Supporting Information

Recovery of Bulk Proton Magnetization and Sensitivity Enhancement in Ultrafast Magic-Angle Spinning Solid-State NMR

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**Supplementary Figure S1.** (a) Bulk $^1$H longitudinal relaxation rate measured by inversion-recovery. The blue line represents the fit with a mono-exponential recovery curve ($T_1 = 32 \pm 2.2$ s). (b) Decay curve recorded during a $^1$H spin-lock at 13.4 kHz RF. The blue line represents the fit with a mono-exponential decay curve ($T_{lp} = 13.9 \pm 0.4$ ms).

**Pulse sequence to measure $^1$H spin-lock efficiency and $^1$H–$^{13}$C decoupling efficiency**

Used for the measurement of $^1$H spin-lock efficiency (Figure 1a, pulse scheme in Figure 2a) and $^1$H–$^{13}$C decoupling efficiency (Figure 1b, pulse scheme in Figure 2b).

**Options:**

*Spin-lock*

l2=0 No spin-lock pulse
l2=1 $^1$H spin-lock pulse before CP
;spinlock.pp
; Measurement of 1H–13C decoupling efficiency and 1H spin-lock efficiency.

;Options
; l2=0 : No spin-lock pulse
; l2=1 : 1H spin-lock pulse before CP

;--- Reference ---
; Recovery of bulk proton magnetization and sensitivity enhancement in ultra-fast Magic-Angle
; Spinning solid-state NMR, Jean-Philippe Demers, Vinesh Vijayan, Adam Lange, J Phys Chem B, 2015

; $OWNER=nmr
sp0=pl6 ; Syntax for TopSpin 2.x ; 1H CP power level
spw0=plw6 ; Syntax for TopSpin 3.x ; 1H CP power level

;============
; Parameters
;============

;p2  1H 90° pulse length
;p12 1H 90° pulse power level
;p16 1H spin-lock pulse length
;p16 1H spin-lock pulse power level
;p15 13C CP power level
;p16 1H CP power level
;p15 CP contact time
;sp0 1H CP shape
;sp15 13C CP shape
;pl12 1H decoupling power level during acquisition
;d1 Recycling delay between experiments

;============
; Protections
;============

1m
if "p2  >  1000" goto Problem
if "p15 > 10m" goto Problem
if "aq > 31m" goto Problem
if "d1 < 0.025s" goto Problem

goto PassParams
Problem, 1m
print "Parameters not accepted, ending."
goto HaltAcqu
PassParams, 1m

;==============
; Pulse program
;==============

1  ze accumulate into an empty memory
2  d1 do:f2 recycling delay, decoupler off
   lu f=q=0:f2
1ufq=cnst15:f1 ; frequency offset on 13C channel for band-selective CP schemes
10u p12:f2 p15:f1 ; set initial power levels

;--- 90° 1H ---
p2:f2 ph1

;--- 1H Spin-lock ---
if (l2==1)
{
  1u p16:f2 (p16 ph0):f2
}

;--- 1H --> 13C Cross-polarization ---
1u p16:f2 (p15 ph2):f1 (p15:sp0 ph0):f2
1u p112:f2 ; 1H decoupling power level
1u cpds2:f2 ; Acquisition 1H decoupling on

;--- Acquisition ---
go=2 ph31
```
1m do:ff  ; decoupler off
100m wr #0  ; save data to disk
HaltAcqu, 1m  ; jump address for protection files
exit  ; quit

# Phase cycle
#-------------------
ph1= 1 3  ; 1H 90° pulse
ph0= 0  ; 1H CP pulse
ph2= 0 0 2 2  ; 13C CP pulse
ph31= 0 2 2 0  ; 13C acquisition
```
Pulse sequence for flip-back experiment

Used for the measurement of sensitivity curve (Figure 4b) and signal enhancement (Figure 5), pulse scheme in Figure 2c.

Parameters:

The following composite pulse decoupling (CPD) programs must be employed:

```
cpdprg1='xix.cpd', cpdprg2='cw.cpd', cpdprg3='cw0_flip270.cpd', cpdprg4='cw0_flip90.cpd'
```

Options:

**Cross-polarization**

- $l_3=1$: Rectangular pulse on both $^1$H and $^{13}$C channels
- $l_3=2$: Shaped pulse on $^1$H, rectangular pulse on $^{13}$C
- $l_3=3$: Rectangular pulse on $^1$H, shaped pulse on $^{13}$C

**Decoupling**

- $l_4=0$: Reference (No flip pulse)
- $l_4=2$: Flip-back pulse
- $l_4=4$: Flip-down pulse
- $l_4=1$: Use alternative CPD program as specified by cpdprg1 (e.g. ‘xix.cpd’)

--- Reference ---


```
;flipback.pp

; Measurement of sensitivity curve and signal enhancement.

;i3=1 : Rectangular pulse on both 1H and 13C channels
;i3=2 : Shaped pulse on 1H, rectangular pulse on 13C
;i3=3 : Rectangular pulse on 1H, shaped pulse on 13C
;i4=0 : Reference (No flip pulse)
;i4=2 : Flip-back pulse
;i4=4 : Flip-down pulse
;i4=1 : Use alternative CPD program as specified by cpdprg1

;--- Reference ---


;OWNER=nmrsu

"sp0=p16" ;Syntax for TopSpin 2.x ; 1H CP power level
"spw0=p16" ;Syntax for TopSpin 2.x ; 1H CP power level
"sp15=p15" ;Syntax for TopSpin 2.x ; $^{13}$C CP power level
"spw15=p15" ;Syntax for TopSpin 2.x ; $^{13}$C CP power level
"cnst25=0" ;Counter for current scan number
```
Parameters

- `p2`  1H 90° pulse length
- `pl2`  1H 90° pulse power level
- `pl5`  13C CP power level
- `pl6`  1H CP power level
- `p15` CP contact time
- `sp0`  1H CP shape
- `sp15` 13C CP shape
- `p25` Duration of 1H CW decoupling pulse during acquisition
- `pl25` 1H CW decoupling power
- `pl12` 1H decoupling power level for alternative CPD program (cpdprg1, set l4=1)
- `d1`  Recycling delay between experiments

 Protections

```plaintext
1m
if "p2 > 1000" goto Problem
if "p15 > 10m" goto Problem
if "aq > 31m" goto Problem
if "d1 < 0.025s" goto Problem
goto PassParams
Problem, 1m
print "Parameters not accepted, ending."
goto HaltAcqu
PassParams, 1m
```

Pulse program

```plaintext
1 ze ;accumulate into an empty memory
2 d1 do:f2 ;recycling delay, decoupler off
1u efq=0:f2
1u f=qcnst15:f1 ;frequency offset on 13C channel for band-selective CP schemes
10u pl2:f2 pl5:f1 ;set initial power levels

;--- 90° 1H ---
p2:f2 ph1

;--- 1H --> 13C Cross-polarization ---
1u pl6:f2 ;1H CP power level
if (l3==1)
    (p15 ph2):f1 (p15 ph0):f2 ;rectangular pulse on both channels
if (l3==2)
    (p15 ph2):f1 (p15:sp0 ph0):f2 ;shaped pulse on 1H, rectangular on 13C
if (l3==3)
    (p15:sp15 ph2):f1 (p15 ph0):f2 ;rectangular pulse on 1H, shaped on 13C

;--- 1H Decoupling during acquisition ---
if (l4==0)
    1u cpds2:f2 ;cw.cpd, CW decoupling pulse along X
else
    if (l4==1)
        1u pl12:f2
        1u cpds1:f2 ;Alternative CPD program
    else
        //--- Decoupling programs containing flip pulses ---
        ; Phase cycling instructions contained in CPD programs are ignored by some versions
        ; of TopSpin. To implement phase cycling of the last 90° pulse (‘flip pulse’), we use
        ; two CPD programs (cpdprg3 and cpdprg4) which alternate every scan.
        ; For the flip-back, the ‘flip’ pulse always has an opposite phase relative to ph1 (3 1),
        ; in order to flip 1H magnetization back to the Iz axis.
```
; For the flip-down, the 'flip' pulse always has the same phase as ph1 (1 3), further
; pushing the 1H magnetization down to the -Iz axis.
if "(l4/2+cnst25+ds)%2=1"
{    
  lu cpds3:2  ;cw0_flip270.cpd
  ; This CPD program contains a CW pulse along X, then a 90° pulse along -Y
  ; It is executed on odd scans for flip-back, and even scans for flip-down.
}
if "(l4/2+cnst25+ds)%2=0"
{    
  lu cpds4:2  ;cw0_flip90.cpd
  ; This CPD program contains a CW pulse along X, 90° pulse along Y
  ; It is executed on even scans for flip-back, and odd scans for flip-down.
  "cnst25=cnst25+1"
}
}

;--- Acquisition ---
go=2 ph31
  
1u do:2  ;decoupler off
100m wr #0  ;save data to disk
HaltAcqu, 1m
  ;jump address for protection files
exit  ;quit

;----------------
; Phase cycle
;----------------

ph1 = 1 3  ; 1H 90° pulse
ph0 = 0  ; 1H CP pulse
ph2 = 0 0 2 2  ;13C CP pulse
ph31= 0 2 2 0  ;13C acquisition
Composite pulse decoupling (CPD) programs

**cw.cpd**

```plaintext
;OWNER=nmrsu

;--- 1H CW decoupling/spin-lock pulse, phase along X ---
1 p25:0 pl=pl25

;--- Do not pulse for the rest of the sequence ---
2 5m
jump to 2
```

**cw0_flip270.cpd**

```plaintext
;OWNER=nmrsu

;--- 1H CW decoupling/spin-lock pulse, phase along X ---
1 p25:0 pl=pl25

;--- 1H 90° flip pulse, phase along -Y ---
 p2:270 pl=pl2

;--- Do not pulse for the rest of the sequence ---
2 5m
jump to 2
```

**cw0_flip90.cpd**

```plaintext
;OWNER=nmrsu

;--- 1H CW decoupling/spin-lock pulse, phase along X ---
1 p25:0 pl=pl25

;--- 1H 90° flip pulse, phase along Y ---
 p2:90 pl=pl2

;--- Do not pulse for the rest of the sequence ---
2 5m
jump to 2
```

**xix.cpd (Example of alternative CPD program)**

```plaintext
0.3u fq=cnst21
0.5u pl=pl12
1 pcpd:0
   pcpd:180
jump to 1
```
Pulse sequence to measure remaining magnetization and magnetization recovery curves

Used for the measurement of $^1$H remaining magnetization (Figure 3) and recovery curve (Figure 4a), pulse scheme in Figure 2d.

Parameters:

The following composite pulse decoupling (CPD) programs must be employed:

cpdprg1=’xix.cpd’, cpdprg2=’cw.cpd’, cpdprg3=’cw0_flip270.cpd’, cpdprg4=’cw0_flip90.cpd’

Options:

Cross-polarization

l3=1 Rectangular pulse on both $^1$H and $^{13}$C channels
l3=2 Shaped pulse on $^1$H, rectangular pulse on $^{13}$C
l3=3 Rectangular pulse on $^1$H, shaped pulse on $^{13}$C

Content of the ‘mock’ experiment

l5=1 Reference experiment (no ‘mock’ experiment executed)
l5=2 Only the $^1$H 90° pulse and $^1$H spin-lock are executed in the ‘mock’ experiment
l5=3 The $^1$H 90° pulse and $^1$H–$^{13}$C CP are executed in the ‘mock’ experiment
l5=4 The full ‘mock’ experiment ($^1$H 90°, $^1$H–$^{13}$C CP and CW $^1$H decoupling) is executed
l5=5 Full ‘mock’ experiment (reference, no flip pulse), magnetization recovery curve
l5=6 Full ‘mock’ experiment and flip-back pulse, magnetization recovery curve
l5=7 Full ‘mock’ experiment and flip-down pulse, magnetization recovery curve

Pre-saturation

l6=0 No pre-saturation
l6=2 Pre-saturation

---

recovery.pp

; Measurement of 1H remaining magnetization and recovery curve.

; Options
; l3=1 : Rectangular pulse on both 1H and 13C channels
; l3=2 : Shaped pulse on 1H, rectangular pulse on 13C
; l3=3 : Rectangular pulse on 1H, shaped pulse on 13C
; l5=1 : Reference experiment (no ‘mock’ experiment executed)
; l5=2 : Only the 1H 90° pulse and 1H spin-lock are executed in the ‘mock’ experiment
; l5=3 : The 1H 90° pulse and 1H–13C CP are executed in the ‘mock’ experiment
; l5=4 : The full ‘mock’ experiment (1H 90°, 1H–13C CP and CW 1H decoupling) is executed
; l5=5 : Full ‘mock’ experiment (reference, no flip pulse), magnetization recovery curve
; l5=6 : Full ‘mock’ experiment and flip-back pulse, magnetization recovery curve
; l5=7 : Full ‘mock’ experiment and flip-down pulse, magnetization recovery curve
; l6=0 : No pre-saturation
; l6=2 : Pre-saturation
--- Reference ---

$OWNER=nmrsu

"sp0=p16" ;Syntax for TopSpin 2.x ; 1H CP power level
"spv0=p16v" ;Syntax for TopSpin 3.x ; 1H CP power level
"sp15=p15v" ;Syntax for TopSpin 2.x ; 13C CP power level
"spw15=p15w" ;Syntax for TopSpin 3.x ; 13C CP power level

--- Parameters ---

%;p2 1H 90° pulse length
%;p27 Duration of one high-power pre-saturation pulse (two pulses, X and -X, are executed).
%;pl2 Power level for 1H 90° pulse and high-power pre-saturation pulses
%;pl5 13C CP power
%;pl6 1H CP power
%;p15 CP contact time
%;sp0 1H CP shape
%;sp15 13C CP shape
%;pl12 1H decoupling power during acquisition ('Read' experiment)
%;p25 Duration of decoupling pulse during 'mock' experiment
%;p15 1H decoupling power during 'mock' experiment
%;d1 Recycling delay before the 'mock' experiment
%;d2 Recovery delay between the 'mock' and the 'read' experiment

--- Protections ---

1m
if "p1  > 1000" goto Problem
if "p2  > 1000" goto Problem
if "p15 > 10m" goto Problem
if "p27 > 10m" goto Problem
if "aq > 31m" goto Problem
if "dl < 0.025s" goto Problem
goto PassParams
Problem, 1m
print "Parameters not accepted, ending."
goto HaltAcqu
PassParams, 1m

--- Pulse program ---

1 ze ;accumulate into an empty memory
2 lu do:f2 ;decoupler off
1u f=0:f2
1u f=cnst15:f1 ;frequency offset on 13C channel for band-selective CP schemes

--- 1H Pre-saturation ---

if (16=0)
| 1u p12:f2
| p2:f2 ph21 ;90° 1H pulse along Y
| p27*0.5:f2 ph10 ;1H spin-lock presat pulse along X
| p27*0.5:f2 ph12 ;1H spin-lock presat pulse along -X
| d1 ;recycling delay before the 'mock' experiment

--- Mock experiment: 90° 1H ---

if (15<5)
| 1u p12:f2
| p2:f2 ph1 ;For measurement of remaining 1H magnetization amounts, the transverse 1H magnetization generated by the 'mock' experiment is preserved by the phase cycling (ph1).
} else {
| 1u p12:f2
| p2:f2 ph21 ;For measurement of the 1H recovery behavior, the transverse 1H magnetization generated by the 'mock' experiment is discarded by the phase cycling (ph21).
if (l5==2) {
    if (l3==2)
    {
        (p15:sp0 ph20):f2
        ;shaped pulse on 1H
    }
    else
    {
        (p15 ph20):f2
        ;rectangular pulse on 1H
    }
}
if (l5>2) {
    ;--- Mock experiment: 1H --> 13C Cross-polarization ---
    1u pl5:f1 pl6:f2
    ;13C and 1H CP power level
    if (l3==1)
    {
        (p15 ph2):f1 (p15 ph20):f2
        ;rectangular pulse on both channels
    }
    if (l3==2)
    {
        (p15 ph2):f1 (p15:sp0 ph20):f2
        ;shaped pulse on 1H, rectangular on 13C
    }
    if (l3==3)
    {
        (p15:sp15 ph2):f1 (p15 ph20):f2
        ;rectangular pulse on 1H, shaped on 13C
    }
}
    ;--- Mock experiment: 1H decoupling ---
    if (l5>3)
    {
        1u pl25:f2
        ;1H decoupling power for 'mock' experiment
        (p25 ph20):f2
        ;CW decoupling on 1H
    }
    ;--- Mock experiment: Flip pulses ---
    1u pl12:f2
    if (l5==6)
    {
        p2:f2 ph23
        ;1H 90° flip-back (opposite phase to initial 90° pulse)
    }
    if (l5==7)
    {
        p2:f2 ph21
        ;1H 90° flip-down (same phase to initial 90° pulse)
    }
};-------------------
; 'Read' experiment
;-------------------
;Detection experiment with the same CP conditions
; as the 'mock' experiment but with XIX decoupling during acquisition

if (l5>4)
{
    d2
    ;Delay between the 'mock' and the 'read' experiment.
    p2:f2 ph1
}
;For measurement of remaining 1H magnetization amounts, the 'read' experiment starts directly
;after the 'mock' experiment, without any delay. The remaining transverse 1H magnetization
;is then directly spin-locked by the 1H CP pulse of the 'read' experiment.

if (l5>3)
{
    1u pl5:f1 pl6:f2
    ;13C and 1H CP power level
    if (l3==1)
    {
        (p15 ph2):f1 (p15 ph0):f2
        ;rectangular pulse on both channels
    }
    if (l3==2)
    {
        (p15 ph2):f1 (p15:sp0 ph0):f2
        ;shaped pulse on 1H, rectangular on 13C
    }
if (l3==3)
{
    (p15:sp15 ph2):f1 (p15 ph0):f2  ; rectangular pulse on 1H, shaped on 13C
}
1u p112:f2  ; 1H decoupling power level
1u cpds1:f2  ; Acquisition 1H decoupling on

--- Acquisition ---
go=2 ph31
1u do:f2  ; decoupler off
wr #0  ; save data to disk
HaltAcqu, 1m
    ; jump address for protection files
exit  ; quit

--- Phase cycle ---

--- Mock experiment phases ---
ph21= 1  ; 1H 90° (pre-sat. and 'mock' experiment)
ph10= 0  ; 1H presat X
ph12= 2  ; 1H presat X
ph20= 0  ; 1H spin-lock
ph22= 1  ; 13C spin-lock (SOCP)
ph23= 3  ; 1H flip-back

--- 'Read' experiment phases ---
ph1 = 1 3  ; 1H 90°
ph0 = 0 0 0 0 2 2 2 2  ; 1H CP pulse
ph2 = 0 0 2 2 0 0 2 2 1 1 3 3 1 1 3 3  ; 13C CP pulse
ph31= 0 2 2 0 2 0 0 2 1 3 3 1 3 1 3  ; 13C acquisition
Full references


