

Supporting Information

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SI Text

¹²⁹Xe NMR

Variable cross-polarization time experiments, Fig. S1 and Fig. S2, showed that the optimum CP time was 3 ms, for which all resonances were close to their maximum intensity.

The quench-recovered sample showed an increased sI signal intensity at 153 K as compared to 77 K. Also, further increases in the amount of sI were observed when spinning at speeds of 4 and 5 kHz, Fig. S3. Faster spinning elevates the temperature in the rotor by a few degrees above the cooling gas temperature and thus may accelerate the conversion to sI.

The large widths of the MAS lines for both HS-I and sI at 153 K (seen in Fig. 3 and Fig. S3) are a consequence of the frozen-in disorder of the water protons of the cages, which effectively produces a large distribution of slightly different cage configurations and environments for Xe. At temperatures above ≈ 200 K reorientations of the water molecules would become rapid enough on the NMR timescale to average out this effect, leading

to much sharper MAS lineshapes than observed here. Unfortunately HS-I decomposes near 160 K.

At high temperatures, where the proton disorder is dynamic, the relatively distinct Xe patterns reflect the time averaged symmetry of the cages (that is, the symmetry as determined from the space averaged diffraction patterns). At low temperature, the proton disorder freezes in and the true local symmetry of the cages is reflected in the Xe patterns as a broadening of the fine structure, although the space averaged symmetry (diffraction pattern) does not change. Disorder from oxygen (water) shows up as extra line broadening in the NMR patterns, as the local symmetry of individual cages is affected in addition to the effects of the proton disorder. If there is oxygen (water) disorder visible in the diffraction pattern, this certainly would show up in the NMR as well. The ¹²⁹Xe NMR MAS lines are also relatively broad indicating a distribution in chemical shifts and therefore of Xe environment. This is entirely consistent with the proton disorder in the water framework, but also will reflect any positional disorder of the O atoms.

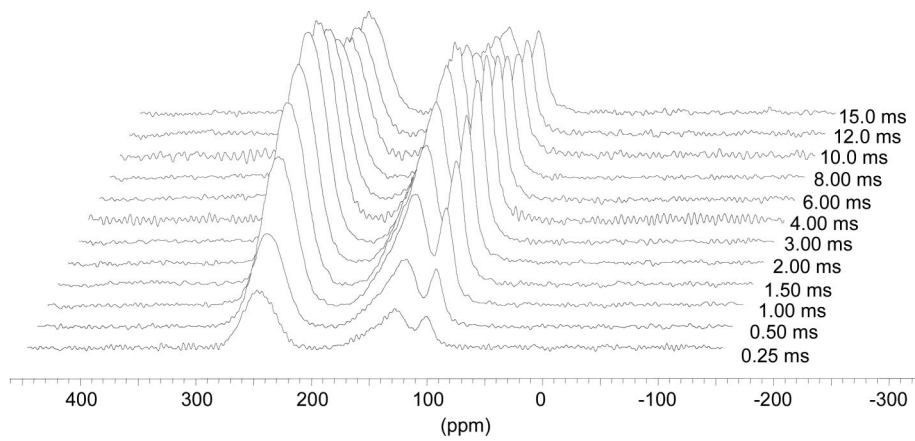


Fig. S1. Static ^{129}Xe NMR spectra as a function of cross-polarization time for the quenched HS-I/Str.I sample at 77K.

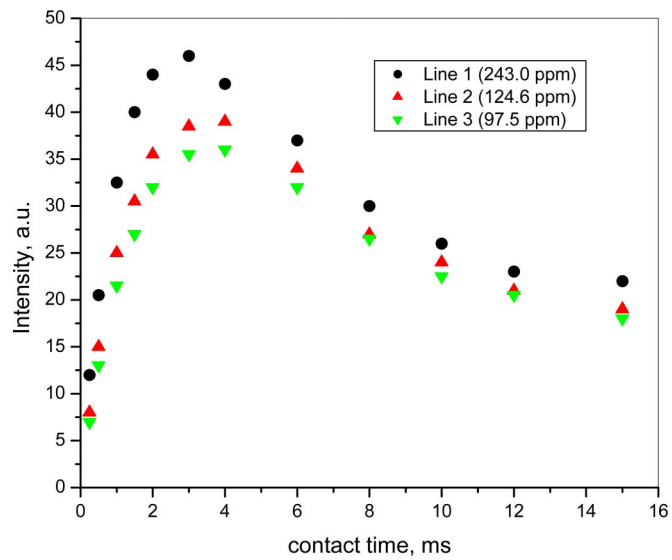


Fig. S2. Static ^{129}Xe NMR signal intensities as a function of cross-polarization time for HS-I at 77K.

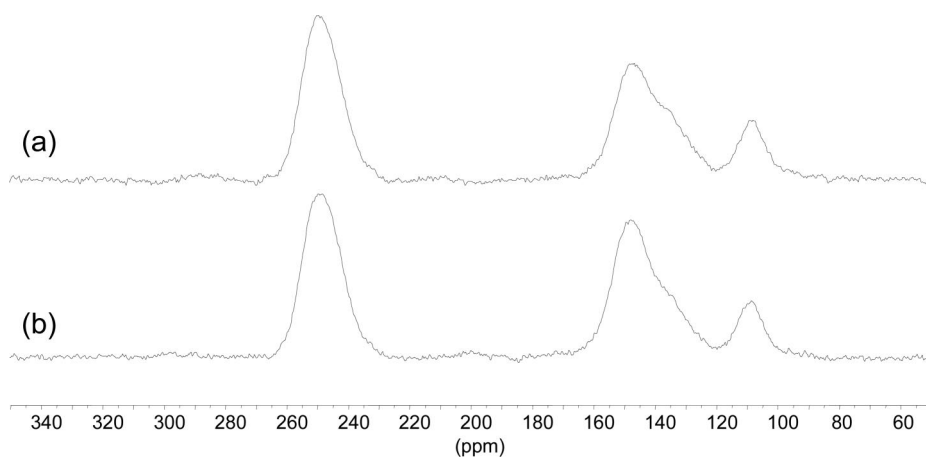


Fig. S3. ^{129}Xe NMR MAS spectra of the quenched HS-I/sl sample at spinning speeds of (a) ≈ 4 kHz and (b) ≈ 5.1 kHz, gas temperature 153 K. Note the increased intensity of the sl line at 148 ppm as the spin rate was increased.