Distance measurements between carbon and bromine using a split-pulse PM-RESPDOR solid-state NMR experiment

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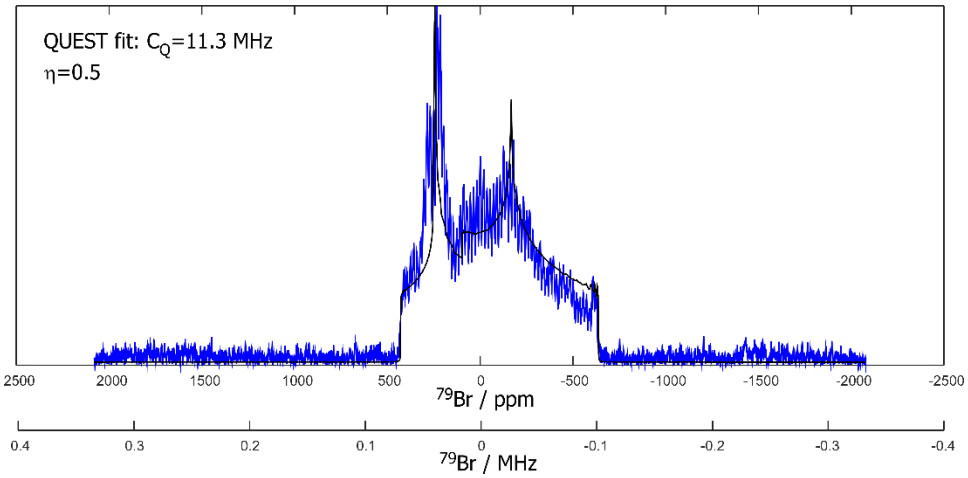
SUPPORTING INFORMATION

Figure S1: ^{79}Br WURST-QCPMG static spectra and fits using QUEST software [Perras, Widdifield, Bryce, SSNMR 45-46, 36-44, 2012].

^{79}Br WURST-QCPMG spectrum of butyl-triphenylphosphonium bromide (BrBuPPh3). C_Q=11.3 MHz, η=0.5. For ^{81}Br, C_Q=9.5 MHz.



^{79}Br WURST-QCPMG spectrum of tetra-n-butylammonium bromide (TBAB). C_Q=12.6 MHz, η=0.16. For ^{81}Br, C_Q=10.5 MHz.

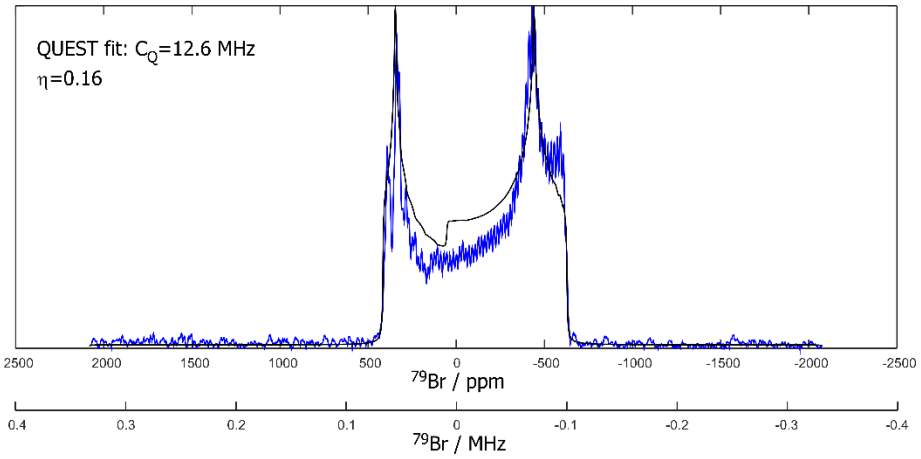


Figure S2:

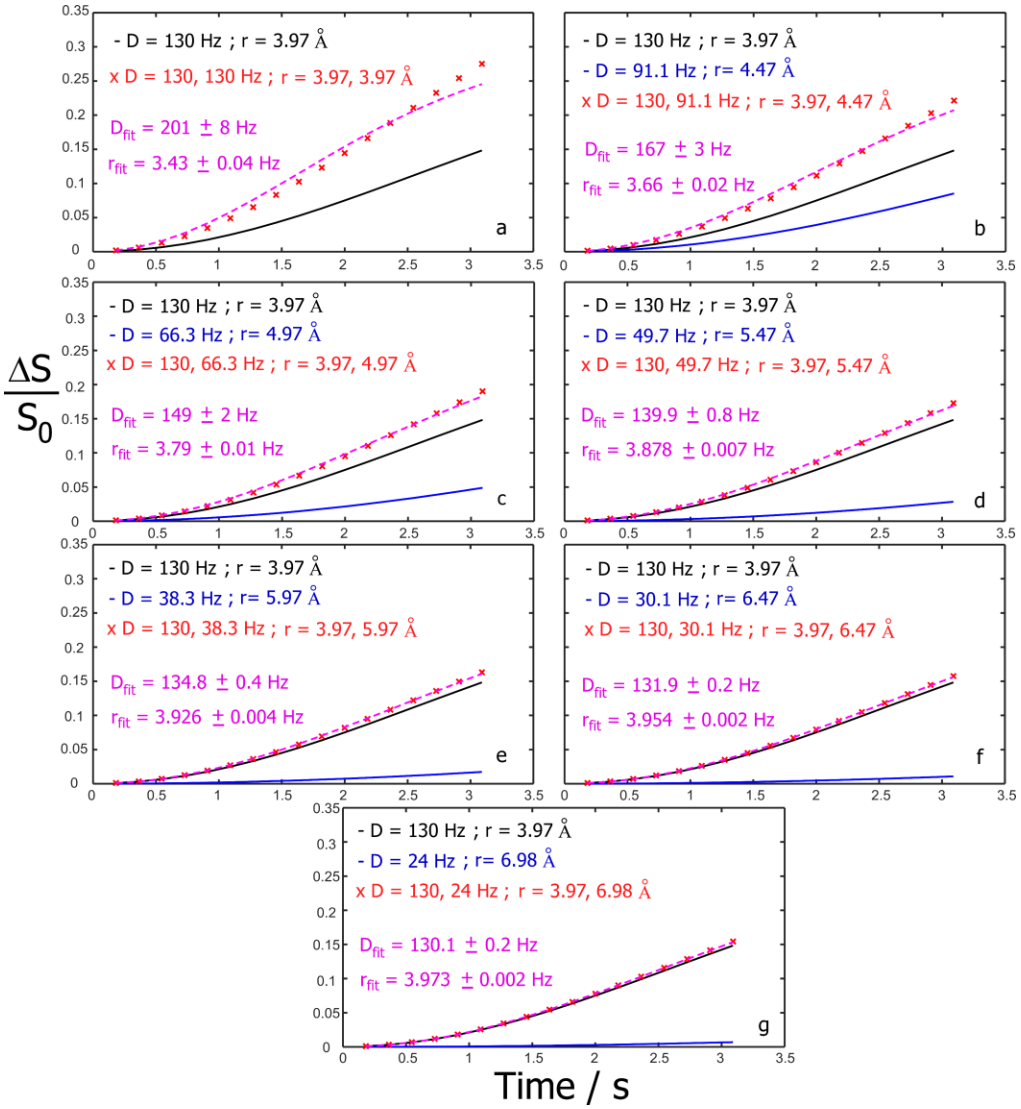
A. Split-PM-RESPDOR recoupling curves for a three spin system containing a single ^{13}C and two Br nuclei at natural abundance – 50% ^{79}Br-^{81}Br pair, 25% ^{79}Br-^{79}Br pair (no ^{81}Br and therefore no recoupling), 25% ^{81}Br-^{81}Br pair. One ^{13}C-Br distance is fixed, and the other is at increasing distances (decreasing dipolar coupling).

'x' symbols - simulations of the three-spin system.

'—' Solid black line – simulation of the close bromine (D=130 Hz, ~3.97Å).

'—' Solid blue line – simulation of the remote bromine.

'---' Purple dash line – fit of the three-spin system with a single spin-pair.



B. A plot of r_{fit}/r as a function of difference in distance Δr, where r_{fit} is the distance extracted by the purple curves above, and r=3.97Å. The dash lines indicate r_{fit}/r=0.9 and 1.1.

Following similar calculations, data points corresponding to a single bromine with D=121 Hz (r=4.07Å) can be fit with 2Br with D=110.1, 58 Hz (r=4.2Å, 5.2Å).
Similarly, a single Br with D=130 Hz (r=3.97Å) corresponds to 2Br with D=118.3, 61.5 Hz (r=4.1Å, 5.1Å).

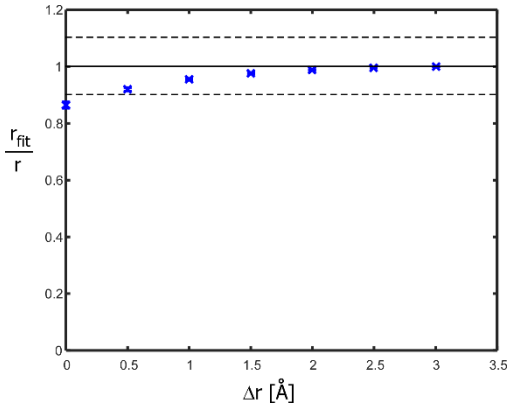


Figure S3: Split-PM-RESPDOR recoupling curves for a spin-1/2 coupled to a spin-3/2 having a nuclear quadrupolar coupling constant of 200 MHz. D=130 Hz, the gap is 26.3μs, PM pulse lengths are $10T_R$ for the red squares, $100T_R$ for the blue crosses. The solid line is the analytical Bessel function for a spin-3/2 shown in Eq. 1 of the main article.

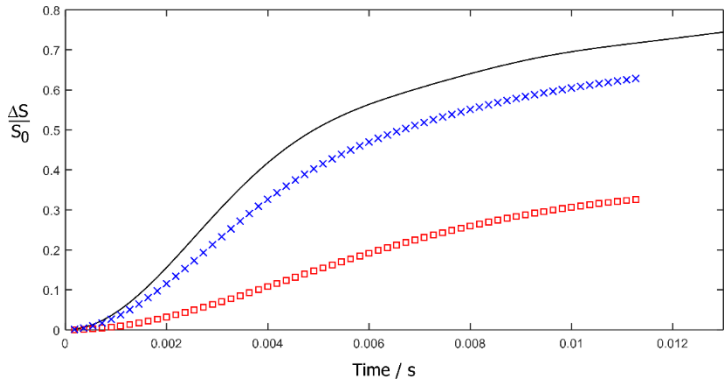
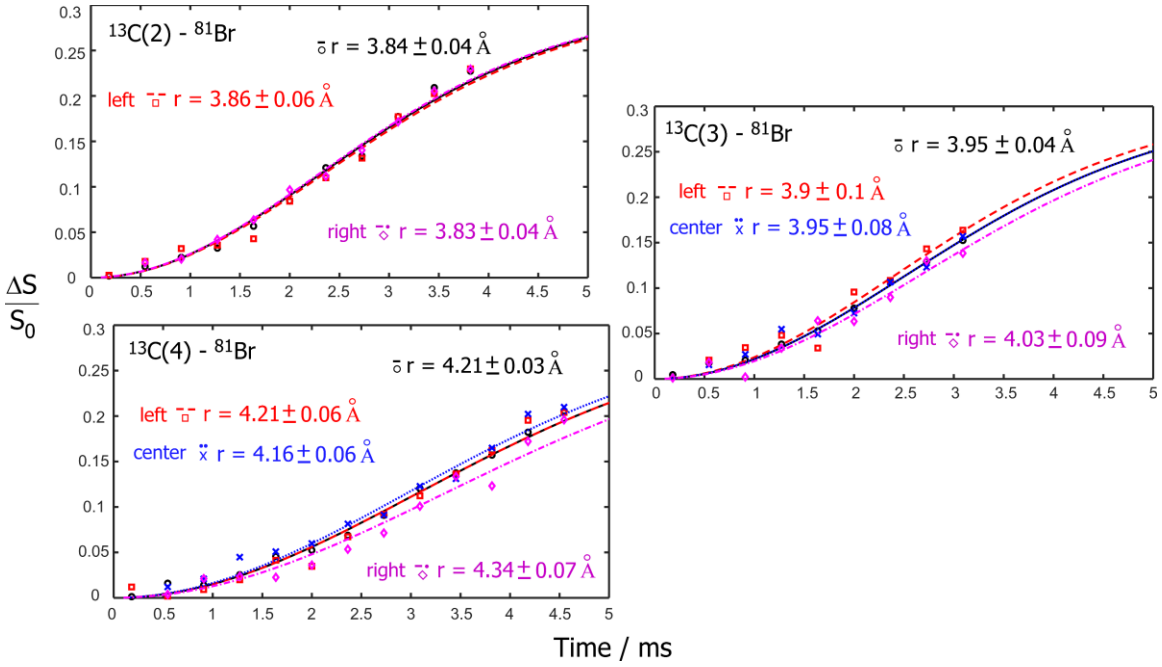


Figure S4: Fits of the individual signals of each of C2, C3, C4 using a very small line broadening of 1 Hz. These signals are shown in the ^{13}C-CPMAS spectrum shown in Figure 5. Even with this small line broadening, C1 cannot be decomposed to individual peaks. The differences in the fit distance between the different components of each carbon are within 0.1Å. In the main manuscript, the fits of figure 6 are to a spectrum that was line-broadened with 100 Hz and a single distance was obtained for each carbon. Those fits are indicated here in black.



Item S5: Bruker pulse program for split-PM-RESPDOR and the corresponding shape files.

Pulse program:

```
;split-PM-RESPDOR pulse program
;based on the papers by Nimerovsky, Makrinich, Goldbourt:
;10.1016/j.jmr.2014.03.003; 10.1016/j.ssnmr.2018.04.001
;Adapted to include a split in the PM pulse
;Avance III version (original II+)
;parameters:
;p3 : proton 90 at power level pl3
;p15 : contact time at pl1 (f1) and pl2 (f2)
;pcpd2 : pulse length in decoupling sequence
;cpdprg2 : cw, tppm (at pl12),
;cpdprg6 : PM phases, first half
;cpdprg7 : PM phases, second half
```

```
;pl33: PM pulse power (0W or 120db for S0)
;p31 : pulse length for phase modulated pulses
;p30 : pulse lenth for phase 225 degree
;p32 : gap length
;cnst31 : spin rate >1 kHz
;l0 : 1,3.... has to be odd
;l10 : l0-1 - number of pi pulses in each REDOR block
;l2 : # of rotor periods of coupled spin pulse
;d1 : recycle delay
;d31 : used to check spin rate
;pl1 : X power level for contact
;pl11 : X power level for 180
;sp0 : proton power level during contact
;pl12 : proton power level for decoupling
;pl3 : H90 power level for 90
;spnam0 : file name for variable amplitude CP
;$COMMENT=REDOR experiment, cp for excitation, interleaved acquisition
of S and S0 signals, inverse sequence
;$CLASS=Solids
;$DIM=1D
;$TYPE=cross polarisation
;$SUBTYPE=REDOR

;$OWNER=Bruker

;calculate sync. delays
define delay del25
"del25=(0.25s/cnst31)"
define delay del26
"del26=(0.25s/cnst31)-(p12/2)"
define delay del27
"del27=l2*0.5*(1s/cnst31)-(p12)"
define delay del28
"del28=l2*0.5*(1s/cnst31)-(p12/2)-(p32/2)"
define delay del29
"del29=(p32/2)-(p12/2)-(1u)"
;define loopcounter nfid
;"nfid=td1/2"
"d31=1s/cnst31"
;cnst11 : to adjust t=0 for acquisition, if digmod = baseopt
"acqt0=1u*cnst11"
"l10=(l0-1)"
1 ze
  d31
2 10m do:f2
  d1
#include <p15_prot.incl>
                  ;make sure p15 does not exceed 10 msec
                  ;let supervisor change this pulseprogram if
                  ;more is needed
#include <aq_prot.incl>
                  ;allows max. 50 msec acquisition time, supervisor
                  ;may change  to max. 1s at less than 5 % duty cycle
```

```
                  ;and reduced decoupling field
#include <rot_prot.incl>
                  ;protect against misset cnst31, must be >1000
  2u rpp4
  2u rpp9
  2u rpp8
  (p3 pl3 ph1):f2
  (p15 pl1 ph2):f1 (p15:sp0 ph10):f2
  del25  cpds2:f2
if "l0 == 1" goto sk3
3 del26
  (p12 pl11 ph8^):f1
  del26
  lo to 3 times l10
sk3,  del26
  (p12 pl11 ph2):f1
  del26
  del25
 (p12 pl11 ph4^):f1
 1u
 0.1u cpds6:f3
 del28
 0.1u do:f3
 del29
 (p12 pl11 ph4^):f1
 del29
 1u
 0.1u cpds7:f3
 del28
 0.1u do:f3
 del25
if "l0 == 1" goto sk4
4 del26
  (p12 ph9^):f1
  del26
  lo to 4 times l10
sk4,  del26
  (p12 ph2):f1
  del26
  del25
  go=2 ph31
  1m do:f2
  30m wr #0


HaltAcqu, 1m
exit

ph1= 1 3
ph2= 0 0 1 1 2 2 3 3
ph4= 0 1 0 1 1 0 1 0
ph8= 0 1 0 1 1 0 1 0
ph9= 0 1 0 1 1 0 1 0
```

```
ph10= 0
ph31= 0 2 1 3 2 0 3 1
```

Shape files:

Shape before X-channel π pulse (cpds6):	Shape after X-channel π pulse (cpds7):
1 p30: 225.00 pl=pl33 p31: 80.51923 pl=pl33 p31: 2.236028 pl=pl33 p31: 244.9407 pl=pl33 p31: 92.52825 pl=pl33 p31: 275.7416 pl=pl33 p31: 98.55024 pl=pl33 p31: 330.2784 pl=pl33 p31: 348.0776 pl=pl33 p31: 126.2695 pl=pl33 p31: 265.2453 pl=pl33 p31: 349.2809 pl=pl33 p31: 23.86148 pl=pl33 p31: 24.11632 pl=pl33 p31: 23.8011 pl=pl33 p31: 92.37856 pl=pl33 p31: 6.6659 pl=pl33 p30: 225.00 pl=pl33 p31: 319.617 pl=pl33 p31: 75.59648 pl=pl33 p31: 242.7034 pl=pl33 p31: 95.8332 pl=pl33 p31: 340.9066 pl=pl33 p31: 226.5105 pl=pl33 p31: 48.00275 pl=pl33 p31: 38.06114 pl=pl33 p31: 5.261435 pl=pl33 p31: 44.36102 pl=pl33 p31: 145.7639 pl=pl33 p31: 303.2499 pl=pl33 p31: 139.6619 pl=pl33 p31: 336.7204 pl=pl33 p31: 95.65318 pl=pl33 p31: 341.3066 pl=pl33 jump to 1	1 p31: 80.51923 pl=pl33 p31: 2.236028 pl=pl33 p31: 244.9407 pl=pl33 p31: 92.52825 pl=pl33 p31: 275.7416 pl=pl33 p31: 98.55024 pl=pl33 p31: 330.2784 pl=pl33 p31: 348.0776 pl=pl33 p31: 126.2695 pl=pl33 p31: 265.2453 pl=pl33 p31: 349.2809 pl=pl33 p31: 23.86148 pl=pl33 p31: 24.11632 pl=pl33 p31: 23.8011 pl=pl33 p31: 92.37856 pl=pl33 p31: 6.6659 pl=pl33 p30: 225.00 pl=pl33 p31: 319.617 pl=pl33 p31: 75.59648 pl=pl33 p31: 242.7034 pl=pl33 p31: 95.8332 pl=pl33 p31: 340.9066 pl=pl33 p31: 226.5105 pl=pl33 p31: 48.00275 pl=pl33 p31: 38.06114 pl=pl33 p31: 5.261435 pl=pl33 p31: 44.36102 pl=pl33 p31: 145.7639 pl=pl33 p31: 303.2499 pl=pl33 p31: 139.6619 pl=pl33 p31: 336.7204 pl=pl33 p31: 95.65318 pl=pl33 p31: 341.3066 pl=pl33 p30: 225.00 pl=pl33 jump to 1