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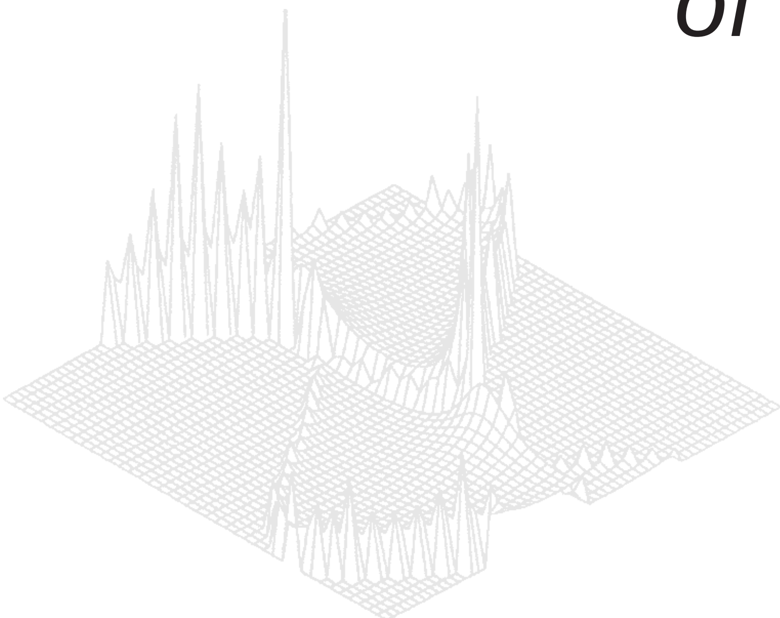

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Nuclear Spin-system Dynamics affected by Double Inhomogeneity under Multipulse Excitation in Statistical Tensor Formalism*

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Abstract

New coherent transient effects formed due to double inhomogeneity, i.e. inhomogeneity in the main precession frequency (Larmor inhomogeneous broadening) and of the rf amplitude expressed in frequency units (Rabi inhomogeneous broadening), influencing the nuclear spin-system dynamics during rf pulse excitation, have been predicted and investigated by use of the method of concatenation of perturbation factors (CPF) in statistical tensors (ST) formalism. Multiple pulse excitation under double inhomogeneity is examined when the repetition period of a pulse sequence is shorter than T_1.

1. Introduction

In this paper we discuss a number of transient coherent effects detected in NMR and NMR on Oriented Nuclei (NMRON), all of which are inherently due to complications from severe Larmor inhomogeneous broadening (LIB) and Rabi inhomogeneous broadening (RIB) under rf pulse excitation. Thus, the effect of the rf pulse is isochromat frequency and Rabi frequency dependent, whereas the LIB only is important for interpulse dynamics. The LIB and RIB naturally occur simultaneously in ferromagnets but can also be synthesised in non-magnetic media with appropriate application of non-homogeneous dc and rf fields. Among the coherent transients considered due to the double inhomogeneity are:

In NMR: (a) single pulse echo (SPE), first observed by Bloom (1955) and subsequently examined by a number of authors (Chekmarev *et al.* 1979, 1988; Tsifrinovich *et al.* 1985; Kuz'min *et al.* 1990; Kiliptary and Tsifrinovich 1991, 1992) and recently interpreted by Shakhmuratova *et al.* (1997*a*); (b) notched- and locked-type echoes (observed by Kunitomo *et al.* 1980, 1982 but under pure LIB on protons); and (c) intriguing multiple structure echo in NMR from ferromagnets, experimentally observed but under various conditions by Kinnear *et al.* (1980), Reingardt *et al.* (1983), Fowler *et al.* (1985) and Kiliptary and Kurkin (1990).

In NMRON: (a) two-pulse stimulated echo in NMRON (Shakhmuratova *et al.* (1996*b*, 1997*b*) and (b) oscillatory free induction decay (OFID) in NMRON (Shakhmuratova *et al.* 1993; Hutchison *et al.* 1993; Chaplin *et al.* 1995*a*, 1995*b*), including the SPE-type effect.

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The vital role of double inhomogeneity for the formation of coherent transients in pulsed NMR and NMRON is demonstrated, including high repetition rate, i.e. small repetition period T of a pulse sequence as compared to the longitudinal relaxation time T_1 for conventional NMR. For higher rank statistical tensors (STs) the high repetition rate is not needed, since the extension of the signal duration due to rank dependence may provide a similar circumstance to utilisation of high repetition rate effect, as is demonstrated below. The possibility to examine the dynamics of a spin system, complicated by these factors simultaneously, is provided by a flexible concatenation of perturbation factors (CPF) in the ST formalism presented below.

General Formalism

The ST formalism, established by Matthias *et al.* (1971), Alder and Steffen (1975) and Blum (1981), but more widely used in the theory of perturbed angular distributions (PAD) of γ-radiation from radioactive nuclei, is applied in the study of coherent transient effects. The ST are related to the density matrix through the Clebsch–Gordan coefficients:

$$\rho_q^\lambda = \sum_{m,m'} \langle m|\rho(I)|m'\rangle (-1)^{I+m} \langle I-m,\ Im'|\lambda q\rangle; \tag{1a}$$

$$\langle m|\rho(I)|m'\rangle = \sum_{\lambda,q} \rho_q^\lambda \langle I-m,\ Im'|\lambda q\rangle\,, \tag{1b}$$

thus providing identical information. On the other hand, one can take advantage of using the ST formalism, since ρ_q^λ, the ST of order q, $|q| \le \lambda$, and rank λ, $0 \le \lambda \le 2I$, where I is the nuclear spin, is easily transformed through the rotation Wigner functions $D^\lambda_{q'q}(z' \to z)$ (Edmonds 1974) when the frame is rotated (Matthias *et al*. 1971):

$$\rho_q^\lambda(t)_z = \sum_{q'\lambda'} D^{(\lambda)}_{q'q}(z' \to z)^* \rho_q^\lambda(t)_{z'}\,. \tag{2}$$

Evolution of the ST in time can be presented as

$$\rho_q^\lambda(t) = \sum_{q'\lambda q'} G^{q'q}_{\lambda'\lambda}(t)^* \rho_{q'}^{\lambda'}(0)\,, \tag{3}$$

where $G^{q'q}_{\lambda'\lambda}(t)$ are the perturbation factors (PF) defined by the external interactions, and in general, it may change both the rank and order of the ST. The PF are well defined for various interaction Hamiltonians, i.e. pure magnetic dipole and electric quadrupole, as well as when they are combined, see Alder and Steffen (1975) and Matthias *et al*. (1971). Under multiple rf pulse excitation, when the Hamiltonian is changed during various periods of time evolution of a quantum system, the CPF method (Shakhmuratova 1985, 1986) proves to be useful. Thus Fig. 1 below shows the composite time domain sequence for multiple rf pulse excitation. The final PF is composite of the constituent PFs:

$$G^{q'q}_{\lambda'\lambda}(t) = \sum_{q_1\lambda_1} \cdots \overline{G}^{q_2q_2}_{\lambda_2\lambda}(\tau_2) \tilde{G}^{q_1q_2}_{\lambda_1{}'\lambda_2}(\Delta t_2) \overline{G}^{q_1q_1}_{\lambda_1\lambda_1}(\tau_1) \tilde{G}^{q'q_1}_{\lambda'\lambda_1}(\Delta t_1)\,, \tag{4}$$

with

$$\overline{G}^{qq}_{\lambda\lambda}(\tau) = \exp(-\mathrm{i}q\omega_{\mathrm{L}}\tau) = D^{(\lambda)}_{qq}(\omega_{\mathrm{L}}\tau,\ 0,\ 0)\,, \tag{5a}$$

$$\tilde{G}^{q_1q_2}_{\lambda\lambda}(\Delta t) = \sum_p d^{(\lambda)}_{q_1p}(\beta) d^{(\lambda)}_{q_2p}(\beta) \times \exp(-\mathrm{i}[q_2\omega t_2 - q_1\omega t_1 + q\omega_{\mathrm{e}}\Delta t + (q_2 - q_1)\phi])\,. \tag{5b}$$

Here ω_L is the Larmor frequency, $\Delta\omega = \omega_L - \omega,\ \Delta t = t_2 - t_1,\ \omega_e = \sqrt{\omega_1^2 + \Delta\omega^2}$; while $\omega_q,\ \phi,\ \omega$ are the amplitude in frequency units (Rabi frequency), phase and frequency of the rf field, and tan $\beta = \omega_1/\Delta\omega$. In equations (5a) and (5b) the PF are additionally presented through the Wigner rotation function $D^{(\lambda)}_{qp}(\alpha,\ \beta,\ \gamma)$, which is applicable only for pure magnetic dipole interactions, and $d^{(\lambda)}_{qp}(\beta) = D^{(\lambda)}_{qp}(0,\ \beta,\ 0)$ is the reduced Wigner rotation function (Edmonds 1974). The transient effects formation under electric quadrupolar interactions in terms of the ST formalism has been examined elsewhere (Shakhmuratova 1995). Here we consider pure magnetic dipole interactions only and the formation for coherent transients through the CPF using equations (5a) and (5b). It is interesting to note that equation (5b) can be presented in the form of the Wigner rotation function under pure magnetic interactions:

$$\tilde{G}^{q_1\,q_2}_{\lambda\,\lambda}(\Delta t) = D^{(\lambda)}_{q_1q_2}[-(\omega t_1 + \phi - A),\ B, \omega t_2 + \phi - \pi + C]\,,$$

$$\cot\ A = \cot C = \cos\ \beta\ \tan(\omega_{\mathrm{e}}\Delta t/2)\,; \tag{5c}$$

$$\cos\ B = \cos^2\ \beta + \sin^2\ \beta\ \cos(\omega_{\mathrm{e}}\Delta t)\,.$$

In the case of resonant rf pulses, i.e. $\Delta\omega = 0,\ \beta = \pi/2$ and thus $A = C = \pi/2,\ B = \omega_e\Delta t$. Under these conditions, corresponding to on-resonance nuclei only, the PF in (5b) can be expressed in terms of the Wigner function as

$$\tilde{G}^{q_1q_2}_{\lambda\lambda}(\Delta t) = D^{(\lambda)}_{q_1q_2}\Big(-\Big(\omega t_1 + \phi - \frac{\pi}{2}\Big),\ \omega_1\Delta t,\ \omega t_2 + \phi - \frac{\pi}{2}\Big)\,. \tag{5d}$$

In this paper we are concerned with coherent transient formation under severe LIB so that the dynamics under rf pulse excitation is different for various isochromats (spin packets). Thus the PF should be specified for a certain Larmor precession frequency ω_j (instead of a common Larmor frequency ω_L for all spins). As a result, in equation (4) there will appear PF defined by equations (5a) and (5b), but with $\omega_{ej} = \sqrt{\omega_1^2 + \Delta\omega_j^2},\ \Delta\omega_j = \omega_j - \omega$, and tan $\beta_j = \omega_1/\Delta\omega_j$, thus providing the total PF for an isochromat with specific Rabi frequency. Averaging over the LIB has to be carried out. Additionally the pulse area may be different for various nuclei due to the inhomogeneity in Rabi frequency. This can be incorporated through averaging of the PF over the spread of rf amplitudes.

The formalism of CPF, with specification for a certain isochromat ω_j (Larmor frequency) and Rabi frequency ω_1, can be applied to rank $\lambda,\ 0 \le \lambda \le 2I$, ST

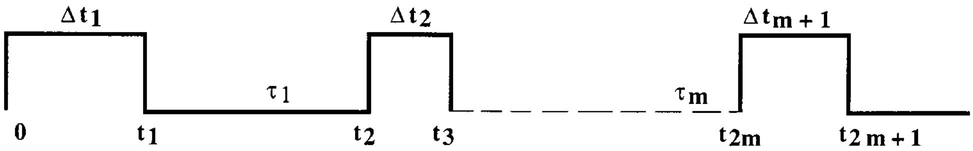


Fig. 1. Timing diagram for the multipulse excitation.

dynamics. Using the CPF formalism the following relation has been demonstrated for the magnetisation vector detected in conventional pulsed NMR (Shakhmuratova 1995):

$$\frac{m_X(t)}{m_0} = \sqrt{2}\mathrm{Re}(G_{1\,1}^{0-1}(t))\,, \qquad \frac{m_Y(t)}{m_0} = -\sqrt{2}\,\mathrm{Im}(G_{1\,1}^{0-1}(t))\,, \tag{6}$$

which provides flexible tools to tackle the multiple pulse excitation of a spin system under severe LIB, and additionally to include RIB. In NMRON the second and fourth rank ST are displayed and the formalism of CPF with LIB and RIB is taken into account.

2. First Rank ST Effects

The formation of an OFID and oscillatory spin-echo (OSE) signals under strong inhomogeneous broadening in the main precession frequency has been investigated in optical resonance and NMR on protons. The conditions for their formation have been formulated (Schenzle *et al.* 1980; Kunitomo *et al.* 1980, 1982), which include: (1) severe LIB $T_2^* \ll T_2$, where T_2^*, T_2 are the transverse reversible and irreversible relaxation times, and $T_2^* \sim 1/\Delta$, where Δ is the halfwidth at half height of the inhomogeneously broadened line (LIB); (2) $R = \omega_1 T_2^* \ll 1$, where ω_1 is the magnitude of the rf amplitude in angular frequency units, i.e. the Rabi frequency; and (3) the pulse area is large, i.e. $\omega_1 \Delta t \geq 2\pi$. Thus the OFID emerges under single pulse excitation, meeting these conditions, and has oscillatory character, depending on the pulse area. The signal is nonzero during a time interval equal to the pulse duration (measured from the trailing edge of the pulse) and zero beyond that interval. The OSE formation for two-pulse excitation, i.e. notched (the first pulse area is large) and locked (the second pulse area is large) type echoes (Kunitomo *et al.* 1980, 1982), where these conditions are effective only for one of the pulses in a sequence, as well as for two large area pulses, has been investigated for proton NMR (Kunitomo and Kaburagi 1984).

In ferromagnets there is typically severe LIB due to inhomogeneity in magnetic hyperfine interactions, most commonly for pure ferromagnets and 3d impurities due to a distribution of demagnetising fields. In addition, for multidomain ferromagnets the inhomogeneity in the enhancement factor (EF) for the rf amplitude in domain walls will generally dominate the RIB, and as demonstrated below strongly modifies the oscillatory character of the OFID and OSE. Recently, a study (Shakhmuratova *et al.* 1996*a*) of coherent transient effects under double inhomogeneity, i.e. LIB plus RIB, effective under pulsing and pure LIB between the pulses, proved itself to be fruitful in the description and understanding of Bloom's SPE and multiple-structure echoes formed by two unequal large area pulses $\bar{\omega}_1 \Delta t_i \geq 2\pi$ $(i = 1,\ 2)$, where $\bar{\omega}_1$ is the average Rabi frequency.

Additionally the case when the two-pulse sequence repetition period is shorter than the longitudinal relaxation time T_1 is demonstrated to be profoundly important in the formation of coherent transients under double inhomogeneity.

In this section we consider the SPE, notched- and locked-type echoes (including their multiple structures) from multidomain ferromagnets formed under double inhomogeneity. Both high and low repetition rates of corresponding pulse sequences are examined. The possibility of SPE formation due to other mechanisms of RIB, i.e. the skin-effect, is demonstrated. Note that the aforementioned conditions for coherent transients under pure LIB apply when the RIB is included, as soon as ω_1 is replaced by $\bar{\omega}_1$, which is the average value in the case of the inhomogeneous EF or the surface value in the case of the skin-effect Rabi frequency. Additionally the situation when these conditions are not strictly met and R becomes large enough, $R \sim 1$, is demonstrated to destroy the SPE formation.

(2a) Single Pulse Echo

SPE is a phenomenon first observed and discussed by Bloom (1955) from protons in water under artificially created severe LIB. However, the single-pulse excitation with LIB only incorporated in the theory did not replicate SPE formation but only the OFID (Schenzle *et al*. 1980; Kunitomo *et al*. 1980, 1982). Neither experimental nor theoretical study unambiguously demonstrated SPE formation under severe LIB exclusively, except when pulse distortions are included (Tsifrinovich *et al*. 1985) or nonresonant pulse excitation takes place (Kuz'min *et al*. 1990). Recently both theoretical and experimental examinations of SPE formation from multidomain ferromagnets have been carried out (Shakhmuratova *et al*. 1997*a*). Theoretically the LIB and RIB, simultaneously effective during pulsing, have been included, the RIB being due to inhomogeneity of the rf amplitude EF in the domain walls. It is well known that the main contribution to the NMR signal is from the domain wall nuclei due to their very much larger enhancement factor compared with domain nuclei. The averaging of the magnetisation vector obtained utilising equation (6) [which is similar to the magnetisation components in Bloom's (1955) paper] over LIB of the gaussian lineshape

$$g(\Delta\omega_j)\mathrm{d}(\Delta\omega_j) = \sqrt{\frac{\ln 2}{\pi\Delta^2}}\exp\left(-\ln 2\left(\frac{\Delta\omega_j}{\Delta}\right)^2\right)\mathrm{d}(\Delta\omega_j)$$

$$= \sqrt{\frac{\ln 2}{\pi}}R\exp(-\ln 2(Rx)^2)\mathrm{d}x \tag{7}$$

gave results similar to those previously obtained (Schenzle *et al*. 1980; Kunitomo *et al*. 1980, 1982), i.e. the OFID signal. Henceforth we use the following notation: $x = \Delta\omega_j/\bar{\omega}_1$, $R = \bar{\omega}_1/\Delta$ where Δ is the halfwidth at half height of the inhomogeneously broadened line (LIB); η and $\bar{\eta}$ are the EF and its mean value; and $\omega_1 = \eta\omega_1^{appl}$, $\bar{\omega}_1 = \bar{\eta}\omega_1^{appl}$ is the mean value of the rf amplitude in frequency units. However, the additional averaging over RIB with the form factor (Kinnear *et al*. 1980; Fowler *et. al.* 1985)

$$P(\eta)\mathrm{d}\eta = \frac{1}{\bar{\eta}}\exp(\eta/\bar{\eta})\mathrm{d}\eta = \exp(-a)\mathrm{d}a\,, \tag{8}$$

where $a = \eta/\bar{\eta}$, including the reverse enhancement of the signal, gives the averaged value for the magnetisation vector Y-component:

$$\left\langle \frac{m_Y(b,y;x,a)}{m_0} \right\rangle_{x.a} = \int_0^\infty \eta P(\eta) \left\langle \frac{m_Y(b,y;x,\eta)}{m_0} \right\rangle_x \mathrm{d}\eta$$
$$= \bar{\eta} \int_0^\infty a \mathrm{e}^{-a} \left\langle \frac{m_Y(b,y;x,a)}{m_0} \right\rangle_x \mathrm{d}a \,, \qquad (9)$$

where the oscillations are finally removed. Here we assume the repetition period is longer than the longitudinal relaxation time, i.e. $T > T_1$, $b = \bar{\omega}_1 \tau$ (dimensionless) characterises the time interval after the pulse excitation and is measured from the trailing edge of the pulse, while $y = \bar{\omega}_1 \Delta t$ is the mean value for the pulse area and Δt is the pulse duration. However, the RIB unexpectedly causes the small step formation exactly before the signal becomes zero, which we consider to be the precursor of the SPE. This behaviour of the signal is observed in a computed curve for final R presented in Fig. 1*b* of Shakhmuratova *et al.* (1997*a*). For infinitely small $R = \bar{\omega}_1/\Delta \to 0$ (extremely large LIB), the averaging over the double inhomogeneity is carried out algebraically demonstrating the similar behaviour through terms of the form

$$S_\epsilon = 1/(1 + y^2 - b^2)^\epsilon \,, \qquad (10)$$

with half integer ϵ, occurring in the final result for the magnetisation vector components. But still the total duration of the signal does not exceed the pulse width, Δt (i.e. b), though having now a non-oscillatory form. The terms of the type given in equation (10) may cause only the step at the end of the signal, since for $\tau > \Delta t$ ($b > y$) the signal is zero. Note that the form factor in equation (8) for the spread of the enhancement factor η cannot be considered to be ideal, since in ferromagnets the enhancement of the rf field is realised through the hyperfine interactions, and thus RIB and LIB are correlated. This could be examined as a next step with the additional complexity to include RIB due to the skin-effect for metallic ferromagnets. However, the results obtained, based purely on the form factor in equation (8) for RIB, are useful as a first approach to spin dynamics complicated both by LIB and RIB, and provide good support for the experimentally observed signals (see Shakhmuratova *et al.* 1997*a*).

As a further development of the existing theory of single pulse excitation we consider the situation when the rf pulse is repeated with a period T shorter than the longitudinal relaxation time T_1, i.e. $T_1 \gg T > T_2 \gg T_2^*$, so that each rf pulse starts with the longitudinal component of the magnetisation vector, already containing information about its previous dynamics for previous pulse excitations, but with zero transverse components. Taking advantage of CPF in accordance with equation (4) under these conditions, when only the PF with $q = 0$ are significant between the subsequent pulses and directly lead to the accumulation of a signal, the final PF for an $(n{+}1)$ pulse train is

$$G_{1\,1}^{0-1}(t) = [\tilde{G}_{1\,1}^{0\,0}(\Delta t)]^n \ \tilde{G}_{1\,1}^{0-1}(\Delta t) \exp(\mathrm{i}\omega_j \tau) \,. \qquad (11)$$

Thus according to equations (5), (6) and (11) the $Y-$ and $X-$ components of the magnetisation vector can be derived:

$$\frac{m_Y(t)}{m_0} = \{1 - \sin^2\beta_j(1 - \cos\theta_j)\}^n$$

$$\times [-\sin\beta_j\cos\beta_j(1 - \cos\theta_j)\sin(bx + \phi) + \sin\beta_j\sin\theta_j\cos(bx + \phi)]$$

$$\frac{m_X(t)}{m_0} = \{1 - \sin^2\beta_j(1 - \cos\theta_j)\}^n$$

$$\times [\sin\beta_j\cos\beta_j(1 - \cos\theta_j)\cos(bx + \phi) + \sin\beta_j\sin\theta_j\sin(bx + \phi)] \qquad (12)$$

where θ_j and β_j are j-isochromat related angles, which now include both Rabi (through a) and Larmor (through x) frequency dependencies:

$$\sin\beta_j = a/\sqrt{a^2 + x^2}, \quad \cos\beta_j = x/\sqrt{a^2 + x^2}, \quad \theta_j = y\sqrt{a^2 + x^2}\,.$$

In equation (12) ϕ is the phase of the rf pulse which is assumed to be zero. As a result, averaging over the LIB conserves only the Y-component of the magnetisation vector, since the X-component is an even function of x. Note that equation (12) can also be applied for single pulse excitation, i.e. low repetition rate, by taking $n = 0$, thus producing a result similar to that given by Kunitomo *et al*. (1980, 1982). In accordance with the coherent transients theorem (Schenzle *et al*. 1980; Kunitomo *et al*. 1980, 1982) in the case of multiple pulse excitation the total duration of the resulting signal, measured from the trailing edge of the final pulse, is now $\tau = (n + 1)\Delta t$ [or [$b = (n + 1)y$] extending from single pulse duration to (n+1) pulse widths, and becoming zero beyond this point, i.e. when $\tau \geq (n + 1)\Delta t$ [or $b \geq (n + 1)y$].

In equation (12) for the magnetisation vector Y-component there are terms with the duration of integer times pulse duration, the longest being of $(n{+}1)\Delta t$. Additionally it contains terms contributing to the formation of the signal formed before $\tau = \Delta t$. Thus the step mentioned, which is formed before $\tau = \Delta t$ and would not develop further under single pulse excitation, for (n+1)-pulse excitation is strengthened due to additional terms, and superimposed on the signal of longer duration. Thus the presence of a nonzero signal out of the limit $\tau = \Delta t$ occurs. As a result the SPE of dispersive form is produced centred at $\tau = \Delta t$, the left-hand component (previously a step) being more developed than the right-hand side one. The inclusion of pure LIB under high repetition rate of pulse excitation demonstrates the developing SPE. However, the double inhomogeneity provides the most unambiguous sharp form of the SPE and the occurrence of its secondaries. Thus, when RIB is incorporated the SPE signal and its secondaries have a profound sharp form even with a small number of pulses.

The formation of secondary echoes is produced by multiple (n+1)-pulse excitation which results in creating terms similar to those given by equation (10), but with py ($p = 2, 3...(n{+}1)$) instead of y there. Each of these terms corresponds to separate signals of duration $\tau = p\Delta t$ ($b = py$), where $p = 2, 3...(n{+}1)$. Thus, under similar conditions the corresponding echo signals

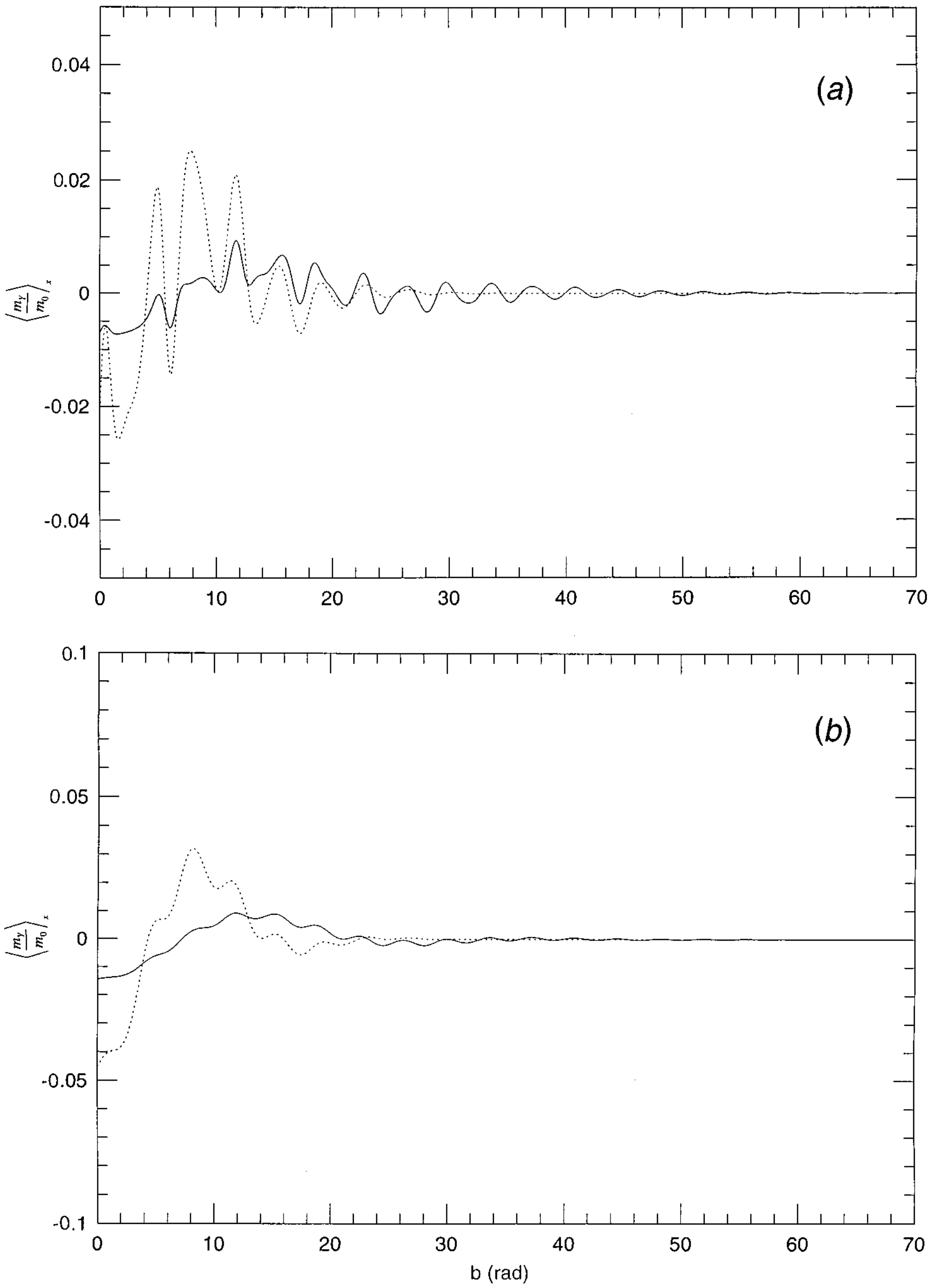


Fig. 2. Computed curves of $\langle m_Y(t)/m_0\rangle_x$ for single pulse excitation under pure LIB and high repetition rate for $n = 10$ (dashed line), $n = 50$ (solid line) and $y = 2\pi$: (a) $R = 0{\cdot}5$ and (b) $R = 1$.

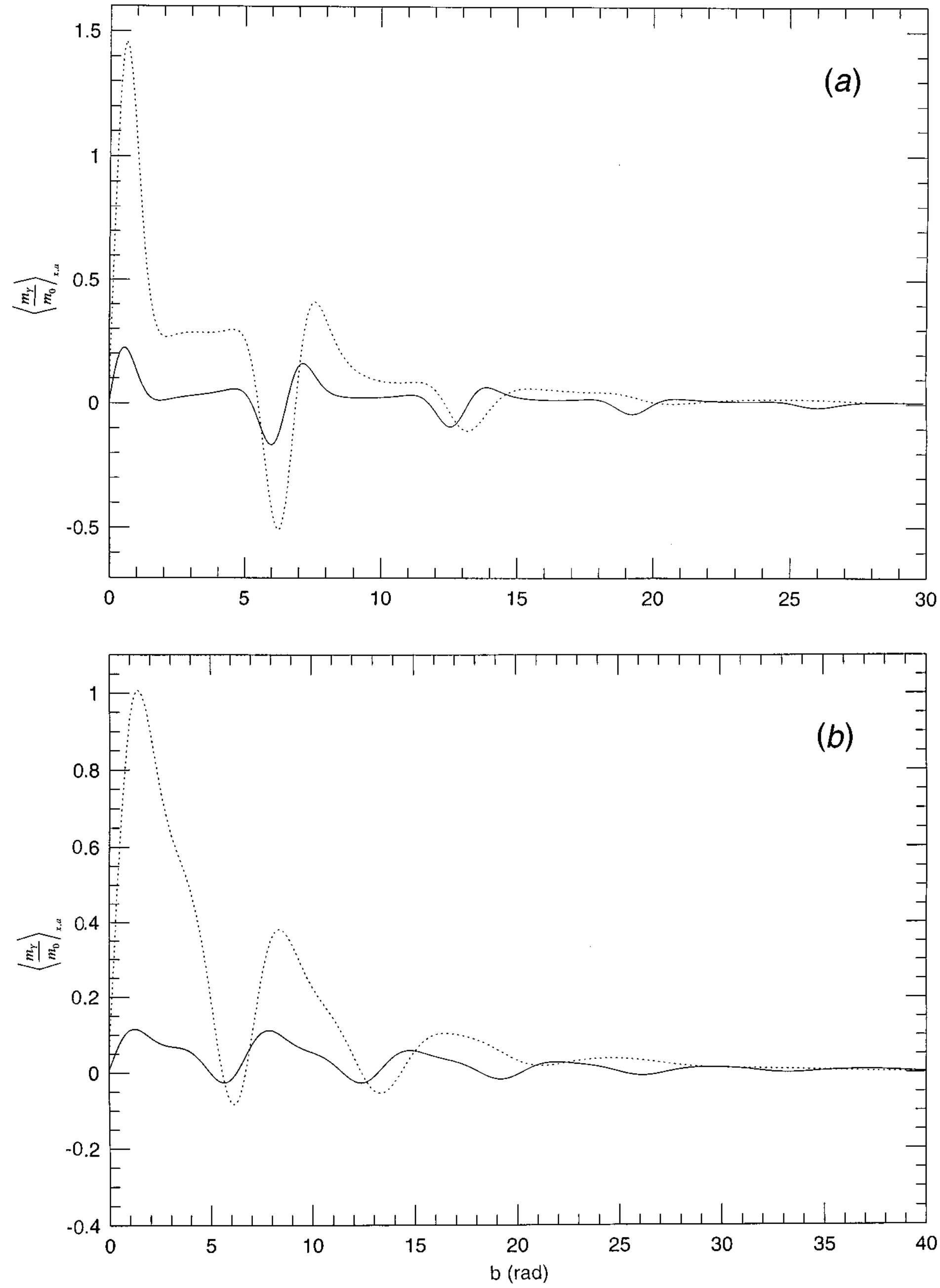


Fig. 3. Computed curves of $\langle m_Y(t)/m_0\rangle_{x,a}$ for single pulse excitation under double inhomogeneity (RIB due to enhancement factor inhomogeneity) and high repetition rate for $n = 10$ (dashed line), $n = 50$ (solid line), $y = 2\pi$ and $\bar{\eta} = 100$: (*a*) $R = 0{\cdot}5$ and (*b*) $R = 1$. SPE and its secondaries are well observed.

of dispersive form are produced at $\tau = p\Delta t$ $(b = py)$, $p = 1, 2, 3...n$ of smaller intensity. But for the latest moment of time related to $p = (n{+}1)$ only the step should be formed, since the total signal becomes zero when $\tau \geq (n{+}1)\Delta t$ $[b \geq (n{+}1)y]$.

In addition to the computed curves demonstrating the formation of SPE and its secondaries formation presented in the paper by Shakhmuratova *et al.* (1997*a*) for small values of R, i.e. $R \ll 1$, here we show the effect of larger values of R (Figs 2 and 3), so that when $R \sim 1$ the SPE is washed out under pure LIB as well as double inhomogeneity, with a high repetition rate in both cases. For bigger R, the LIB loses its role, providing the isochromat dependent spin dynamics during pulsing. However, it is worth noting that even for intermediate R, but $R < 1$, the SPE is still observable, especially with double inhomogeneity.

In order to further investigate the RIB effect, the influence of the skin effect as the source of the rf amplitude inhomogeneity, but additionally affecting the rf field phase as well, has been examined. Note that since m_X in equation (12) is an even function of x when $\phi = 0$, averaging over LIB will eliminate the X-component of the magnetisation vector, and as a result the RIB due to the EF inhomogeneity will finally provide only the Y-component $\langle m_Y\ (b,\, y;\, x,\, a)\rangle_{x,a}$. However, with the skin effect ϕ varies with the depth of the probe nuclei. Thus, both m_X and m_Y will emerge after averaging over the skin-effect parameter and contribute to the final signal. According to equation (6), the X- and Y-components are simultaneously contained in the PF $G^{0-1}_{1\,1}$. The averaging over RIB, which includes the reverse skin effect (Mehring *et al.* 1972), has been carried out then for $G^{0-1}_{1\,1}$ according to

$$\langle G^{0-1}_{1\,1}\rangle_{x.\text{skin-effect}} = \frac{1}{d}\int_0^d a(r)\langle G^{0-1}_{1\,1}(a(r),\, \phi(r);\, b,\, y,\, x)\rangle_x \mathrm{d}r\,, \tag{13}$$

where $b = \bar{\omega}_1\tau$, $y = \bar{\omega}_1\Delta t$, $x = \Delta\omega/\bar{\omega}_1$ (as before), $a = \omega_1/\bar{\omega}_1 = \exp(-z)$, $\phi = z = r/\sigma$, r is the distance from the surface for the location of a nucleus, σ is the skin depth, $w = d/\sigma$, d is the total depth of location for the probe nuclei, and $\bar{\omega}_1$ is the rf amplitude on the surface of a specimen. Note that $0 \leq r \leq d$, and when $w \gg 1$ (i.e. d is large enough compared with the skin depth) the upper limit in equation (13) should be taken as infinity (which is typical in NMR experiments) both for numerical integration and algebraic analyses. But when the location of probe nuclei is within a thin layer of a metal specimen then w, in principle, has to be specified. For a bulk metal specimen with layers thin compared to the skin depth σ, the amplitude and phase dependencies on the location of a nucleus will have a different form (see Kotzur *et al.* 1972), which is not considered here. The computed curves, for $w = 1{\cdot}5$, demonstrate that the RIB caused by the skin effect also provides SPE formation under a high repetition rate, but with a smaller intensity in contrast to the more potent inhomogeneity in the rf field EF (Fig. 4). This case may not be typical for conventional NMR experiments with skin-effect, though still well demonstrates the effect of double inhomogeneity. It can be easily shown algebraically, using infinity for the upper limit of integration in equation (13), that with the skin effect the terms of the form given by (10) will also emerge, eliminating the oscillatory feature of the signal along with multipulse excitation due to a high repetition rate.

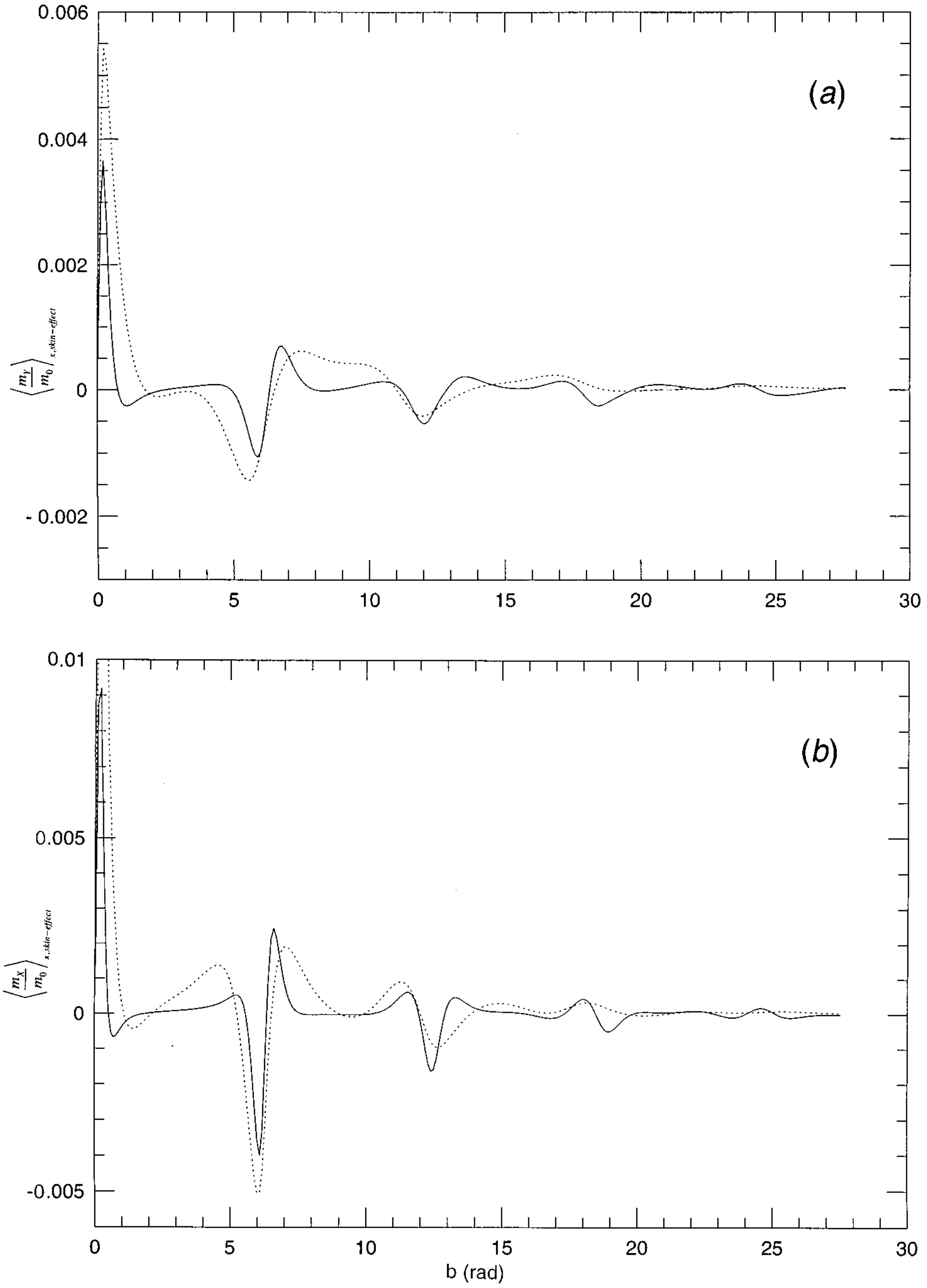


Fig. 4. Computed curves of (a) $\langle m_Y(t)/m_0\rangle_{x,\text{skin-effect}}$ and (b) $\langle m_X(t)/m_0\rangle_{x.\text{skin-effect}}$ for single pulse echo formed under double inhomogeneity, RIB due to skin-effect, and high repetition rate for $n = 10$ (dashed lines), $n = 50$ (solid lines), $R = 0{\cdot}1$, $y = 2\pi$, $w = d/\sigma = 1{\cdot}5$, where σ is the skin depth and d is the depth in a specimen with probe nuclei.

(2b) Notched- and Locked-type Echo Formation

The study of locked-type and notched-type echo signals formation under pure LIB (Kunitomo *et al*. 1980, 1982), efficient for protons in water, and the low repetition rate of a two-pulse sequence revealed the oscillatory character specific for each of the signals, which are difficult to split into separate parts and specify as a multiple structure. The total duration of the OSE, measured from the trailing edge of the second pulse, is $\tau_2 \approx \tau_1 + \Delta t_i$ $(i = 1,\ 2)$ and indicates the duration of the large area pulse. Here we consider theoretically for the first time the notched- and locked-type echoes from multidomain ferromagnets formed under double inhomogeneity, including both high and low repetition rates of a pulse sequence.

Under two-pulse excitation with repetition time T, $T_1 \gg T > T_2 \gg T_2^*$, the corresponding total PF with an $(n{+}1)$ times repeated two-pulse sequence may be presented according to equation (4) as

$$G^{0\,-1}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1, \tau_2) = [G^{0\,0}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1)]^n G^{0\,-1}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1)\exp(\mathrm{i}\Delta\omega_j \tau_2)\,, \quad (14)$$

with the following PF for two-pulse sequences, producing axial and transverse components of the magnetisation vector, respectively:

$$G^{0\,0}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1) = \sum_q \tilde{G}^{q\,0}_{1\,1}(\Delta t_2)\overline{G}^{q\,q}_{1\,1}(\tau_1)\tilde{G}^{0\,q}_{1\,1}(\Delta t_1)\,, \quad (15a)$$

$$G^{0\,-1}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1) = \sum_q \tilde{G}^{q\,-1}_{1\,1}(\Delta t_2)\overline{G}^{q\,q}_{1\,1}(\tau_1)\tilde{G}^{0\,q}_{1\,1}(\Delta t_1)\,. \quad (15b)$$

It is worth noting that due to the relation $T_1 \gg T > T_2 \gg T_2^*$ the longitudinal component is only important in the time interval between the subsequent two-pulse sequences (thus $q = 0$ for the PF for the dynamics within T). Consequently, each two-pulse excitation starts with a pure longitudinal component of the magnetisation vector, assumed undamped by longitudinal relaxation. Thus the train of n two-pulse sequences can be considered as preparatory (accumulating the spin dynamics within pulses and the time interval separating these two-pulses in the sequence) and the last $(n{+}1)$th two-pulse sequence additionally converts the axial magnetisation vector component onto the XY plane. This results in the formation of the echo signals, the location of which is ruled by interpulse separation as well as by pulse durations on the timescale triggered after the last $(n{+}1)$th two-pulse sequence. Note that equations (14) and (15) can be applied in the case of low repetition rate when $T \gg T_1$ as well, if we put $n = 0$, thus providing the general approach in the examination of coherent transients formation.

In order to investigate the formation of echo signals under a high repetition rate of a pulse sequence it is convenient to present equations (15) in the following way:

$$G^{0\,0}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1) = A_1 \exp\{-\mathrm{i}(\Delta\omega_j \tau_1 + \phi_2 - \phi_1)\}$$
$$+ A_{-1}\exp\{(\Delta\omega_j \tau_1 + \phi_2 - \phi_1)\} + A_0\,, \quad (16a)$$

$$G^{0\,0}_{1\,1}(\Delta t_1, \Delta t_2, \tau_1) = B_1 \exp\{-\mathrm{i}(\Delta\omega_j \tau_1 - (2\phi_2 - \phi_1))\}$$

$$+ B_{-1}\exp\{i(\Delta\omega_j\tau_1 + \phi_1)\} + B_0 \exp\{\mathrm{i}\phi_2\}\,, \qquad (16b)$$

with

$$A_q = \sum_{p_1,p_2} d^{(1)}_{0\,p_2}(\beta_j) d^{(1)}_{q\,p_2}(\beta_j) d^{(1)}_{q\,p_1}(\beta_j) d^{(1)}_{0\,p_1}(\beta_j) \exp\{-\mathrm{i}\omega_{ej}(p_1\Delta t_1 + p_2\Delta t_2)\}$$

$$A_{-1} = A^*_1\,; \qquad (17a)$$

and

$$B_q = \sum_{p_1,p_2} d^{(1)}_{-1p_2}(\beta_j) d^{(1)}_{qp_2}(\beta_j) d^{(1)}_{qR}(\beta_j d^{(1)}_{0p_1}(\beta_j) \exp\{-\mathrm{i}\omega_{ej}(p\Delta t_1 + p_2\Delta t_2)\}\,. \qquad (17b)$$

Here the well known expressions for the PF under rf pulse excitations given in equations (4), i.e. $\tilde{G}^{0\,0}_{1\,1}(\Delta t_1)$ and $\tilde{G}^{0-1}_{1\,1}(\Delta t_2)$, were used with common notation for the Wigner rotation functions $d^{(1)}_{qp}(\beta_j)$ and tan $(\beta_j) = \bar{\omega}_1/\Delta\omega_j = 1/x$. As a result equation (14) can be transformed into the form:

$$G^{0-1}_{1\,1}(y_1, y_2, b_1, b_2, n; x, a) =$$

$$(A_1 \exp\{-\mathrm{i}(b_1 x + (\phi_2 - \phi_1))\} + A_{-1}\exp\{\mathrm{i}(b_1 x + (\phi_2 - \phi_1))\} + A_0)^n \qquad (18)$$

$$\times\, (B_1 \exp\{-\mathrm{i}(b_1 x - (2\phi_2 - \phi_1))\} + B_{-1}\exp\{\mathrm{i}(b_1 x + \phi_1)\} + B_0 \exp\{\mathrm{i}\phi_2\})\exp\{\mathrm{i}b_2 x\}\,.$$

Now from this equation the formation of the main and secondary echo signals can be demonstrated, the $m_Y(y_1, y_2, b_1, b_2, n; x, a)$ component of the magnetisation vector defined by the imaginary part of the PF in equation (18), according to equation (6). Here dimensionless parameters convenient for algebraic analysis, and which were introduced in the previous section, are used, i.e. a, x and $y_i = \bar{\omega}_1\Delta t_i$, $b_i = \bar{\omega}_1\tau_i$; $\Delta\phi = \phi_2 - \phi_1$ is the phase difference for two-pulses in the sequence. All echo-signals are contained in equation (18) when n is defined, and if $n = 0$ the low repetition rate of a two-pulse sequence result is reproduced, identical to that given by Kunitomo *et al.* (1980, 1982).

The algebraic averaging, which is not presented here, is accomplished in the extreme case of infinitely large LIB, $R \to 0$, effective only for the pulse of large area. The dynamics of all isochromats during the short pulses is indistinguishable. The RIB is also unimportant under rf field impact on a spin system due to the short duration of the pulse. However, the large area pulse incorporates the effect of both inhomogeneities, i.e. LIB and RIB. Algebraic analysis demonstrates the formation of the main echo at $\tau_2 = \tau_1$, where τ_1 is the pulse separation and τ_2 is measured from the trailing edge of the last pulse in the train of a two-pulse sequence. In the case of low repetition rate, the multiple signals are formed additionally, determined by the long pulse durations, at $\tau_2 = \Delta t_i$, $\tau_1 + \Delta t_i$, $\tau_1 - \Delta t_i$, where i is the label for the pulse of large area. Note that in the case of equal

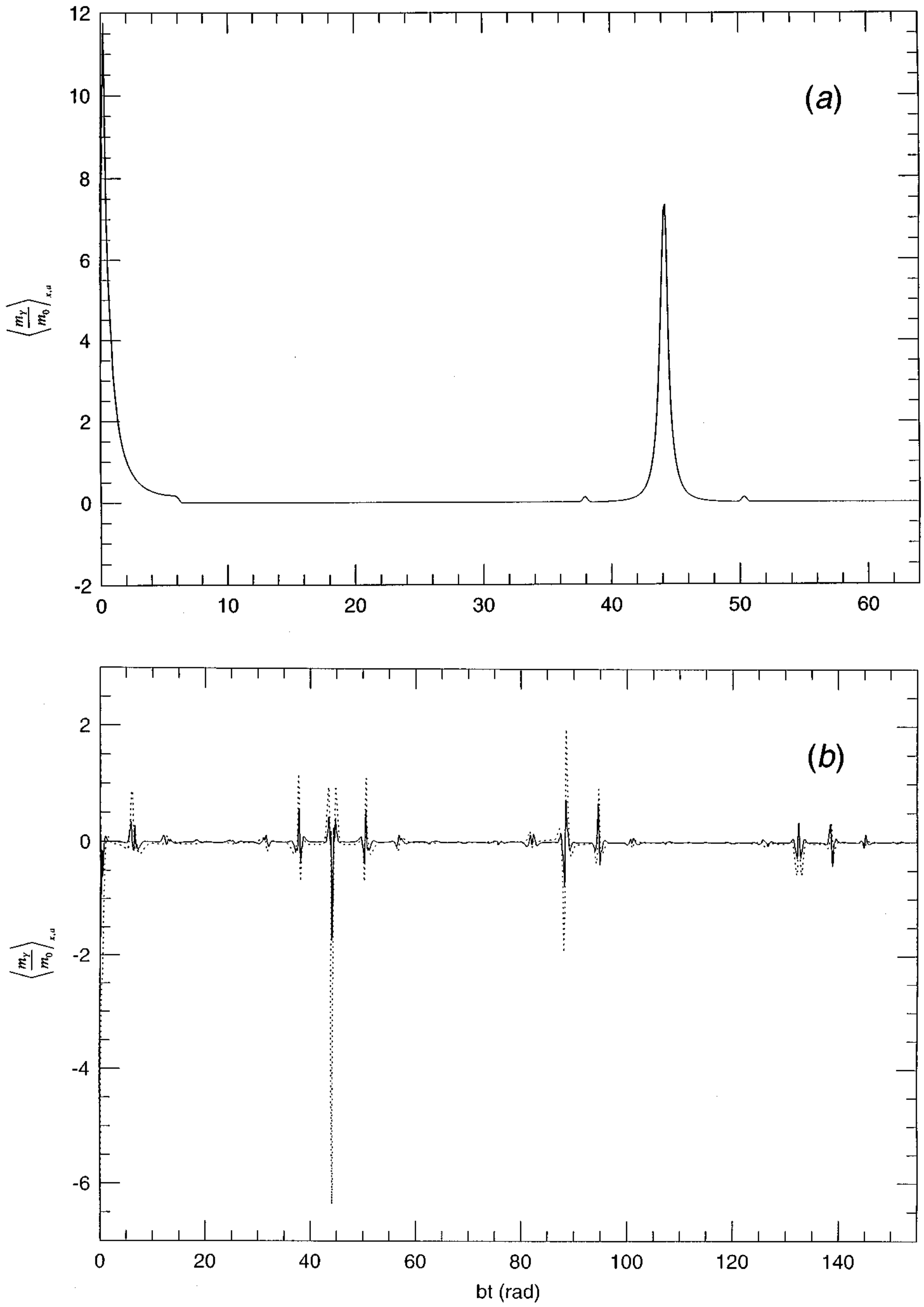
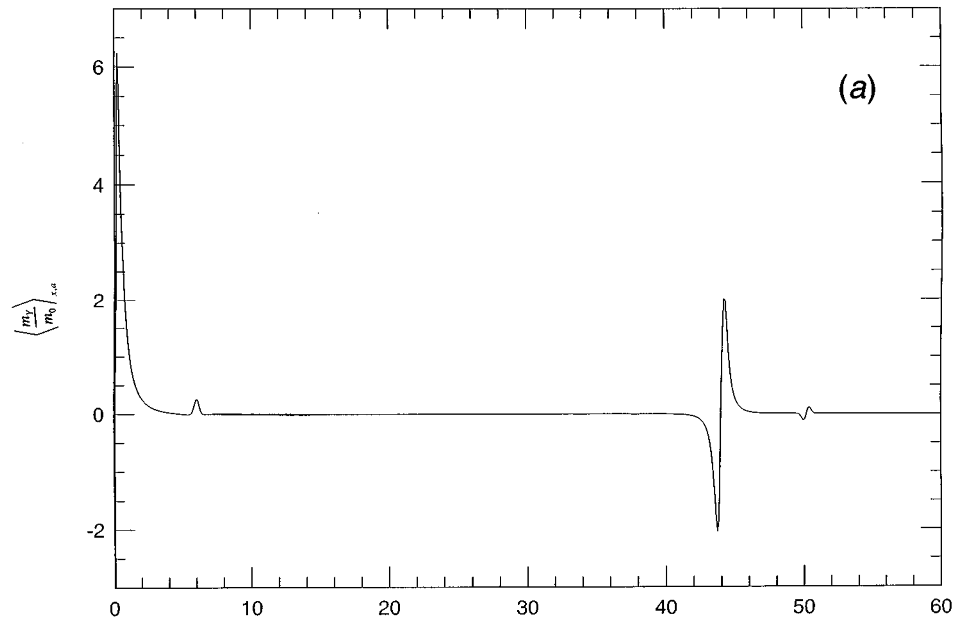


Fig. 5. (a) Locked-type echo (inverted) with double inhomogeneity and *low* repetition rate, i.e. $T > T_1$, for $0 \cdot 1\pi - 14\pi - 2\pi$ pulse sequence, $R = 0 \cdot 1$, $\bar{\eta} = 100$, and $bt - \bar{\omega}_1 \tau_1$ is for pulse separation in a two-pulse sequence. (b) Locked-type echo with double inhomogeneity and *high* repetition rate, i.e. $T < T_1$, $n = 10$, (dashed line), $n = 50$ (solid line), for $0 \cdot 1\pi - 14\pi - 2\pi$ pulse sequence, $R = 0 \cdot 1$, $\bar{\eta} = 100$, and $bt = \bar{\omega}_1 \tau_2$.



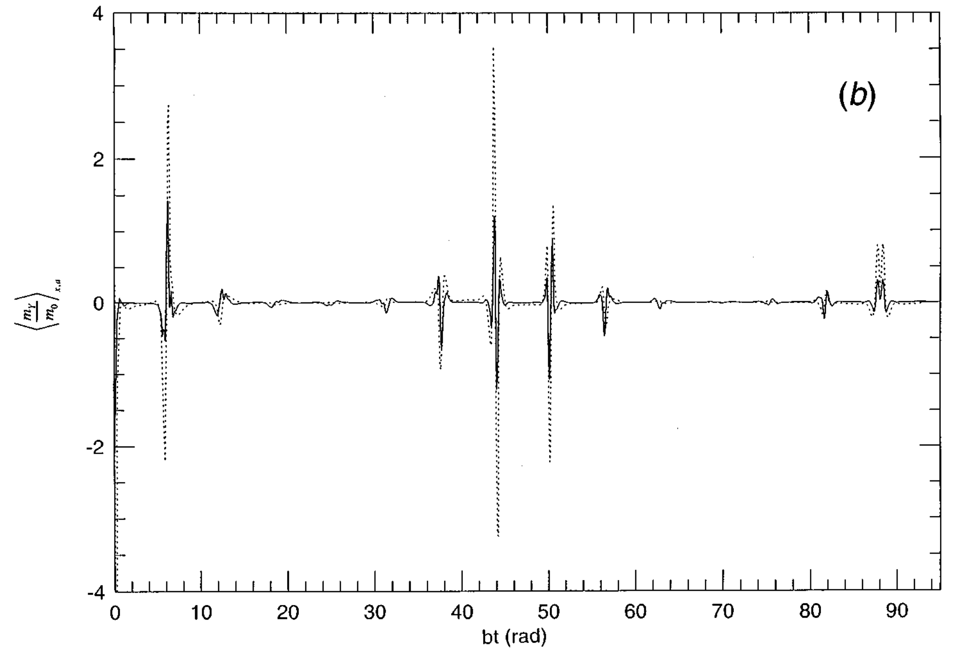


Fig. 6. (a) Notched-type echo (inverted) with double inhomogeneity and *low* repetition rate, i.e. $T > T_1$, for $2\pi - 14\pi - 0{\cdot}1\pi$ pulse sequence, $R = 0{\cdot}1$, $\bar{\eta} = 100$, and $bt = \bar{\omega}_1\tau_1$. ($b$) Notched-type echo with double inhomogeneity and *high* repetition rate, i.e. $T < T_1$, $n = 10$ (dashed line), $n = 50$ (solid line), for $2\pi - 14\pi - 0{\cdot}1\pi$ pulse sequence, $R = 0{\cdot}1$, $\bar{\eta} = 100$, and $bt = \bar{\omega}_1\tau_2$.

amplitude rf pulses, the large area pulse will have longer duration, which is the case under consideration.

In Figs 5 and 6 the computed curves for locked- and notched-type echoes are presented for finite but small values of R respectively. With a low repetition rate (Figs 5a and 6a) the main echo, formed at $\tau_2 = \tau_1$, is accompanied by satellite echoes, which are located symmetrically around the main echo and separated by the long pulse duration from its central point. Note that the main locked- and notched-type echoes have different forms. The satellite echo signals are well observed in the case of the locked-type echo (the main echo is symmetrical as well), but for the notched-type echo (the main echo signal is of dispersive form) the left-hand side component is not noticeable. Additionally there is a stimulated echo-type signal separated from the trailing edge of the second pulse by the long pulse duration. It has the form of a step for the locked-type echo case and a hump for the notched-type echo formation. These signals are related to the terms in the total PF of long pulse duration and become prominent since the total signal duration after the trailing edge equals the sum of long and short pulse durations, i.e. $\tau_2 \leq \Delta t_1 + \Delta t_2$, and then the signal becomes zero beyond the interval $\tau_1 - \Delta t_1 - \Delta t_2 \leq \tau_2 \leq \tau_1 + \Delta t_1 + \Delta t_2$, in accordance with the coherent transients theorem modified for the case of multipulse excitation. At a high repetition rate these signals look more sharp and well distinguished among the additional secondary echoes, which according to equation (18) are formed at $\tau_2 = p\Delta t_i,\ n\tau_1 + p\Delta t_i,\ n\tau_1 - p\Delta t_i$. Thus $n = 2$, 3... define the location of the secondary main echoes when $p = 0$; but $p = 1$, 2, 3... determine those symmetrically located around the main echo (when $n = 1$) and its secondaries (when $n = 1,\ 2,\ 3...$), the secondary multiple echo signals ruled by the long pulse duration; also the stimulated echo and its secondaries are formed at $\tau_2 = n\tau_1$ $(p = 1, 2, 3...)$. All these signals can be clearly observed in Figs 5b and 6b. Note that originally the effects of the long and short pulses were not theoretically differentiated in equation (18) which has the most general form for two-pulse excitation; they are manifested through definition of the pulse areas while numerical averaging of the magnetisation vector component over LIB and RIB.

The results for multiple echo structure formed under excitation by two long pulses, so that LIB and RIB become effective for the both pulses, are presented elsewhere.

3. Second and Fourth Rank ST Effects

The double inhomogeneity effect on the formation of coherent transients for the second and fourth rank ST is displayed in NMRON. In this section we consider the case similar to OFID and OSE signal formation in conventional NMR, when LIB has to be incorporated during pulsing, since the dynamics of spins are strongly isochromat dependent, but as applied to higher rank ST. In contrast to first rank ST transient coherents considered in the previous section, in NMRON experiments the RIB is mainly due to the skin effect since the probe nuclei are predominantly located within domains. Additionally, the transient coherents detected via γ-radiation from nuclei oriented at low temperatures is experimentally carried out under population sensitive axial geometry. As a result an extra read pulse is needed to convert the transverse components of nuclear spins, sensitive to LIB, into axial components in order to trace the dynamics in the transverse plane at a certain moment of time. Thus the three-pulse stimulated echo formation in conventional pulsed NMR corresponds to the four-pulse excitation in NMRON (Chaplin and Wilson 1986). Effects such as the two-pulse stimulated echo (Shakhmuratova *et al.* 1995, 1996*a*, 1996*b*, 1997*b*) and the OFID signal formation for the second rank ST (Shakhmuratova 1984; Shakhmuratova *et al.* 1993; Hutchison *et al.* 1993; Chaplin *et al.* 1995*a*, 1995*b*), but under double inhomogeneity and additionally using the extra 'read' pulse, are examined.

(3a) Two-pulse Stimulated Echo

The two-pulse excitation of oriented nuclei with the spin dynamics detected via γ-radiation within the second pulse, i.e. as a function of the read pulse duration, has been investigated both theoretically and experimentally by Shakhmuratova *et al.* (1995, 1996*a*, 1996*b*, 1997*b*). Thus, in contrast to experiments previously carried out in pulsed NMRON the mandatory read pulse is varied in duration (i.e. pulse area) and LIB and RIB is effective for the read pulse as well. Now this extra pulse cannot be considered as pure read pulse only, but it is important for the coherent transient effect formation detected within its duration—the two-pulse stimulated echo. The corresponding PF for the axial geometry of the experiment (i.e. with $q=0$) and higher rank ST displayed in NMRON (second and to a smaller extent fourth) can be presented as

$$G^{0\,0}_{\lambda\,\lambda}(\tau,\Delta t_1,\Delta t_2)=\sum_{|q|\leq\lambda}\tilde{G}^{q\,0}_{\lambda\,\lambda}(\Delta t_2)\overline{G}^{q\,q}_{\lambda\,\lambda}(\tau)\tilde{G}^{0\,q}_{\lambda\,\lambda}(\Delta t_1)\,, \tag{19}$$

where each PF is defined according to equations (5a) and (5b). The total PF for an isochromat can be expanded as

$$G^{0\,0}_{\lambda\,\lambda}(\tau,\Delta t_1,\Delta t_2,\Delta\omega_j)=$$

$$[d^{(\lambda)}_{0\,0}(\beta_j)]+2\sum_{|p_i|\leq\lambda}{}'\{[d^{(\lambda)}_{0\,p_1}(\beta^2_j)]^2[d^{(\lambda)}_{0\,p_2}(\beta_j)]\cos\omega_{ej}(p_1\Delta t_1+p_2\Delta t_2)\}$$

$$+\,2\sum_{|p_1|\leq\lambda}\{d^{(\lambda)}_{0\,p_1}(\beta_j)d^{(\lambda)}_{1p_1}(\beta_j)d^{(\lambda)}_{0\,p_2}(\beta_j)d^{(\lambda)}_{1p_2}(\beta_j)\cos(\omega_{ej}(p_1\Delta t_1+p_2\Delta t_2\tau)+\Delta\omega_j)\}$$

$$+\,\{d^{(\lambda)}_{0\,p_1}(\beta_j)d^{(\lambda)}_{2p_1}(\beta_j)d^{(\lambda)}_{2p_1}(\beta_j)\cos(\omega_{ej}(p_1\Delta t_1+p_2\Delta t_2)+2\Delta\omega_j\tau)\}\,, \tag{20}$$

where the second term with the prime stands for summation over one combination of the signs of p_1 and p_2 [e.g. if (1, -2) is included then (-1, 2) is omitted], and (p_1, p_2) are not simultaneously zero, as this case is contained in the first term of equation (20). Examination of (20) provides an understanding of the phasing and dephasing leading to two-pulse echo formation, including the sub-harmonic echoes. The term of two-pulse stimulated echo is provided by the following examination of PF in equations (19) and (20). From (19) and (5) it is evident that the $q=0$ condition leads to no precession between pulses, since $\overline{G}^{0\,0}_{\lambda\,\lambda}(\Delta\omega_j\tau)=1$. Possible compensation of dephasing of isochromats occurring during the first pulse may occur only when the second pulse is switched on. At the times of occurrence of spin echo formation, δt^e_2, the dependence on the nutational frequency scatter,

ω_{ej}, is eliminated in the cosine arguments in equation (21), and terms with $q = 0$ [the second term in equation (20)] correspond to the nutational stimulated two-pulse echo formation. From (20) the nutational two-pulse stimulated echo is formed when $p_1\Delta t_1 = -p_2\Delta t_2$ ($|p_i| \leq \lambda$), i.e. at $\Delta t_2^e = \Delta t_1/2,\ \Delta t_1,\ \Delta t_1$ for $\lambda = 2$ and $\Delta t_2^e = \Delta t_1/2, \Delta t_1/3, \Delta t_1, 3\Delta t_1/4,\ \Delta t_2^e = \Delta t_1,\ 4\Delta t_1/3,\ 2\Delta t_1,\ 3\Delta t_1, 4\Delta t_1$ for $\lambda = 4$, i.e. fourth rank ST. There is definitely the possibility of the formation of other echo signals, except for the stimulated echo and its subharmonics within the second pulse duration, which are those obtained from equation (20) when $q \neq 0$ and ruled out not only by pulse durations but by interpulse separation as well. However, under strong LIB the terms with $q \neq 0$ in (19) and (20) lead to OFID formation, the duration of which is $\tau_{\mathrm{OFID}} = \lambda(\Delta t_1 + \Delta t_2)$, according to the extension of the well known theorem on coherent transients for the higher rank ST (Shakhmuratova 1984; Shakhmuratova *et al.* 1993; Hutchison *et al.* 1993; Chaplin *et al.* 1995*a*, 1995*b*), and allowing for the obligatory read pulse Δt_2. Thus, after the second pulsed rf field is switched on, for $\lambda = 2$ and when $\tau > 2(\Delta t_1 + \Delta t_2)$, terms with $q = 0$ in equations (19) and (20) are the only ones remaining; those with $q \neq 0$ have decayed to zero. Since $\Delta t_2 = 2\Delta t_1$ is the latest subharmonic spin-echo signal time of occurrence, therefore only terms with $q = 0$ are present for the region of principal echo and subharmonic echo formation for $\tau > 6\Delta t_1$. The averaging over the skin depth is performed without the reverse skin effect as it was for NMR in equation (13), but according to

$$\langle G^{\cdots}_{\cdots}\rangle_{x,\text{skin-effect}} = \frac{1}{w}\int_0^w \langle G^{\cdots}_{\cdots}(x, y_1, y_2, b; a(z))\rangle_x \mathrm{d}z\,. \tag{21}$$

Here $a = \exp(-z)$, $z = r/d$, $w = d/\sigma$, σ is the skin depth, d is the depth of the radioactive profile (Isbister and Chaplin 1990). Note that under axial geometry of the experiment [when only the PF $G^{q_1\,q_2}_{\lambda\,\lambda}(t)$ with $q_1 = q_2 = 0$ are detected] the skin effect is effective only through the rf amplitude, but not the rf phase, since the corresponding PF loses its rf field phase dependence due to final cancellation.

From the results presented in the previous section it is obvious that the pure LIB provides the oscillatory feature of the signal within the second pulse width, which is difficult to interpret as coherent transients. But when RIB is additionally included the oscillatory character is removed and the multistructural character of the signal is provided. The corresponding numerically computed curves are presented in Fig. 1 in Shakhmuratova *et al.* (1997*b*). The coherence is made observable due to the influence of the metallic skin effect, as a result the RIB removing strong competition from single pulse nutation.

(3b) Oscillatory Free Induction Decay (OFID)

The OFID was first predicted and observed for the first rank ST. Later on these ideas of OFID formation have been extended to higher rank ST (Shakhmuratova 1984), and the unique opportunity to test these results by pulse NMRON was recognised (Shakhmuratova *et al.* 1993; Hutchison *et al.* 1993; Chaplin *et al.* 1995*a*, 1995*b*). From utilisation of the axial geometry of the experiment the read pulse rotates the transverse components of the ST ρ_q^λ into an axial ρ_0^λ. In contrast with two-pulse stimulated echo in NMRON the read pulse is of constant duration, while the interpulse separation is changed to trace the dynamics of a spin system as a function of time elapsing from the trailing edge of the first pulse. The PF for arbitrary rank under two-pulse excitation may be presented in the form:

$$G^{0\,0}_{\lambda\,\lambda}(\Delta t_1, \Delta t_2, \tau) = \sum_q \tilde{G}^{q\,0}_{\lambda\,\lambda}(\Delta t_2)\overline{G}^{0\,0}_{\lambda\,\lambda}(\tau)\tilde{G}^{0\,q}_{\lambda\,\lambda}(\Delta t_1)\,, \tag{22}$$

the signal being detected at the end of the read pulse.

Two cases should be considered, one when the read pulse's rotation is isochromate independent and its role is purely to study the dynamics of a spin system in the transverse plane as a function of interpulse separation (Chaplin and Wilson 1986) and one when only during the first pulse is the spin dynamics influenced by severe LIB. Then according to equations (4) and (5) the total PF $G^{0\,0}_{\lambda\,\lambda}(y_1, b, y_2)$ from equation (22), but with the notation $b = \bar{\omega}_1\tau,\ y_i = \bar{\omega}_1\Delta t_i$ ($i = 1,\,2$) for dimensionless parameters can be derived in an explicit form for each λ, $\lambda = 1,\,2,\,3,\,4$ ($\lambda = 2$ and 4 are displayed in NMRON, $\lambda = 1$ and 3 are examined to trace the rank dependencies). Through an algebraic analysis of the PF in (22) averaged over LIB in the extreme case of $R \to 0$, the following results are obtained for durations of different terms emerging in the corresponding PF for various λ:

$\lambda = 1$

$$0 \le \tau \le \Delta t_1\ \ (0 \le b \le y_1); \tag{23a}$$

$\lambda = 2$

$$\begin{aligned}&(1)\ 0 \le \tau \le 0{\cdot}5\Delta t_1\ (0 \le b \le 0{\cdot}5y_1)\,,\\ &(2)\ 0 \le \tau \le \Delta t_1\ \ (0 \le b \le y_1)\,,\\ &(3)\ 0 \le \tau \le 2\Delta t_1\ \ (0 \le b \le 2y_1)\,;\end{aligned} \tag{23b}$$

$\lambda = 3$

$$\begin{aligned}&(1)\ 0 \le \tau \le \Delta\tfrac{1}{3}t_1\ \ (0 \le b \le \tfrac{1}{3}y_1), \qquad (2)\ 0 \le \tau \le 0{\cdot}5\Delta t_1\ \ (0 \le b \le 0{\cdot}5y_1)\,,\\ &(3)\ 0 \le \tau \le \tfrac{2}{3}\Delta t_1\ \ (0 \le b \le \tfrac{2}{3}y_1), \qquad (4)\ 0 \le \tau \le \Delta t_1\ \ (0 \le b \le y_1)\,,\\ &(5)\ 0 \le \tau \le 1{\cdot}5\Delta t_1\ \ (0 \le b \le 1{\cdot}5y_1),\\ &(*)(6)\ 0 \le \tau \le 2\Delta t_1\ \ (0 \le b \le 2y_1), \qquad (*)(7)\ 0 \le \tau \le 3\Delta t_1\ \ (0 \le b \le 3y_1)\,;\end{aligned} \tag{23c}$$

$\lambda = 4$

$$(1)\ 0 \le \tau \le \tfrac{1}{4}\Delta t_1\ \ (0 \le b \le \tfrac{1}{4}y_1), \qquad (*)(2)\ 0 \le \tau \le \tfrac{1}{3}\Delta t_1\ \ (0 \le b \le \tfrac{1}{3}y_1)\,,$$

(3) $0 \le \tau \le \frac{1}{2}\Delta t_1$ $(0 \le b \le \frac{1}{2}y_1)$, (*)(4) $0 \le \tau \le \frac{2}{3}\Delta t_1$ $(0 \le b \le \frac{2}{3}y_1)$,

(5) $0 \le \tau \le \frac{3}{4}\Delta t_1$ $(0 \le b \le \frac{3}{4}y_1$, (6) $0 \le \tau \le \Delta t_1$ $(0 \le b \le y_1)$,

(*)(7) $0 \le \tau \le 1\frac{1}{3}\Delta t_1)$ $(0 \le b \le 1\frac{1}{3}y_1)$, (8) $0 \le \tau \le 1{\cdot}5\Delta t_1$ $(0 \le b \le 1{\cdot}5y_1)$,

(9) $0 \le \tau \le 2\Delta t_1$ $(0 \le b \le 2y_1)$, (*)(10) $0 \le \tau \le 3\Delta t_1$ $(0 \le b \le 3y_1)$,

(*)(11) $0 \le \tau \le 4\Delta t_1$ $(0 \le b \le 4y_1)$. (23d)

The results presented in equations (23) can be easily obtained from an analysis of the total PF in (22), since it can be demonstrated that the separate terms have durations defined through the long pulse duration and ST rank as $\tau = (m/n)\Delta t$, with $0 < m,\ n \le \lambda$. The terms marked with the asterisk stand for those which become zero under a certain value of hard read pulse area (i.e. the LIB and RIB are not effective) for each rank ST, thus shortening the OFID duration. But with soft read pulse (i.e. the LIB and RIB are effective) due to RIB the pulse area is varying through the skin depth, thus providing different read pulses for different locations of probe nuclei. As a result the effect of leakage of the OFID signal with skin effect occurs (Chaplin *et al*. 1995).

Except for the extension of the OFID signal by $b = \lambda y_1$ as follows from analyses of the PF in (22), which is well investigated theoretically by now, the general damping of the oscillations under double inhomogeneity, i.e. the RIB due to skin effect, should be expected. In order to analyse the character of these modifications of the OFID attention should be paid to the terms of shorter duration, since after averaging of the PF over RIB [according to equation (21)] terms of the form given in equation (10) will emerge, and thus pure oscillatory character related to Rabi frequency is removed. At certain moments of time for each ST rank from (23) the branching points will provide the formation of SPE-type features, the total signal duration being $\tau = \lambda\Delta t$. Since there is a number of these sort of points for each rank of ST PF, they may provide the nonregular oscillatory type signal. In fact, due to double inhomogeneity, there are SPE-type effects formed at $\tau = (m/n)\Delta t$ $(0 < m, n \le \lambda)$, corresponding to the termination of each term as defined in equation (23). Thus it may be concluded that without the high repetition rate the total signal duration is extended to rank dependent times pulse width (when read pulse is hard) and SPE-type features emerge, which is well observed for example in Fig. 5 (Hutchison *et al*. 1993) for an interpulse separation equal to a single pulse duration for the second rank ST.

However, the picture is more complicated if the second read pulse is soft and its duration (or area) is comparable with that of the first pulse, which is often closer to the experimental situation. Then in equations similar to (23) not only Δt_1 i.e. y_1) but also Δt_2 (i.e. y_2) and $(\Delta t_1 + \Delta t_2)$ i.e. $(y_1 + y_2)$ will emerge. This will cause an increase in the number of branching points, unless two equal area pulses are utilised, i.e. $y_1 = y_2 = y$, since then only the sum of pulse durations (areas) and the single pulse duration (area) dependent terms are pertinent. But as the damping of the OFID signal is rank dependent the branching points at $b = y/2,\ y$ are more profound as compared to $b = 2y$.

4. Conclusions

An examination of various coherent transient effects formed under double inhomogeneity, i.e. LIB plus RIB, demonstrates that the second inhomogeneity, i.e. RIB, plays a vital role in many aspects. It modifies the oscillatory character of the signal, typical for severe LIB, since the frequency of these oscillations is related to the Rabi frequency. Algebraically, the inhomogeneity additional to LIB in the Rabi frequency provides the formation of branching points in the case of an infinitely wide linewidth, i.e. $R \to 0$. Thus numerically, for finite values of R, it results in echo signal formation, ruled by pulse durations as well as interpulse separation, or single pulse echo-type effects. These conclusions can be extended to a wider number of experiments in optical resonance, NMR and EPR carried out under the conditions specified earlier for pulse excitation.

A high repetition rate of a pulse sequence for the first rank ST provides the extension of the signal beyond the point separated from the trailing edge of the last pulse in a sequence by an integer times the long pulse duration, which is in accordance with the coherent transients theorem. On the other hand, it consolidates the echo signal formation due to the constructive effect of all pulses at these moments of time (produced by additional terms of various durations equal to an integer times the long pulse width). The simple oscillatory character of the signal related to the rf amplitude is severely mixed under a high repetition rate due to superposition of the dynamics during many rf pulses, but still the echo signals are discernible among these oscillations at the moments of time, measured from the trailing edge of the latest pulse in the sequence, equal to the integers of the long pulse durations (or combinations of the various long pulse durations). The RIB plays the most important role in removing all these oscillations and making the echo signals profound and sharp, especially when related to the enhancement factor inhomogeneity.

As for coherent transients observed for higher rank ST, $\lambda > 1$, the high repetition rate is not necessary, since the total signal observed under the pulsing is extended to λ times the pulse duration, thus providing the non-zero signal beyond the single pulse duration (or combination of large area pulse durations). As a result the RIB may have a severe effect on the Rabi frequency related oscillations through formation of echo signals without a high repetition rate at the moments of time that are shorter than the rank dependent total duration of a signal. Interestingly, a similar effect can be expected in NMR and optical resonance (Manson 1996) when due to multipulse excitation, e.g. three-pulse stimulated echo formation with at least one large area pulse, will provide the observation of three stimulated echoes at $\tau = \tau_1,\ \tau_1 \pm \Delta t$, the total signal being of the duration $\tau = \tau_1 + \tau_2 + \Delta t$ in accordance with the coherent transients theorem, where τ_1, τ_2 are pulse separations in a three-pulse sequence and τ is measured from the trailing edge of the third pulse. Thus, in this case the extension of the siganal is due to multiple pulse excitation with a few long interpulse separations in a sequence. The formation of new coherent transient effects under various types of double inhomogeneity is expected with formation of multi-structural signals, ruled by pulse durations.

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