Supplementary Material

S1 Tables of experimental conditions

When compiling the experimental data shown in Fig.4, it was sometimes necessary to adjust slightly the rf amplitude, the rf phase shifts, and the DQ excitation time, in order to optimize the DQ filtering efficiency. Adjustments in the DQ excitation time are expected theoretically since the scaling factor of the DQ dipolar interaction depends on the symmetry numbers. The required adjustment in the rf phase shifts are due to a combination of second-order CSA terms (see for example ref.[24]), and to small phase errors (in the region of 0.2°) known to be generated by the quadrature hybrid hardware of the Infinity+ spectrometer.

All tables employ the following notation:

$|\kappa|$ = Magnitude of scaling factor for recoupled heteronuclear dipole-dipole interaction;

$\omega_{nut}^{S} / 2\pi = N\omega_r / N$ = theoretical nutation frequency for ^{13}C field;

$\Delta^S / 2\pi =$ difference between optimized experimental ^{13}C nutation frequency and theoretical value;

$\phi = \pi\nu / N$ = theoretical phase shift for RN_n^ν symmetry;

$\Delta\phi$ =difference between optimized experimental phase shift and theoretical value;

q = number of R elements used for DQ excitation and reconversion;

τ = excitation and reconversion times

DQF$_0$ = experimental DQ filtering efficiency with no decoupling

DQF$_{120}$ = experimental DQ filtering efficiency with a decoupling nutation frequency of 120 kHz.

S1.1 DAF

Diammonium [2,3-$^{13}C_2$]- Fumarate (DAF)

$\omega_r / 2\pi = 6.000$ kHz

Symmetry	$\lvert\kappa\rvert$	$(\omega_{nut}^S / 2\pi)$ /kHz	$(\Delta^S / 2\pi)$ /kHz	ϕ	$\Delta\phi$	q	τ/ms	DQF_0	DQF_{120}
note	a	b	c	d	e	f	g	h	i
$R12_2^5$	0.170	36	-1.06	75°	-0.2°	12	0.333	3.1 %	39.5 %
$R14_2^6$	0.172	42	-2.58	77.1°	-0.1°	14	0.333	6.8 %	35.5 %
$R16_2^7$	0.173	48	-3.47	78.7°	-0.2°	16	0.333	18.5 %	41.5 %
$R18_2^8$	0.174	54	-5.63	80°	-0.2°	18	0.333	22.4 %	40.5 %
$R20_2^9$	0.174	60	-8.44	81°	-0.3°	20	0.333	29.4 %	34.2 %
$R24_2^{11}$	0.175	72	-8.89	82.5°	-0.3°	24	0.333	34.9 %	-
$R28_2^{13}$	0.175	84	-12	83.5°	-0.4°	28	0.333	33.5 %	-
$R32_2^{15}$	0.176	96	-11.83	84.4°	-0.3°	32	0.333	36.5 %	-
$R36_2^{17}$	0.176	108	-11.06	85°	-0.4°	36	0.333	36.8 %	-
$R40_2^{19}$	0.176	120	-9.63	85.5°	-0.3°	40	0.333	36.6 %	-

Diammonium [2,3-$^{13}C_2$]- Fumarate (DAF)

$\omega_r / 2\pi = 12.000$ kHz

Symmetry	$\lvert\kappa\rvert$	$(\omega_{nut}^S / 2\pi)$ /kHz	$(\Delta^S / 2\pi)$ /kHz	ϕ	$\Delta\phi$	q	τ/ms	DQF_0	DQF_{120}

$R12_2^5$	0.170	72	-10.20	75°	-0.6°	24	0.333	26.8 %	22.3%
$R14_2^6$	0.172	84	-8.50	77.1°	-0.7°	28	0.333	37.8 %	-
$R16_2^7$	0.173	96	-12.47	78.7°	-0.6°	32	0.333	43.0 %	-
$R18_2^8$	0.174	108	-13.00	80°	-0.7°	36	0.333	39.5 %	-
$R20_2^9$	0.174	120	-13.00	81°	-0.7°	40	0.333	48.3 %	-

S1.2 GLY

[^{15}N,^{13}C$_2$]-glycine

$\omega_r / 2\pi = 6.000$ kHz

Symmetry	$\lvert\kappa\rvert$	$(\omega_{nut}^S$ $/2\pi)$ /kHz	$(\Delta^S$ $/2\pi)$ /kHz	ϕ	$\Delta\phi$	q	τ /ms	DQF$_0$	DQF$_{120}$
$R12_2^5$	0.170	36	-1.70	75°	-0.2°	18	0.500	0.4 %	24.1 %
$R14_2^6$	0.172	42	-2.56	77.1°	-0.2°	20	0.476	1.7 %	33.5 %
$R16_2^7$	0.173	48	-0.01	78.7°	-0.2°	24	0.500	5.3 %	31.5 %
$R18_2^8$	0.174	54	-0.84	80°	-0.2°	26	0.481	7.0 %	32.8 %
$R20_2^9$	0.174	60	-2.72	81°	-0.2°	28	0.467	10.6 %	20.6 %
$R24_2^{11}$	0.175	72	-2.033	82.5°	-0.2°	34	0.472	16.7 %	7.0 %
$R28_2^{13}$	0.175	84	-5.46	83.5°	-0.2°	40	0.476	25.9 %	4.6 %
$R32_2^{15}$	0.176	96	-2.02	84.4°	-0.2°	46	0.479	27.2 %	1.4 %
$R36_2^{17}$	0.176	108	-15.39	85°	-0.3°	52	0.481	27.5 %	0.3 %
$R40_2^{19}$	0.176	120	-10.59	85.5°	-0.2°	56	0.467	28.2 %	-

[^{15}N,^{13}C$_2$]-glycine

$\omega_r / 2\pi = 12.000$ kHz

Symmetry	$\lvert\kappa\rvert$	$(\omega_{nut}^S$ $/2\pi)$	$(\Delta^S$ $/2\pi)$	ϕ	$\Delta\phi$	q	τ /ms	DQF$_0$	DQF$_{120}$

		/kHz	/kHz						
$R12_{2}^{5}$	0.170	72	-4.77	75°	-0.6°	36	0.500	8.6 %	14.3 %
$R14_{2}^{6}$	0.172	84	-12.65	77.1°	-0.9°	42	0.500	21.2 %	2.7 %
$R16_{2}^{7}$	0.173	96	-10.59	78.7°	-0.7°	48	0.500	24.4 %	3.0 %
$R18_{2}^{8}$	0.174	108	-8.53	80°	-0.7°	54	0.500	26.8 %	-
$R20_{2}^{9}$	0.174	120	-8.53	81°	-0.8°	60	0.500	35.9 %	-

S1.3 ALA

[2,3-$^{13}C_2$]-alanine

$\omega_r / 2\pi = 6.000$ kHz

Symmetry	$\lvert\kappa\rvert$	$(\omega_{nut}^{S} / 2\pi)$ /kHz	$(\Delta^{S} / 2\pi)$ /kHz	ϕ	$\Delta\phi$	q	τ/ms	DQF_0	DQF_{120}
$R12_2^5$	0.170	36	-1.36	75^o	-0.2^o	18	0.500	6.0 %	49.1 %
$R14_2^6$	0.172	42	-2.56	77.1^o	-0.2^o	20	0.476	8.9 %	45.3 %
$R16_2^7$	0.173	48	-4.10	78.7^o	-0.3^o	24	0.500	18.3 %	46.0 %
$R18_2^8$	0.174	54	-0.84	80^o	-0.3^o	28	0.519	19.2 %	44.0 %
$R20_2^9$	0.174	60	-1.70	81^o	-0.3^o	30	0.500	32.8 %	38.3 %
$R24_2^{11}$	0.175	72	-7.17	82.5^o	-0.4^o	36	0.500	36.5 %	12.8 %
$R28_2^{13}$	0.175	84	-5.11	83.5^o	-0.3^o	42	0.500	41.6 %	12.3 %
$R32_2^{15}$	0.176	96	-8.20	84.4^o	-0.3^o	48	0.500	41.9 %	7.1 %
$R36_2^{17}$	0.176	108	-15.39	85^o	-0.3^o	54	0.500	27.0 %	-
$R40_2^{19}$	0.176	120	-10.24	85.5^o	-0.4^o	60	0.500	41.2 %	-

[2,3-$^{13}C_2$]-alanine

$\omega_r / 2\pi = 12.000$ kHz

Symmetry	$\lvert\kappa\rvert$	$(\omega_{nut}^S / 2\pi)$ /kHz	$(\Delta^S / 2\pi)$ /kHz	ϕ	$\Delta\phi$	q	τ/ms	DQF_0	DQF_{120}
$R12_2^5$	0.170	72	-0.32	75^o	-0.6^o	36	0.500	26.3 %	27.2 %
$R14_2^6$	0.172	84	-5.11	77.1^o	-0.6^o	42	0.500	34.1 %	4.3 %
$R16_2^7$	0.173	96	-6.82	78.7^o	-0.7^o	48	0.500	48.8 %	2.4 %
$R18_2^8$	0.174	108	-1.68	80^o	-0.7^o	54	0.500	33.2 %	-
$R20_2^9$	0.174	120	-6.82	81^o	-0.8^o	60	0.500	47.6 %	-

S2 SIMPSON input files

S2.1 Diammonium [2,3-$^{13}C_2$]- Fumarate (DAF) at MAS frequency of 6 kHz using the sequence $R12_2^5$.

```
# R_n^nu sequence for homonuclear recoupling of two spin-1/2 nuclei in the presence of two 1H
#  the 1H decoupling power is varied
#  R element is (90)0(270)180



# define the spin system

#(parameters for 2,3-13C-DAF 13C info from Carravetta et al JACS
# (2001) 123, 10628-38)

spinsys {
    channels 13C 1H
    nuclei   13C 13C 1H 1H
    shift  1   0p  94p  0.59   -65 -102  9
    shift  2   0p  94p  0.59   -65 -102  9
    shift  3   0p   0   0        0    0  0
    shift  4   0p   0   0        0    0  0

    dipole 1 2 -3127          0    0    0
    dipole 1 3 -20938         0  120    0
    dipole 2 4 -20938         0   60  180
    dipole 1 4 -3057          0  153  180
    dipole 2 3 -3057          0   27    0
    dipole 3 4 -3821          0  142  180
}

#
```

```
# define specific parameters for the calculation
#
# Make sure that maxHdec is an integer multiple of stepHdec
#

par {
    variable N   12.
    variable n       2.
    variable nu      5.
    spin_rate        6000
    variable nRexc   12
    variable nRrec   12

    variable maxHdec 120000
    variable stepHdec 3000

    sw              1000000/stepHdec
    np              maxHdec/stepHdec +1

    start_operator   Inz
    detect_operator  -I1z-I2z

    gamma_angles     10
    crystal_file     rep100
    proton_frequency 300e6

    method          direct
    verbose          1111
    use_cluster      1
}

#
# start the pulse program
#
proc pulseq {} {
```

```
  global par
  maxdt 1

  set phi     [expr 180*$par(nu)/$par(N)]
  set rf [expr $par(spin_rate)*$par(N)/$par(n)]
  set tR [expr 1e6/$rf]
  set pw90     [expr 0.25*$tR]
  set pw270   [expr 0.75*$tR]

  matrix set 2 totalcoherence {-2 +2}

 for {set d 0} {$d <= [expr $par(np)-1]} {incr d} {

   reset
   set Hdec     [expr $d*$par(stepHdec)]


  for {set i 1} {$i <= [expr $par(nRexc)/2]} {incr i} {

# R element
    pulse $pw90   $rf  [expr (+1)*$phi +   0]  $Hdec  0
    pulse $pw270  $rf  [expr (+1)*$phi + 180]  $Hdec  0

# R' element
    pulse $pw90   $rf  [expr (-1)*$phi -   0]  $Hdec  0
    pulse $pw270  $rf  [expr (-1)*$phi - 180]  $Hdec  0
   }

    filter 2

  for {set i 1} {$i <= [expr $par(nRrec)/2]} {incr i} {

# R element
    pulse $pw90   $rf  [expr (+1)*$phi +   0]  $Hdec  0
    pulse $pw270  $rf  [expr (+1)*$phi + 180]  $Hdec  0
```

```
 # R' element
     pulse $pw90   $rf  [expr (-1)*$phi -   0]  $Hdec  0
     pulse $pw270  $rf  [expr (-1)*$phi - 180]  $Hdec  0
    }

     acq
}

}

proc main {} {
    global par
    set f [fsimpson]
    fsave $f $par(name).fid
    funload $f
}
```

S2.2 SIMPSON spin system parameters for U-^{13}C-^{15}N-glycine (GLY).

Parameters for 2,3-13C2-Glycine are taken from JMR 156, 79-96 (2002) and Acta Cryst. (1972). B28, 1827.

```
spinsys {
    channels 13C 1H
    nuclei   13C 13C 1H 1H
    shift  1   66.6p  -74.55p  0.88   -0.7 88.5  52.5
    shift  2  -66.6p  -19.43p  0.98   99.4 146.0  138.9
    shift  3   0p   0   0        0    0  0
    shift  4   0p   0   0        0    0  0

    dipole 1 2 -2138.4            0   180.0      0
    dipole 1 3 -23328             0    69.5    240
    dipole 2 4 -3073.33           0    28.8    120
    dipole 1 4 -23328.4           0    71.2    120
    dipole 2 3 -2982.3            0    28.1    240
    dipole 3 4 -21368.4           0    91.0     90.2
}
```

S2.3 SIMPSON spin system parameters for 2,3-13C2-Alanine (ALA).

(parameters for 2,3-13C-Alanine are taken from JMR 156, 79-96 (2002) and other derivated from JACS 1972, 94, 2657)

```
spinsys {
    channels 13C 1H
    nuclei   13C 13C 1H 1H 1H 1H
    shift  1   15.5p  -11.7p  0.76   39    77    -53
    shift  2  -15.5p  -0.44p  0.44   82    24     29
    shift  3    0p     0       0       0     0      0
```

```
    shift  4    0p     0      0       0     0      0
    shift  5    0p     0      0       0     0      0
    shift  6    0p     0      0       0     0      0

    dipole 1 2   -2147       0       0       0
    dipole 1 3  -23137       0      69.6     0
    dipole 2 4     390       0       0       0
    dipole 2 5     390       0       0       0
    dipole 2 6     390       0       0       0
    dipole 4 5   11118       0      90       0
    dipole 4 6   11118       0      90       0
    dipole 5 6   11118       0      90       0
    dipole 1 4   -2006       0       0       0
    dipole 1 5   -2006       0       0       0
    dipole 1 6   -2006       0       0       0
    dipole 2 3   -2985       0     152       0
    dipole 3 4   -7676       0     156       0
    dipole 3 5   -7676       0     156       0
    dipole 3 6   -7676       0     156       0
}
```

S3 Calculation of Scaling Factors

S3.1 Loading the Mathematica packages

These example calculations use the set of Mathematica packages called **mPackages**, which is available for free download on the website *http://www.mhl.soton.ac.uk/research/software/mPackages/.*

The code below is compatible with Mathematica 5.1 and later, and mPackage version 2.00 and later. Mathematica is produced by Wolfram Research (*http://www.wolfram.com/*).

Use of **mPackages** requires the appropriate directory to be loaded into the Mathematica variable **$Path**. Instructions for doing this are on the **mPackages** website.

mPackages contains a package **NMR`CandRsymmetries`**, which is loaded by executing the following instruction:

```
In[1]:= Needs["NMR`CandRsymmetries`"]
```

S3.2 Single-channel sequences

The symmetry-allowed first-order homonuclear DD coupling terms for the symmetry $R20_2^9$ may be determined by executing:

```
In[2]:= SymmetryAllowedH1Terms[{"R", {20, 2, 9}}, "DD"]

Out[2]= {{DD, {2, -1}, {2, 2}}, {DD, {2, 1}, {2, -2}}}
```

The output indicates that the terms $\{\ell, m, \lambda, \mu\} = \{2, \pm1, 2, \mp2\}$ are symmetry-allowed.

A basic *R*-element of the form $R_0 = (\pi/2)_0 (3\pi/2)_\pi$ is defined by the following code:

```
In[3]:= BasicRelement = {{1 / 4, Pi / 2, 0}, {3 / 4, 3 Pi / 2, Pi}}
```

Out[3]= $\left\{\left\{\frac{1}{4}, \frac{\pi}{2}, 0\right\}, \left\{\frac{3}{4}, \frac{3\pi}{2}, \pi\right\}\right\}$

The first element in each sublist indicates the fraction of time occupied by each pulse; the second element in each sublist indicates the flip angle; the third element in each sublist indicates the phase. If desired, the time fractions may be adjusted to control the relative rf field of each pulse; the time fraction may be set to zero to indicate an infinitely strong and short rf pulse. The flip angle may be set to zero to indicate an interval with no rf field. In the example above, the rf amplitude is constant.

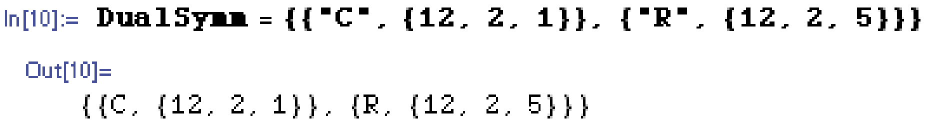
The complex scaling factor for the term $\{\ell, m, \lambda, \mu\} = \{2, 1, 2, -2\}$ under the symmetry $R20_2^9$ and the basic element $R_0 = (\pi/2)_0 (3\pi/2)_\pi$ is calculated by executing

```
ScalingFactor[
 {"R", {20, 2, 9}},
 {"DD", {2, 1}, {2, -2}},
 BasicRelement
]
```

Out[9]= $-0.174319 - 8.01234 \times 10^{-18}\, i$

S3.2 Dual-channel sequences

A dual symmetry such as $CR12_2^{1,5}$ on 2 rf channels is set up by defining



```
In[10]:= DualSymm = {{"C", {12, 2, 1}}, {"R", {12, 2, 5}}}

  Out[10]=
     {{C, {12, 2, 1}}, {R, {12, 2, 5}}}
```

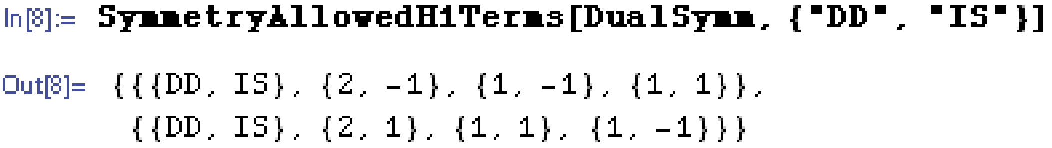
Consider the case where the C-element applied to the I-spin channel is given by $C_0 = \left[\delta_{\pi/2}(\pi/2)\right](2\pi)_0\left[\delta_{-\pi/2}(\pi/2)\right]$where the symbol $\delta_\phi(\beta)$ indicates an infinitely strong, infinitely short pulse with flip angle $\beta$and phase ϕ. This element may be defined using the syntax

```
In[6]:= Cel = {{0, Pi / 2, Pi / 2}, {1, 2 Pi, 0}, {0, Pi / 2, -Pi / 2}};
```

The R-element on the S-channel is defined as above:

```
In[7]:= Rel = {{1 / 4, Pi / 2, 0}, {3 / 4, 3 Pi / 2, Pi}};
```

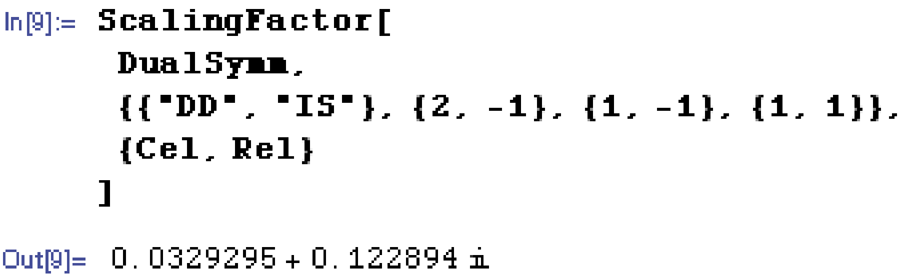
The symmetry-allowed heteronuclear dipole-dipole coupling terms for the symmetry $CR12_2^{1,5}$ are determined by executing



```
In[8]:= SymmetryAllowedH1Terms[DualSymm, {"DD", "IS"}]

Out[8]= {{{DD, IS}, {2, -1}, {1, -1}, {1, 1}},
         {{DD, IS}, {2, 1}, {1, 1}, {1, -1}}}
```

which shows that the only symmetry-allowed first-order heteronuclear dipole-dipole coupling terms have quantum numbers $\{\ell, m, \lambda_I, \mu_I, \lambda_S, \mu_S\} = \{2, \pm 1, 1, \pm 1, 1, \mp 1\}$. The scaling factor for one of these terms is calculated as follows:



```
In[9]:= ScalingFactor[
          DualSymm,
          {{"DD", "IS"}, {2, -1}, {1, -1}, {1, 1}},
          {Cel, Rel}
        ]

Out[9]= 0.0329295 + 0.122894 i
```

S3.3 Heteronuclear Interference for CW decoupling

The discussion in the manuscript shows that CW decoupling applied to the *I*-spin channel at the same time as a RN_n^ν sequence is applied to the *S*-spin channel may be described in terms of the symmetry $CRN_n^{\nu_I,\nu_S}$, where $\nu_S = \nu$ and $\nu_I = n\omega_{nut}^I / \omega_r$. The average Hamiltonian symmetry theory may be used to analyze this case providing that ν_I is an integer.

The basic *I*-spin C-element in this case is given by $C_0 = (2\pi\nu_I / N)_0$, i.e. a rotation by the angle $2\pi\nu_I / N$ about the rotating-frame x-axis. For example, consider the symmetry $CR12_2^{1,5}$ which corresponds to an *I*-spin rf field given by $\omega_{nut}^I = \frac{1}{2}\omega_r$. The rotation angle induced by the decoupler field during each *R*-element on the *S*-spins is $\beta = \pi / 6$. The code generates a warning when the scaling factor is calculated for this case:

```
In[28]:= Cel = {{1, Pi / 6, 0}};
         Rel = {{1 / 4, Pi / 2, 0}, {3 / 4, 3 Pi / 2, Pi}};
```

```
In[30]:= ScalingFactor[
          DualSymm,
          {{"DD", "IS"}, {2, -1}, {1, -1}, {1, 1}},
          {Cel, Rel}
         ]

     ValidBasicElementQ::InvalidC :
      Warning: The basic element appears to be unsuitable for C-symmetry.

 Out[30]=
     -0.0173266 - 0.0180362 i
```

This is because the basic *C* element must usually be a cycle, i.e. a rotation through an even multiple of 2π.

Nevertheless, the existing code may be adapted to the problem of CW decoupling by using a trick. Insert two infinitely short $\pi / 2$ rotations before and after each element:

```
In[39]:= Cel = {{0, Pi / 2, -Pi / 2}, {1, Pi / 6, 0}, {0, Pi / 2, +Pi / 2}};
```

The scaling factor for this dual sequence may be calculated as follows:

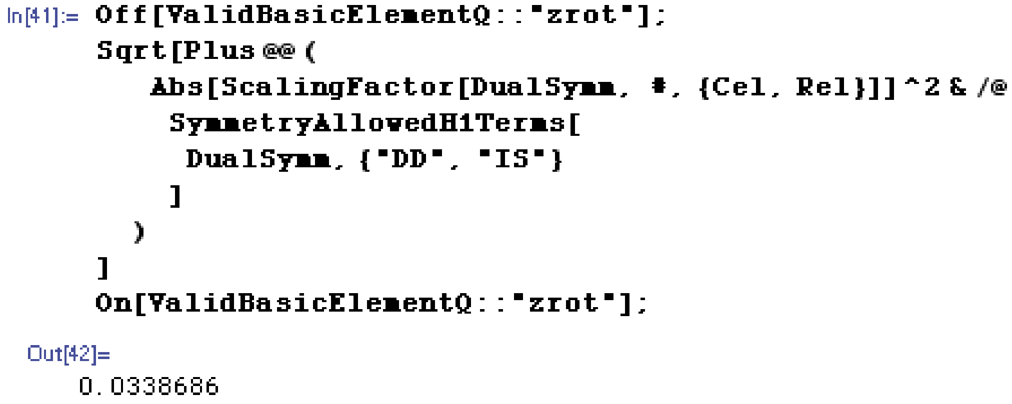
```
In[40]:= ScalingFactor[
          DualSymm,
          {{"DD", "IS"}, {2, -1}, {1, -1}, {1, 1}},
          {Cel, Rel}
         ]

     ValidBasicElementQ::zrot :
      Warning: The basic element leads to a rotation by -30. degrees about the z-axis.

 Out[40]=
     -2.00309 × 10^-18 + 0.0239487 i
```

As indicated by the warning, this sandwich of three elements generates a rotation by -30° degrees about the z-axis, which is equivalent to a phase shift by +30°. A succession of identical rotation sandwiches (with no phase shifts in between) therefore generates the desired $C12_2^1$ symmetry. The entire sequence behaves exactly like CW decoupling, since the infinitesimal rotation at the end of each element cancels the infinitesimal rotation at the beginning of the next one. In this way the current problem may be tackled without modifications of the standard mPackages code.

The $\mathfrak{R}$ factor for this sequence may be calculated using the following syntax:



```
In[41]:= Off[ValidBasicElementQ::"zrot"];
         Sqrt[Plus @@ (
            Abs[ScalingFactor[DualSymm, #, {Cel, Rel}]]^2 & /@
             SymmetryAllowedH1Terms[
              DualSymm, {"DD", "IS"}
             ]
           )
         ]
         On[ValidBasicElementQ::"zrot"];
 Out[42]=
        0.0338686
```

S4 Heteronuclear Interference for C-sequences

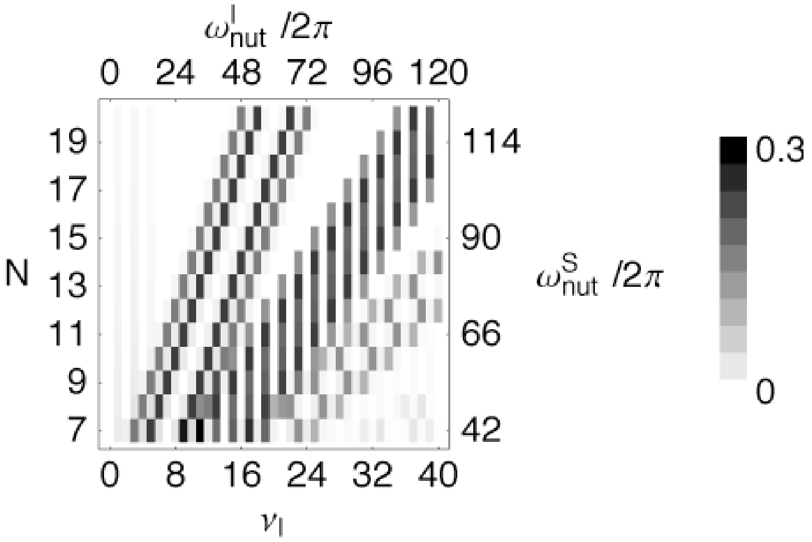
The theory of CN_n^{ν} sequences in the presence of a heteronuclear decoupling field closely resembles that of RN_n^{ν} sequences, as described in the main paper. The relevant dual-channel symmetry is denoted $CN_n^{\nu_I,\nu_S}$ where the I-spin winding number is defined by Eq.18, and $\nu_S = \nu$. The relevant first-order selection rule is

$$\bar{H}^{(1)}_{1,m,\lambda_I,\mu_I,\lambda_S,\mu_S} = 0 \quad \text{if} \quad mn - \mu_I \nu_I - \mu_S \nu_S \neq NZ$$

where Z is any integer. The heteronuclear interference factor may be calculated for arbitary combinations of winding numbers as follows:

$$\Re = \Re(N,n,\nu_I,\nu_S) = \underset{\substack{\{m,\mu_I,\mu_S\}\\ \text{symm allowed}}}{} \left|\kappa_{2,m,1,\mu_I,1,\mu_S}(CN_n^{\nu_I,\nu_S})\right|^2 \quad {}^{1/2}$$

which is almost identical to Eq.(21). A plot of $\Re$ against the symmetry numbers N and ν_I is shown below, for the set of sequences CN_2^1, assuming the basic element $C^0 = 90_0 360_{180} 270_0$:



The top and right-hand axes are labelled with nutation frequencies corresponding to a spinning frequency of 6 kHz.

This plot is very similar to that in Fig.8. We therefore anticipate that CN_2^1 sequences based on the element $C^0 = 90_0 360_{180} 270_0$ will have very similar heteronuclear interference characteristics to $RN_2^{-1+N/2}$ sequences based on the element $R^0 = 90_0 270_{180}$, as studied in the main part of this paper.

very similar performance for the C and R-seqences, with respect to heteronuclear decoupling.