

Zero- to ultra-low field NMR spectroscopy of azobenzene hyperpolarized by SABRE

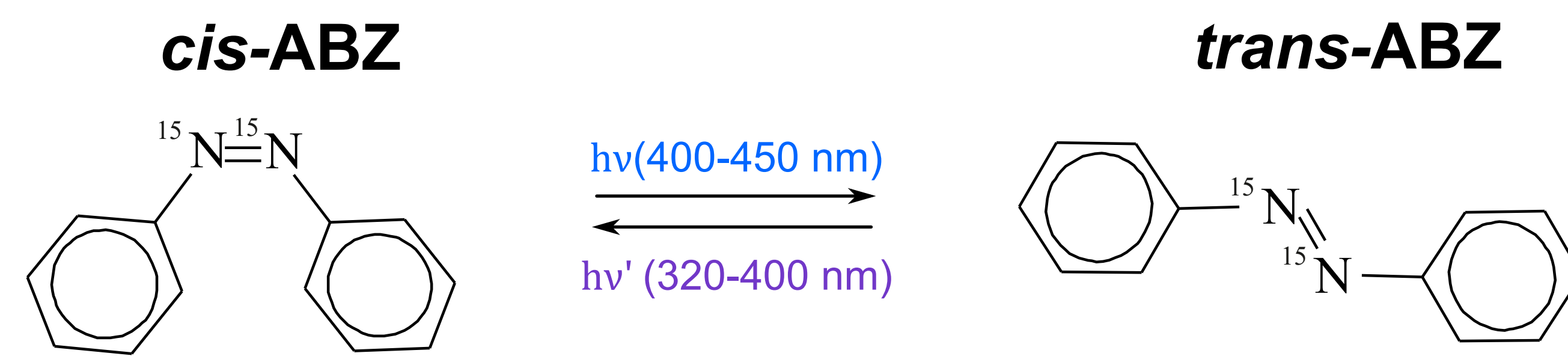
Kirill Sheberstov¹, Vitaly Kozinenko^{2,3}, John W. Blanchard¹, Konstantin Ivanov^{2,3}, Alexey Kiryutin^{2,3}, Hans-Martin Vieth^{2,4}, Herbert Zimmermann⁵, Dmitry Budker^{1,6}, Alexandra Yurkovskaya^{2,3}

1. Helmholtz-Institut Mainz, Johannes Gutenberg-Universität, 55128 Mainz, Germany
 2. International Tomography Center, Siberian Branch of the Russian Academy of Science, Novosibirsk 630090, Russia
 3. Novosibirsk State University, Novosibirsk, 630090, Russia

4. Freie Universität Berlin, Berlin, 14195, Germany
 5. Department of Biomolecular Mechanisms, Max-Planck-Institut für Medizinische Forschung, 69120 Heidelberg, Germany
 6. Department of Physics, University of California, Berkeley, California 94720-300, USA

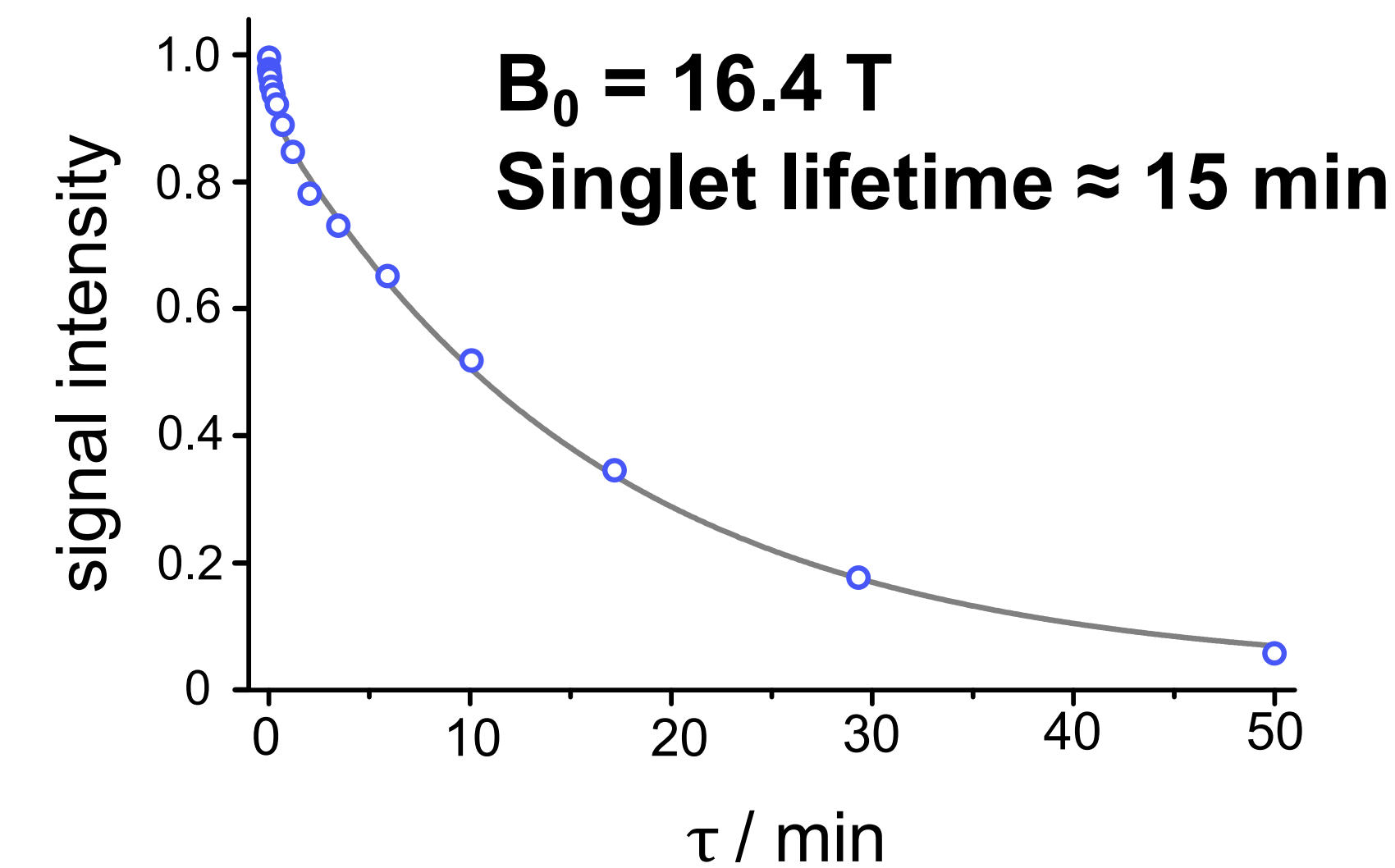


Photochromic properties of azobenzene



- Azobenzene (ABZ) can be reversibly photo-switched
- *trans*-ABZ exhibits long-lived states (LLS) of nuclear spins
- *cis*-ABZ can be efficiently hyperpolarized by SABRE
- We are developing experimental protocol to combine SABRE, photo-switching and storage of hyperpolarization in LLS

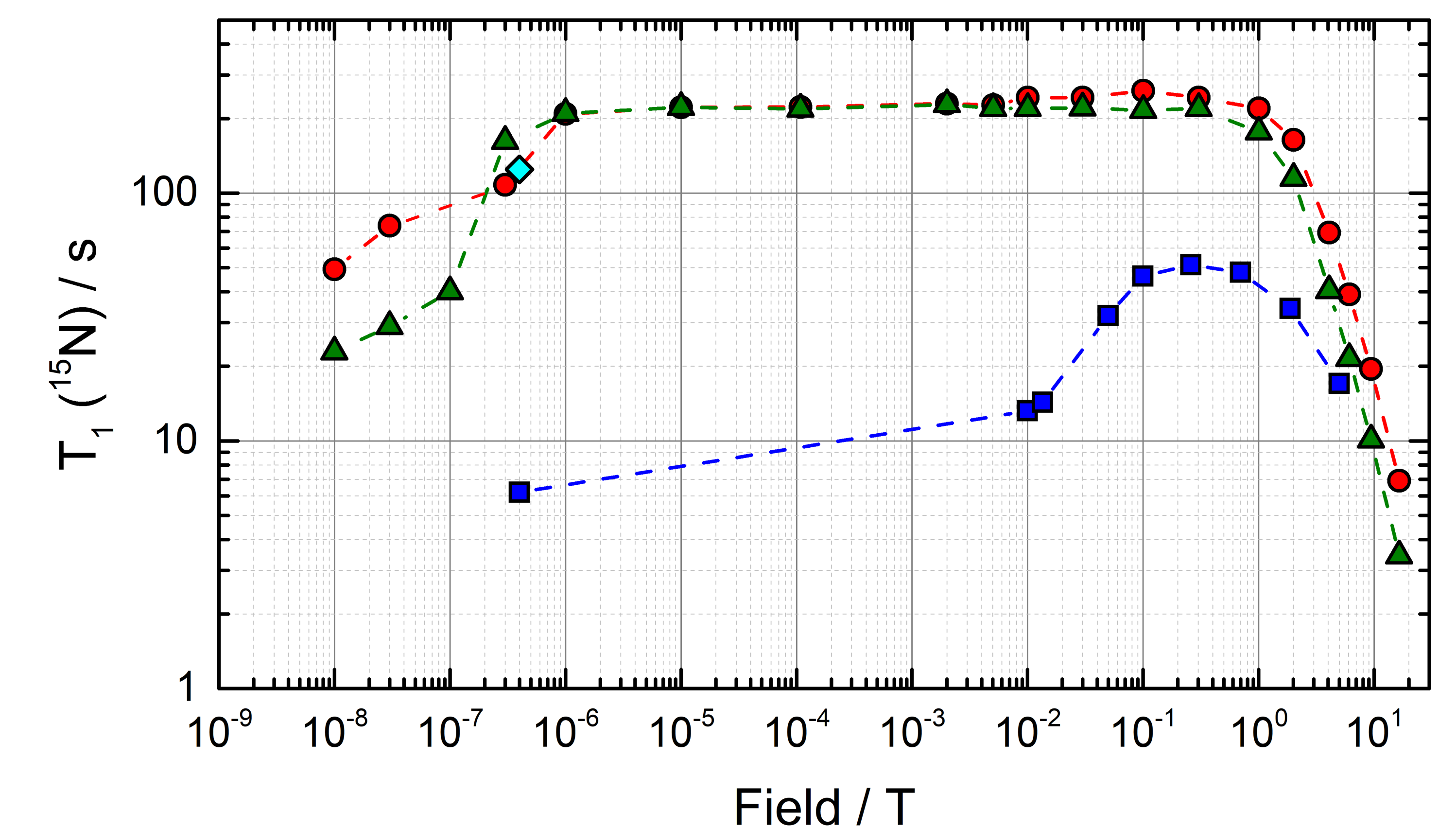
Long-lived states



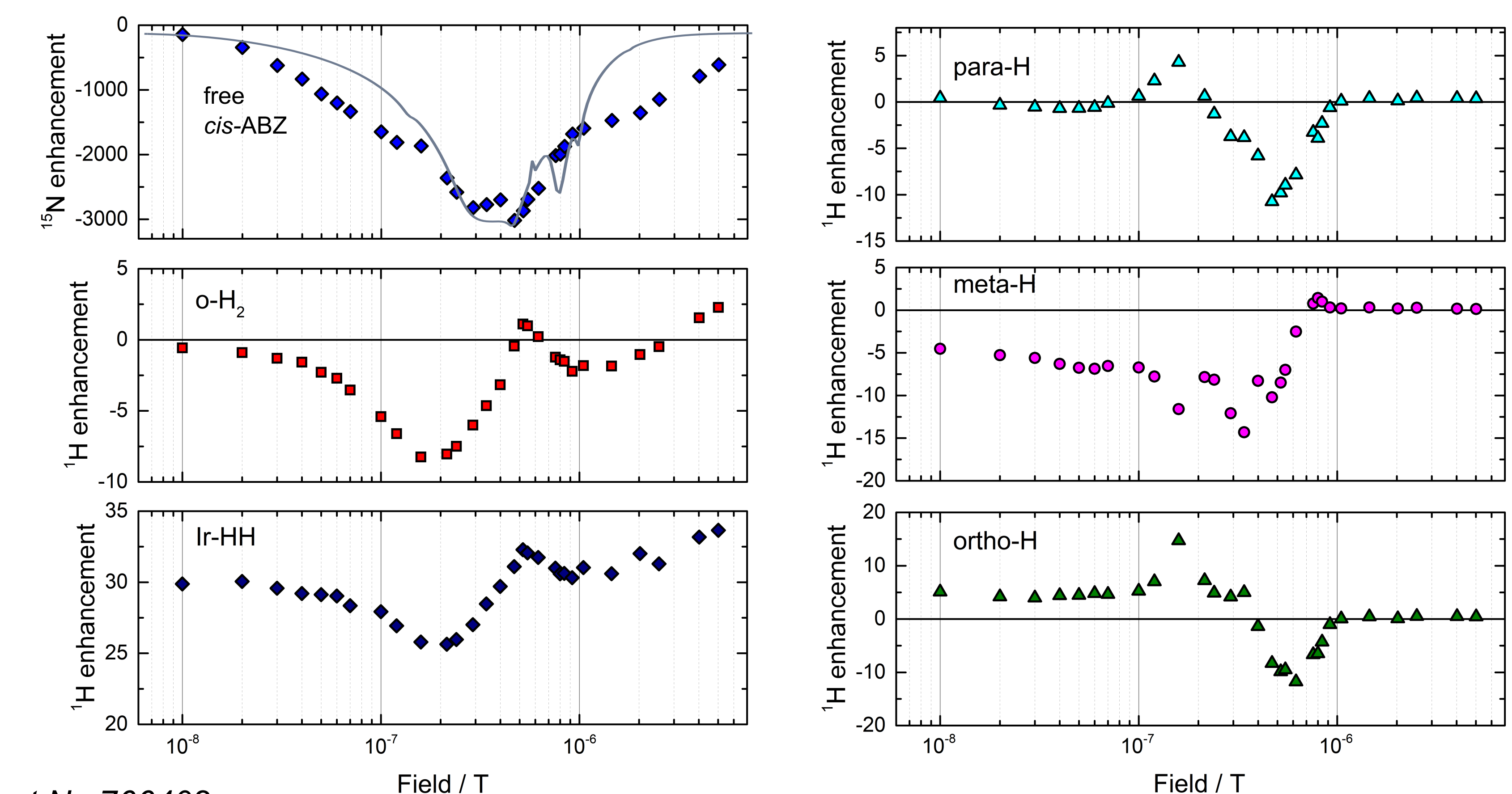
- LLS was observed only in *trans*-ABZ
- Extra-ordinarily long lifetime for high-field experiments

Relaxation field dependencies

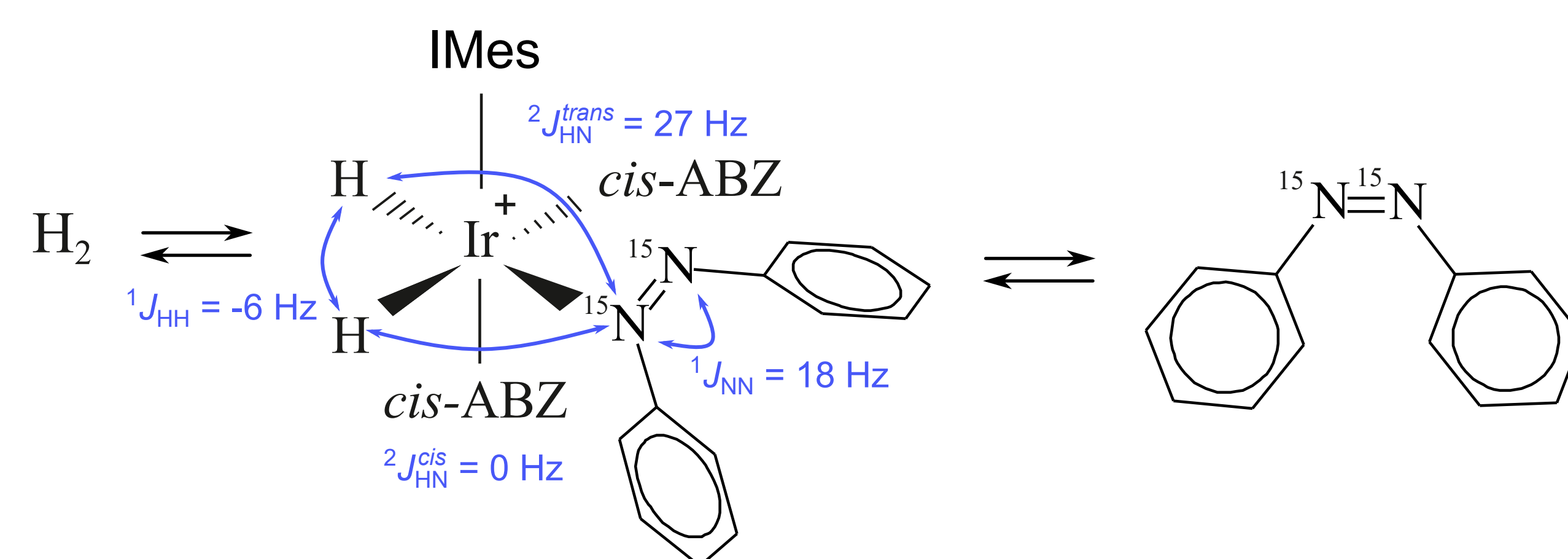
- \square *cis*-ABZ in SABRE solution (1 mM IrMes, 22 mM *cis*-ABZ in MeOD)
- \bullet *cis*-ABZ in acetonitrile
- \blacktriangle *trans*-ABZ in acetonitrile
- \blacklozenge *trans*-ABZ in SABRE solution



SABRE field dependencies



Signal amplification by reversible exchange

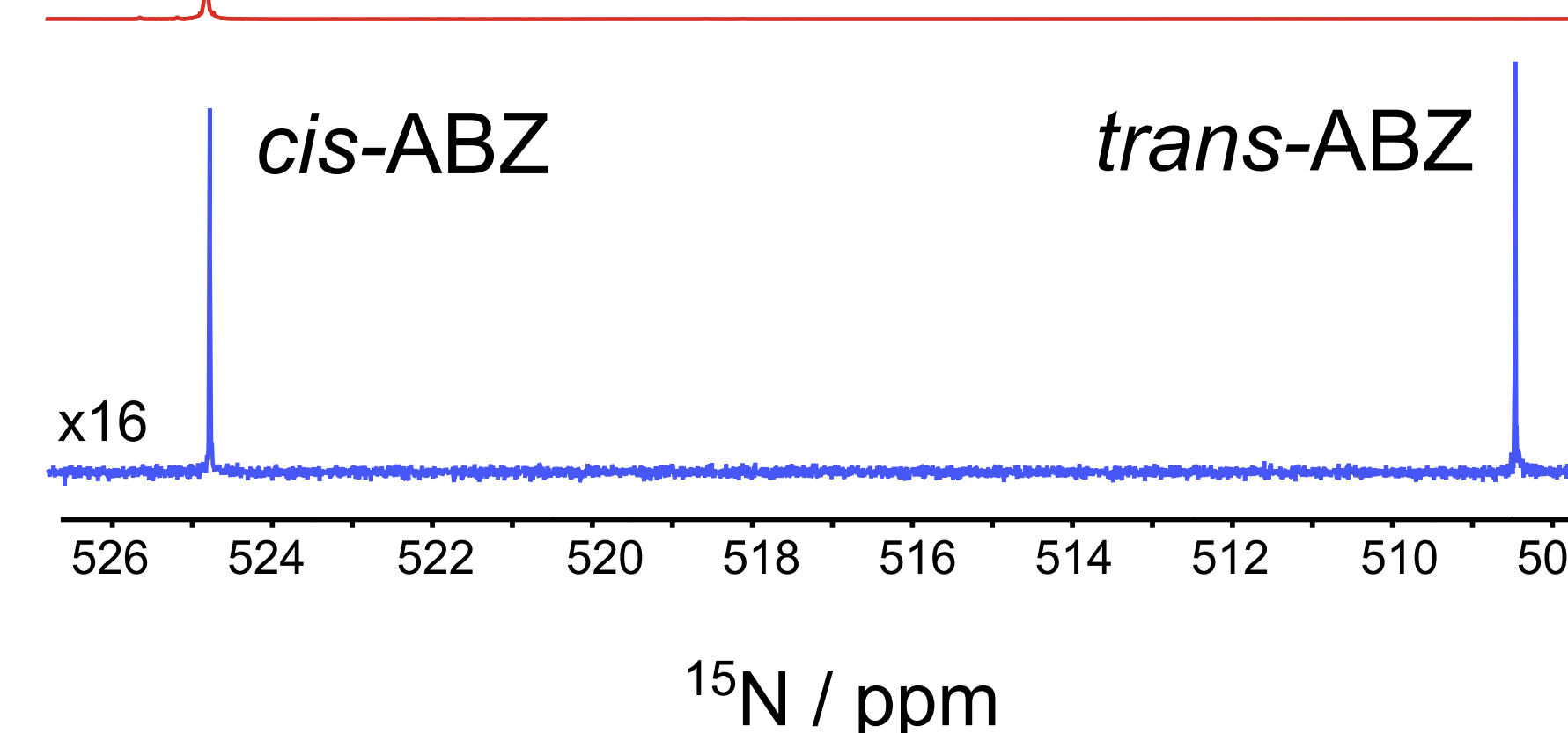


- Reversible formation of the complex enables to repeat hyperpolarization for many times
- J-coupling constants were determined from ¹⁵N and ¹H SABRE spectra acquired at 5 °C
- SABRE SHEATH (Shield Enables Alignment Transfer to Heteronuclei) enables transfer of p-H₂ singlet order to ¹⁵N magnetization in zero- to ultra-low fields (ZULF)

SABRE SHEATH

Enhancement ≈ 2500 times
 Bubbling p-H₂ (95%, 2.6 bar, 10s) at $5 \cdot 10^{-7} \text{ T}$

- only *cis*-ABZ is polarized



Outlook

Long T_1 relaxation time of the ¹⁵N spins in *trans*-ABZ ($\sim 2 \text{ min}$) at the optimal magnetic field for SABRE SHEATH experiment ($5 \cdot 10^{-7} \text{ T}$) will facilitate transfer of the hyperpolarization to *trans*-ABZ by photo-switching of the hyperpolarized *cis*-ABZ

ZULF NMR is a perspective approach for in situ observation of this process

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 766402.