the resonance offset Hamiltonian,

$$\tilde{H}_\Delta(t) = \omega/2^{1/2}(I_+\exp\{if(t)2\pi/3\} + I_-\exp\{-if(t)2\pi/3\}), \tag{2}$$

$\tilde{H}_d(t)$ is the secular dipolar interaction,

$$\tilde{H}_d(t) = \sum_{\sigma=\pm 1,\pm 2} V^\sigma \exp\{if(t)\sigma\, 2\pi/3\} , \tag{3}$$

$$V^{\pm 1} = 1/2^{1/2} \sum_{i,j} b_{ij}(t) I_{Zi} I_{\pm j} \; , \quad V^{\pm 2} = 1/2 \sum_{i<j} b_{ij}(t) I_{\pm i} I_{\pm j} .$$

The coefficients $b_{ij}(t) = 1/2\,\gamma^2\hbar(1-3\cos^2\theta_{ij})/r_{ij}^3$ are dependent on the lattice motion via r_{ij} and θ_{ij}; periodic function of time f(t) is shown on Fig. 1b.

The equations of motion for $M_0 = M_Z$, $M_\pm = M_X \pm M_Y$ (where M_X; M_Y and M_Z are the magnetizations along X,Y and Z axes of tilted frame, respectively) were derived (ZOBOV and PONOMARENKO, 1979) by projection operator method:

$$\frac{dM_p(t)}{dt} = -ip\omega M_p(t) - \sum_{q=0,\pm 1} \int_0^t \overline{R_{pq}(t,t')} e^{-i\omega(pt-qt')} M_q(t')dt', \quad (4)$$

where

$$R_{pq}(t,t') = \sum_{n=1} R_{pq}^{(2n)}(t,t') , \quad (5a)$$

$$R_{pq}^{(2)}(t,t') = - \sum_{\sigma,\sigma'} \exp\left\{i\frac{2\pi}{3}(f(t)\sigma + f(t')\sigma')\right\} \frac{\langle [B_d^{\sigma}(t), I_{-p}][B_d^{\sigma'}(t'), I_q] \rangle}{\langle I_{-p} I_p \rangle}, \quad (5b)$$

$$R_{pq}^{(2n)}(t,t') = \sum_{\sigma,\dots,\sigma'} \int_{t'}^{t} dt_1 \dots \int_{t'}^{t_{2n-3}} dt_{2n-2} \exp\left\{i\frac{2\pi}{3} \sum_k \sigma_k f(t_k)\right\} (i)^{2n} \langle [B_d^{\sigma}(t), I_{-p}] \times \frac{(1-\hat{P})[B^{\sigma_1}(t_1), \dots, (1-\hat{P})[B^{\sigma_{2n-2}}(t_{2n-2}), [B_d^{\sigma'}(t'), I_q] \dots] \rangle}{\langle I_{-p} I_p \rangle}, \quad (5c)$$

$\hat{P}$ is the projection operator,

$$\hat{P}A = \sum_p \frac{\langle I_{-p} A \rangle}{\langle I_{-p} I_p \rangle} I_p , \quad \langle \dots \rangle = Sp\{\dots\}/Sp\{1\} ,$$

$$B_d^{\sigma}(t) = V^{\sigma} \exp\{i\sigma\omega t\} + V^{-2\sigma} \exp\{-i2\sigma\omega t\} ,$$

$$B^{\sigma}(t) = B_d^{\sigma}(t) + \omega/2^{1/2} I_{\sigma} \exp\{i\sigma\omega t\} .$$

The line over $R_{pq}(t,t')$ means averaging over thermal motion. The first term of the expansion in small quantity $(\tau/T_2) \ll 1$ (5), $R_{pq}^{(2)}(t)$, contains a fast oscillation with the period 6τ. It is the leading term in the fast motion case ($\tau_c \ll T_2$, τ_c is the time of thermal motions correlation). In the rigid lattice and in the slow motion case ($\tau_c \gg T_2$) the leading term is one with n=3, in which the fast oscillations vanish ("resonance term"). The expression for this term was derived from (5c) by integration by parts and is (ZOBOV and PONOMARENKO, 1979)

$$R^*_{pq}(t,t') = -\tau^4/(18)^2 \langle [F(t), I_{-p}][F(t'), I_q] \rangle / \langle I_{-p} I_p \rangle , \quad (6)$$

where

$$F(t) = [B_d^+(t) - B_d^-(t), [B_d^+(t), B_d^-(t)]] \quad (7)$$

(at t=0, using the notation of HAEBERLEN, 1976 we have $\tau^2 F(0)/18 = \bar{H}_d^{(2)}$). Using Eq.(5) and regrouping the operators in F(t) as follow

$$Q^{+1}(t)=3[V^{+1},[V^{+1},V^{-1}]]+3[V^{-2},[V^{+1},V^{+2}]]+3[V^{+1},[V^{-2},V^{+2}]] ,$$

$$Q^{+2}(t)=3[V^{+2},[V^{+1},V^{-1}]]+3[V^{+2},[V^{+2},V^{-2}]]+3[V^{-1},[V^{+2},V^{+1}]] ,$$

$$Q^{+3}(t)=Q^{0}(t)=0 , \quad Q^{+4}(t)=3[V^{+1},[V^{+1},V^{+2}]] ,$$

we have

$$F(t) = \sum_{m=1}^{4} Q^{m}(t)\exp\{im\omega t\} + C.C. . \tag{8}$$

Now we must carry out the average over thermal motion. Assuming the usual exponential correlation function, corresponding to a random Markoff process, we have

$$\overline{b_{ij}(t)b_{ij}(t')} = b_{ij}^2 \exp\{-|t-t'|/\tau_c\} . \tag{9}$$

That is enough for calculation of $\bar{R}_{pq}^{(2)}$. However, in $\bar{R}_{pq}^{(6)}$ there are products of six coefficients $b_{ij}(t)$, for example in the form of

$$\overline{b_{ij}(t)b_{jk}(t)b_{kl}(t)b_{ij}(t')b_{jk}(t')b_{kl}(t')} = g_{ijkl}(t,t') .$$

To calculate g_{ijkl} we will need to know how b_{ij} transforms under thermal motion of atoms or molecules. Let us consider for simplicity a random Markoff <u>process</u>: thermal motion results in jumps of b_{ij} to b'_{ij} so that $\overline{b_{ij}b'_{ij}}=0$, and the mean time between consecutive jumps is τ_c. Let us consider two limiting cases:

1). Completely uncorrelated motion, i.e. b_{ij}, b_{jk} and b_{kl} change quite independently. Then

$$g_{ijkl}(t,t') = b_{ij}^2 b_{jk}^2 b_{kl}^2 \exp\{-3|t-t'|/\tau_c\} . \tag{9a}$$

2). Completely correlated motion. Then

$$g_{ijkl}(t,t') = b_{ij}^2 b_{jk}^2 b_{kl}^2 \exp\{-|t-t'|/\tau_c\} . \tag{9b}$$

Eqs. (9) have a simple structure: the thermal motion results in appearance of exponent at "rigid" term $b_{ij}^2 b_{jk}^2 b_{kl}^2$. Extending this property on more complicated expressions, we assume that

$$\langle[Q^{m}(t),I_{-p}][Q^{-m}(t),I_{p}]\rangle/\langle I_{-p}I_{p}\rangle = -M_6^{(p)}(m)\exp\{-|t-t'|/\tau_k\} , \tag{10}$$

where

$$M_6^{(p)}(m) = -\langle [Q^m, I_{-p}][Q^{-m}, I_p] \rangle / \langle I_{-p} I_p \rangle \quad .$$

τ_k changes from τ_c to $\tau_c/3$ depending on the extent of the correlated motion.

RESULTS AND DISCUSSION

Using Eqs.(4)-(10), we obtain in the usual way

$$\frac{dM_p(t)}{dt} = -ip\omega M_p(t) - M_p(t)/T_p \quad , \tag{12}$$

where $1/T_p = 1/T_{1p} + 1/T_{2p}$. The relaxation terms with the decay constants T_{2p} and T_{1p} are obtained from the terms of Eq.(4) containing R^*_{pq} and $R^{(2)}_{pq}$, respectively. Thus,

$$1/T_{2p} = \sum_m M_6^{(p)}(m) \frac{\tau_k}{1 + (\omega m \tau_k)^2} \frac{\tau^4}{18^2} \quad , \tag{13}$$

$$1/T_{1p} = 1/3 M_2 \tau^2/\tau_c \quad , \quad M_2 = 3I(I+1) \sum_j b_{ij}^2 \quad . \tag{14}$$

Now suppose the resonance offset and therefore, corresponding magnetic field are equal to zero. In this case the projections of magnetizations on the toggling frame axes relax independently (ZOBOV, 1979). Therefore, it is convenient to return to the old untilted frame. Following the outlined procedure of calculation, we obtained

$$1/T_{2s} = \tau^4 M_6^{(s)} \tau_k / 18^2 \quad , \tag{15}$$

where s = x,y and z,

$$M_6^{(s)} = -\langle [[H_d^x - H_d^y, [H_d^x, H_d^y]], I_s]^2 \rangle / \langle I_z^2 \rangle \quad , \tag{16}$$

$$H_d^s = \sum_{i<j} b_{ij} (3 I_{si} I_{sj} - \vec{I}_i \vec{I}_j)$$

The relaxation terms of second order have been considered in (VEGA and VAUGHAN, 1978). The authors have obtained at $\tau_c \gg \tau$

$$1/T_{1x} = 1/T_{1z} = 2/9 \, M_2 \tau^2/\tau_c \quad , \quad 1/T_{1y} = 5/9 \, M_2 \tau^2/\tau_c \quad . \tag{17}$$

Thus, on resonance the x,y and z directions of the toggling frame are "principal axes" of relaxation (VEGA and VAUGHAN, 1978).

Off resonance there is the effective field $H_{eff} = \omega/\gamma$ in the toggling frame. This field mixes the x,y and z magnetizations during the relaxation process and, for a sufficiently large resonance offset ($\Delta T_{2e} \gg 1$), the parallel and perpendicular to the effective field magnetizations relax independently with time constants T_0, $T_{\pm 1}$. From Eq.(13) we see that T_0 and T_{+1} have the same orders of magnitude and the similar dependences of parameters. Since $M_{\pm 1}$ decay and oscillate but M_0 decays only, $T_{\pm 1}$ gives a line width of a multiple-pulse line-narrowing experiment. In real samples the decay of M_0 results from spin-lattice interaction, whereas the decay of the oscillations ($M_{\pm 1}$) does not necassarily. For example, the chemical shift dispersion makes contribution to rate of this decay. Therefore T_0 may be convenient to study of thermal motion. The calculated dependences of the relaxation rate ($1/T_{2e}$) on τ_c for some values of τ, Δ and τ_c/τ_k are shown in Figure 2.

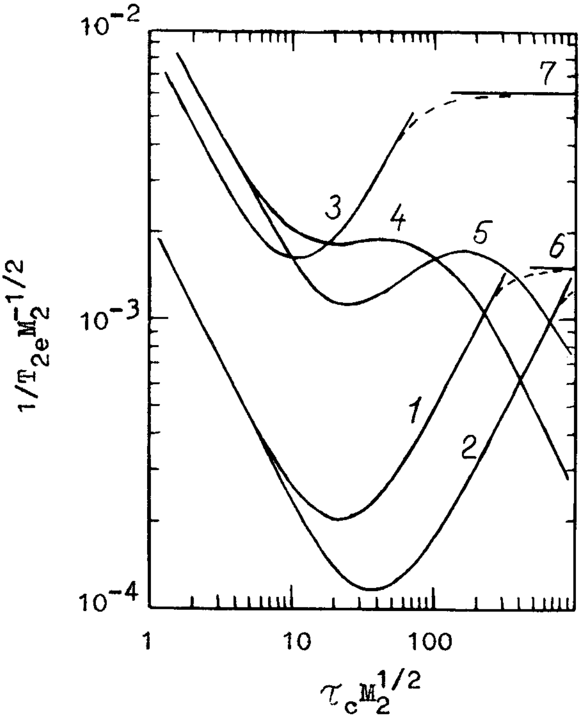

Fig. 2: Dependence of relaxation rate $1/T_{2e}$ on the correlation time τ_c (1-5); (6,7) - values of $1/T_{2e}$ in the rigid lattice limit. 1-3, 6, 7 - $\Delta = 0$ (1 - $k=1$, $\tau M_2^{1/2} = 0,1$; 2 - $k=3$, $\tau M_2^{1/2} = 0,1$; 3 - $k=1$, $\tau M_2^{1/2} = 0,2$). 4,5 - $\Delta/3^{1/2} = 0,01 M_2^{1/2}$ (4 - $k=1$, $\tau M_2^{1/2} = 0,2$; 5 - $k=3$, $\tau M_2^{1/2} = 0,2$), $k = \tau_c/\tau_k$.

On resonance the relaxation rate of z-magnetization $1/T_{2e} = 1/T_{1z} + 1/T_{2z}$ was calculated using Eqs.(15) and (17) and estimation $M_6^{(z)}=15M_2^3$. For $\omega=0,01M_2$ the parallel magnetization rate $1/T_{2e}=1/T_o$ was calculated using Eq.(13) and following estimation

$$M_6^{(0)}(\pm 1)/2 = M_6^{(0)}(\pm 2) = M_6^{(0)}(\pm 4) = 3M_2^3 \quad .$$

The two terms $1/T_{1s}$ and $1/T_{2s}$ (or $1/T_{1p}$ and $1/T_{2p}$ for $\Delta \neq 0$) have different τ_c dependences. Therefore, either $1/T_{1s(p)}$ (fast motion) or $1/T_{2s(p)}$ (slow motion) is a leading term for the different values of τ_c. Let us first analyse the on-resonance case. In the rigid lattice limit ($\tau_c \rightarrow \infty$) $T_{1z} \rightarrow \infty$ and we obtain, using Eqs.(4) and (6),

$$M_z(t) = M_z(0)\ (1-t^2/2\ M_6^{(z)}\tau^4/18^2\ \ +\ldots)$$

and we can estimate the relaxation rate:

$$(1/T_{2z})_\infty = \tau^2(M_6^{(z)}/2)^{1/2}/18 \quad .$$

From this estimation one can conclude that the slow motion effects on the value of T_{2z} if

$$\tau_c < (T_{2z})_\infty \sim 18/(\tau^2(M_6^{(z)}/2)^{1/2}) \quad .$$

In increase the thermal motion intensity (τ_c decreases) the $1/T_{2z}$ decreases, but $1/T_{1z}$ increases and will overcome $1/T_{2z}$ for $\tau_c < \tau_c'$. By comparing Eq.(15) and Eq.(16), we get

$$\tau_c' = 6(2M_2k)^{1/2}/(\tau\,(M_6^{(z)})^{1/2}) \ .$$

Off resonance the τ_c dependences of $1/T_{1p}$ and $1/T_{2p}$ have the same form as $1/T_{1z}$ and $1/T_{2z}$ for $\tau_c\Delta < 1$, but for $\tau_c\Delta > 1$ and in the slow motion and rigid lattice limits the relaxation rate $1/T_{2o}$ is decreased by resonance offset. Thus, the maximum at $\Delta\tau_c/k=3^{1/2}$ will appear in the τ_c dependence of $1/T_{2o}$. One can see that the both values, $1/T_{2o}$ and $1/T_{2z}$, depend on the extent of correlated motion $k=\tau_c/\tau_k$. To find k in the case of $\Delta=0$ we must calculate $M_6^{(0)}$. But for $\Delta \neq 0$, when the additional maximum of $1/T_{2o}$ occurs at $\tau_c=k/\omega$, this difficulties can be avoided: knowing the Δ and the values of τ_c for different temperatures, one may obtain k from temperature dependence of T_{2e}.

MREV eight-pulse sequence (HAEBERLEN, 1976) which is less sesitive on pulse imperfections, can be more convenient to study this effect. The MREV-8 cycle consists of two subcycles: The first is the WAHUHA cycle, the second is again a WAHUHA, but the P_x and P_{-x} pulses are interchanged. Therefore, the spin-lattice relaxation rates have the same values as it is in a WAHUHA sequence.

The effect considered above may be masked by chemical shift dispersion in powders, polimers and other compounds. To supress the chemical shift DYBOWSKI and PEMBLETON, 1979 proposed to add the 180° converting pulse in the MREV-8 cycle (the 17

-pulse DNCP sequence). The 180° pulse leads to reversing of the resonance offset sign with the period 24τ. Taking into account this fact we obtained that for $24\tau\Delta \gtrsim 1$ the chemical shift is not eliminated. When the averaging condition $24\tau\Delta \ll 1$ is fulfiled, the relaxation is the same as for $\Delta = 0$.

The chemical shift anisotropy may be supressed by additional spinning a sample about an axis tilted by the "magic angle" 54°44' to the H_0 (LIPPMAA et al., 1977). However, in this case the averaged over spinning part of F(t) is not equal to zero and averaging resonance offset is preserved. The partial averaging of the dipolar interaction decreases $M_6^{(0)}$ but the form of the τ_c dependence of the relaxation rate $1/T_{2o}$ is preserved.

In conclusion, we note that changing the pulse cycles, one can change the number of spins in the effective interaction, i.e. one may, in principle, study the correlation of thermal motion of various number of atoms.

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