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

Distance measurements between boron and carbon at natural abundance using magic-angle spinning REAPDOR NMR and a universal curve

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We show here the explicit dependence of the REAPDOR fraction $\Delta S/S_0$ upon the modifications of physical (ν_Q, ν_D) and experimental (ν_1, ν_R) parameters. Figure S1-S4 show the dependence on the Euler angle relating the dipolar and quadrupolar tensors (S1), on the RF irradiation strength ν_1 (S2) on the quadrupolar frequency (S3), which for a spin-3/2 is given by $\nu_Q = \frac{3e^2qQ}{2Ih(2I-1)} = C_Q/2$ and on the asymmetry η of the electric field gradient tensor (S4). The Universal curve $0.75\left(1 - e^{-(1.75Dt)^2}\right)$ is always shown with D=150 Hz (solid line) and for 15% deviations below and above D (dashed lines). It shows that above a threshold which is given by $\frac{\nu_1^2}{\nu_Q\nu_R}$, the universal curve always provides the correct results within the given margin. In figure S5, we show and briefly discuss the effect of chemical shift anisotropy of the detected spin on the measured REAPDOR fraction. In Figure S6 we discuss the effect of 11B-11B homonuclear couplings on the recoupling curve. In Figure S7 we show additional experimental results performed by fitting data from two different spinning speeds.

Figure S1 - Dependence of the $\Delta S/S_0$ REAPDOR recoupling curve on the Euler angle β relating the dipolar and EFG tensors. Simpson simulations were performed with a quadrupolar coupling constant C_Q = 2 MHz, ^{11}B RF irradiation strength of ν_1 = 60 kHz, a spinning frequency of ν_R = 5 kHz and a dipolar coupling constant of 150 Hz. The values correspond to an adiabaticity parameter $\alpha = \nu_1^2/(\nu_Q \cdot \nu_R)$ = 0.72. The left figure shows the range valid for extraction of the distance using the universal curve and the right for a larger time scale.

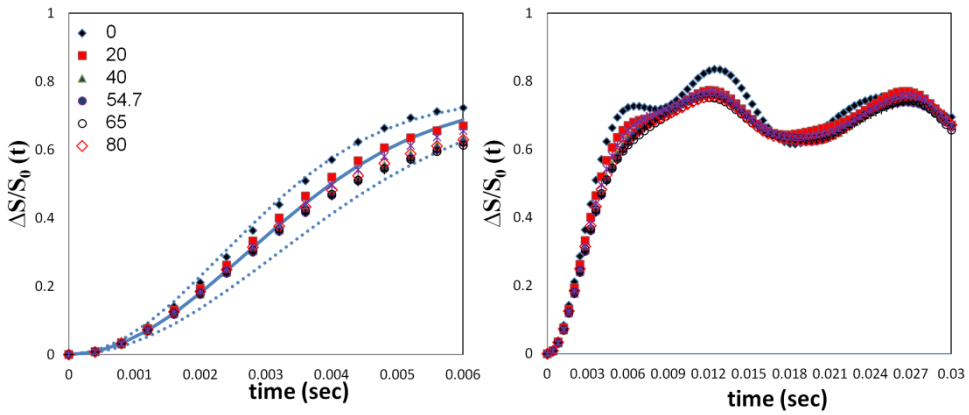

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Figure S2 - Dependence of $\Delta S/S_0$ on the RF irradiation strength applied to the spin-3/2 nucleus. Simpson simulations were performed with a quadrupolar coupling constant C_Q = 3 MHz, a spinning rate of 5 kHz, a dipolar coupling constant of 150 Hz and collinear dipolar and EFG tensors. Variations of ν_1 between 10-85 kHz correspond to α variation between 0.013 to 0.96.

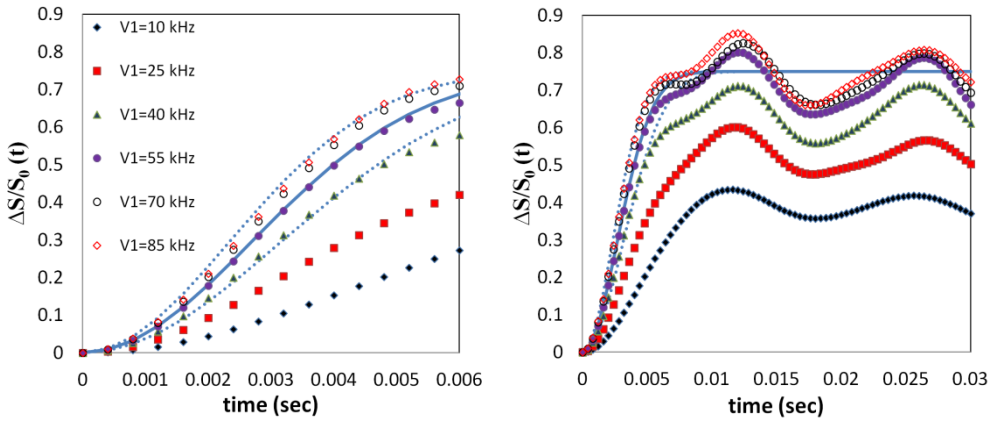

Figure S3 - Dependence of $\Delta S/S_0$ on a spin-3/2 quadrupolar coupling frequency ν_Q. Simpson simulations were performed with an RF power level of ν_1 = 70 kHz, a spinning rate of 10 kHz, a dipolar coupling constant of 150 Hz and collinear dipolar and quadrupolar tensors.

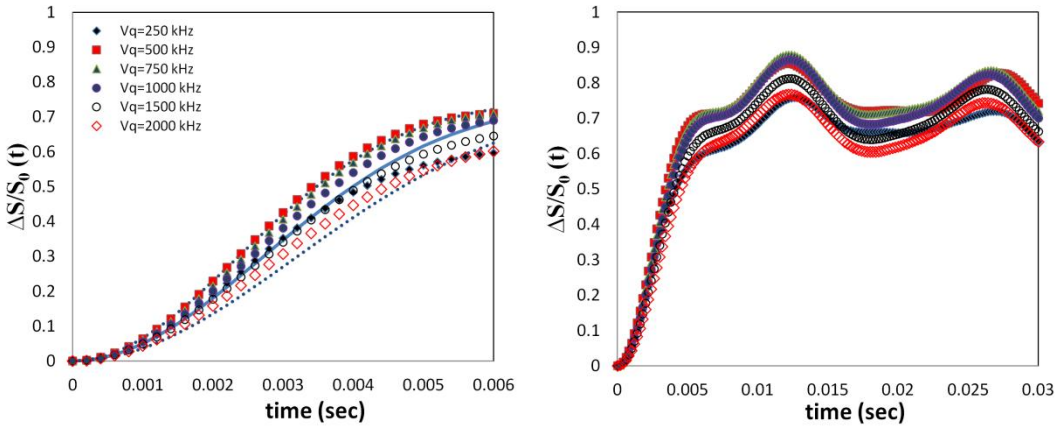

Figure S4 - Dependence of $\Delta S/S_0$ on the asymmetry of the EFG tensor for two values of the adiabaticity parameter. The entire range of η=0.0 to η=1.0 is shown for simulations at a spinning rate of 3 kHz, quadrupolar coupling constant of 3 MHz and RF irradiation strength of 75 kHz, i.e. α=1.25. These curves correspond to the empty circles shown in Figure 1. Simulations with twice the spinning speed are plotted for asymmetry values of 0.0 and 1.0. The dipolar coupling here was 100 Hz.

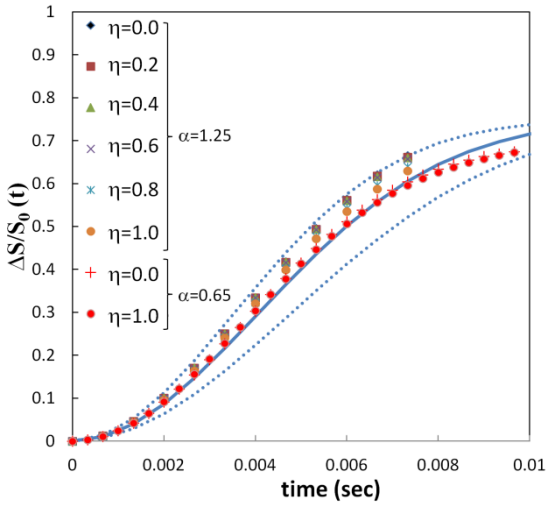

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Figure S5 - The effect of chemical shift anisotropy of the detected spin on $\Delta S/S_0$.

Typical CSA values of carbon range 20-300 ppm, or between a few kHz and up to several tens of kHz on a 14.1T field. For other spin-1/2 nuclei such as P31 and F19 these values could take larger values in kHz. Since the main effect of the CSA occurs during the pulse and is determined by the ratio ν_1/ν_{CSA}, we simulated REAPDOR curves for CSA values ranging up to 400 ppm with an irradiation strength of 50 kHz. A calculation of only S_0 shows a significant decreases in the reference signal (averages 0.88, 0.6, 0.31, 0.14 for CSA values of 100-400 ppm, respectively) and can generate very low experimental signal-to-noise however as long is the pulse is able to invert the spin magnetization, the REAPDOR fraction is not very significantly affected at least up to ~300 ppm. Our simulations suggested that up to $\lambda=Dt$ values of ~0.5 there is a complete overlap of all $\Delta S/S_0$ points and some deviations only start to appear for $\lambda > 0.6$. Above 300 ppm (or ν_1/ν_{CSA} value of ~0.5) significant oscillations occur, the *S* signal takes negative values (not shown) and the data analysis cannot be reliably performed. Simulations have been performed with a spinning rate of 9.5 kHz, quadrupolar coupling constant of 1.6 MHz, asymmetry of 0.4 and a dipolar coupling constant of 505 Hz. The RF irradiation field was set between 50-60 kHz hence the anisotropies are between a ν_1/ν_{CSA} ratio of 3.3 to 0.83.

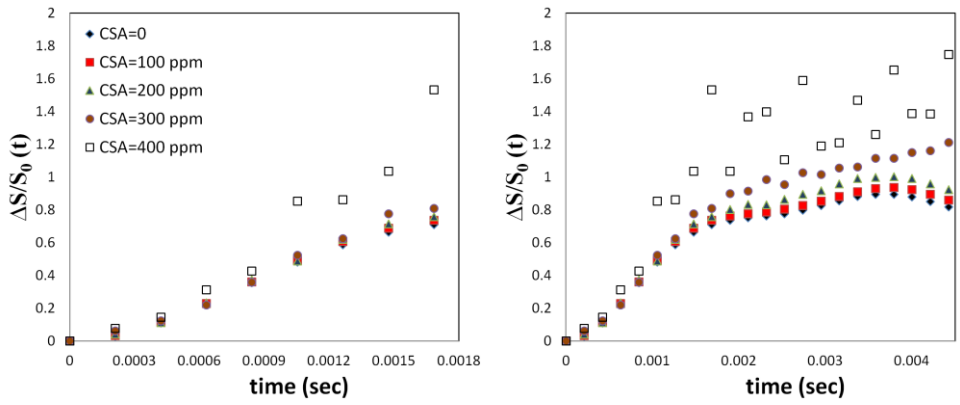

Figure S6 - The effect of homonuclear boron-boron coupling on the REAPDOR recoupling curve.

The effect of the ^{11}B-^{11}B homonuclear coupling on the REAPDOR universal curve was investigated by SIMPSON simulations. In the reported structure of 4-(Hydroxymethyl)phenylboronic acid MIDA ester, this coupling is ~80 Hz and slightly affects the calculated curve at long recoupling times (top left), while in the region corresponding to the validity of the universal curve the effect is negligible (bottom left). Even when the ^{11}B-^{11}B distance is a short as 3.14Å (D = 400 Hz), the homonuclear coupling has a negligible effect on the curve (right). While ^{13}C-^{13}C couplings can affect the curve due to the application of two pulses every rotor period, only a single pulse is applied to the boron spins, at an intensity which is much larger than $D_{11B\text{-}11B}$, hence the dipolar coupling is not directly recoupled. Other parameters used in the calculations are ν_{1B} = 66 kHz, ν_R = 9.5 kHz, $D_{13C\text{-}11B}$ = 505 Hz, ν_Q=0.8 MHz.

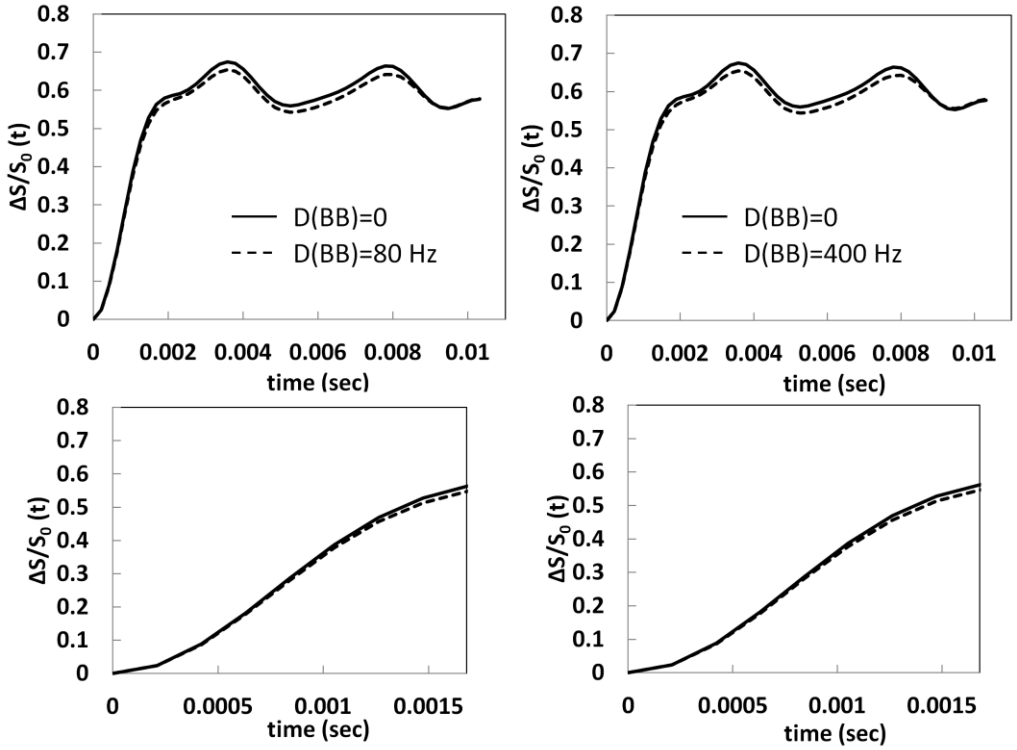

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Figure S7 - Additional experimental REAPDOR results. (a) Experimental $\Delta S/S_0$ points for the methyl carbon taken from experiments at spinning rates of 8.1 (red squares) and 10 (blue diamonds) kHz. A mutual fit of all points yield a dipolar coupling of 475 Hz, or a distance of 2.73 Å. (b) $\Delta S/S_0$ for the ortho carbon having two distances of 2.61 and 3.92 (or 2.59 and 5.19). The corresponding dipolar couplings are 545 and 161 Hz (or 558 and 69 Hz). The experimental results yield a dipolar coupling of 539. (c) $\Delta S/S_0$ for one of the meta carbons. The two carbons have two very similar dipolar couplings to two different boron spins (166 and 155 Hz or 166 and 85 Hz), hence fitting to a single distance using the universal formula causes an overestimation of the distance by ~9% (3.57 Å instead of 3.88 Å). In such cases full simulations have to be performed and the method is not accurate enough.