X International Voevodsky Conference "Physics and Chemistry of Elementary Chemical Processes" (VVV-2022)

2022 Novosibirsk 05-09 Sep 2022

Application an antiphase-to-inphase signal shape conversion to parahydrogen-induced polarization for operando MRI study of a heterogeneous reactor

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[2] Novosibirsk State University

[3] Boreskov Institute of Catalysis SB RAS

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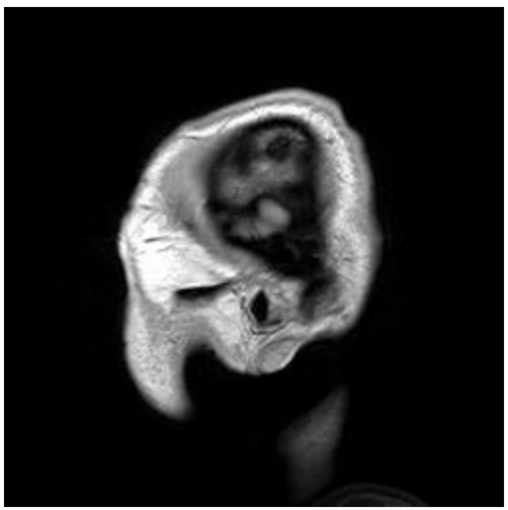
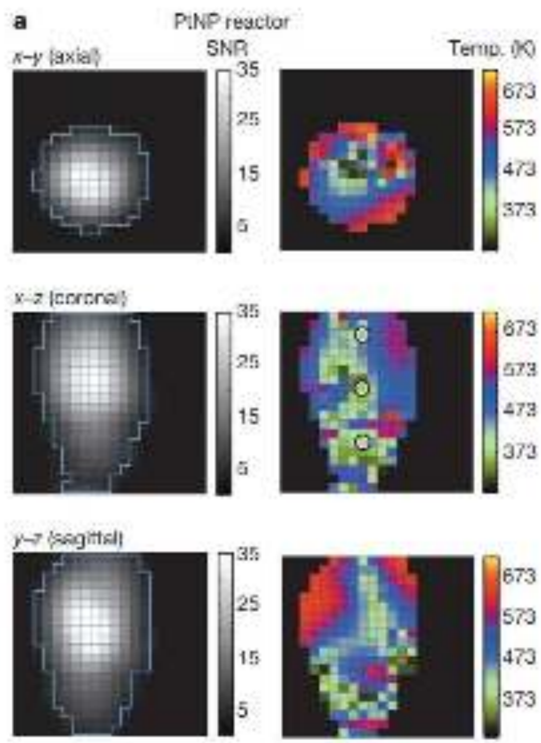
Relevance

Functional MRI

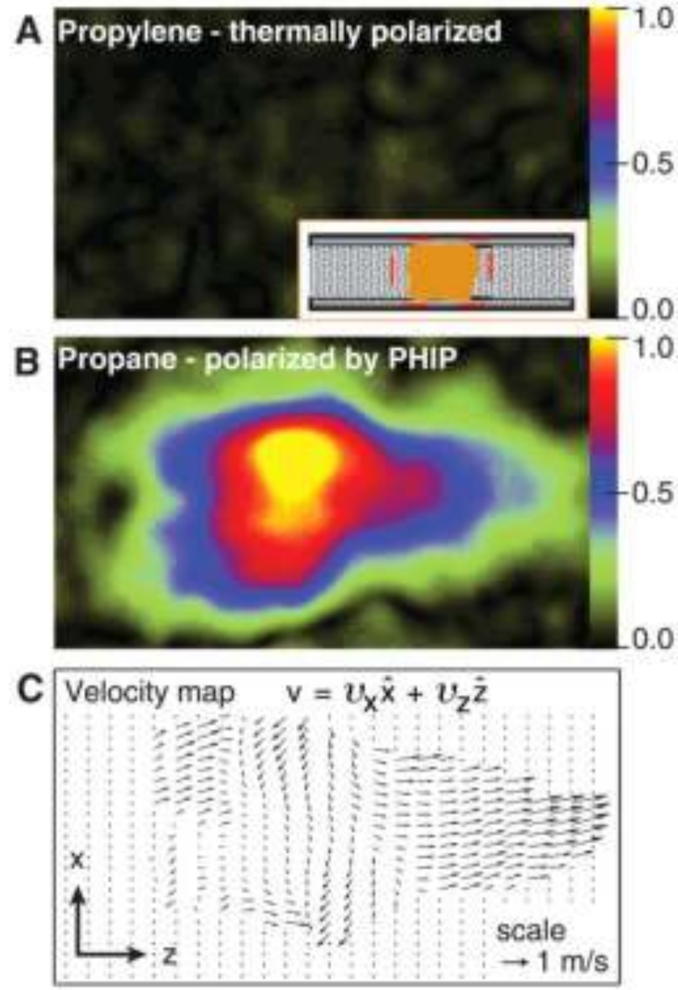


Propane Temperature Distribution Maps in a Heterogeneous Hydrogenation Reactor



Thermal maps of gases in heterogeneous reations
N.N. Jarenwattananon, S. Gloggler, et al, Nature, 2013
DOI: 10.1038/nature12568

Packed Propane Catalyst Distribution and Flow Velocity Map

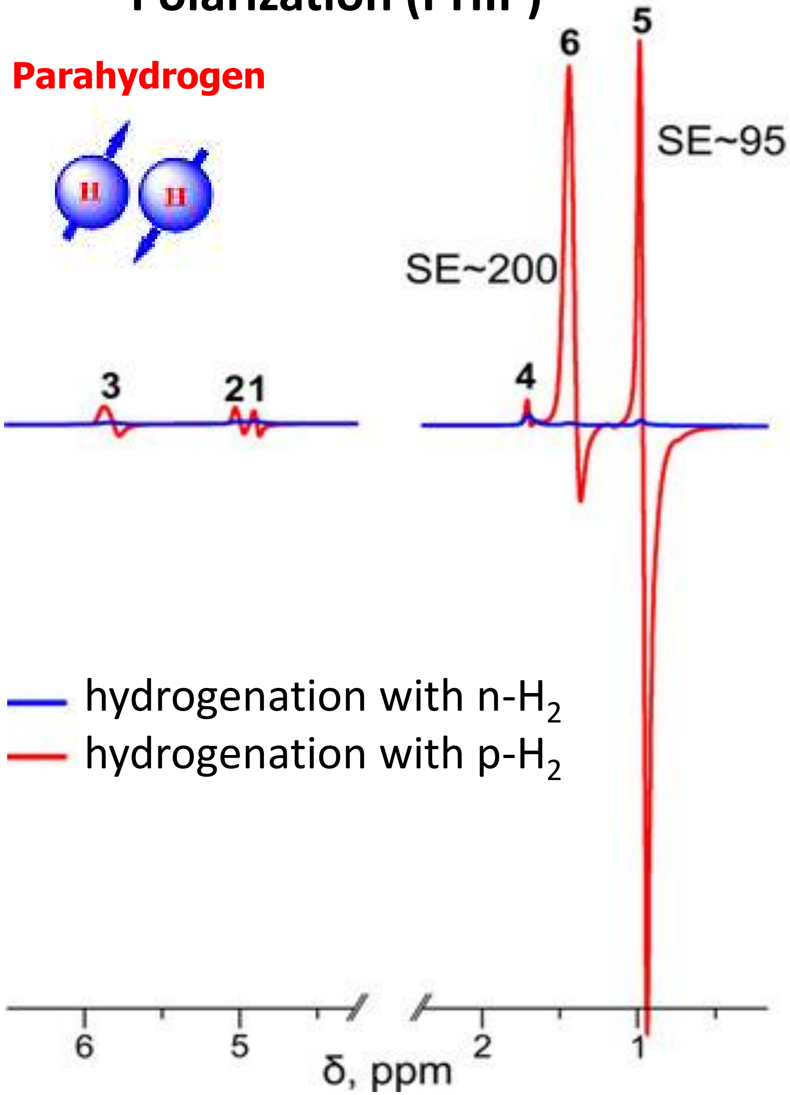


NMR Imaging of Catalytic Hydrogenation in Microreactors with the Use of para-Hydrogen
L.S. Bouchard, S. R. Burt, et al, Science, 2008
DOI: 10.1126/science.1151787

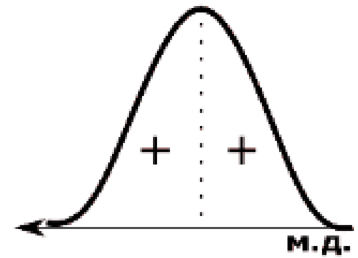
Low sensitivity problem

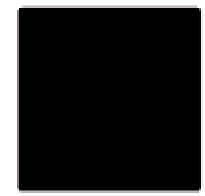
Parahydrogen-Induced Polarization (PHIP)

Parahydrogen

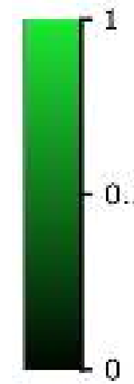


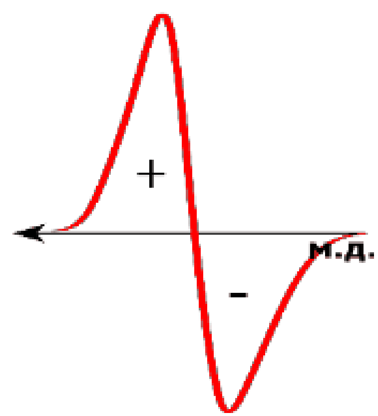
MRI with using PHIP

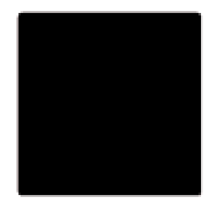




Signal intensity per pixel





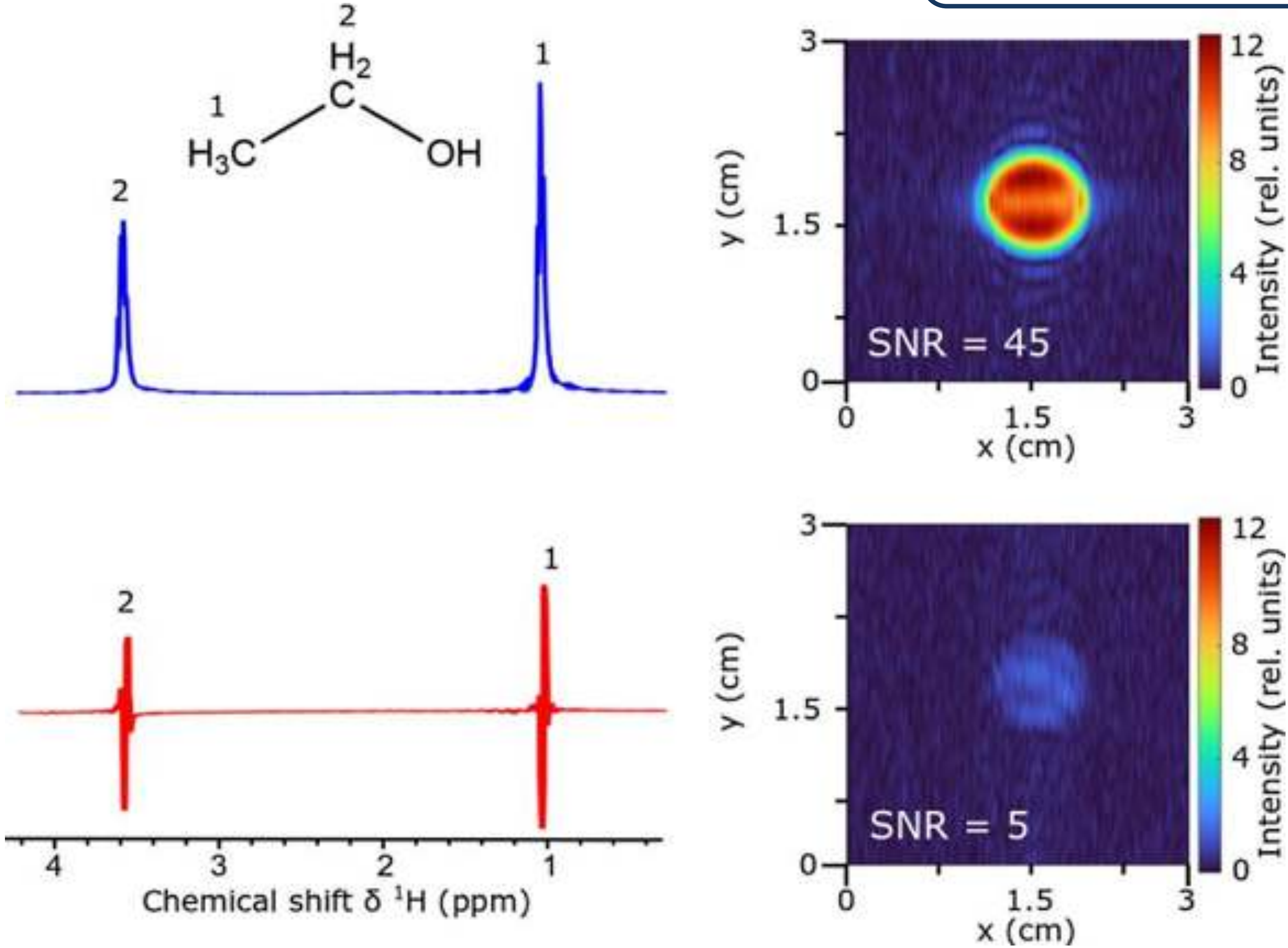


Signal intensity per pixel

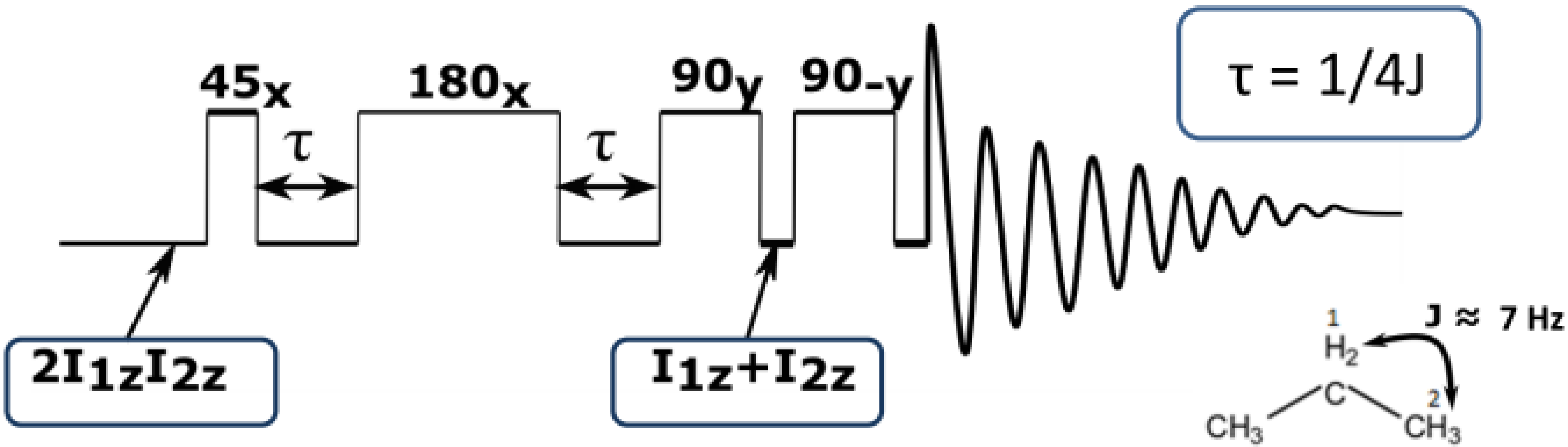
Mechanistic in situ investigation of heterogeneous hydrogenation over Rh/TiO2 catalysts: selectivity, pairwise route and catalyst nature
E. V. Pokochueva, D. B. Burueva, et al., Faraday Discuss., 2021, DOI: 10.1039/C9FD00138G

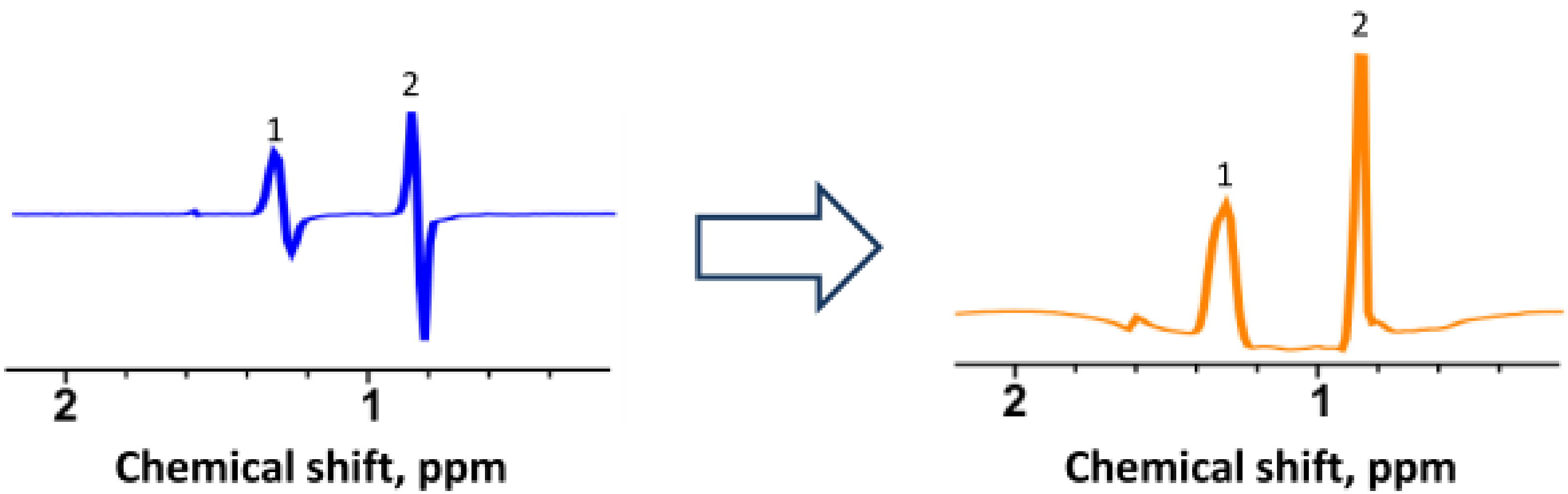
Effect of the antiphase signal on the MRI

10% $C_2H_5OH + D_2O$

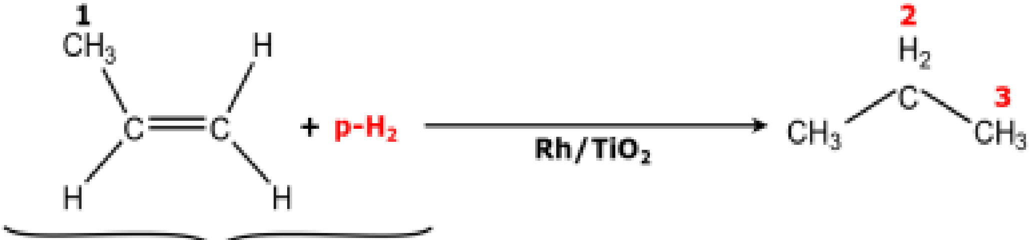


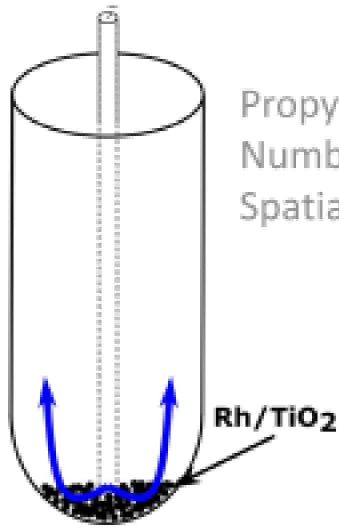
Conversion of antiphase signals



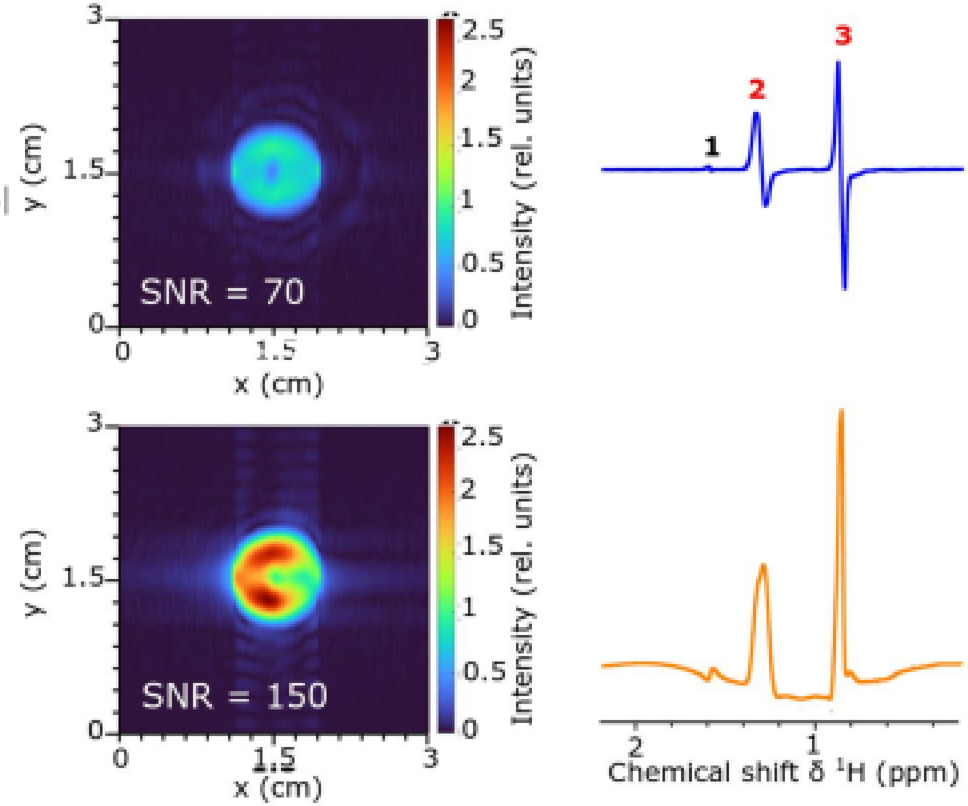


2D MRI of propane



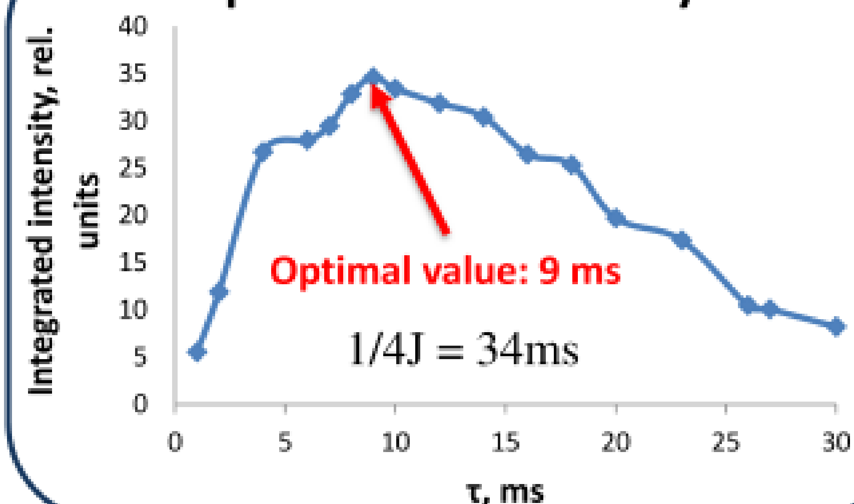


Propylene: parahydrogen = 1:4
Number of averages: 128
Spatial resolution:
0.006×0.194 cm^2/pixel



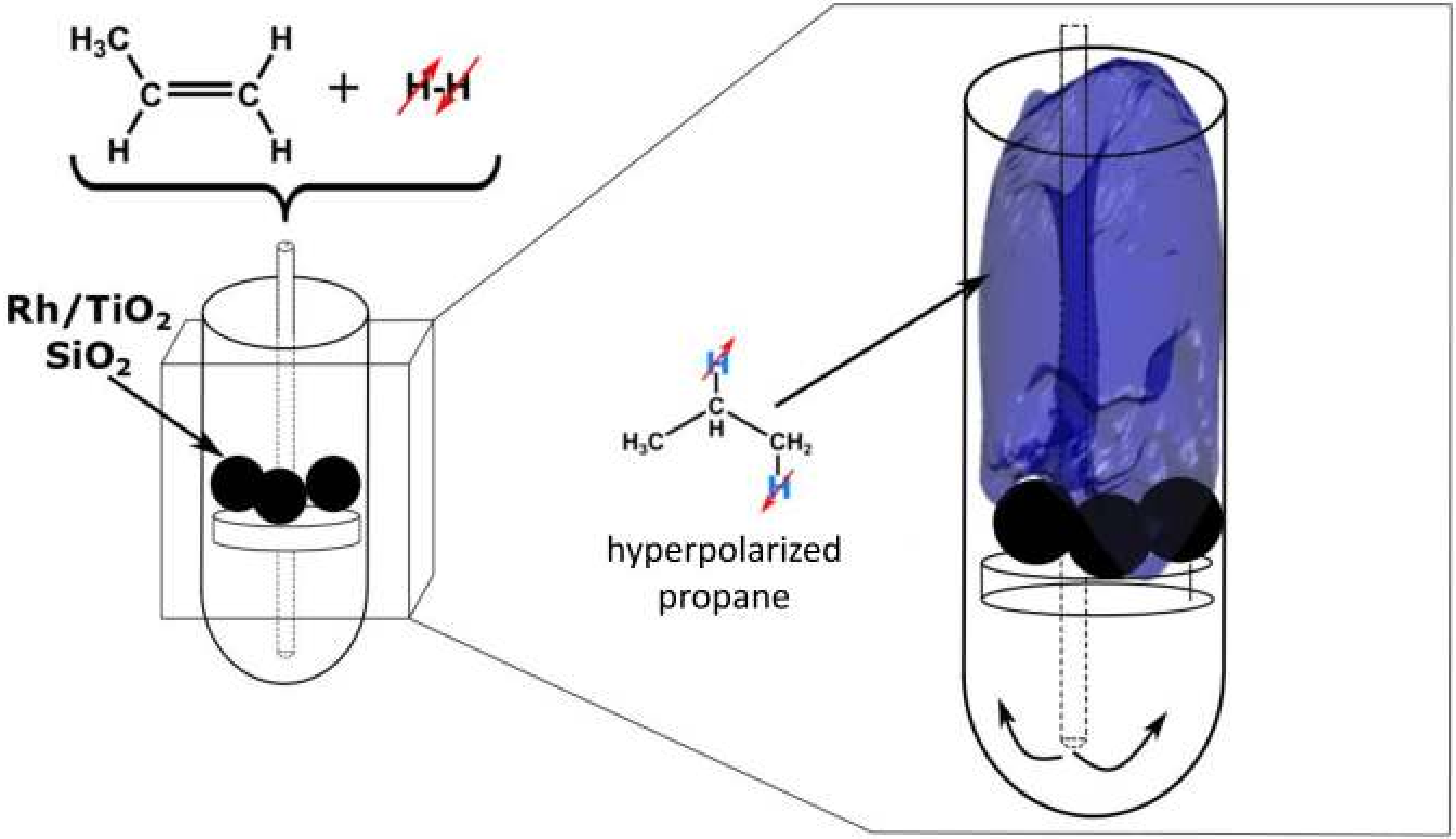
SNR is 2 times more!

Optimization of τ delay



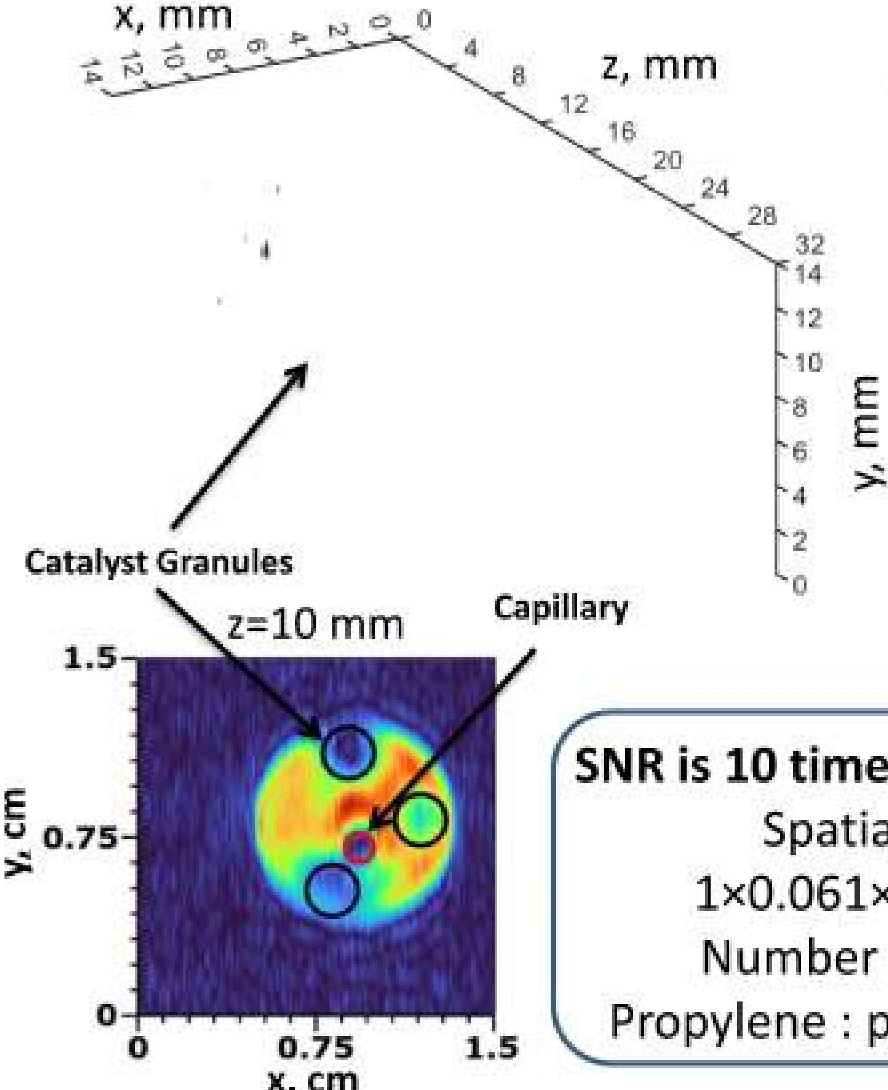
3D MRI of propane

Reaction conditions:
1 atm, 25°C

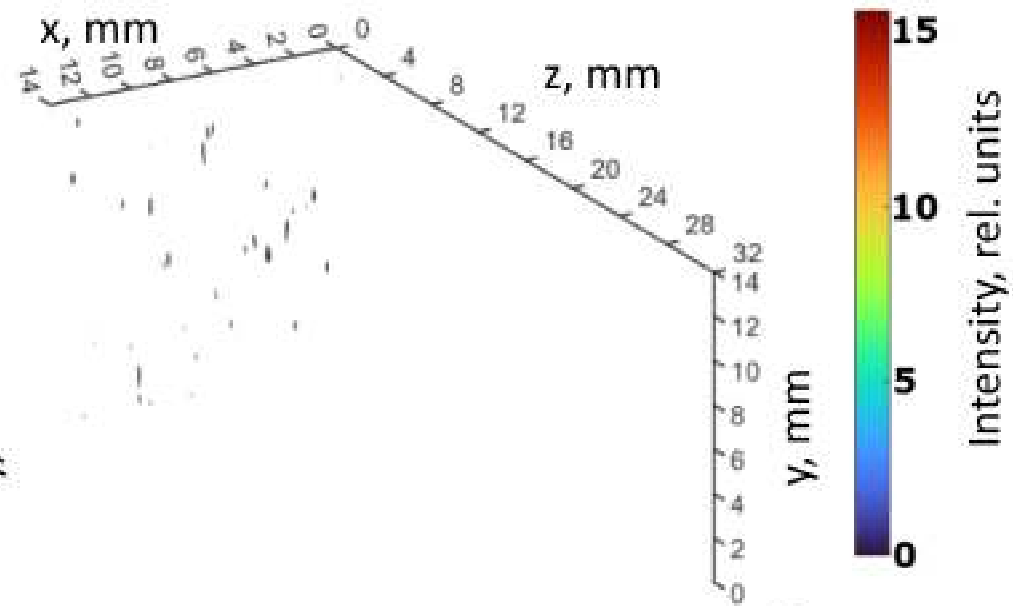


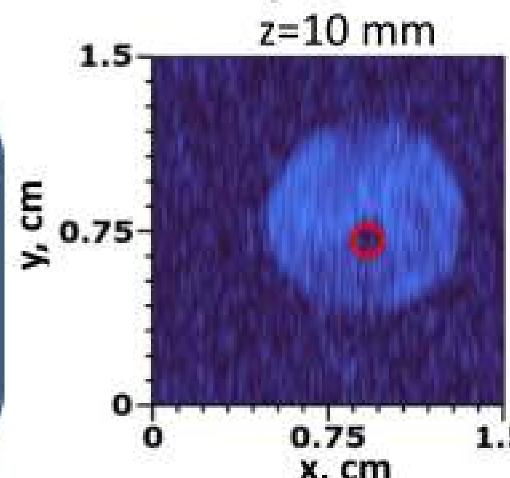
3D MRI of propane

Inphase



Antiphase





SNR is 10 times greater in layer 17!

Spatial resolution:

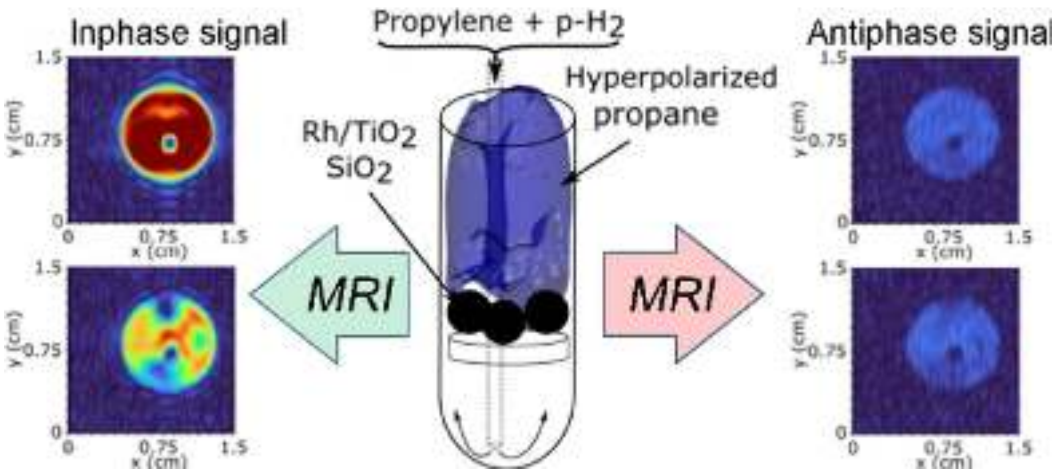
1×0.061×0.97mm3/pixel

Number of averages: 16

Propylene : parahydrogen = 1 : 4

Conclusions:

- it was shown the necessity of converting the antiphase signal of PHIP experiments in a strong magnetic field into an in-phase form in MRI experiments for the most effective use of the high signal intensity obtained due to hyperpolarization for visualizing the products of the heterogeneous hydrogenation reaction in the gas phase;
- it was first time demonstrated that the combined use of the PHIP method in a strong magnetic field and a pulse sequence that converts an antiphase NMR signal into an in-phase one makes it possible to visualize the position of heterogeneous catalyst granules inside a model reactor in a gas-phase hydrogenation reaction by MRI.



Getting the Most out of Parahydrogen-Induced Signal Enhancement for MRI of Reacting Heterogeneous Systems
Elizaveta S. Kononenko, Alexandra I. Svyatova, Ivan V. Skovpin, Larisa M. Kovtunova, Evgeny Yu. Gerasimov, and Igor V. Koptyug,
The Journal of Physical Chemistry C
DOI: 10.1021/acs.jpcc.2c05218

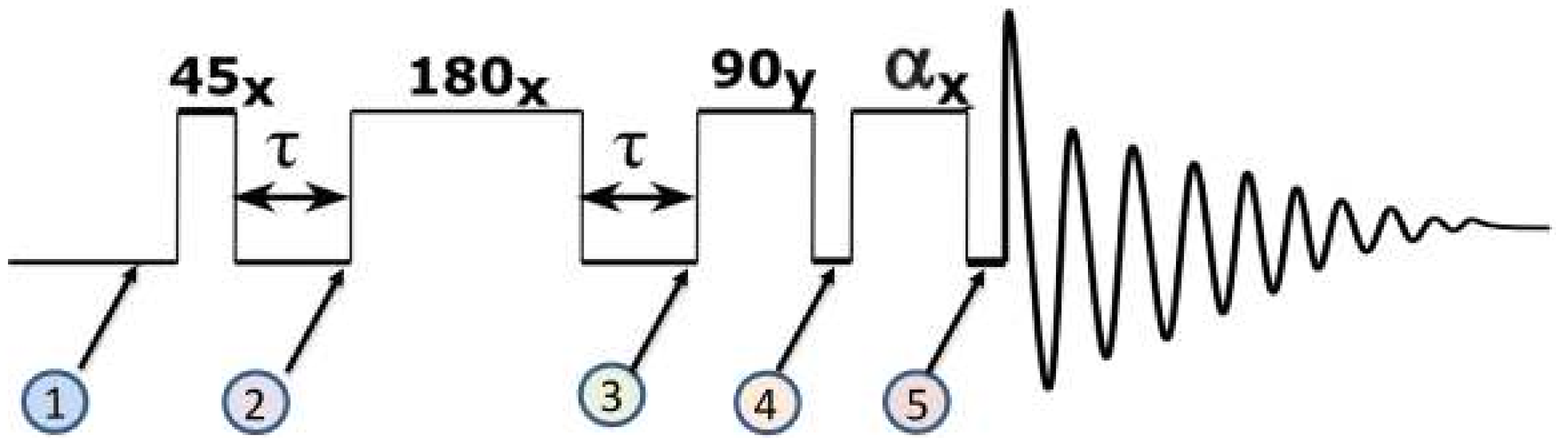
Acknowledgment

Laboratory of Magnetic Resonance Microimaging International Tomography Center SB RAS

Thank you for your attention!

Additional slides

Conversion of antiphase signals



1

2

$$2\hat{I}_z\hat{S}_z \xrightarrow{(45^\circ)_{\hat{I}_x};(45^\circ)_{\hat{S}_x}} -\hat{I}_y\hat{S}_z - \hat{I}_z\hat{S}_y + \hat{I}_z\hat{S}_z + \hat{I}_y\hat{S}_y;$$

non-observable terms

3

$$-\hat{I}_y\hat{S}_z - \hat{I}_z\hat{S}_y \xrightarrow{(2\pi J\tau)_{\hat{I}_z\hat{S}_z}} \xrightarrow{(180^\circ)_{\hat{I}_x};(180^\circ)_{\hat{S}_x}} \xrightarrow{(2\pi J\tau)_{\hat{I}_z\hat{S}_z}} (\hat{I}_y\hat{S}_z - \hat{I}_z\hat{S}_y)\cos(2\pi J\tau) + \frac{1}{2}(\hat{I}_x + \hat{S}_x)\sin(2\pi J\tau).$$

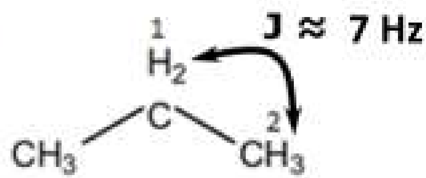
cos(2πJτ)=0 => τ = 1/4J

4

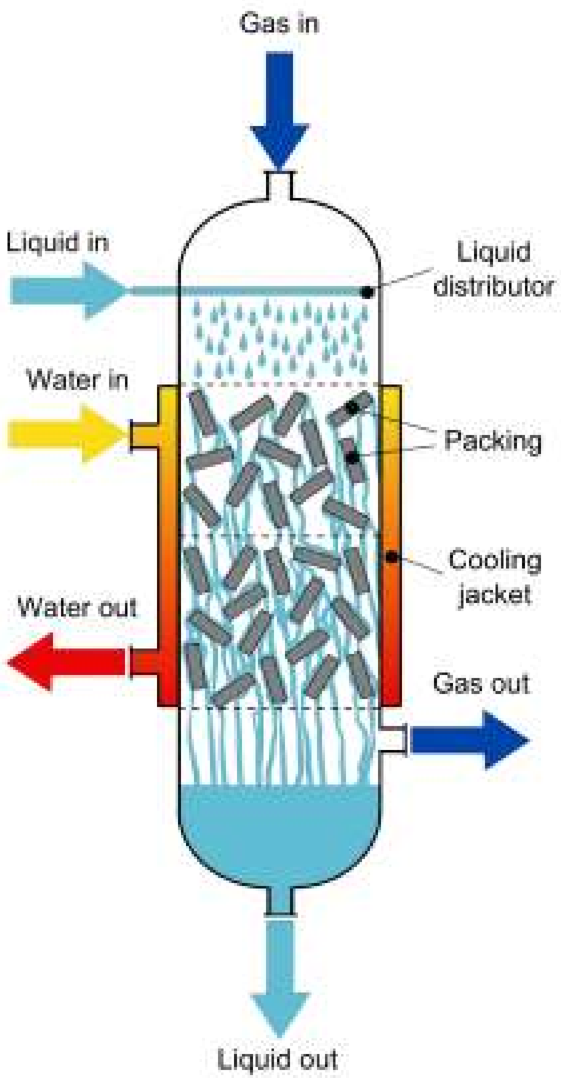
$$\frac{1}{2}(\hat{I}_x + \hat{S}_x) \xrightarrow{(90^\circ)_{\hat{I}_y};(90^\circ)_{\hat{S}_y}} \frac{1}{2}(-\hat{I}_z - \hat{S}_z)$$

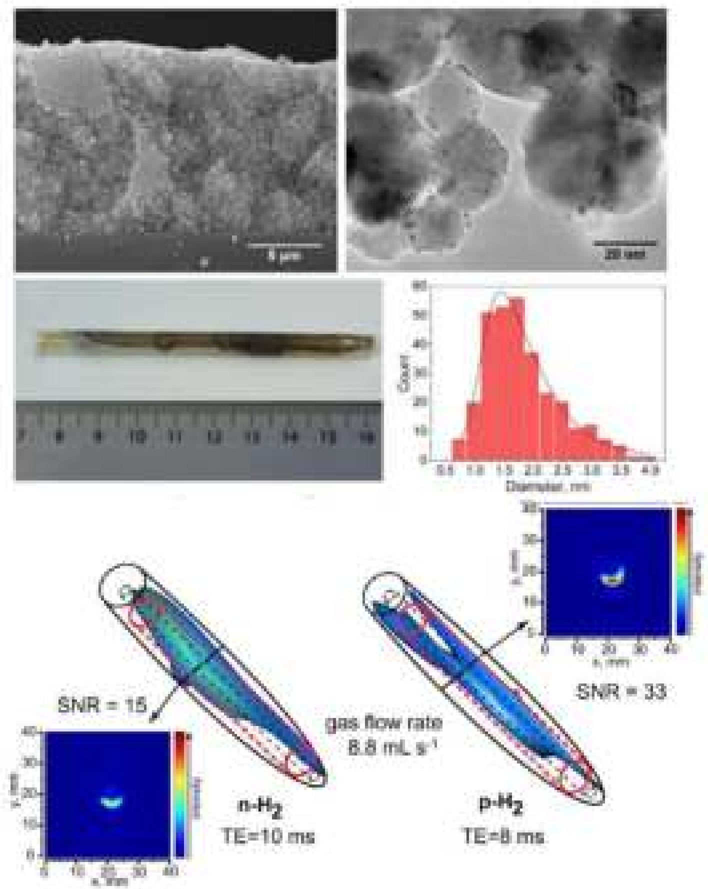
5

$$\xrightarrow{(\alpha^\circ)_{\hat{I}_x};(\alpha^\circ)_{\hat{S}_x}} \frac{1}{2}(-\hat{I}_z - \hat{S}_z)\cos(\alpha) + \frac{1}{2}(\hat{I}_y + \hat{S}_y)\sin(\alpha).$$



MRI compatible catalytic reactors





K. V. Kovtunov *et al.*, "Robust In Situ Magnetic Resonance Imaging of Heterogeneous Catalytic Hydrogenation with and without Hyperpolarization," *ChemCatChem*, vol. 11, no. 3, pp. 969–973, 2019.

Hyperpolarization techniques

Thermally equilibrium population:

$$\frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx 10^{-4} - 10^{-5}$$

Spin-Exchange Optical Pumping (SEOP)

- Complex and expensive equipment
- Low reactivity of hyperpolarized gases

Dynamic Nuclear Polarization (DNP)

- Complex and expensive equipment
- The need to introduce a paramagnetic substance into the sample

Signal Amplification By Reversible Exchange (SABRE)

- No change structure of matter

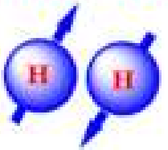
Parahydrogen Induced Polarization (PHIP)

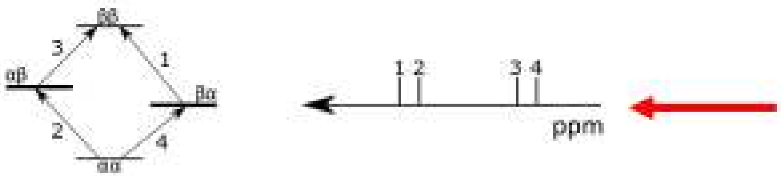
- Polarization transfer from parahydrogen nuclei to during catalytic hydrogenation
- Doesn't require complicated and expensive equipment

Parahydrogen Induced Polarization (PHIP)

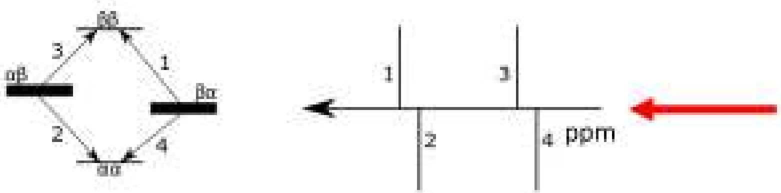
- I=0 for para-H_2 and thus it is NMR inactive! (i.e. it's an A_2 spin system)
- Need magnetically inequivalent H's, use a chemical reaction (AX spin system)

Parahydrogen



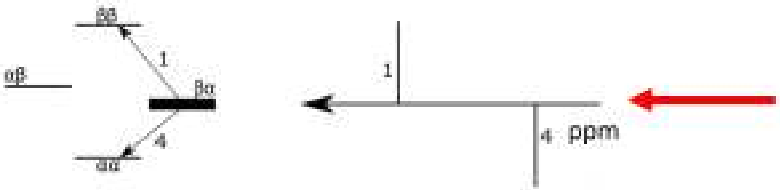


Hydrogenation with normal hydrogen



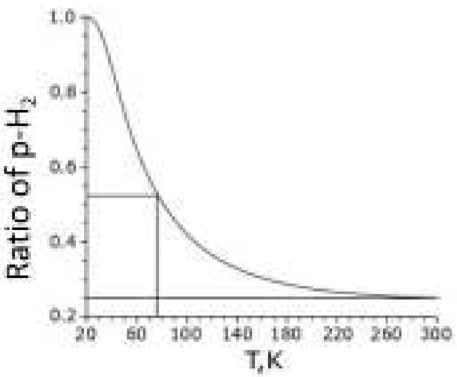
PASADENA

$(|\gamma \Delta\delta B_0| \gg |2\pi J|)$



ALTADENA

$(|\gamma \Delta\delta B_0| < |2\pi J|)$



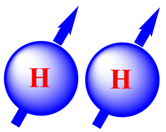
Parahydrogen

$$|T_{-1}\rangle = |\beta\beta\rangle$$

$$|T_0\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle + |\beta\alpha\rangle\right)$$

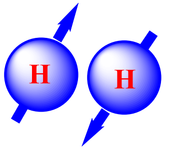
$$|T_{+1}\rangle = |\alpha\alpha\rangle$$

Triplet state → orthohydrogen

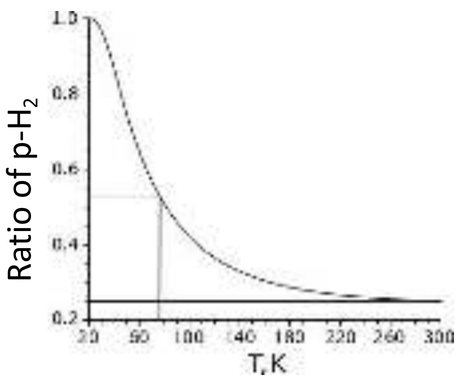


$$|S_0\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle - |\beta\alpha\rangle\right)$$

Singlet state → parahydrogen



Normal hydrogen: 75% ortho-H_2 : 25% para-H_2

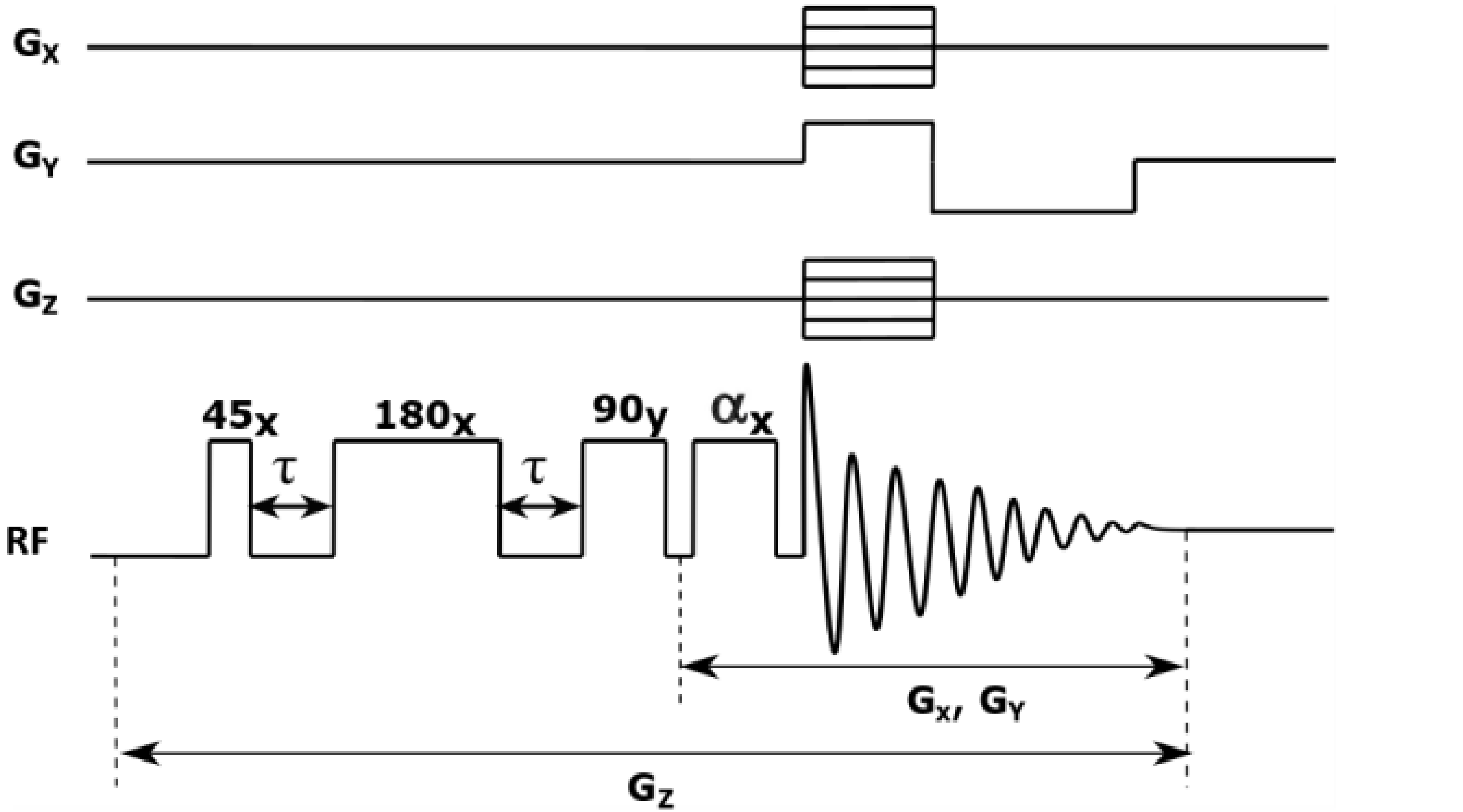


$$\frac{N_{ortho}(T)}{N_{para}(T)} = \frac{3\sum_{j=1,3,\ldots}(2j+1)e^{-j(j+1)\theta_{rot}/T}}{1\sum_{j=0,2,\ldots}(2j+1)e^{-j(j+1)\theta_{rot}/T}},$$

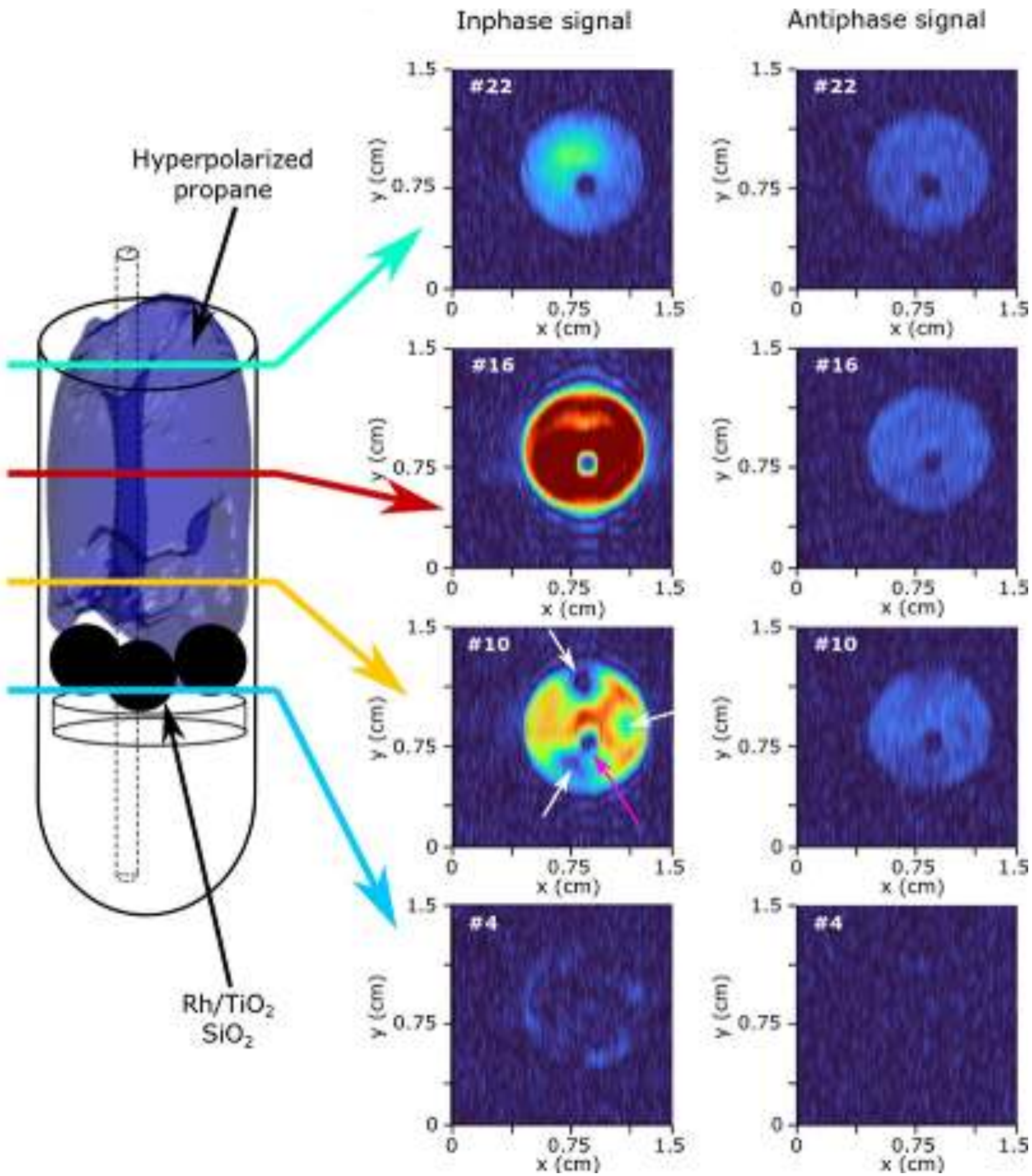
Parahydrogen enrichment

- low temperature 77K → 50% ortho : 50% para
- a suitable catalyst (FeOOH , charcoal..)
- Can be stored at RT without back conversion for a long time

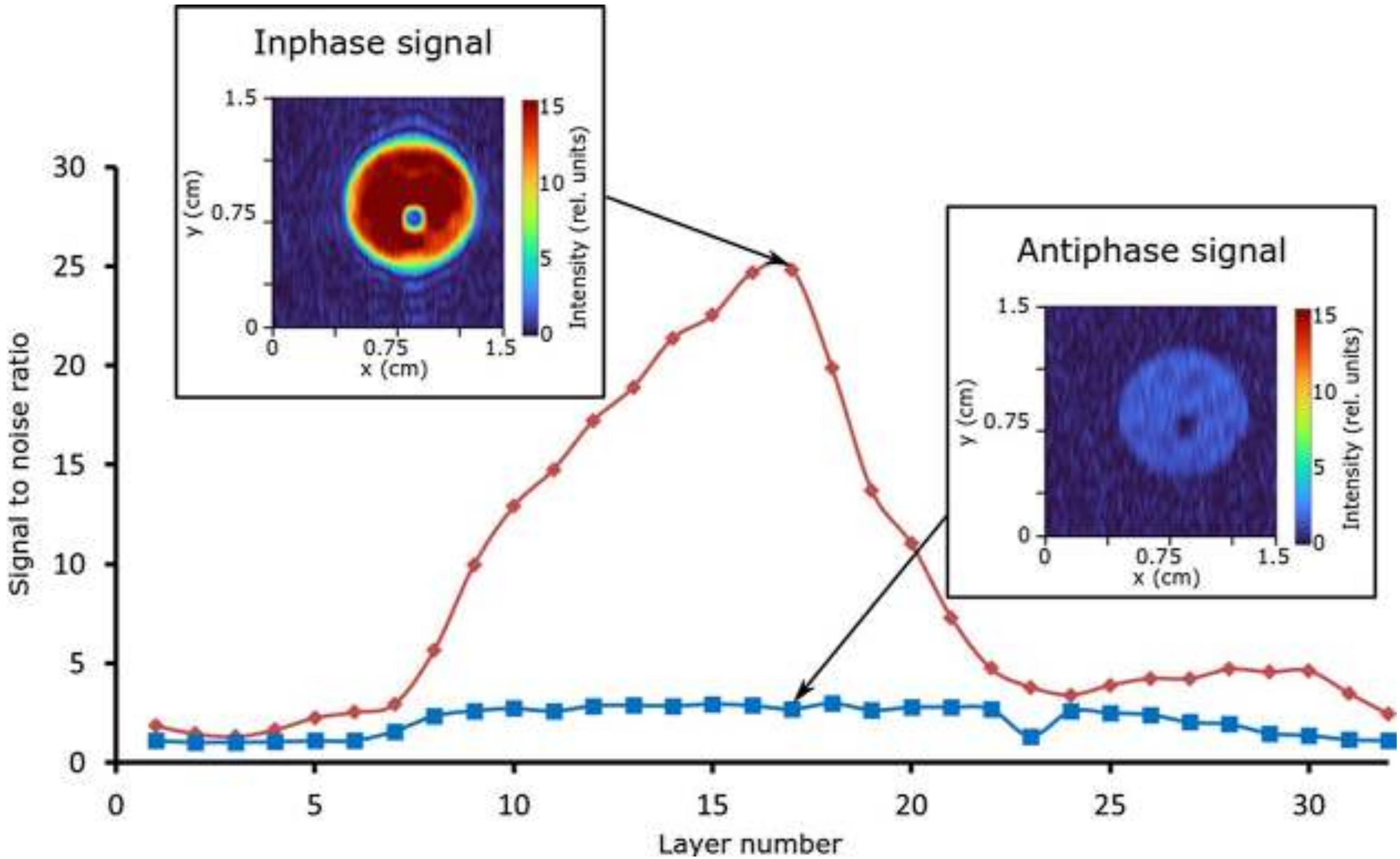
Conversion of antiphase signals



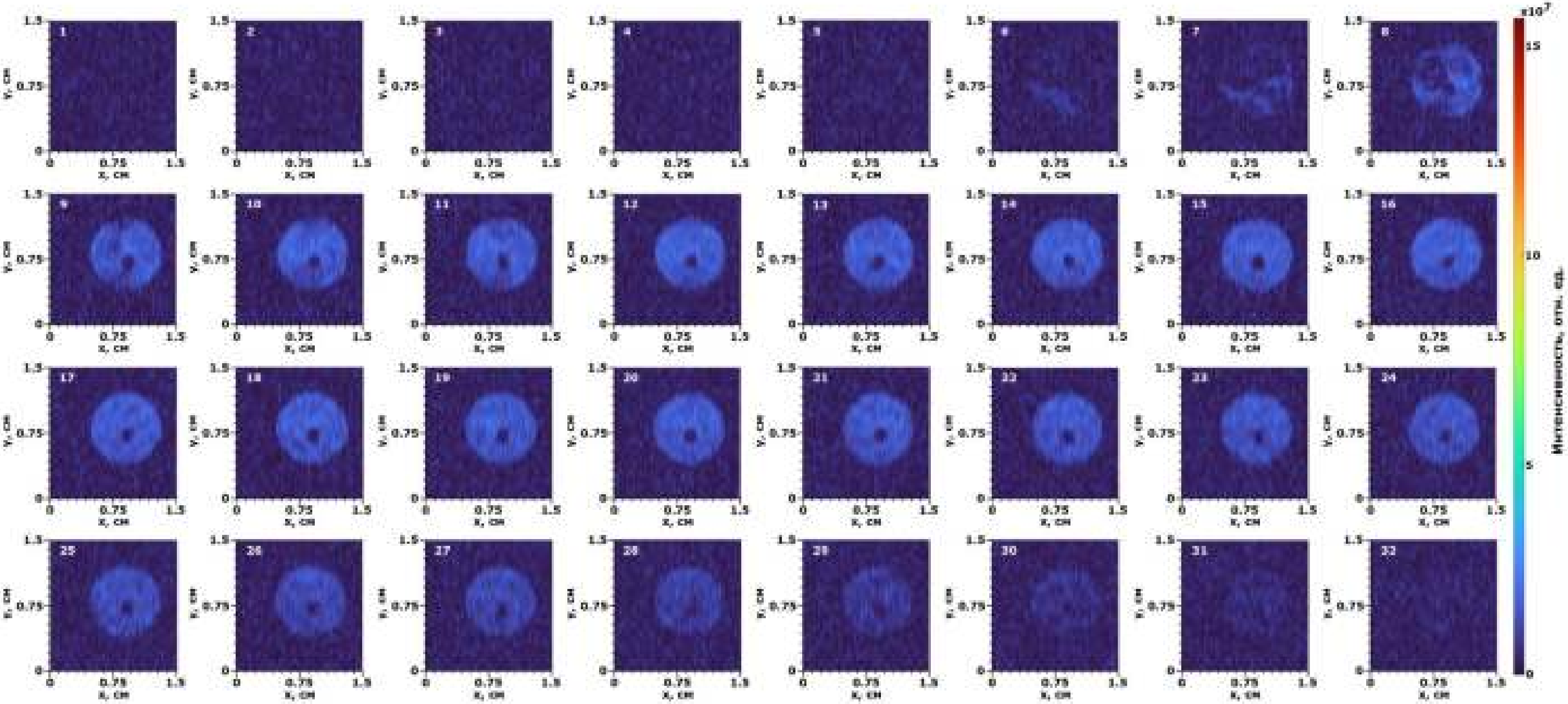
3D MRI of hyperpolarization propane



Dependence of the SNR on the layer number of the 3D MR image



Slices of a 3D ^{1}H MR image of hyperpolarized propane obtained without a pulse sequence converting an antiphase signal to inphase form



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