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Supporting information

Excitation of singlet-triplet coherences in pairs of nearly-equivalent spins

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1. Maximal achievable enhancement of the OST transitions

A common problem in singlet-state NMR is to calculate the maximal amplitude b_{max} of spin order conversion that can be achieved by transforming an initial operator $\hat{A}$ into an operator $\hat{B}$:

$$\hat{U}\hat{A}\hat{U}^{\dagger} = b_{max}\hat{B} + \hat{C}$$

where the operator $\hat{C}$ is orthogonal to $\hat{B}$:

$$Tr\{\hat{B}^{\dagger}\hat{C}\} = 0$$

The b_{max} value can be evaluated using unitary bounds for spin evolution [1, 2].

In the present case, the initial state of density operator is given by $(\hat{I}_{az} + \hat{I}_{bz})$ operator, the final state, corresponding to generation of the OST coherences, is as follows:

$$\frac{\exp(-i\varphi)}{\sqrt{2}}(|3\rangle\langle 1| - |3\rangle\langle 4|) + \frac{\exp(i\varphi)}{\sqrt{2}}(|1\rangle\langle 3| - |4\rangle\langle 3|)$$

For a pair of chemically inequivalent spins there are no symmetry constraints [3] with a consequence that the eigenvalues of the initial and target spin operators are sorted within a single manifold of states. Both operators have the same set of the eigenvalues (when written in the ascending or descending order):

$$\Lambda_{z\uparrow} = \Lambda_{OST\uparrow} = \{1,0,0,-1\}$$

Hence, the maximal spin order conversion efficiency is equal to

$$b_{max} = \frac{\Lambda_{OST\uparrow}.\Lambda_{z\uparrow}}{\|\Lambda_{OST\uparrow}\|^2} = 1$$

This b_{max} value means that the $(\hat{I}_{az} + \hat{I}_{bz})$ state can be completely transformed into the OST coherences.

The “forbidden” transitions corresponding to the OST coherences will be enhanced by the factor of χ as compared to the case of NMR detection using excitation by a single $\frac{\pi}{2}$ pulse.

In the same way, one can show that the IST coherence can be also generated from the $(\hat{I}_{az} + \hat{I}_{bz})$ spin order with 100% efficiency.

[1] O.W. Sørensen, Polarization Transfer Experiments in High-Resolution NMR-Spectroscopy, Prog. Nucl. Magn. Reson. Spectrosc. 21 (1989) 503-569.
[2] O.W. Sørensen, A Universal Bound on Spin Dynamics, J. Magn. Reson. 86 (1990) 435-440.
[3] M.H. Levitt, Symmetry constraints on spin dynamics: Application to hyperpolarized NMR, J. Magn. Reson. 262 (2016) 91-99.

1. J-CPMG ISTz pulse program for AVANCE III

```
;J –CPMG ISTz sequence
;pseudo 2D sequence
;
;$CLASS=HighRes
;$DIM=2D
;$TYPE=zg

#include <Avance.incl>
#include <Grad.incl>

"p2=p1*2"
"d20=1/(4*cnst10)"

1 ze
        10u pl1:f1
2 30m
        d1
        10u pl1:f1
        (p1 ph1):f1   ;90*flip

3       d20                                     ;CPMG block
  (p1 ph2):f1
        (p2 ph1):f1
        (p1 ph2):f1
        d20
        lo to 3 times l1

        (p1 ph3):f1

        10u UNBLKGRAD
        p30:gp1
        10u BLKGRAD

        vd

        (p1 ph4):f1
4       d20                                     ;CPMG block
  (p1 ph2):f1
        (p2 ph1):f1
        (p1 ph2):f1
        d20
        lo to 4 times l1

        go=2 ph31
   30m wr #0 if #0 ivd
  lo to 1 times td1
exit

ph1 = 0 0
ph2 = 1 1
ph3 = 1 3
ph4 = 1 1
ph31= 1 3
```

;p1: duration of 90* pulse
;d20 : delay in J-CPMG echo train
;l1 : number of echoes for J-CPMG
;plw1 : power 90 hard pulse
;cnst10 : square root of (J*J + delta*delta)[Hz]
;p30 : duration of gradient
;gp1 : gradient strength
;pl1: power of 90* pulse

1. J-CPMG ISTx pulse program for AVANCE III

```
;J –CPMG ISTx with CW during variable delay sequence
;pseudo 2D sequence
;
;$CLASS=HighRes
;$DIM=2D
;$TYPE=zg

#include <Avance.incl>

"p2=p1*2"
"d20=1/(4*cnst10)"


1 ze
        10u pl1:f1
2 30m
        d1
        10u pl1:f1
        (p1 ph3):f1   ;90*flip

3       d20                                     ;J-CPMG block
  (p1 ph2):f1
        (p2 ph1):f1
        (p1 ph2):f1
        d20
        lo to 3 times l1

        10u pl9:f1
  d22 cw:f1 ph1
        10u do:f1

        10u pl1:f1
4       d20                                     ;J-CPMG block
  (p1 ph2):f1
        (p2 ph1):f1
        (p1 ph2):f1
        d20
        lo to 4 times l1

        go=2 ph31
  30m wr #0 if #0 id22
  lo to 1 times td1
exit

ph3 = 0 2
ph1 = 0 0
ph2 = 1 1
ph31= 1 3

;p1: 90* detection pulse
;d20 : delay in J-CPMG echo train
;d22 : starting value of variable delay
;id22: increment for d22
```

;l1 : number of echoes for J-CPMG
;plw9 : power of CW (spin-locking on-resonance RF field) during variable delay
;plw1 : power 90 hard pulse
;cnst10 : square root of (J*J + delta*delta)[Hz]
;pl1: power of 90