Electronic Supporting Information for:

Symmetry-Amplified $J$ Splittings for Quadrupolar Spin Pairs: 
A Solid-State NMR Probe of Homoatomic Covalent Bonds

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Experimental

Compound 1 was purchased from Aldrich and compounds 2 and 4 were purchased from Strem Chemicals; all were used without further purification.

Synthesis of compound 3

78.1 mg of 1 and 100.0 mg of 2 were dissolved in 5 mL of dry toluene and mixed for two hours under an inert atmosphere. A fine precipitate of 3 quickly formed which was then decanted, washed with a small amount of cold toluene, and dried under vacuum. The purity of the compound was determined using $^{13}$C CPMAS NMR and $^{11}$B MAS NMR, where no traces of the starting materials were observed. The $^{13}$C chemical shifts are listed in Table S1 and the $^{13}$C NMR spectrum is shown in Figure S1. The $^{11}$B MAS NMR spectrum is shown in Figure 2(c) of the main text and the $^{11}$B NMR parameters are listed in Table S2.

NMR Spectroscopy

All powdered samples were tightly packed into 4 mm o.d. ZrO$_2$ rotors under inert conditions. NMR experiments were performed at an applied magnetic field of 9.4 T using a Bruker AVANCE III 400 NMR spectrometer equipped with a triple resonance 4 mm MAS probe. SPINAL-64 decoupling$^1$ was used during both the acquisition and evolution periods in all protonated samples.

$^{55}$Mn NMR

The $^{55}$Mn NMR experiments were all performed under 10 kHz MAS with the use of 25 $\mu$s central transition selective 90° pulses and 50 $\mu$s central transition selective 180° pulses (i.e., RF power of 3.3 kHz).

The regular $J$-resolved experiment was performed using 72 $t_1$ increments of 400 $\mu$s (2.5 kHz spectral window). 64 transients were acquired for each slice with a recycle delay of 1 s.

The $J$-based DQF $J$-resolved spectrum was acquired using a total double-quantum excitation and reconversion period of eight rotor cycles. 2048 transients were acquired for each of the 72 $t_1$ increments and a 0.5 s recycle delay was used.

The dipolar-based DQF $J$-resolved spectrum was acquired using two BR2$^1$ recoupling cycles (eight rotor cycles for both the excitation and reconversion periods) and thus the total DQF period lasted ten rotor cycles. 1440 scans were acquired for each of the 72 $t_1$ increments and a 0.5 s recycle delay was used. A second spectrum was acquired

$^1$ Fung, B. M.; Khitrin, A. K.; Ermolaev, K. J. Magn. Reson. 2000, 142, 97.
using four BR2$^1$ cycles as opposed to two. As the peak at zero frequency grew in this spectrum, it is likely that it originates from intermolecular dipolar recoupling (see Figure S3).

The $J$-resolved spectra are processed in magnitude mode. Apparent distortions are caused by the tail of the non-modulated signal.

$^{11}$B NMR

The $^{11}$B $J$-based DQF $J$-resolved experiments were all performed using 20 $\mu$s central transition selective 90° pulses and 40 $\mu$s central transition selective 180° pulses (i.e. RF power of 6.25 kHz) and a 2 s recycle delay. For compound 1, 15 kHz MAS was used and the total double quantum excitation and reconversion time was 36 rotor cycles. 768 transients were acquired for each of the 24 $t_1$ increments of 1.33 ms. For compound 4, 13.5 kHz MAS was used and the total double quantum excitation and reconversion time was 24 rotor cycles. In this case, the sample was cooled to 0°C to increase the $T_2$. 384 transients were acquired for each of the 16 $t_1$ increments of 740 $\mu$s. For compound 3, 12.5 kHz MAS was used and the total double quantum excitation and reconversion time was 88 rotor cycles. 320 transients were acquired for each of the 40 $t_1$ increments of 1.6 ms.

DFT calculations

All DFT calculations of the $J$ coupling constants were performed using the CPL module$^2$ of the Amsterdam Density Functional software (v. 2009.01).$^3$ Calculations for 1 and 4 were performed at the TPSS/QZ4P$^4$ level of theory using the molecular structures extracted from the published crystal structures$^5$ whereas a TPSS/TZ2P optimized structure was used for 3 where the mesityl groups were replaced by methyl groups.

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$^2$ (a) Dickson, R. M.; Ziegler, T. J. Phys. Chem. 1996, 100, 5286; (b) Autschbach, J.; Ziegler, T. J. Chem. Phys. 2000, 113, 936; (c) Autschbach, J.; Ziegler, T. J. Chem. Phys. 2000, 113, 9410.

$^3$ (a) Guerra, C. F.; Snijders, J. G.; te Velde, G.; Baerends, E. J. Theor. Chem. Acc. 1998, 99, 391; (b) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. J. Comput. Chem. 2001, 22, 931; (c) ADF2009, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

$^4$ (a) Tao, J.; Perdew, J. P.; Starovenov, V. N.; Scuseria, G. E. Phys. Rev. Lett. 2003, 91, 146401; (b) van Lenthe, E.; Baerends, E. J.; J. Comput. Chem. 2003, 24, 1142.

$^5$ (a) Kleeberg, C.; Crawford, A. G.; Batsanov, A. S.; Hodgkinson, P.; Apperley, D. C.; Cheung, M. S.; Lin, Z.; Marder, T. B. J. Org. Chem. 2012, 77, 785; (b) Clegg, W.; Elsegood, M. R. J.; Lawlor, F. J.; Norman, N. C.; Pickett, N. L.; Robins, E. G.; Scott, A. J.; Nguyen, P.; Taylor, N. J.; Marder, T. B. Inorg. Chem. 1998, 37, 5289.
For the calculations of the $J$ coupling constant as a function of the bond length, a constrained geometry optimization was performed at the TPSS/TZ2P level of theory and the $J$ coupling calculation was performed at the TPSS/DZP level of theory. $J$ coupling constant values calculated with this smaller basis set differed by 5% from the values calculated with the QZ4P basis set.

**Theoretical description of $J$-resolved experiments**

All central transitions in an $A_2$ spin pair are characterized by $\Delta I = 0$ ($I$ being the total spin of the system). We can then treat a spin system of two homonuclear coupled quadrupolar nuclei of spin $S$ as an ensemble of isolated ‘nuclei’ with spins of $2S$, $2S-1$…0.$^6$ The triplet states ($I=1$) may be represented as a nucleus with a spin of 1. Both transitions involving the triplet states can be associated with the central transitions, and thus all of the transitions are manipulated when using central transition selective pulses. A $90^\circ$ pulse excites single quantum transitions and the scaled density matrix takes the following form:

$$
\rho(0) = \begin{bmatrix}
0 & -1 & 0 \\
1 & 0 & -1 \\
0 & 1 & 0
\end{bmatrix}.
$$

The propagator for evolution under the homonuclear $J$ coupling (assuming that the transmitter is on resonance) is the following:

$$
U_J(t) = \exp\left[-\frac{iJt}{4} \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & \frac{-iJt}{4} \\
\frac{-iJt}{4} & 0 & 0
\end{bmatrix}\right]
$$

and the propagator for a $180^\circ$ pulse is given by

$$
U_{180} = \begin{bmatrix}
0 & 0 & -1 \\
0 & -1 & 0 \\
-1 & 0 & 0
\end{bmatrix}.
$$

The density matrix after a spin echo sequence ($t/2$-$180^\circ$-$t/2$) is calculated as:

$$
\rho(t) = U_J(t/2)U_{180}U_J(t/2)\rho(0)U_J^\dagger(t/2)U_{180}^\dagger U_J^\dagger(t/2)
$$

$^6$ Perras, F. A.; Bryce, D. L. *J. Chem. Phys.* 2013, 138, 174202.
The two single quantum transitions are then modulated as a function of $t$ as

$$\cos\left(\frac{Jt(2S + 3)(2S - 1)}{8}\right) + i\sin\left(\frac{Jt(2S + 3)(2S - 1)}{8}\right)$$

and

$$\cos\left(\frac{Jt(2S + 3)(2S - 1)}{8}\right) - i\sin\left(\frac{Jt(2S + 3)(2S - 1)}{8}\right)$$

so that the total signal amplitude is proportional to $\cos\left(\frac{Jt(2S + 3)(2S - 1)}{8}\right)$.  

The splitting between the resonances in a 2D $J$-resolved experiment would then be $(2S+3)(2S-1)/4J$ which amounts to a splitting of $3J$ for $S = 3/2$ and $8J$ for $S = 5/2$.

If we now consider the states with total spin $I = 2$, the initial density matrix following a central transition selective 90° pulse is the following:

$$\rho(0) = \begin{bmatrix}
1.5 & -0.5 & 0 & 0 & 0 \\
-0.5 & 1.5 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1.5 & -0.5 \\
0 & 0 & 0 & -0.5 & -1.5
\end{bmatrix}. $$

The propagator during free evolution under the $J$ coupling is:

$$U_J(t) = \exp\left[\frac{iJt(S(S+1) - 9/4)}{2} \begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{iJt(S(S+1) - 9/4)}{2}
\end{bmatrix}\right].$$
and that for the CT selective 180° pulse is:

\[
U_{180} = \begin{bmatrix}
    0 & -1 & 0 & 0 & 0 \\
    1 & 0 & 0 & 0 & 0 \\
    0 & 0 & 1 & 0 & 0 \\
    0 & 0 & 0 & 0 & -1 \\
    0 & 0 & 0 & 1 & 0
\end{bmatrix}.
\]

If we then calculate the signal after a spin-echo sequence,

\[
\rho(t) = U_j (t/2)U_{180} U_j (t/2) \rho(0) U_j (t/2) U_{180}^+ U_j^+ U_j (t/2),
\]

we obtain

\[
\rho(t) = \begin{bmatrix}
    1.5 & -0.5 & 0 & 0 & 0 \\
    -0.5 & 1.5 & 0 & 0 & 0 \\
    0 & 0 & 0 & 0 & 0 \\
    0 & 0 & 0 & -1.5 & -0.5 \\
    0 & 0 & 0 & -0.5 & -1.5
\end{bmatrix},
\]

which is identical to the density matrix at the start of the experiment. The J coupling in these pentet states is then refocused with a central-transition selective spin-echo. As the total spin of the states increases, the CT coherences are more greatly isolated. The J coupling is refocused for all states with the exception of the triplet states.

The observed spin can be coupled to the 2S+1 different states of the other nucleus and only two of these correspond to the central states. As discussed earlier, only those can become J modulated when central transition selective pulses are applied. It follows that only 1/(S+1/2) of the central transition signal is J modulated, and similarly, only this same fraction can be excited in central transition-selective DQ-SQ correlation experiments.

In the case of AX spin systems, the effect of the central transition selective spin echo can be described analogously to the spin-1/2 case.\(^7\)

The line widths in the indirect dimension are dictated by the spin-spin relaxation time constant \((T_2)\). In order for the J coupling to be measurable, the splitting (either J or \((2S+3)(2S-1)/4J\) in the AX and A\(_2\) cases) needs to be greater than \(\sim 1/T_2\). \(T_2\) can usually be systematically increased by decreasing the sample temperature.

\(^7\) Duma, L.; Lai, W. C.; Caravetta, M.; Emsley, L.; Brown, S. P.; Levitt, M. H. \textit{ChemPhysChem} \textbf{2004}, 5, 815.
Figure S1. $^{13}$C CPMAS NMR spectrum of compound 3 acquired at 9.4 T under 10 kHz MAS. Spinning sidebands are marked with asterisks.

Figure S2. $^{11}$B MAS NMR spectrum (bottom) and the simulation (top) for compound 4. $B_0 = 9.4$ T.
Figure S3. Comparison of D-DQF results for manganese decacarbonyl using (a) two and (b) four recoupling blocks. The intensity of the non-modulated signal is higher in the latter.
Table S1. $^{13}$C chemical shifts for compound 3

|                  | chemical shifts / ppm                           |
|------------------|-----------------------------------------------|
| methyl           | 22.5, 22.0, 18.6, 17.4, 16.8; 16.1              |
| aromatic         | 153.1, 152.8, 149.0, 148.1, 141.4, 138.3,      |
|                  | 137.6, 135.4, 134.9, 133.2, 130.2, 129.4,      |
|                  | 128.3, 124.9, 122.8, 122.0, 119.7, 116.7,      |
|                  | 112.5, 111.9, 109.6, 109.0                      |
| carbene          | 164.5                                          |

Table S2. $^{11}$B NMR parameters

| compound                  | $\delta_{iso}$ / ppm | $C_Q$ / MHz   | $\eta$     |
|---------------------------|-----------------------|---------------|------------|
| 1a                        | 30.5 ± 1.0            | 2.85 ± 0.05   | 0.85 ± 0.05|
| 4                         | 31.5 ± 0.5            | 2.70 ± 0.05   | 0.85 ± 0.10|
| 3 (three-coordinate)      | 34.3 ± 0.5            | 3.0 ± 0.1     | 0.89 ± 0.05|
| 3 (four-coordinate)       | $\delta_{peak} = 1 ± 1^b$ | N/A           | N/A        |

$^a$ Parameters from ref. 6.  
$^b$ Due to the lack of a second-order quadrupolar line shape, only the peak position could be determined.