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Supporting information for the paper

Transfer of SABRE-derived hyperpolarization to spin ½ heteronuclei

Andrey N. Pravdivtsev,[a,b] Alexandra V. Yurkovskaya,[a,b] Herbert Zimmermann,[c]
Hans-Martin Vieth,[d] Konstantin L. Ivanov[a,b]*

[a] *International Tomography Center, Siberian Branch of the Russian Academy of Science, Institutskaya 3a, Novosibirsk, 630090, Russia*
[b] *Novosibirsk State University, Pirogova 2, Novosibirsk, 630090, Russia*
[c] *Max-Planck-Institut für Medizinische Forschung, Jahnstrasse 29, Heidelberg, 69028, Germany*
[d] *Freie Universität Berlin, Arnimallee 14, Berlin, 14195, Germany*

* Corresponding author; e-mail: ivanov@tomo.nsc.ru; tel.: +7(383)330-8868; fax: +7(383)333-1399

This supporting information file contains the following items:

(A) 2D-HSQC spectra of SABRE complexes;

(B) SABRE spectra with the two SABRE catalysts used measured after polarization formation at high and low magnetic fields;

(C) description of the protocol for low-field relaxation measurements; experimental data for T_1-relaxation measurements at ultralow and high magnetic fields; calculation results for the magnetic field dependence of T_1-relaxation times in ^{15}N-labeled pyridine.

A. Characterization of the SABRE complexes by two-dimensional NMR spectroscopy

To assign signals in ^{15}N SABRE spectra we obtained two-dimensional HSQC spectra of our samples. Since NMR assignments are known for protons, analysis of the HSQC cross-peaks provides unambiguous assignment of the nitrogen signals. HSQC experiments have been done on thermally polarized spins.

HSQC spectra are shown for complexes with the IMes catalyst and with Crabtree's catalyst are shown in Figures 1S and 2S, respectively.

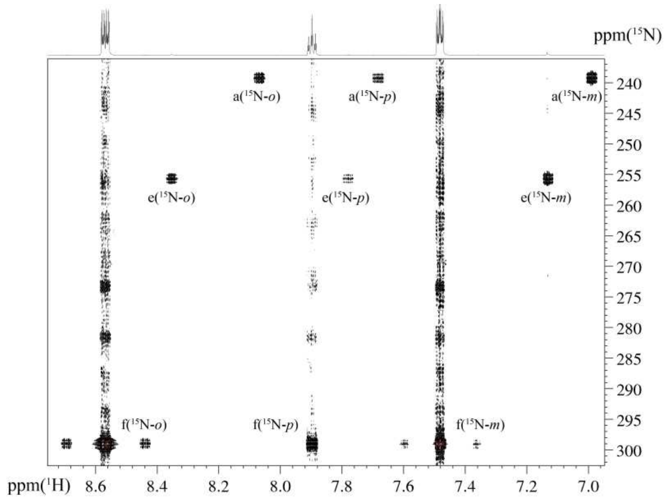


Figure 1S. HSQC spectrum of ^{15}NPy-h$_5$ and the IrImesCODCl complex in methanol after bubbling by H$_2$. The cross-peaks between ^{15}N and ^{1}H are assigned: f, e, a stand for the 'free', 'equatorial' and 'axial' pyridine (Py); *o*, *m*, *p* stand for the 'ortho', 'meta' and 'para' protons of Py.

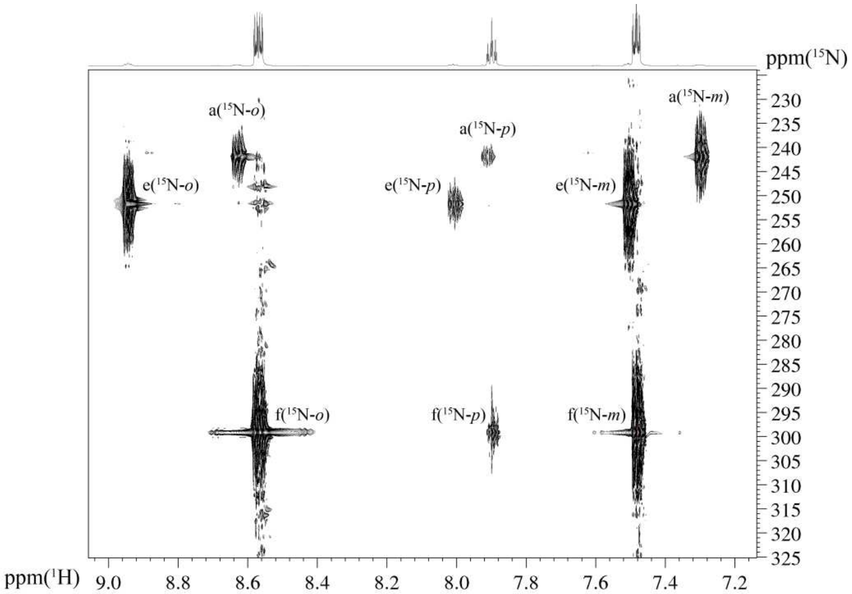


Figure 2S. HSQC spectrum of ^{15}NPy-h$_5$ with Crabtree's catalyst in MeOD after bubbling by H$_2$. The cross-peaks between ^{15}N and ^{1}H are assigned: f, e, a stand for the 'free', 'equatorial' and 'axial' pyridine (Py); *o*, *m*, *p* stand for the 'ortho', 'meta' and 'para' protons of Py.

B. SABRE spectra

Here we show supplementary SABRE spectra for protons and nitrogen with the two SABRE catalysts used measured after polarization formation at high and low magnetic fields.

Proton SABRE spectra obtained with the two SABRE catalysts using different experimental protocols are shown in Figures 3S and 4S. ^{15}N-SABRE spectra obtained with Crabtree's catalyst using different experimental protocols are shown in Figure 5S and 6S.

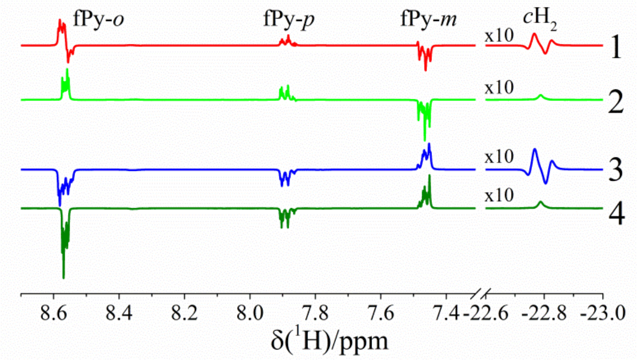


Figure 3S. ^{1}H NMR spectra of ^{15}NPy (70 mM) with IrImes (2 mM). Spectra were measured using 45° RF-pulse after the preparation of hydrogenation at Earth magnetic field (traces 1 and 2) and in µ-box (traces 3 and 4). Spectra 2 and 4 were measured using ^{15}N decoupling.

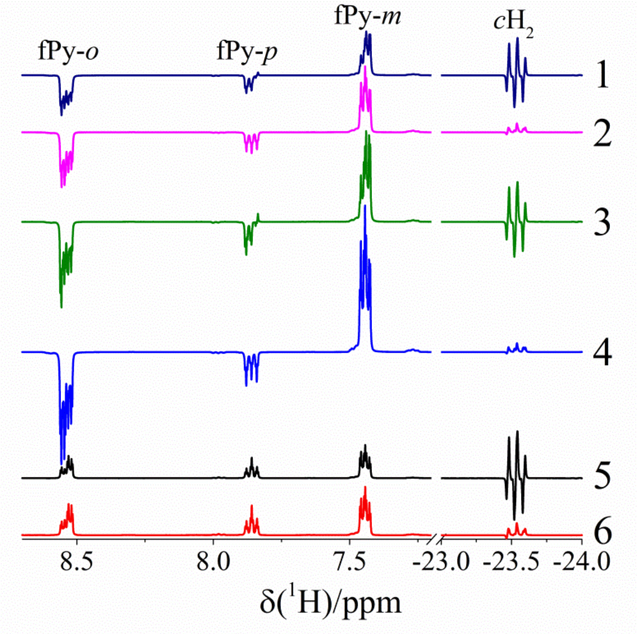


Figure 4S. ^{1}H NMR spectra of ^{15}NPy (70 mM) with Crabtree's catalyst (2 mM). Spectra 1, 3 and 5 were measured using 45° RF-pulse and spectra 2,4 and 6 were measured using 90°-pulses. Polarization was prepared in µ-box (traces 1 and 2), at the Earth magnetic field (traces 3 and 4) and at high field of NMR spectrometer $B_0 = 9.4$ Tesla (traces 5 and 6).

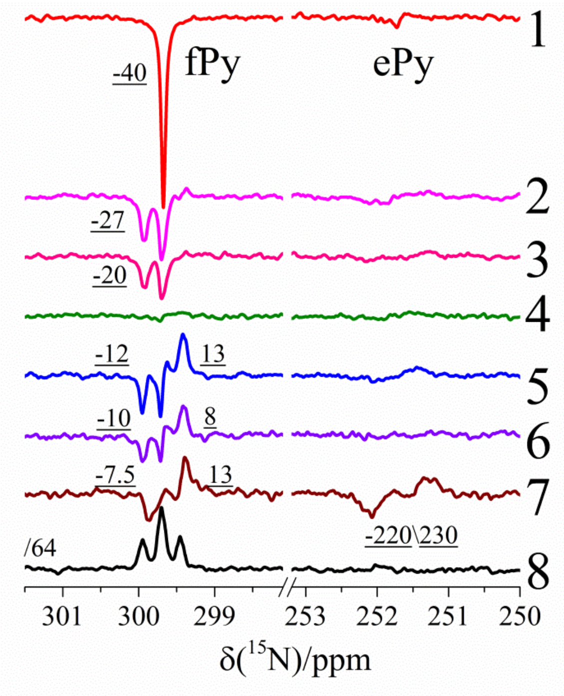


Figure 5S. Nitrogen SABRE spectra obtained for solutions of ^{15}NPy (70 mM) with 2 mM Crabtree's catalyst. Ultralow-field SABRE spectra are detected by a 90^{o} pulse with ^{1}H decoupling (trace 1) and without decoupling (trace 2) and also with a 45^{o} pulse (trace 3). Earth-field SABRE spectra are detected by a 90^{o} pulse with ^{1}H decoupling (trace 4) and without decoupling (trace 5) and by a 45^{o} pulse (trace 6). High-field SABRE spectrum is detected by a 45^{o} pulse (trace 7); the corresponding NMR spectrum is shown by trace 8, which has been obtained using a 90^{o} pulse and 2048 acquisitions (17.2 hours of acquisition); spectrum 8 is also divided by a factor of 64. Underlined numbers stand for the enhancement of the corresponding lines.

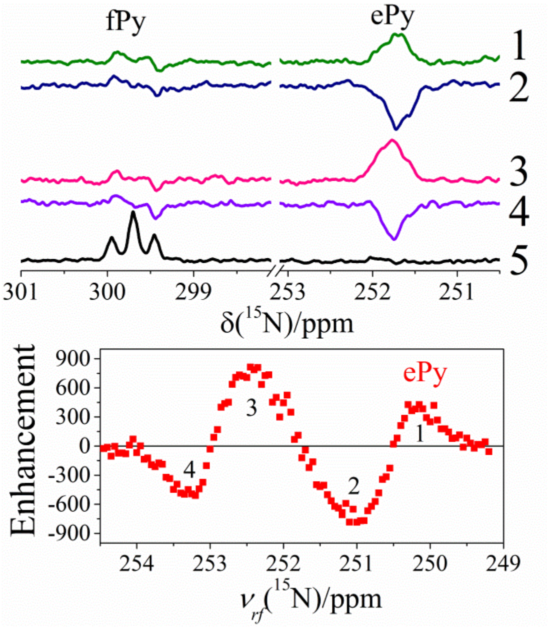
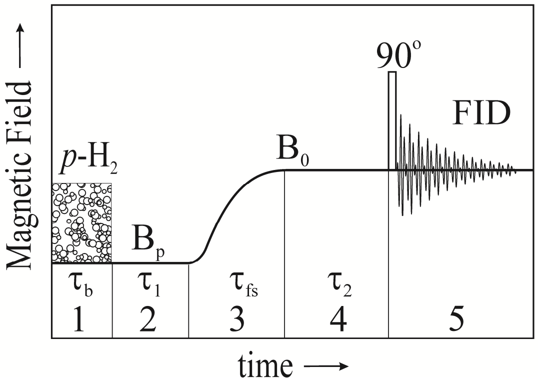


Figure 6S. SABRE formation from ^{1}H to ^{15}N by adiabatic passage through an LAC. Here the mixture of 2 mM Crabtree's catalyst and 70 mM ^{15}N-Py in MeOD was used. (top) SABRE spectra obtained using the following parameters of the two RF-fields: v_1(^{1}H)= 75 Hz, v_{rf}(^{1}H)= -3.517 ppm, v_1^o(^{15}N)= 80 Hz, τ_{off} = 0.7 s and ν_{rf}(^{15}N) = 250.15 ppm (trace 1), 251 ppm (trace 2), 253.35 ppm (trace 3), 254.45 ppm (trace 4); the amplitude of the RF$_{\mathrm{N}}$ field was linearly reduced to zero. The corresponding NMR spectrum shown by trace 5 has been detected using a 90^{o} pulse and 2048 acquisitions (17.2 hours of acquisition); spectrum 8 is also divided by a factor of 64. (bottom) SABRE-derived enhancement for the ePy signal as a function of ν_{rf}(^{15}N) in the range between 249 and 254.5 ppm.

C. ^{15}N T_1-relaxation measurements

Experiments were performed using the experimental protocol shown in Scheme 1S.



Scheme 1S. Scheme of measuring lifetime of hyperpolarization at low (B_p) and high (B_0) magnetic fields. **Stage 1**: hyperpolarization is generated by means of SABRE at the magnetic field B_p. **Stage 2**: spins relax to thermal equilibrium at the field B_p during the time period τ_1. **Stage 3**: the sample is manually transferred from the field B_p to the detection field B_0 during the time period τ_{fs}~5 s. **Stage 4**: free evolution at the field B_0. **Stage 5**: Measuring the Free Induction Decay (FID) after application of a 90° RF-pulse. When τ_1 is varied and $\tau_2 = \text{const}$ one can measure hyperpolarization lifetime at the low field B_p. When τ_2 is varied and $\tau_1 = \text{const}$ one can measure the lifetime of polarization at the high field B_0. Low magnetic fields B_p were accessed by placing the sample inside a μ-metal box.

Using this protocol we have measured the relaxation kinetics of SABRE-derived polarization of shown in Figure 7S.

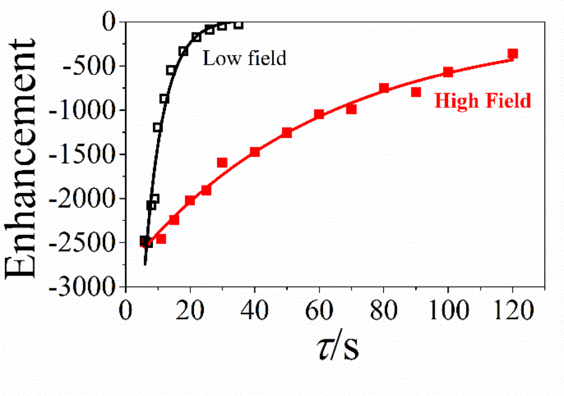


Figure 7S. ^{15}N relaxation kinetics measured in ^{15}NPy at $B_0 = 9.4$ Tesla (red filled squares) and at ultralow B_p (black open squares). The experiment was carried out according to the protocol shown in Scheme 1S. Prior to the measurement, polarization was created inside the μ-box and during a time period of 5 s inserted into the NMR spectrometer and measured. Data are fitted by exponential decay functions (solid lines of the corresponding color) yielding the decay times $T = 6 \pm 1$ s and $T = 60 \pm 8$ s in the case of low and high field, respectively.

This behavior of relaxation can be modeled using an approach developed in our previous works [1], which predicts that strongly coupled spins tend to relax with a common T_1-relaxation time. Transition from weak to strong coupling upon decreasing the magnetic field thus conditions the field dependence of relaxation. In our case, strong coupling of protons and nitrogens means that the difference in their NMR frequencies, $(\nu_H - \nu_N)$, is smaller than or comparable to the proton-nitrogen interaction, J_{NH}; otherwise the weak coupling regime is operative. The calculation results are shown in Figure 6S.

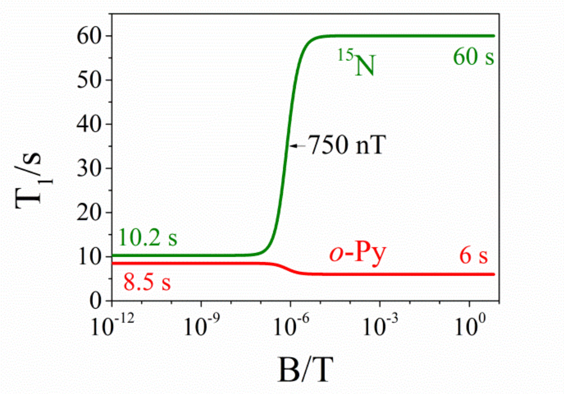


Figure 8S. Theoretical field dependence of T_1-relaxation times for a model three-spin system of the type A_2X; here A_2 model the two *ortho*-protons of pyridine (*o*-Py) and X is ^{15}N nucleus of pyridine. The calculation was performed using the following NMR parameters: J(*o*-Py$_1$,*o*-Py$_2$)= -1 Hz, J(*o*-Py,^{15}N)= 9.94 Hz – J-couplings; T_1^{HF}(*o*-Py)= 6 s, T_1^{HF}(^{15}N)= 60 s – high-field relaxation times. The Redfield theory was used in the same way as previously [1]; relaxation of spins due to local fluctuating fields was considered.

References

[1] K. L. Ivanov, A. V. Yurkovskaya, H.-M. Vieth. «High resolution NMR study of T_1 magnetic relaxation dispersion. I. Theoretical considerations of relaxation of scalar coupled spins at arbitrary magnetic field», *J. Chem. Phys.*, **129** (23), 234513 (2008) **DOI:** 10.1063/1.3040272.