PHASE SHIFTS INDUCED BY TRANSIENT BLOCH–SIEGERT EFFECTS IN NMR

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It is shown by simulation and experiment that selective pulses designed to invert or excite magnetization over a limited frequency window induce significant phase shifts over a bandwidth much larger than the chosen window. These phase shifts affect all experiments where selective pulses are used after exciting transverse magnetization or generally p-quantum coherence. The phase shifts may be compensated by modifying the phases of the rf pulses during the experiments or in some cases by suitable data transformations.

1. Introduction

Bloch–Siegert shifts are known to occur in all double-resonance experiments where a continuous monochromatic irradiation of magnitude ω_1 is applied at a frequency ω_{rf} [1,2]. In the absence of the double-resonance field, a spin I_k precesses at its offset (chemical shift) $\Omega_k = \omega_k - \omega_{rf}$. If the rf amplitude fulfills the condition $0 < \omega_1 \ll \Omega_k$ however, the I_k signal appears at a frequency $\Omega'_k \approx \Omega_k + \omega_1^2/2\Omega_k$. The Bloch–Siegert shift disappears as soon as the irradiating field is switched off, as in so-called "gated" Overhauser measurements for example, where it is possible to use difference spectroscopy to unveil weak enhancements. In selective decoupling experiments, on the other hand, it is necessary to irradiate the coupling partners during observation, and the Bloch–Siegert shift makes it difficult to use the principle of difference spectroscopy [3–5]. The shift also affects two-dimensional spectra, particularly when continuous irradiation is applied, for example to saturate the solvent resonance, in either the evolution *or* detection period [6]. By and large however, it is generally assumed that Bloch–Siegert shifts can only have treacherous effects when the double-resonance field is actually switched on during sampling. In this Letter, it is shown that *transient* Bloch–Siegert effects can profoundly affect a range of experiments that were hitherto believed to be quite safe from this type of interference.

Many experimental schemes involve selective pulses designed to invert or excite magnetization over a limited frequency window. Usually, the effects of such selective pulses are predicted by calculating the offset dependence of the M_z and M_{xy} responses. In fact, it turns out that selective pulses also induce rotations about the z-axis. We will demonstrate how, if there is any transverse magnetization, or in general p-quantum coherence, these z-rotations can lead to significant phase shifts. The effects occur at surprisingly large offsets Ω_k from the carrier frequency ω_{rf} of the selective pulses, well outside the frequency window in which the selective pulses are intended to invert or excite the magnetization. Clearly, these pernicious phase shifts will not manifest themselves in the usual simulations of the offset dependence of the M_z or M_{xy} responses.

2. The basic phenomenon

Consider a simple experiment where the beginning of data acquisition is delayed after initial excitation by an interval t_p (fig. 1a). In a frame rotating at ω_{rf} the magnetization associated with a spin I_k at an offset Ω_k from the carrier of the exciting pulse builds up a phase

$$\phi_k = \Omega_k t_p \quad (1)$$

which is due to free precession about the z-axis of the

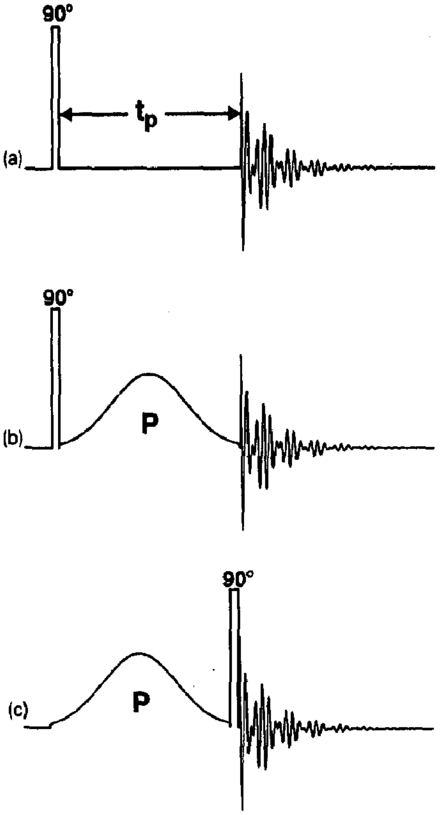

Fig. 1. Experimental schemes suitable to demonstrate transient Bloch–Siegert effects. (a) Hard 90° pulse followed by acquisition after a delay t_p. (b) Hard 90° pulse followed by application of a time-dependent irradiation P of duration t_p before acquisition. (c) Same as (b) but with permutation of the hard and soft pulses. The pulse P is shown as a truncated Gaussian, but it could be defined by an arbitrary envelope function.

rotating frame for a time t_p. However, if an rf pulse of constant amplitude ω_1 is applied along the y-axis during t_p, the precession occurs about an effective vector $\omega_{k\,\mathrm{eff}}$ which lies in the yz-plane and is tilted with respect to the z-axis by an angle $\theta_{k\,\mathrm{eff}}$. The precession about the effective field gives rise to a phase error ϕ'_k rather than ϕ_k. If we begin with an initial magnetization M_k^0 aligned along the x-axis, it can easily be shown [7] that the x- and y-components of the resultant magnetization are

$$M_{kx}=M_k^0 \cos\beta_{k\,\mathrm{eff}}\,, \tag{2a}$$

$$M_{ky}=M_k^0 \sin\beta_{k\,\mathrm{eff}} \cos\theta_{k\,\mathrm{eff}}\,, \tag{2b}$$

where $\beta_{k\,\mathrm{eff}}$ is the effective flip angle around $\omega_{k\,\mathrm{eff}}$. The phase of the resulting vector is

$$\tan\phi'_k=M_{ky}/M_{kx}=\tan\beta_{k\,\mathrm{eff}}\cos\theta_{k\,\mathrm{eff}}\,,$$

hence

$$\sigma'_k=\arctan(\tan\beta_{k\,\mathrm{eff}}\cos\theta_{k\,\mathrm{eff}})\,. \tag{3}$$

Thus the phase difference $\Delta\phi=\phi_k-\phi'_k$ of the magnetization vectors in the experiments with and without an rf pulse in the t_p interval (see figs. 1a and 1b) is

$$\Delta\phi_k=\phi_k-\arctan(\tan\beta_{k\,\mathrm{eff}}\cos\theta_{k\,\mathrm{eff}})\,. \tag{4}$$

For the purposes of this Letter we are interested in effects that are far from resonance, i.e. where $\Omega_k \gg \omega_1$. It follows that $\theta_{k\,\mathrm{eff}}$ is small and that $\cos\theta_{k\,\mathrm{eff}}\approx 1$. Making this assumption, we can rewrite eq. (4) as

$$\Delta\phi_k\approx\phi_k-\beta_{k\,\mathrm{eff}}\,. \tag{5}$$

At this point we should recall that *any* sequence of rotations $\boldsymbol{R}_1,...,\boldsymbol{R}_i$ about axes $\boldsymbol{n}_1,...,\boldsymbol{n}_i$ can be represented by a total rotation $\boldsymbol{R}_{\mathrm{tot}}$ about an axis $\boldsymbol{n}_{\mathrm{tot}}$ [8]. Thus at a given offset the problem is exactly analogous to the rotation produced under a constant-amplitude pulse and without loss of generality we can assume that $\boldsymbol{n}_{\mathrm{tot}}$ lies in the yz-plane. Eq. (3) is therefore valid for any shaped pulse. Although $\theta_{k\,\mathrm{eff}}$ cannot be calculated analytically for an arbitrary pulse, $\cos\theta_{k\,\mathrm{eff}}\approx 1$ is true for any pulse provided we are far off-resonance. Thus eq. (5) is also valid for any pulse. The angle $\beta_{k\,\mathrm{eff}}$ is given as

$$\beta_{k\,\mathrm{eff}}=\int\{\Omega_k^2+[\omega_1(t)]^2\}^{1/2}\,\mathrm{d}t=\int\omega_{k\,\mathrm{eff}}(t)\,\mathrm{d}t\,, \tag{6a}$$

where $\omega_{k\,\mathrm{eff}}(t)$ is the time-dependent magnitude of the effective field. Hence

$$\beta_{k\,\mathrm{eff}}=\langle\omega_{k\,\mathrm{eff}}\rangle t_p\,, \tag{6b}$$

where $\langle\omega_{k\,\mathrm{eff}}\rangle$ is the average magnitude of the effective field during t_p. This is equivalent to saying that any pulse shape can be replaced by an equivalent square pulse provided we are far from resonance. Thus, on a scale of offset defined as $\Omega_k/\langle\omega_{k\,\mathrm{eff}}\rangle$, which is not linear with respect to Ω_k since $\langle\omega_{k\,\mathrm{eff}}\rangle$ also contains a term in Ω_k, the phase behaviour should be identical for *all* pulses regardless of their shape. With this in mind, eq. (5) can be conveniently rewritten

$$\Delta\phi_k \approx (\Omega_k - \langle \omega_{k\,\mathrm{eff}} \rangle) t_\mathrm{p} = \langle \Delta\omega_k \rangle t_\mathrm{p} , \qquad (7)$$

where $\langle \Delta\omega_k \rangle$ is the average deviation of $\omega_{k\,\mathrm{eff}}$ from Ω_k.

Fig. 2a shows the M_z response of a simple Gaussian inversion pulse with 2.5% truncation. Inversion is efficient over a very small frequency region [9,10]. In fig. 2b we show the phase shift expected when P of fig. 1b is such a Gaussian pulse as obtained by numerical solution of the Bloch equations, compared to the shift predicted by eq. (7). The agreement is found to be exact at reduced offsets $\Omega_k/\omega_1^{\mathrm{max}} > 2$. Note how the phase shift extends to offsets much larger than those where the longitudinal magnetization component is affected by the pulse. It may initially appear that at reduced offsets greater than around 5, the transient Bloch–Siegert effect is negligible, being less than 20°. However, in fig. 2c the result of subtraction can be seen to be non-negligible even for a reduced offset of 12.6 when the phase difference is as small as 5°.

Fig. 3 compares the phase shifts experienced by

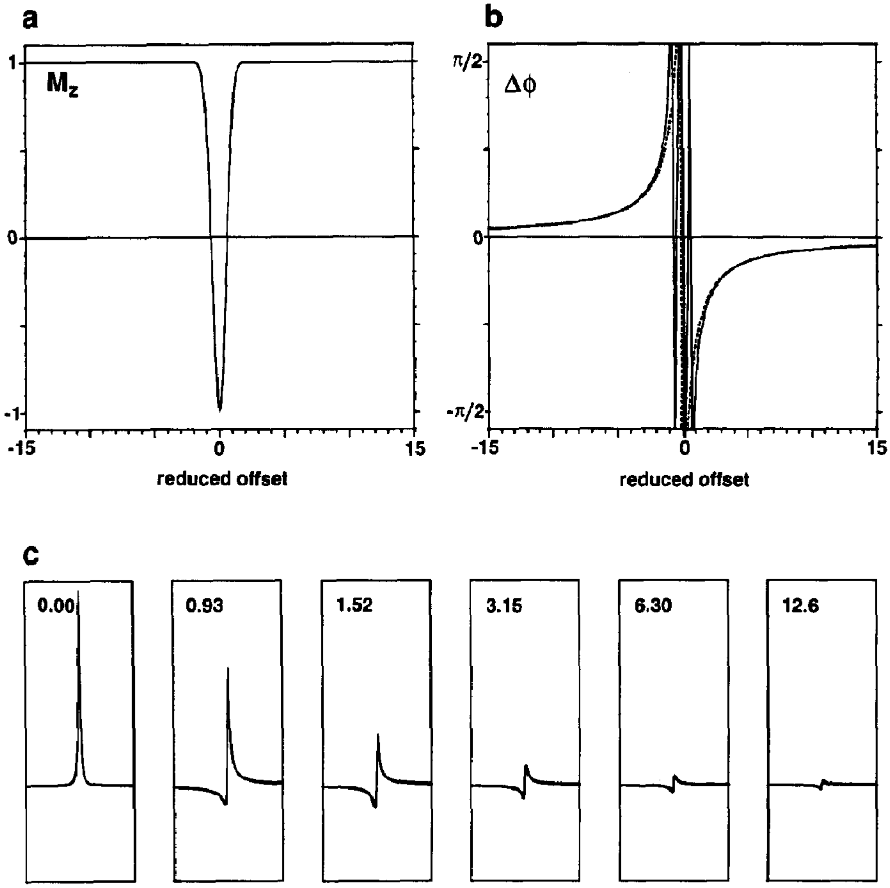

Fig. 2. Offset dependence after a 180° Gaussian inversion pulse of (a) the M_z response and (b) the transient Bloch–Siegert effect. In (b) the solid line corresponds to the phase shift calculated by numerical solution of the Bloch equations and the dashed line corresponds to the shift calculated using eq. (7). (c) Simulations of the residual signal observed after subtraction of two Lorentzian components with the same magnitude but having a phase difference as shown in (b) at the reduced offsets ($\Omega_k/\omega_1^{\mathrm{max}}$) indicated. The signal at zero offset is the reference and corresponds to the difference between two signals of exactly opposite phase. The other signals correspond to residuals observed after Bloch–Siegert phase shifts of, from left to right, 90°, 45°, 20°, 10° and 5°. Even at reduced offsets as large as 12, transient Bloch–Siegert effects clearly cannot be neglected in difference experiments.

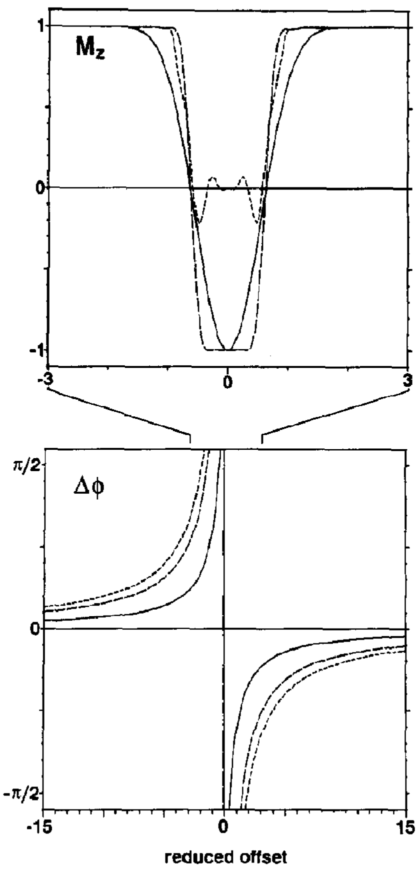

Fig. 3. Offset dependence of $\Delta\phi$ calculated with eq. (7) for various pulse shapes compared to their M_z responses. The solid line is for a simple Gaussian inversion pulse, the long dashes are for a G^3 inversion pulse and the short dashes for a G^4 excitation pulse. Note that the Bloch–Siegert phase shifts are significant over bandwidths more than 30 times wider than the region that is inverted or excited.

transverse magnetization after a truncated Gaussian inversion pulse, a so-called G^3 inversion pulse and a G^4 excitation pulse [11]. The plots are on a reduced scale of offset divided by the maximum pulse amplitude, and it is apparent that on this scale the bandwidth of the M_z perturbation is approximately the same for each pulse. However, we can see how the phase error $\Delta\phi_k$ gets larger as the complexity of the pulse envelope increases in going from G^1 to G^4. This reflects a general phenomenon, implied by eq. (7), that transient Bloch–Siegert effects become more pronounced as pulse shapes become more complex. While ω_1 can be negative if the pulse involves phase modulation, ω_{eff} is always positive and larger than or equal to Ω_k and it can be seen that pulses with complicated envelopes will have a larger phase error $\Delta\phi_k$.

3. Experimental verification

In order to verify the existence of transient Bloch–Siegert effects we have performed a series of experiments according to fig. 1b where the proton resonance of tetramethylsilane (TMS) was put into the transverse plane by a hard 90° pulse, and an off-resonance 180° Gaussian shaped pulse was applied before acquiring the free induction decay. The Gaussian pulse was always set far enough from resonance so that no perturbation of the intensity of the signal would occur. The phase shift originating from transient Bloch–Siegert effects was then assessed by comparing the phase of the signal with that of a control experiment in which all conditions were the same except that the amplitude of the soft pulse was set to zero (as in fig. 1a). The results are shown in fig. 4 compared to those predicted by numerical integration, and the agreement is seen to be excellent.

In fig. 5 we show perturbations due to transient Bloch–Siegert effects on a real example Figs. 5a–5f

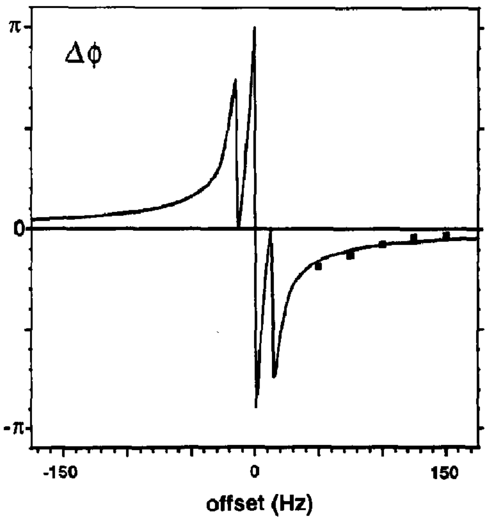

Fig. 4. Experimental confirmation (squares) of the offset dependence of the predicted phase shifts for a Gaussian inversion pulse with 2.5% truncation and peak amplitude $\omega_1^{max}/2\pi = 22$ Hz. See text for experimental details.

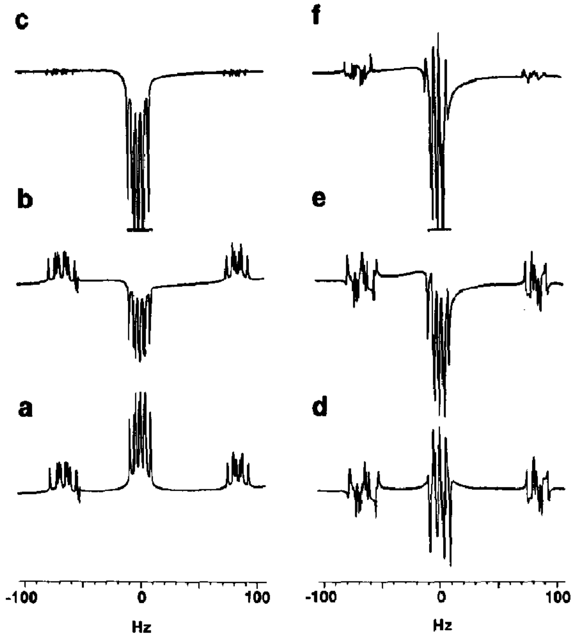

Fig. 5. Transient Bloch–Siegert effects in a 400 MHz proton spectrum of a 1:3 mixture of cis- and trans-2-phenylcyclopropanecarboxylic acid methyl ester. The central multiplet is of the trans isomer and the other multiplets are of the minor cis isomer. (a) Normal spectrum; (b) spectrum acquired with the sequence of fig. 1c. In (b) P is a 50 ms 180° Gaussian inversion pulse with 2.5% truncation. (c) shows the result of subtraction of (a) and (b). As expected the off-resonance multiplets are almost perfectly suppressed. The phase of the soft pulse was alternated while keeping the receiver phase constant, so as to suppress any residual transverse coherence which may have been created by the pulse. (d)–(f) Results of the experiment if the hard and soft pulses are permuted: (d) is acquired according to fig. 1a, (e) is acquired according to fig. 1b, and (f) is the result of subtracting the two spectra. The failure of the subtraction of the outer multiplets in (f) is due to transient Bloch–Siegert effects and is seen to be quite striking. The experimental conditions were the same as for (a)–(c), except for the phase cycling, in that the phase of the hard pulse was alternated in conjunction with the receiver. The same zeroth-order phase correction was applied to all six spectra.

show a region of the 400 MHz proton spectrum of a 1:3 mixture of cis- and trans-2-phenylcyclopropanecarboxylic acid methyl ester. Fig. 5b shows the result of a control experiment using the sequence of fig. 1c, which demonstrates that the effect of the 180° Gaussian inversion pulse is limited to only the central multiplet. Consequently, the outer multiplets disappear almost completely in the difference spectrum of fig. 5c. In fig. 5f we see a striking demonstration of transient Bloch–Siegert effects in the appearance of residual off-resonance multiplets. Since the off-resonance multiplets are both of the cis isomer, while the central multiplet is of the trans, there can be no interference in this experiment from any coherence transfer mechanisms, such as selective population transfer [12], and neither can there be any other effects such as partial refocusing of scalar couplings. The only mechanism for the appearance of the off-resonance multiplets in fig. 5f is through transient Bloch–Siegert shifts. The two multiplets in fig. 5f have residual magnitudes of around 40% and 25% respectively for the left- and right-hand sides of those in fig. 5a.

4. Multiple-quantum coherences

So far we have shown the effect of transient Bloch–Siegert shifts on transverse magnetization, or single-quantum coherences. Bloch–Siegert shifts themselves have been shown also to affect double-quantum coherences [13–15], and it follows that transient Bloch–Siegert shifts should lead to phase shifts of p-quantum coherence.

Double- and zero-quantum coherences in weakly coupled systems are best represented as linear combinations of product operators [7,16], i.e.

$$\{\mathrm{DQC}\}_x = \tfrac{1}{2}(2I_{1x}I_{2x} - 2I_{1y}I_{2y}) \tag{8}$$

and

$$\{\mathrm{ZQC}\}_x = \tfrac{1}{2}(2I_{1x}I_{2x} + 2I_{1y}I_{2y})\ . \tag{9}$$

The propagator for the transformation induced by the irradiating pulse can be represented at suitable offsets from resonance as

$$U = \exp\left(-\mathrm{i}\sum_k \Delta\phi_k I_{kz}\right), \tag{10}$$

that is, as a z-pulse through the offset-dependent flip angle $\Delta\phi_k$ defined in eq. (7). The effect on a double-quantum coherence is easily determined to be

$$\{DQC\}_x \xrightarrow{\Delta\phi_1 I_{1z} + \Delta\phi_2 I_{2z}} \{DQC\}_x \cos(\Delta\phi_1 + \Delta\phi_2) + \{DQC\}_y \sin(\Delta\phi_1 + \Delta\phi_2) . \quad (11)$$

Thus double-quantum coherence experiences a transient Bloch–Siegert phase shift through an angle which is the sum of the phase shifts that would be undergone by individual I_{1x} and I_{2x}. Similarly for zero-quantum coherence,

$$\{ZQC\}_x \xrightarrow{\Delta\phi_1 I_{1z} + \Delta\phi_2 I_{2z}} \{ZQC\}_x \cos(\Delta\phi_1 - \Delta\phi_2) + \{ZQC\}_y \sin(\Delta\phi_1 - \Delta\phi_2) . \quad (12)$$

The zero-quantum coherence is phase shifted through an angle which corresponds to the difference of the two phase shifts. This may, for example, be important if selective inversion pulses are inserted in the recovery intervals of NOESY-type experiments designed to monitor the dynamics of various forms of longitudinal multiple-spin order [17,18]. In such experiments, transient Bloch–Siegert shifts may interfere with phase cycles designed to eliminate p-quantum coherences.

5. Conclusions

Phase shifts induced by transient Bloch–Siegert effects interfere with all experiments where selective pulses are used *after* excitation of single- or multiple-quantum coherence. We have recently encountered problems in variants of soft correlation spectroscopy (soft COSY) involving selective inversion of coupling partners in the evolution period [19]. These methods rely on the subtraction of signals obtained in two complementary experiments, one with and the other without a selective inversion pulse applied well outside the spectral range of interest. Such experiments are useful to determine networks of coupled spins [19,20]. They may be regarded as multiple-quantum filtering schemes using "amplitude alternation" rather than phase cycling of the pulses. It turns out however that the selective pulses not only invert the polarization of a particular passive coupling partner, but also induce phase shifts of the transverse magnetization of the active spins. This makes it difficult to use difference spectroscopy. Similar effects are likely to arise in all forms of so-called "ω_1 decoupling" where a semi-selective refocusing pulse is applied in the middle of the evolution period [21]. In such techniques transient Bloch–Siegert effects will manifest themselves as intensity losses in the resulting spectra, as sequences designed to achieve efficient transfer of coherence usually depend on spins undergoing the same rotation at all offsets. The phase shifts may also affect some multi-slice imaging experiments [22].

Fortunately, the phase shifts induced by transient Bloch–Siegert effects can be readily quantified, and may be compensated for by suitable data transformations using a non-linear phase correction with a frequency dependence according to eq. (7). In situations where only one particular multiplet is observed, the phase shift may be compensated for by the simple expedient of suitably adjusting the phases of rf pulses preceeding or following the off-resonance selective pulse [19].

Much effort has been invested in recent years to "craft" selective pulses that achieve nearly ideal rectangular excitation or inversion [11,23–26]. These efforts have led to sophisticated prescriptions involving the modulation of the rf amplitude and/or phase during the course of the pulse. Transient Bloch–Siegert effects tend to be more pronounced for sophisticated crafted pulses, but even for the simplest rectangular or Gaussian pulse envelopes they are surprisingly large.

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References

[1] F. Bloch and A. Siegert, Phys. Rev. 57 (1940) 522.
[2] N.F. Ramsey, Phys. Rev. 100 (1955) 1191.
[3] R. Freeman and W.A. Anderson, J. Chem. Phys. 37 (1962) 85.
[4] L.D. Hall and J.K.M. Sanders, J. Am. Chem. Soc. 102 (1980) 5703.

[5] J.D. Mersh and J.K.M. Sanders, J. Magn. Reson. 50 (1982) 289.
[6] R.V. Hosur, R.R. Ernst and K. Wüthrich, J. Magn. Reson. 54 (1983) 142.
[7] R.R. Ernst, G. Bodenhausen and A. Wokaun, Principles of nuclear magnetic resonance in one and two dimensions (Clarendon Press, Oxford, 1987).
[8] W.R. Hamilton, Proc. Roy. Irish Acad. 2 (1844) 424.
[9] C. Bauer, R. Freeman, T. Frenkiel, J. Keeler and A.J. Shaka, J. Magn. Reson. 58 (1984) 442.
[10] L. Emsley and G. Bodenhausen, J. Magn. Reson. 82 (1989) 211.
[11] L. Emsley and G. Bodenhausen, Chem. Phys. Letters 165 (1990) 469.
[12] A.J. Shaka, C. Bauer and R. Freeman, J. Magn. Reson. 60 (1984) 479.
[13] J. Margerie and J. Brossel, Compt. Rend. Acad. Sci. (Paris) 241 (1955) 373.
[14] J.A. Hermann and S. Swain, J. Phys. B 7 (1974) 2363.
[15] A. Wokaun and R.R. Ernst, Mol. Phys. 38 (1979) 1579.
[16] O.W. Sørensen, G.W. Eich, M.H. Levitt, G. Bodenhausen and R.R. Ernst, Progr. Nucl. Magn. Reson. Spectry. 16 (1983) 163.
[17] C. Dalvit and G. Bodenhausen, Advan. Magn. Reson., in press.
[18] C. Dalvit and G. Bodenhausen, Chem. Phys. Letters 161 (1989) 554.
[19] L. Emsley and G. Bodenhausen, in preparation.
[20] L. Emsley, P. Huber and G. Bodenhausen, Angew. Chem., in press.
[21] R. Brüschweiler, C. Griesinger, O.W. Sørensen and R.R. Ernst, J. Magn. Reson. 78 (1988) 178.
[22] P.G. Morris, Nuclear magnetic resonance imaging in medicine and biology (Clarendon Press, Oxford, 1986).
[23] W.S. Warren and M.S. Silver, Advan. Magn. Reson. 10 (1988) 1.
[24] J.T. Ngo and P.G. Morris, Magn. Reson. Med. 5 (1987) 217.
[25] L.K. Hedges and D.I. Hoult, J. Magn. Reson. 79 (1988) 391.
[26] H. Geen, S. Wimperis and R. Freeman, J. Magn. Reson. 85 (1989) 620.