INSTYTUT FIZYKI JĄDROWEJ
im. H. Niewodniczańskiego
w Krakowie

MATERIAŁY XXXI OGÓLNOPOLSKIEGO SEMINARIUM

NA TEMAT
MAGNETYCZNEGO REZONANSU JĄDROWEGO
I JEGO ZASTOSOWAŃ

1 - 2 grudnia 1998

KRAKÓW 1999

EFFECTS OF FINITE PULSE WIDTHS ON ECHO SIGNALS IN HETERONUCLEAR SPIN SYSTEMS

N.Sergeev[1)], P.Bilski[2)], J.Wąsicki[2)]

[1)]Institute of Physics US, Szczecin; [2)] Institute of Physics UAM, Poznań

Introduction

The effects of the finite RF pulse width on the free induction decay (FID) and the solid-echo signal in solids with only one nuclear species (homonuclear spin systems) were discussed in [1-4]. It was shown that the FID after the hard 90^0 RF pulse with the finite amplitude and duration (t_1) has its origin at the centre of RF pulse ($t_1/2$). It was shown also that due to the dipole-dipole interactions during the RF pulses the maximum of solid-echo signal was observed at $t_e = 2\tau+t_2-t_1/2$.

The main purpose of this work is the analysis the influence of the finite pulse width on the FID and solid-echo signals in solids with two nuclear species (heteronuclear spin systems).

Results and discussion

Using the formalism described in [3 – 5] we obtained the following expression for the FID signal in homonuclear spin system

$$G(t) = G_0(t-t_1)\, F_0(t_1/2) + M_{2II}\, G_1(t-t_1)\, F_1(t_1/2) + \dots \,, \quad (1)$$

where

$$G_0(t) = \mathrm{Tr}\{\exp(-iH_{int}t)\, I_X \exp(iH_{int}t)\, I_X\}/\mathrm{Tr}(I_X^2) \quad (2)$$

is the FID signal after hard delta 90^0 pulse.

H_{int} is the interaction Hamiltonian of nuclear spin system

$$H = H_{II} + H_{SS} + H_{IS} \,. \quad (3)$$

Here H_{II} is the secular dipolar Hamiltonian of the I-spins

$$H_{II} = \Sigma_{(i>j)}\, D_{ij}\, (2I_{iZ}I_{jZ} - I_{iX}I_{jX} - I_{iY}I_{jY}) \,, \quad (4)$$

H_{SS} is the secular dipolar Hamiltonian of the S-spins

$$H_{SS} = \sum_{(k>l)} B_{ij} (2S_{kZ}S_{lZ} - S_{kX}S_{lX} - S_{kY}S_{lY}) \ . \tag{5}$$

H_{IS} is the interaction Hamiltonian of I and S spins

$$H_{IS} = \sum_{(i,k)} C_{ik} I_{iZ}S_{kZ} \ . \tag{6}$$

In Eq.(1) M_{2II} is homonuclear contribution to the second moment M_2

$$M_2 = M_{2II} + M_{2IS} \ , \tag{7}$$

where M_{2IS} is the heteronuclear contribution to M_2.
In Eq.(1) the function $F_0(t)$ has the form

$$F_0(t) = Tr\{\exp(-iH_{II}t)\, I_X \exp(iH_{II}t)\, I_X\}/Tr(I_X^2) \ . \tag{8}$$

This function is the FID signal which would be observed if $H_{IS} = 0$.
In Eq.(1) the functions $G_1(t)$ and $F_1(t)$ are

$$G_1(t) = -(i/M_2)\, dG_0(t)/dt \ , \tag{9}$$

$$F_1(t) = -(i/M_{2II})\, dF_0(t)/dt \ . \tag{10}$$

If $H_{IS} = 0$ we have homonuclear spin system. For this case the function $F_0(t)$ is equal to the function $G_0(t)$ and from Eq.(1) we obtain the well known result [1 - 3]

$$G(t) = G_0(t-t_1)\, G_0(t_1/2) + M_2\, G_1(t-t_1)\, G_1(t_1/2) + \ldots \approx$$

$$\approx G_0(t-t_1/2) \ . \tag{11}$$

At the short times t and t_1 the good approximations for functions $G_0(t)$ and $F_0(t)$ are

$$G_0(t) = 1 - (M_2/2)\, t^2 + \ldots \ , \tag{12}$$

$$F_0(t) = 1 - (M_{2II}/2)\, t^2 + \ldots \ . \tag{13}$$

Using Eqs.(12), (13) and Eqs.(9), (10) from Eq.(1) we obtain

$$G(t) = 1 - (M_{2II}/2)\, (t - t_1/2)^2 - (M_{2IS}/2)\, (t - t_1)^2 + \ldots \ . \tag{14}$$

From Eq.(14) it follows that the origin (maximum) of the FID signal is observed at

$$t_0 = (t_1/2)\, (1 + M_{2IS}/M_2) \ . \tag{15}$$

So heteronuclear dipolar interactions lead to the shift of the FID's origin from the time $t_0 = t_1/2$(Eq.(11)).

The amplitude of the FID signal at $t = t_0$ is

$$G(t_0) = 1 - t_1^2 \,(M_{2II}\, M_{2IS}/8\, M_2) + \dots \ .$$

Using again the formalism described in [3 - 5] we obtained the following expression for the solid-echo signal ($90^0{}_Y - \tau - 90^0{}_X$) in heteronuclear spin system

$$\begin{aligned} V(t, \tau) &= G_0(t - \tau - t_2)\, F_0(-t_1/2)\, G_0(-\tau + t_1) + \\ &+ M_{2II}\, [\, G_0(t - \tau - t_2)\, F_1(-t_1/2)\, G_1(-\tau + t_1) + \\ &+ G_1(t - \tau - t_2)\, F_0(-t_1/2)\, G_1(-\tau + t_1) + \\ &+ G_1(t - \tau - t_2)\, F_1(-t_1/2)\, G_0(-\tau + t_1)\,] - \\ &- M_{2IS}\, G_0(t - \tau - t_2)\, F_1(-t_1/2)\, G_1(\tau - t_1) + \dots \ . \end{aligned} \tag{16}$$

Here t_1 and t_2 are the RF pulses widths; the times τ and t are measured from the beginning of the first RF pulse.

If $H_{IS} = 0$ from Eq.(16) we have

$$\begin{aligned} V(t, \tau) &= G_0(t - \tau - t_2)\, G_0(-t_1/2)\, G_0(-\tau + t_1) + \\ &+ M_2\, [\, G_0(t - \tau - t_2)\, G_1(-t_1/2)\, G_1(-\tau + t_1) + \\ &+ G_1(t - \tau - t_2)\, G_0(-t_1/2)\, G_1(-\tau + t_1) + \\ &+ G_1(t - \tau - t_2)\, G_1(-t_1/2)\, G_0(-\tau + t_1)\,] + \dots \ . \end{aligned} \tag{17}$$

Using the expression [4]

$$\begin{aligned} G_0(t_1 + t_2 + t_3) &= G_0(t_1)\, G_0(t_2)\, G_0(t_3) + \\ &+ M_2\, [\, G_0(t_1)\, G_1(t_2)\, G_1(t_3) + \\ &+ G_1(t_1)\, G_0(t_2)\, G_1(t_3) + G_1(t_1)\, G_1(t_2)\, G_0(t_3)\,] + \dots \ , \end{aligned} \tag{18}$$

we obtain from Eq.(17) the known result [4]

$$V(t, \tau) \approx G_0(t - 2\tau - t_2 + t_1/2) \ . \tag{19}$$

In the case when $H_{IS} \neq 0$ we again assume that $G_0(t)$ and $F_0(t)$ may be approximate by Eq.(12) and Eq.(13). Using these equations we have from Eq.(16)

$$V(t, \tau) = 1 - (M_{2II}/2)\,(t - 2\tau - t_2 + t_1/2)^2 - $$
$$- (M_{2IS}/2)\,[\,(t - \tau - t_2)^2 + (\tau - t_1)^2\,] + \ldots \quad . \qquad (20)$$

From Eq.(20) it follows that maximum of the solid-echo signal has been observed at

$$t_e = (2\tau + t_2 - t_1/2) - (\tau - t_1/2)\,(M_{2IS}/M_2) \quad . \qquad (21)$$

The amplitude of solid-echo signals is

$$V(t_e, \tau) = 1 - (\tau - t_1/2)^2\,(M_{2II}\,M_{2IS}/2M_2) - (M_{2IS}/2)\,(\tau - t_1)^2 \quad . \qquad (22)$$

If t_1=t_2=0 (the approximation of the delta RF pulses) from Eq.(21) and Eq.(22) it follows the known results [6].

Eq.(21) and Eq.(22) show that the heteronuclear dipole-dipole interactions induce the attenuation and additional shift of the solid-echo signal amplitude.

References

1.D.Barnaal and I.J.Lowe, *Phys.Rev.Lett.*, **11** (1963) 258; *Phys.Rev.*, **148** (1966) 328.

2.M.Bloom, J.H.Davis and M.I.Valic, *Can.J.Phys.*, **58** (1980) 1510.

3.N.A.Sergeev, *Solid State Nuclear Magnetic Resonance*, **8** (1997) 47.

4.N.A.Sergeev, *Solid State Nuclear Magnetic Resonance*, **10** (1997) 45.

5.M.Siergiejew, *Wstęp do kwantowej teorii magnetycznego rezonansu jądrowego*, Wydawnictwo WSP, Słupsk, 1996.

6.M.Siergiejew, A.Sapiga, in: *Materiały XXVII Ogólnopolskiego Seminarium na temat Magnetycznego Rezonansu Jądrowego i jego zastosowań*, Raport Nr 1695/PL., Kraków 1995, str.55.