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Supporting Information

Revisiting Anisotropic Diffusion of Carbon Dioxide in the Metal-Organic Framework Zn_2(dobpdc)

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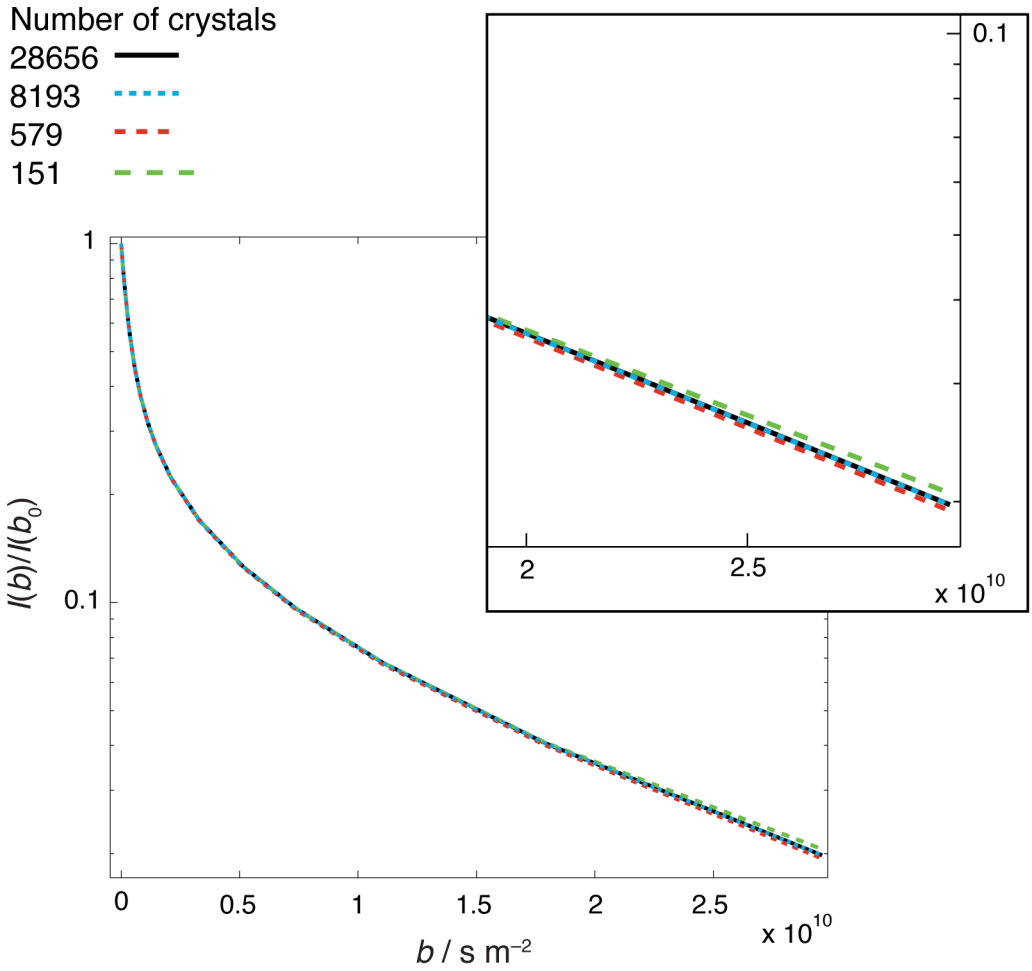

Figure S1. Effect of number of crystals used in simulations on total simualted integrated NMR signal intensity as a function of *b* value. Simulations for 28656 (zcw scheme), 8193 (ASGh), 579 (ASGh) and 151 (LEBh) crystals are shown, with the crystal files used directly from Simpson software.[1] Other simulation parameters: $D_{//} = 6.5 \times 10^{-9}$ m^2 s^{-1}, $\delta_{\perp} = 133.0$ ppm, $\delta_{//} = 114.5$ ppm, Gaussian lineshapes FWHM of 1.7 ppm, and with no weighting function used. Simulations with 28656 and 8193 give converged results to a very good approximation, while simualtions with 579 and 151 crystals show small deviations at large *b* values. 28656 crystals were used for all simulations in the main text. The actual number of crystals in our NMR sample may be roughly estimated using crystal sizes from microscope images from our previous work,[2] and the approximate volume of crystals in the NMR tube (5 mm NMR tube, 10 mm sample height), and is of the order of hundreds of thousands of crystals.

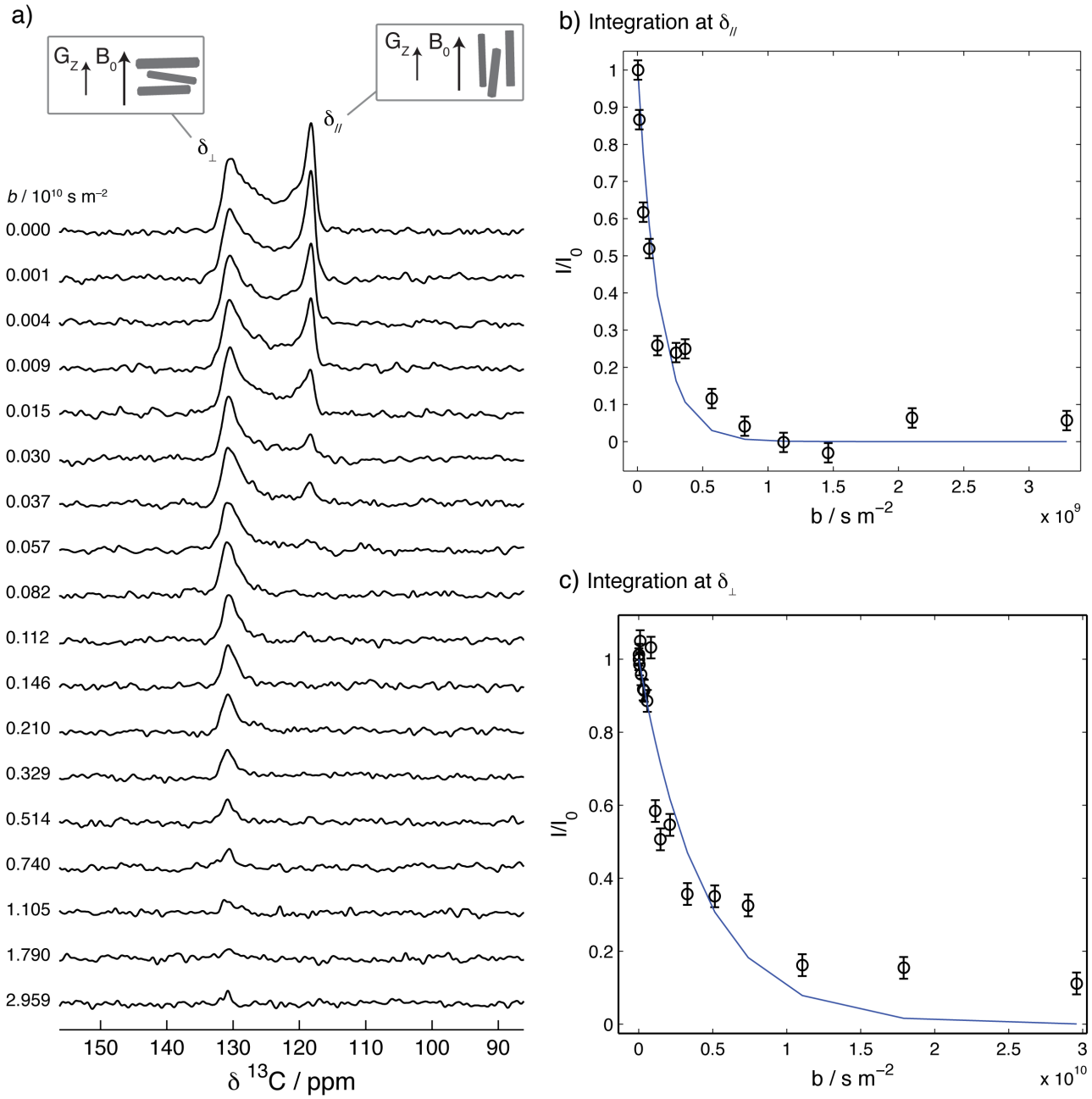

Figure S2. Data analogous to Figure 2 in the main text, except for a gas dosing pressure of 1010 mbar.

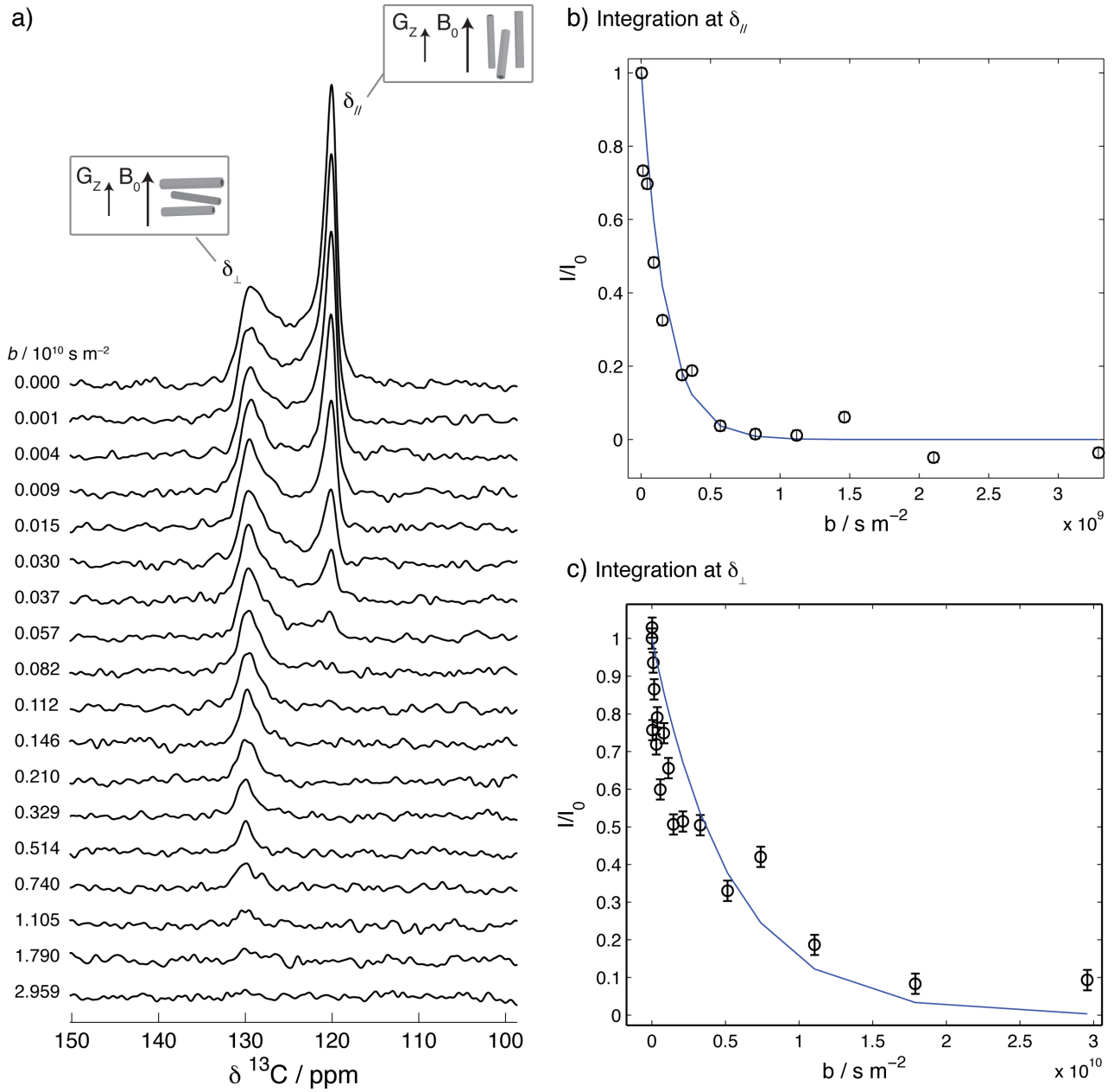

Figure S3. Data analogous to Figure 2 in the main text, except for a gas dosing pressure of 625 mbar.

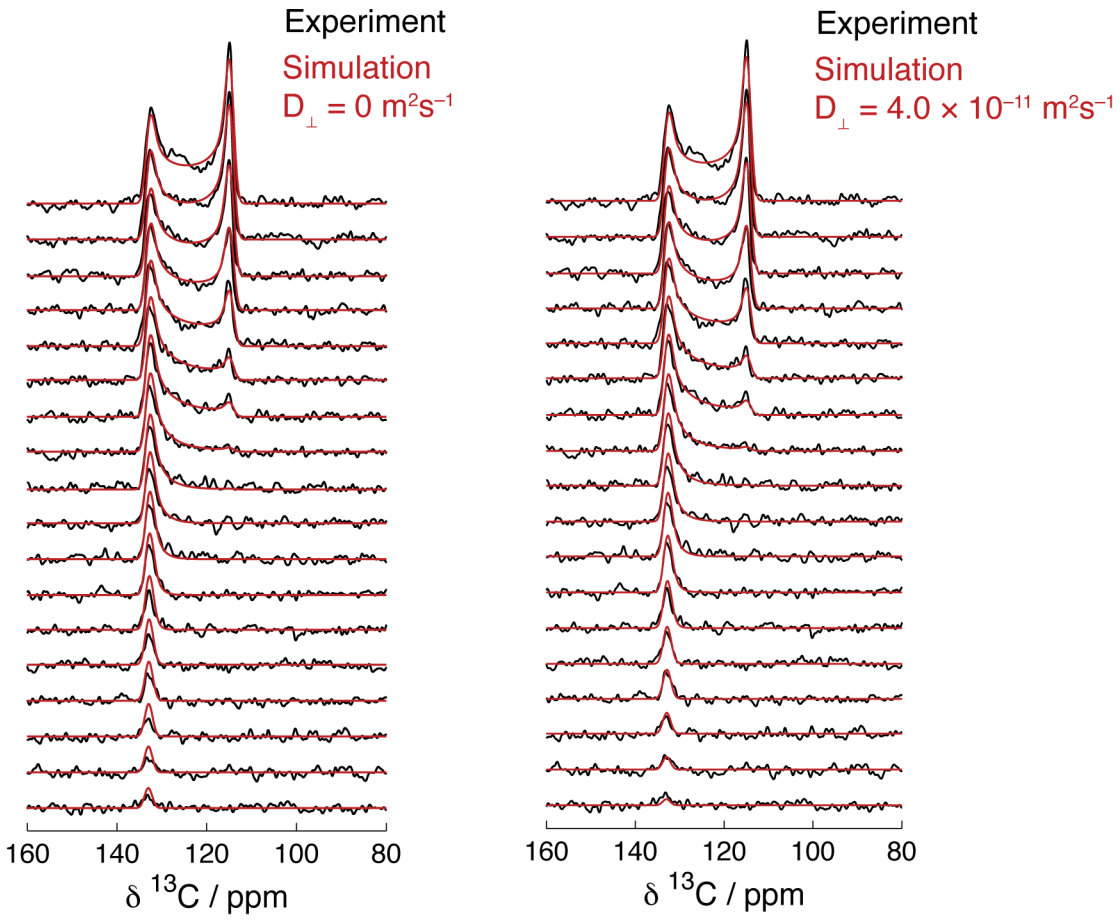

Figure S4. Data is reproduced from Figure 4 in the main text, though with data directly overlaid.

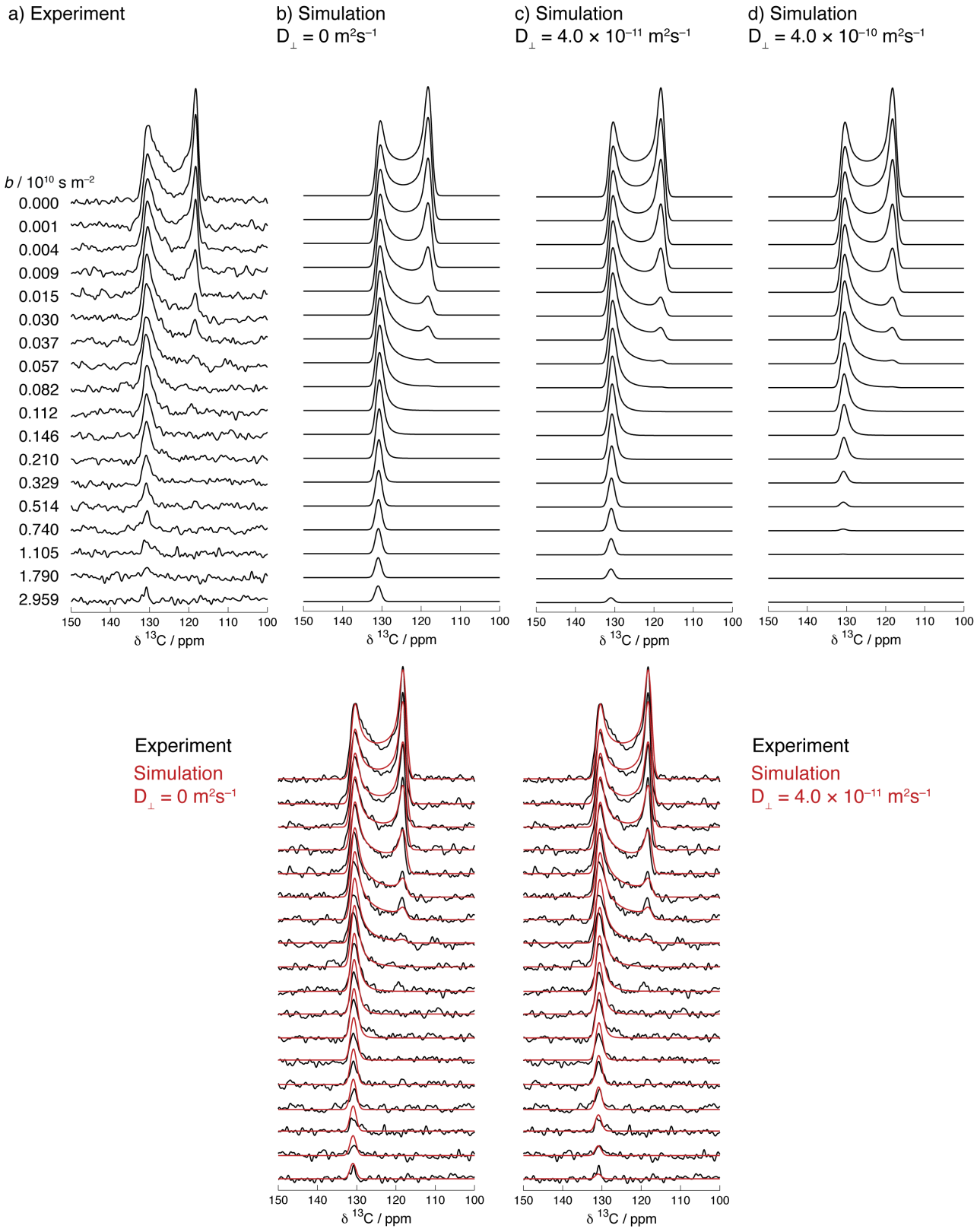

Figure S5. Data is analogous to that in the main text Figure 4, except the gas dosing pressure is 1010 mbar. Simulation parameters: $D_{//} = 6.2 \times 10^{-9}$ m^2 s^{-1}, $\delta_{\perp} = 131.0$ ppm, $\delta_{//} = 117.8$ ppm, Gaussian lineshapes with a FWHM of 1.8 ppm. $D_{\perp}$ was varied in the three different simulations. Overlays are shown at the bottom for ease of comparison.

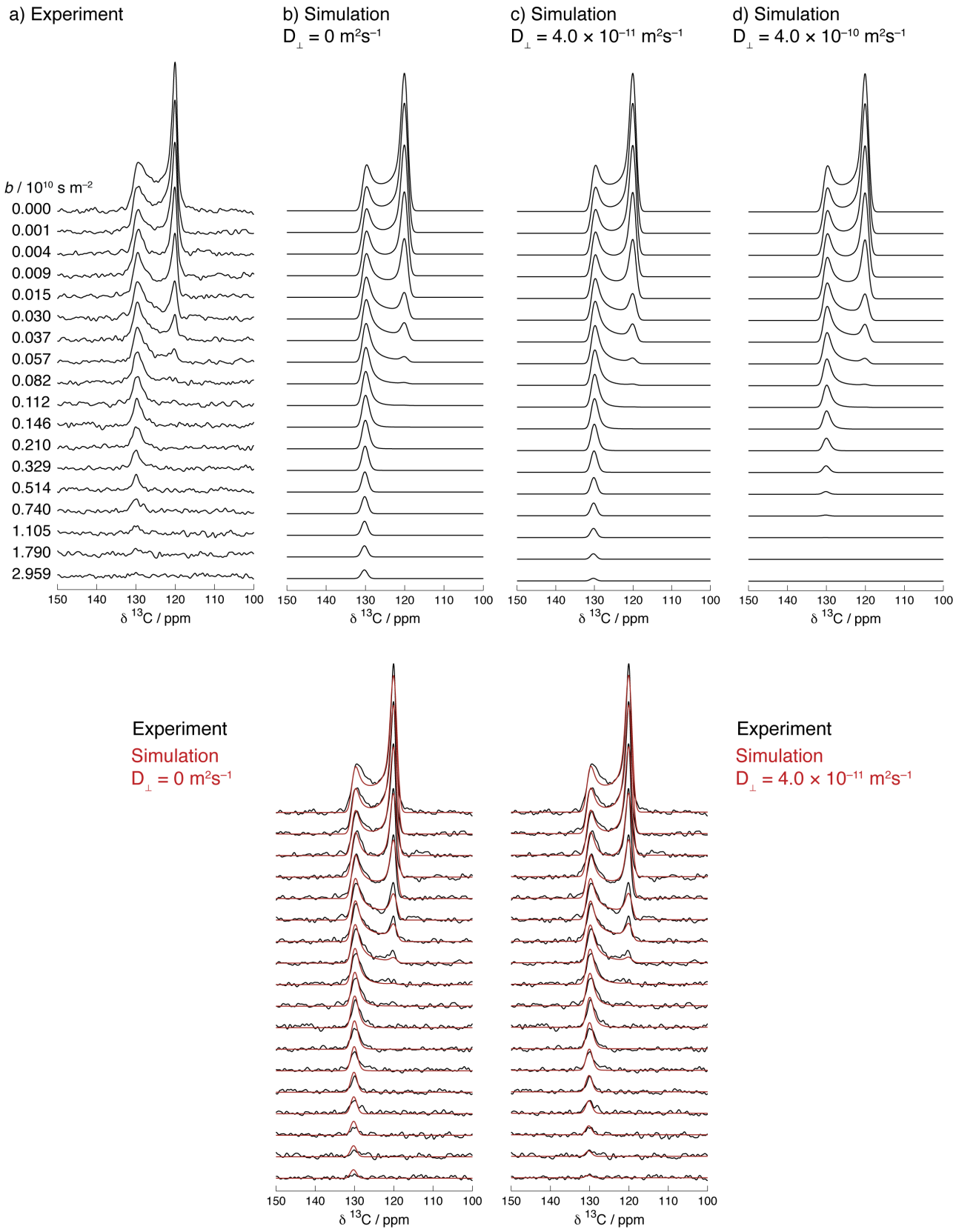

Figure S6. Data is analogous to that in the main text Figure 4, except the gas dosing pressure is 625 mbar. Simulation parameters: $D_{//} = 5.8 \times 10^{-9}$ m^2 s^{-1}, $\delta_{\perp} = 130.3$ ppm, $\delta_{//} = 119.8$ ppm, Gaussian lineshapes with a FWHM of 1.8 ppm. $D_{\perp}$ was varied in the three different simulations. Overlays are shown at the bottom for ease of comparison.

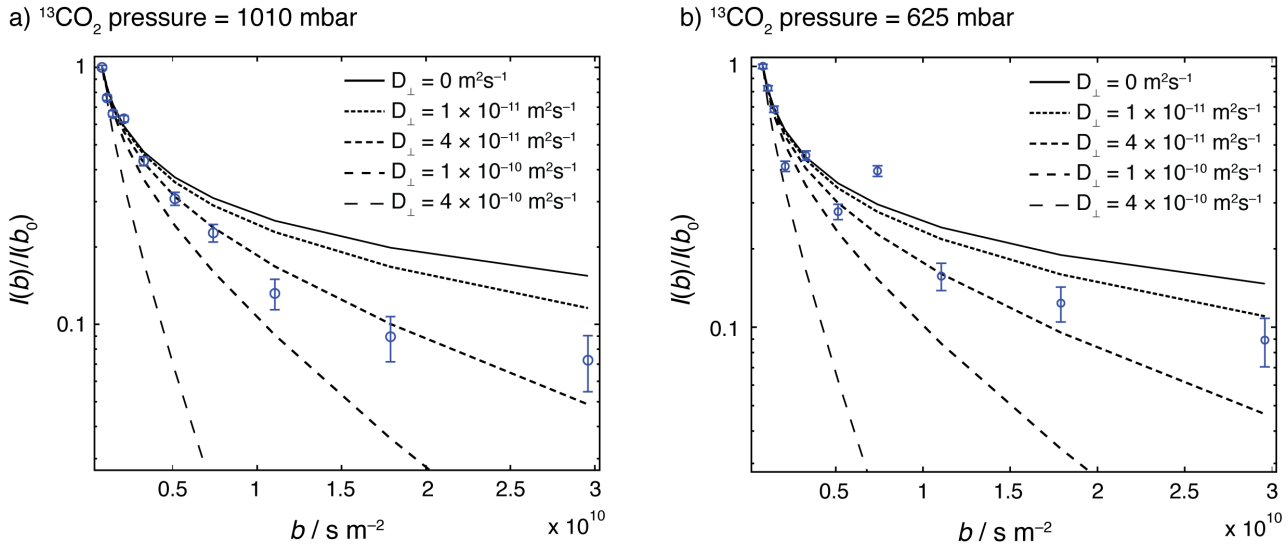

Figure S7. Plots analogous to Figure 5a in the main text, with different $^{13}CO_2$ gas-dosing pressures of a) 1010 mbar and b) 625 mbar.

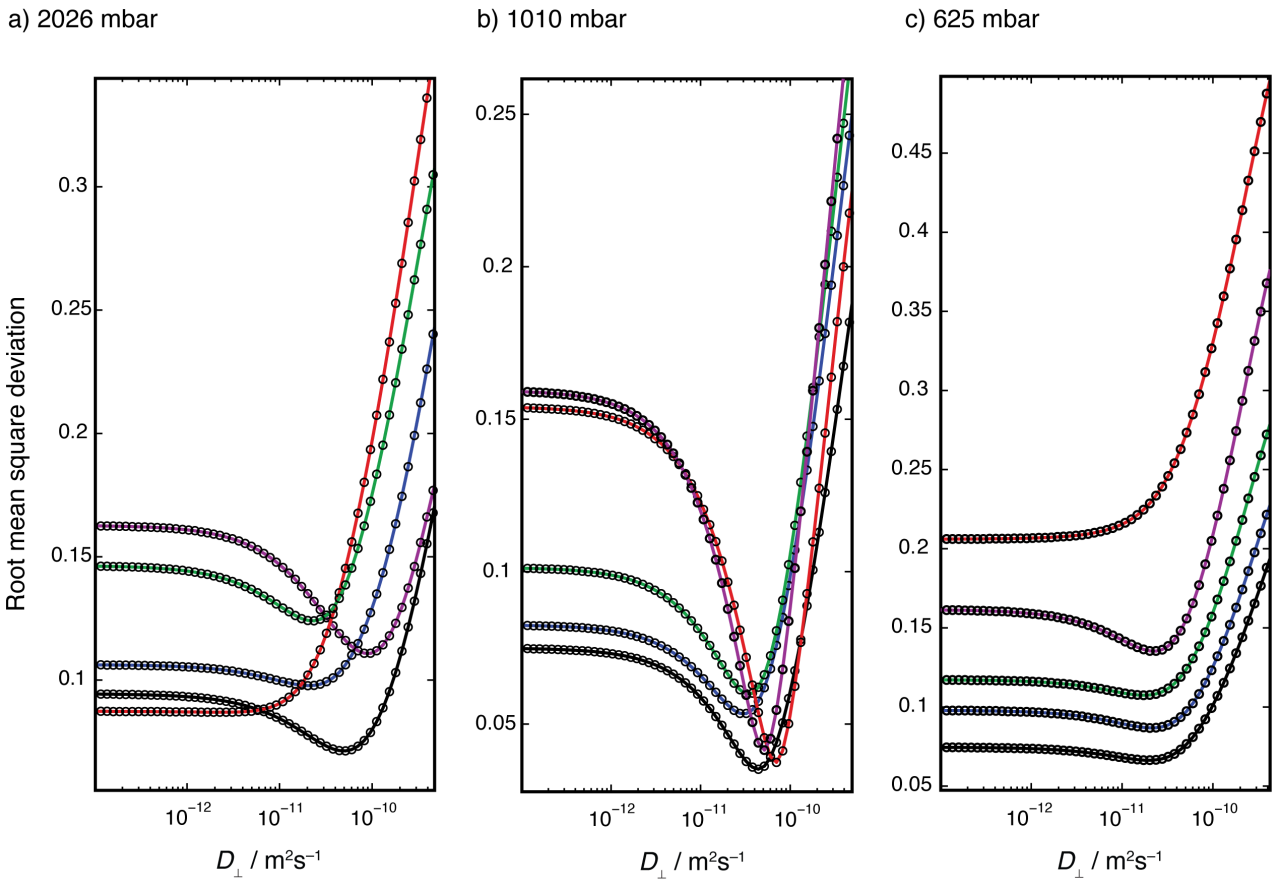

Figure S8. Root mean square deviation plots similar to those shown in the main text, Figure 5b. For each gas pressure, five curves are shown, which correspond to data with, $b \geq 8.2 \times 10^8$ s m^{-2} (black line), $b \geq 1.12 \times 10^9$ s m^{-2} (blue line), $b \geq 1.46 \times 10^9$ s m^{-2} (green line), $b \geq 2.10 \times 10^9$ s m^{-2} (red line), and $b \geq 3.29 \times 10^9$ s m^{-2} (purple line). The root mean square deviations are not normalized to account for the different numbers of data points used in the fits.

References

(1) Bak, M.; Rasmussen, J. T.; Nielsen, N. C. SIMPSON : A General Simulation Program for Solid-State NMR Spectroscopy. *J. Magn. Reson.* **2000**, *147*, 296–330.

(2) Forse, A. C.; Gonzalez, M. I.; Siegelman, R. L.; Witherspoon, V. J.; Jawahery, S.; Mercado, R.; Milner, P. J.; Martell, J. D.; Smit, B.; Blümich, B.; et al. Unexpected Diffusion Anisotropy of Carbon Dioxide in the Metal−Organic Framework Zn2(dobpdc). *J. Am. Chem. Soc.* **2018**, *140*, 1663–1673.