Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

Homonuclear decoupling for spectral simplification of carbon-13 enriched molecules in solution-state NMR enhanced by dissolution DNP

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Pulse program

Pulse program for a Bruker AVANCE-I system used to obtain the experimental spectra of Figs. 2 and 3. The phase list may be generated externally in a spreadsheet and depends on the desired frequencies to be irradiated. In this example, *m* = 6 distinct irradiation frequencies were generated.

```
#include <Avance.incl>
#include <Avancesolids.incl>

"d9=0.1u"
"d25=1.3u"
"d22=5.0u"
define delay dead
"dead=1.2u"
define delay acq
"acq=10.0u"
"d24=d23-dead-acq+0.2u+d25"
"d30=1u+d23+d22+p2+d22+p2++d22+p2+d22+p2+d22+p2+d22+p2+d24+dead+acq+0.2u+d25" ;add extra p2 since
                        using 2 p2's

define loopcounter count   ;make sure td datapoints are sampled
"count=(td/2+1)*decim"
;AV I and AV II hardware: blktr# is transmitter blanking for f# logical channel
;blktr1 for f1 logical channel; blktr2 for f2 logical channel
"blktr2 = 0.7u"

"d11=30m"
"d12=20u"
1 ze
  d11 pl17:f4 LOCKDEC_ON
  50u LOCKH_ON
  d11 H2_PULSE

2 d30 do:f4
  10u reset:f1 reset:f2        ;synchronise pulse and detection RF
  1u pl1:f2                    ;preselect power level for inital pulses
```

```
 STARTADC              ;prepare adc for sampling, set reference frequency
 RESETPHASE            ;reset reference phase
 RGP_ADC_ON            ;open ADC gate
 1u REC_BLK            ;blank the receiving path

 30m H2_LOCK
 6m LOCKH_OFF
 d1
 50u LOCKH_ON
 d12 H2_PULSE
 p1:f2 ph1

 0.1u cpd4:f4

3 1u pl2:f2
 d22
(p2 ph2^):f2
 d22 pl3:f2
 (p2 ph3^):f2
d22 pl5:f2
(p2 ph4^):f2
d22 pl6:f2
(p2 ph5^):f2
d22 pl7:f2
(p2 ph6^):f2
d22 pl8:f2
(p2 ph7^):f2
 d24
 dead
 acq setrtp1|0|1|2     ;open receiver path
 d23
 0.1u setrtp1|7
 0.1u setrtp1^0^1^2^7  ;this is sample macro
 d25                   ;to keep timing if pulsing on f1
 lo to 3 times count   ;make sure td points are sampled
 1m
 rcyc=2                ;next scan
```

```
  30m wr #0        do:f4     ;save data


  d11 H2_LOCK
  d11 LOCKH_OFF
  d11 LOCKDEC_OFF
exit
ph1=1 3
ph2 = (7) 0 1 2 3 4 5 6
ph3 = (92) 91 90 89 88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 70 69 68 67 66 65 64 63 62 61 60 59 58
                57 56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26
                25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
ph4 = (170) 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36
                37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68
                69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99
                100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121
                122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143
                144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165
                166 167 168 169
ph5 = (52) 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37
                38 39 40 41 42 43 44 45 46 47 48 49 50 51
ph6 = (30) 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
ph7 = (19) 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
ph30 = 0
ph31 = 0 2
```

Numerical simulations

Numerical simulations for SIMPSON for a three-spin ^{13}C system where two spins are irradiated in a dichromatic (m = 2) experiment. The phase increments for the two pulses within each dwell time are given by $\Delta\phi_m = \Delta\nu_m\, \Delta t\ 360°/10^6$ where $\Delta\nu_m$ [Hz] is the offset with respect to the carrier frequency that one wishes to irradiate, and Δt [µs] is the dwell time. By setting the *rf* amplitude rfw = 0, one obtains the unperturbed, J-coupled spectrum.

```
spinsys {
   channels 13C
   nuclei 13C 13C 13C
   shift 1 -1500 0 0 0 0 0
   shift 2 500 0 0 0 0 0
   shift 3 1500 0 0 0 0 0
   jcoupling 1 2 -50 0 0 0 0 0
   jcoupling 1 3 -10 0 0 0 0 0
   jcoupling 2 3 -40 0 0 0 0 0
}

par {
   start_operator   Inz
   detect_operator  Inp
   spin_rate       0
   gamma_angles    1
   sw              10000
   crystal_file    alpha0beta0
   np              4096*4
   proton_frequency 400e6
   verbose         01001

   variable        rf        33333.3333333
   variable        rfw                4000
   variable        tp        0.25e6/rf
   variable        tpw       0.25e6/rfw
```

```
   variable       np1       2048
   variable       tdwell    1.0e6/sw
}

proc pulseq {} {
   global par

   reset
   offset 0
   pulse $par(tp) $par(rf) y
   acq
   for {set i 1} {$i < $par(np)} {incr i} {
      delay [expr ($par(tdwell)/2)-1]
      pulse 1 $par(rfw) [expr 0-$i*18]
      delay [expr ($par(tdwell)/2)-1]
      pulse 1 $par(rfw) [expr 0+$i*54]
      acq
      }
}

proc main {} {
   global par
   set f [fsimpson]
   fsave $f $par(name).fid
   fzerofill $f 32768
   faddlb $f 1 0
   fft $f
   fsave $f $par(name).spe
}
```

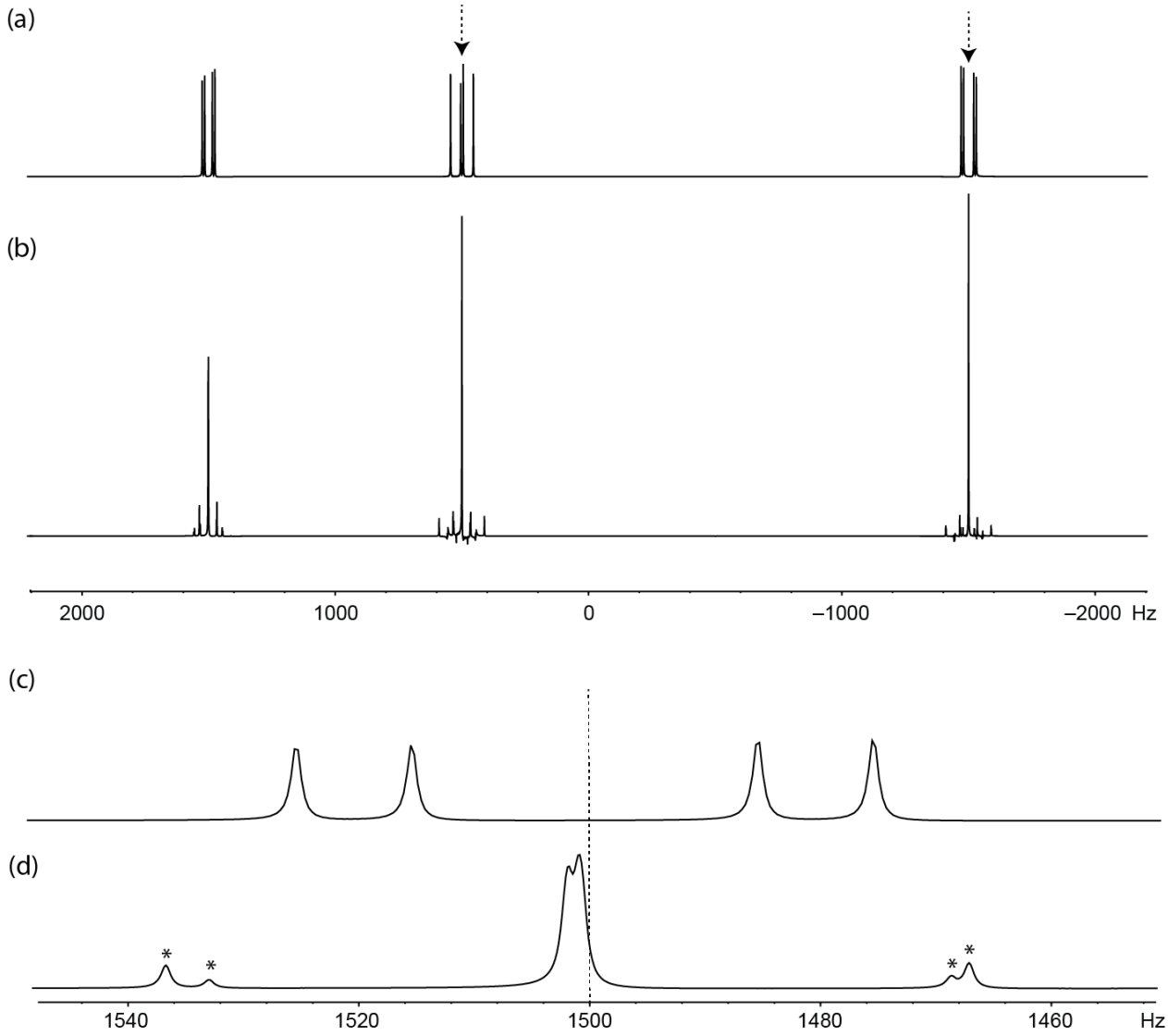

Figure S1 (a) Spectrum resulting from the numerical simulation for the input file given above with a vanishing rf amplitude rfw = 0. (b) Spectrum with rfw = 4000 Hz. Dashed arrows indicate the two irradiation frequencies. (c) Expansion of the multiplet of the non-irradiated spin of (a) centered at 1500 Hz. (d) Expansion of the multiplet of the non-irradiated spin of (b) centered at 1500 Hz. Artifacts caused by the *rf*-irradiation are indicated by asterisks. The isotropic shift of the non-irradiated spin is shown by a dashed vertical line in (c) and (d).