Supporting Information

Quantitative Assessment of Xenon Exchange Kinetics with Cucurbit[6]uril in Physiological Saline

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Saturation transfer experiment

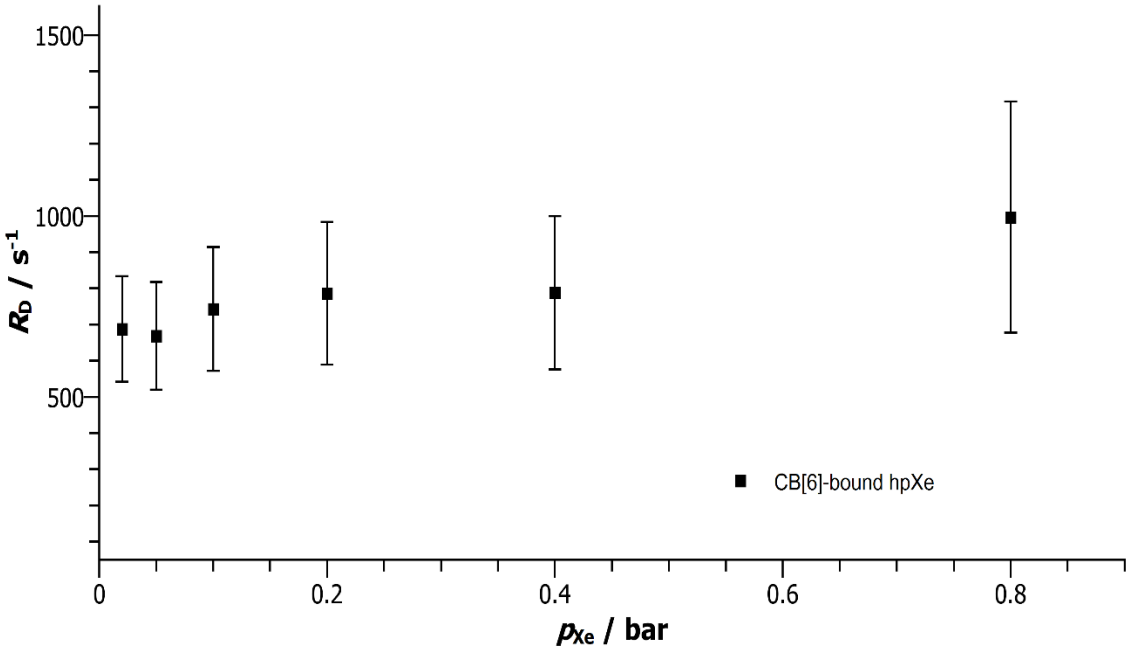

Fig. S1. Depletion rate (k_{off}) for the signal of CB[6]-bound hpXe in dependence of xenon partial pressure determined by saturation transfer from free hpXe for 4.5 mM CB[6] in PBS at 298 K. Saturation was achieved by CW irradiation of amplitude 500 Hz which is the maximum permissible not to directly saturate CB[6]-bound hpXe. The individual depletion rates were obtained by a mono-exponential fit to the signal intensity of free and CB[6]-bound xenon, respectively, in dependence of the exchange period which was varied between 0 and 2.5 ms. Error margins are the standard error from the depletion rate fitting. For the sample saturated with xenon gas at 0.02 bar partial pressure, the exchange rate was k_{off} = 690±148 Hz while the line width of the CB[6]-bound hpXe signal obtained by Lorentzian line fitting of the respective standard spectrum corresponds to the rate 1215±1 Hz in case any contributions other than exchange broadening are ignored (Fig. 1b main text).

Exchange of anti-parallel magnetization generated by selective inversion of free hpXe

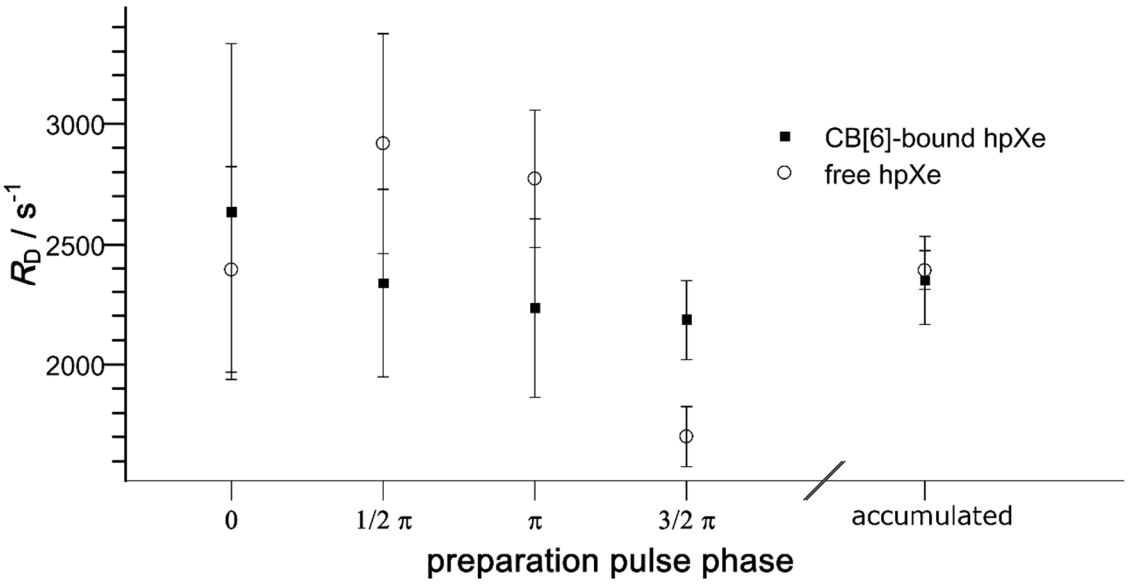

Fig. S2. Depletion rates (k_{off}+k_{on}) for free and CB[6]-bound hpXe in dependence of the preparation pulse phase determined by application of a selective inversion pulse to the free xenon magnetization for the preparation of anti-parallel magnetization with the pulse sequence in Fig. 2a in the main text. The sample was 4.5 mM CB[6] in PBS at 298 K saturated with xenon gas at 0.02 bar partial pressure. For inversion, a Gaussian pulse of 0.7 ms duration was used which is at the limit permitted for clean spectrally selective pulse action not affecting the resonance of CB[6]-bound xenon ~6 kHz shifted up-field. The individual depletion rates were obtained by a mono-exponential fit to the signal intensity of free and CB[6]-bound xenon, respectively, in dependence of the exchange period which was varied between 0 and 2.5 ms. Error margins are the standard error from the depletion rate fitting. With the phase of the read pulse held constant, the depletion rates vary with changing phase of the Gaussian pulse. However, through accumulation of the signal intensities for the different phase settings close to identical depletion rates within narrow error margins are attained, as theoretically expected (Ref. 20). Quantitative exploitation of the latter by division through the scaling factor 1+M_{CXe}/M_{Xe} using the equilibrium magnetization of free and encaged hpXe in the corresponding standard spectrum, M_{Xe} and M_{CXe} , respectively (Eq. 1 main text), yields for the exchange rate the weighted mean k_{off} = 888±76 Hz. This result is an improvement in comparison to the saturation transfer experiment but still falls short of the expectation from the line width consideration in the standard spectrum (Fig. 1 main text).

Exchange of anti-parallel magnetization generated by non-selective pulse action

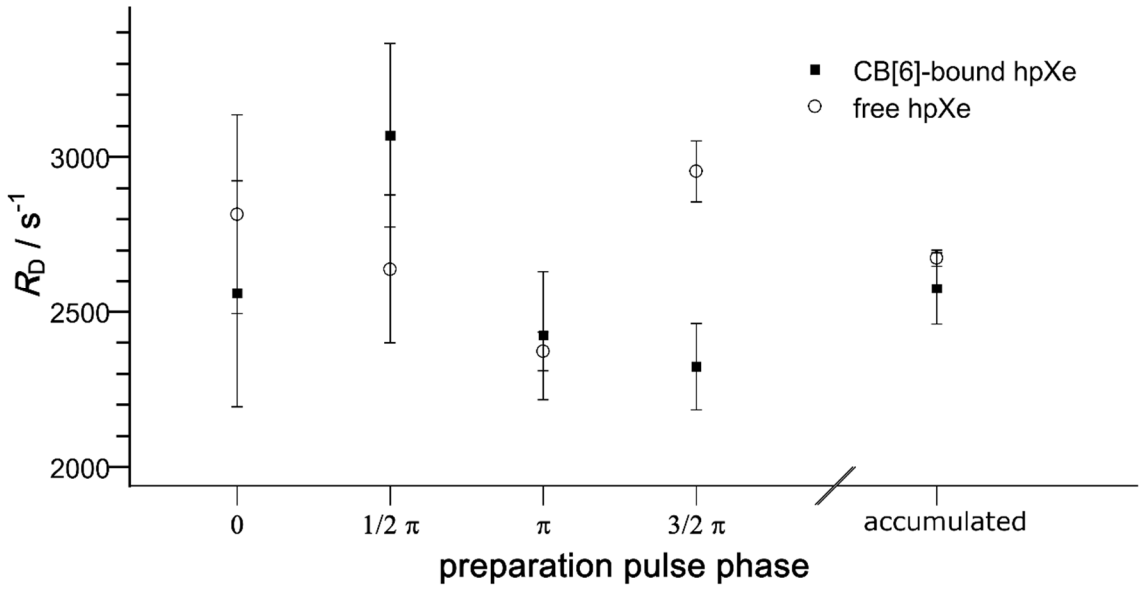

Fig. S3. Depletion rates (k_{off}+k_{on}) for free and CB[6]-bound hpXe in dependence of the preparation pulse phase determined by application of a non-selective preparation pulse for the generation of anti-parallel magnetization with the pulse sequence in Fig. 2a in the main text. The sample was 4.5 mM CB[6] in PBS at 298 K saturated with xenon gas at 0.02 bar partial pressure. The preparation pulse had a duration of 145 µs to invert resonantly the free hpXe magnetization but to cycle the CB[6]-bound xenon ~6 kHz shifted up-field back to its equilibrium position (Fig. 2b main text). The individual depletion rates were obtained by a mono-exponential fit to the signal intensity of free and CB[6]-bound xenon, respectively, in dependence of the exchange period which was varied between 0 and 2.5 ms. Error margins are the standard error from the depletion rate fitting. With the phase of the read pulse held constant, the depletion rates vary with changing phase of the preparation pulse as happened in case of the Gaussian selective inversion (Fig. S2). Again, through accumulation of the signal intensities for the different phase settings close to identical depletion rates within narrow error margins are attained. Quantitative exploitation of the latter by division through the scaling factor 1+M_{CXe}/M_{Xe} using the equilibrium magnetization of free and encaged hpXe in the corresponding standard spectrum, M_{Xe} and M_{CXe} , respectively (Eq. 1 main text), yields for the exchange rate the weighted mean k_{off} = 1192±12 Hz which is reasonable considering the line width in the standard spectrum (Fig. 1 main text).

Rate coefficient quantification at 310 K

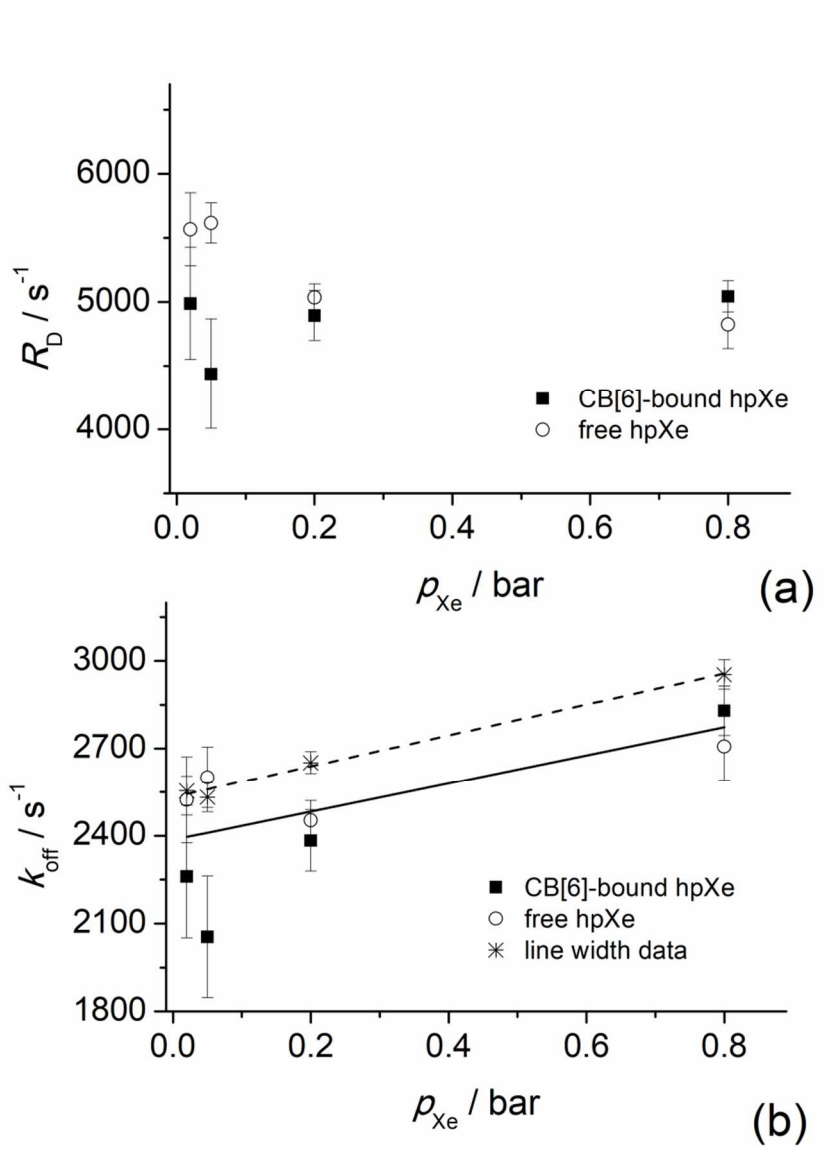

Fig. S4. CB[6]-hpXe chemical exchange at 310 K. (a) Depletion rates in dependence of xenon partial pressure for the signals of free and CB[6]-bound hpXe determined by mono-exponential curve fitting to experimental data (likewise shown in Fig. 2c main text). (b) Same data but divided by $(1+M_{CXe}/M_{Xe})$ derived from standard NMR spectra at respective xenon partial pressure settings to obtain k_{off} for free and CB[6]-bound. The rate coefficients c_- and k are determined as the intercept at vanishing xenon partial pressure and the slope, respectively, by linear fitting to the thus experimentally determined k_{off} as c_-=2390±70 s^{-1} and k=16000±51600 M^{-1}s^{-1} (continuous line). The line width of CB[6]-bound hpXe multiplied by π from standard spectra in dynamic equilibrium and for the various xenon partial pressures is also indicated. The rate coefficient k=175300±14400 M^{-1}s^{-1} derives from the slope in a linear fit (dashed line). The error margin of k from the exchange spectroscopy and the line width includes in addition to the standard error from the fitting a contribution of ±1600 M^{-1}s^{-1} and ±1800 M^{-1}s^{-1}, respectively, from the uncertainty in the xenon solubility when converting the fitted slope to the rate k (see Experimental Section).