Cluster Formation in Solid-state Mixtures Restricts DNP of ^{129}Xe

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Introduction: Recent reports of ^{129}Xe dynamic nuclear polarization (DNP) [1,2] spurred renewed interest in producing large quantities of highly polarized xenon for human-lung MRI. Compared to well-established ^{129}Xe optical pumping schemes, DNP is performed in the solid state, with 10^3 times higher Xe density and, potentially, higher production rates. However, the reported ^{129}Xe polarizations vary widely and are still considerably lower than ^{13}C DNP. One of the reasons for these limitations may be a lack of experimental access to microscopic DNP parameters. Another reason is a poorly understood process of forming a solid sample from a gaseous ingredient. DNP requires an intimate mixture of the target (xenon) with the source of unpaired electron spins, e.g. a free-radical molecule. Crystallization often leads to exclusion of foreign molecules from the solid, therefore a glassing agent (1-propanol) is added to achieve a homogeneous mixture of the radical with the target substance. Glassing behavior, however, is difficult to predict and to control, as slight variations in molecular mobility and affinity during freezing are thought to significantly affect polarization levels in otherwise similar organic molecular targets. To resolve these issues, we used ^{129}Xe NMR spectroscopy with part-per-million (ppm) resolution as a local probe to investigate DNP in xenon/1-propanol/trityl-radical mixtures.

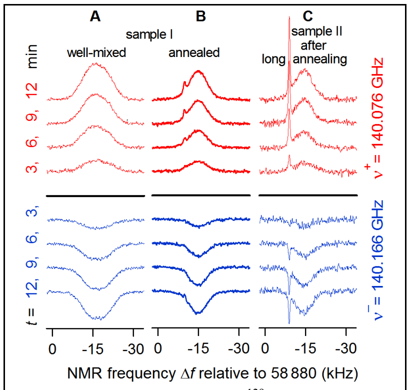

Figure 1: Early evolution of ^{129}Xe NMR spectra under DNP at ν^+=140.067 GHz (red) and ν^-=140.166 GHz (blue) microwave frequencies as a function of DNP time *t*. **A**: Well-mixed sample I. Only one broad peak (corrected FWHM of 10.0 kHz) is observed. **B**: The same sample after undergoing four-hour annealing process at 125 K. Two peaks are observed: the broad peak (FWHM 7.0 kHz) and a much narrower, shifted second peak (FWHM 0.7 kHz). **C**: Sample II after a 21-hour gradual annealing process at T < 125 K. The narrow peak (FWHM 0.5 kHz) is somewhat narrower compared to Sample I, whereas the broad peak (FWHM 6.8 kHz) is within error bars of the broad peak of panel B.

Methods: We built a hybrid DNP/NMR system based on an Oxford TMR7/88/15 Teslatron^{MR} magnet, integrated ^{4}He variable-temperature insert, and Oxford ITC-503 controller. 140-GHz microwaves were generated by a computer-controlled primary source at 7.78 GHz and 18.3 dBm followed by a ×18 frequency multiplier integrated with a narrow-band 140 GHz/70 mW microwave amplifier. Our custom-made probe supported an overmoded cylindrical aluminum microwave chamber (~5 cm in height and diameter), attached to an overmoded circular stainless-steel waveguide. A two-turn copper NMR saddle coil wrapped around a PEEK sample holder accommodated a vertical 5-mm glass sample tube. The samples were prepared using a hermetically-sealed retractable electric stirrer from a 3:1 mixture (by volume) of (a) 3 mg trityl (Finland acid) radical dissolved in 97 mg 1-propanol and (b) liquid ^{129}Xe (BOC Gases, 99.997% purity, <1 ppm O_2) at the 195 K temperature of ethanol/dry ice bath and 4.2 atm pressure. After 1 min of vigorous stirring we changed the bath to liquid nitrogen (LN_2, at 77 K), then transferred the sample tube to our pre-cooled probe within several minutes. ^{129}Xe NMR spectra were acquired with a home-built broadband NMR spectrometer. After applying baseline adjustment, FFT, and zero-phase correction, spectra were fitted to double-Gaussian line shapes, and the individual peak integrals were computed from the fit parameters. In cases where the narrow peak's slightly non-Gaussian tail overlapped the broad peak significantly, a linear combination of a Gaussian and a Lorentzian of the same full width at half max (FWHM) was used to represent the narrow peak in multi-peak fits. Polarization was calculated by normalizing the peak integrals (obtained from the fit parameters) by the corresponding thermally-relaxed values measured without DNP at 1.43 K. The reported areas and widths of the broad Gaussian peaks were corrected for the effects of a 9.5-μs digitizer dead time.

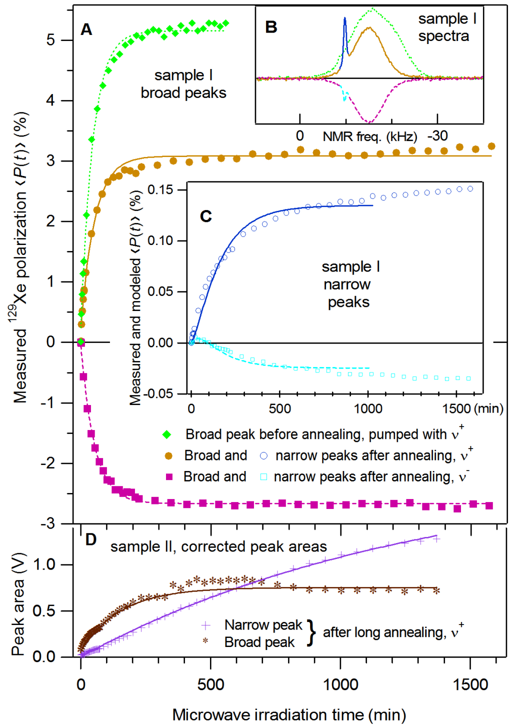

Figure 2: **A**: Polarization of the broad peaks (^{129}Xe in 1-propanol/trityl matrix) in sample I as a function of irradiation time *t* at ν^+=140.067 GHz (♦ well-mixed, ● annealed) and ν^-=140.166 GHz (■ annealed). The lines show exponential fits. **B**: ^{129}Xe spectra in sample I after 9 hours of DNP (well-mixed: ⋯ ν^+; annealed: — ν^+ and ---- ν^-). **C**: Polarization of the narrow peaks (pure Xe clusters) in sample I after annealing: ○ ν^+ and □ ν^-. Note the significantly lower polarizations compared to the broad peaks in A. The lines show a fit of the spherical cluster model to the combined ν^+ and ν^- data. **D**: Areas of the narrow (+) and broad (*) peaks in sample II at ν^+=140.0616 GHz. The lines are exponential fits to the data.

Results and Discussion: Figure 1 shows the early evolution of ^{129}Xe NMR spectra during DNP at ν^+ = 140.076 GHz (polarizing towards the *ground state* of the nuclear Zeeman system), and ν^- = 140.166 GHz (inducing population inversion of nuclear spins). Spectra were taken every 3 min after destroying the polarization by 2000 hard NMR pulses. Fig. 1A illustrates a case of well-mixed, homogeneous Xe/1-propanol/trityl solid-state mixture. The width of the only ^{129}Xe peak is consistent with broadening by uniformly distributed ^{1}H atoms of 1-propanol molecules. This peak directly responds to DNP, growing in the positive (negative) directions due to ν^+ (ν^-) irradiation. Fig. 1B shows the effect of annealing this sample for 4 hours at ~120 K. The broad ^{129}Xe peak is significantly narrower, indicating a reduced local density of surrounding ^{1}H. A second, very narrow ^{129}Xe peak exhibits width and chemical shift relative to the main peak consistent with almost pure xenon clusters. Initially, the narrow peak appears to grow in thermal direction regardless of microwave frequency. However, at some point (Fig. 2C, □) this tendency is overcome by DNP, inverting both peaks in the spectrum of Fig. 2B (----). This peculiar time evolution of ^{129}Xe spin polarization in pure-Xe clusters strongly suggests nuclear spin diffusion from the cluster boundary inward, while at the same time the T_1 process is relaxing the entire cluster towards its thermal equilibrium. Figure 1C shows the early DNP evolution of ^{129}Xe spectra in an extreme case of cluster formation in a different sample, after gradually warming it up to 120 K over 21 hours. The narrow peaks in Fig. 1C are narrower and much larger compared to Fig. 1B, and their response to DNP at ν^- is inverted starting from *t*=0. However, the most striking difference with sample I is in the late-time evolution of the ^{129}Xe signals (Fig. 2D). Even after 24 hours of DNP, ^{129}Xe magnetization in pure xenon clusters keeps growing, exceeding that of ^{129}Xe in the surrounding matrix. However, the average polarization remains fairly low. A simple model, incorporating spin diffusion and T_1 relaxation effects [3] was developed for a pure-xenon spherical cluster surrounded by a well-mixed xenon/1-propanol/trityl matrix, to fit the pure-xenon polarization data as a function of time *t* in Fig. 2C. The assumption of continuous ^{129}Xe polarization across the cluster boundary is not supported by the data (e.g., compare polarizations in Figs. 2A and 2C), nor is it plausible, given the poor spectral overlap of the two ^{129}Xe NMR peaks. Instead a polarization bottleneck at the cluster boundary was introduced, with the magnetization flux across the boundary proportional to the discontinuity in polarization: $\partial P/\partial r = \kappa(P_{inside} - P_{outside})$. The resulting model is rather insensitive to the cluster radius R, but shows a high sensitivity to the intrinsic sample temperature T and a fair sensitivity to T_1 in the clusters. A fit of this model to the data of Fig. 2C gives: $T_1 = 151 \pm 11$ min, $T = 2.8 \pm 0.1$ K, $R = 3.6 \pm 2$ μm, $\kappa = 0.5 \pm 0.2$ μm^{-1}.

Conclusion: We observed that achieving a homogeneous mixture requires vigorous mechanical stirring of liquid xenon and 1-propanol/ trityl-radical solution at 195 K, followed by rapid freezing below 90 K. Inefficient stirring and/or exposure to warm temperatures spontaneously creates pure xenon clusters in the solid-state glassy matrix, ultimately segregating ^{129}Xe spins from the unpaired electrons of the radical molecules. ^{129}Xe atoms inside the clusters cannot be pumped by the DNP process directly, relying instead on the nuclear spin diffusion through a chain of ^{129}Xe neighbors. This process is substantially restricted by the polarization bottleneck at the cluster boundaries and by significant overheating of the sample due to the microwaves.

References: [1] A. Comment *et al.*, Phys. Rev. Lett. **105**, 018104 (2010). [2] J.-H. Ardenkjaer-Larsen *et al.*, US patent 8,003,077, filed 2003, issued 2011.
[3] M. Pourfathi *et al.*, "Modelling T_1 and spin diffusion in pure-xenon clusters during ^{129}Xe DNP", ISMRM (2012).