T-jump spectroscopy under THz radiation: a way to measure T_1 of magnetically concentrated substances

A.R. Melnikov[1,2], A.G. Maryasov[3], Y.V. Getmanov[2,4], D.A. Shevchenko[4], M.V. Fedin[1,2], S.L. Veber[1,2]

[1] International Tomography Center SB RAS, 3a, Institutskaya Str., 630090 Novosibirsk, Russian Federation
[2] Novosibirsk State University, Pirogova Str. 2, 630090, Novosibirsk, Russian Federation
[3] Novosibirsk Institute of Organic Chemistry SB RAS, 9, Lavrentiev Ave., 630090 Novosibirsk, Russian Federation
[4] Budker Institute of Nuclear Physics SB RAS, 11, Lavrentiev Ave., 630090, Novosibirsk, Russian Federation

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E-mail: anatoly.melnikov@tomo.nsc.ru

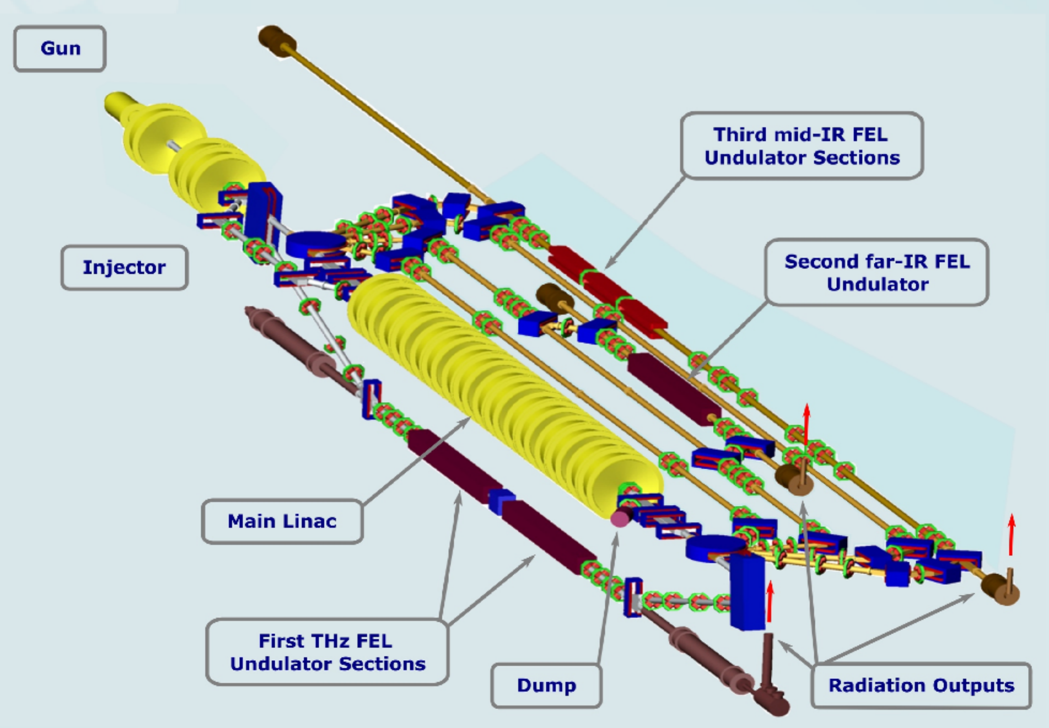
Abstract

Spin-lattice and spin-spin interactions play an important role in a number of physical phenomena. In particular, the low rate of spin-lattice relaxation (T_1) is one of the critical factors that requires a fundamental understanding. To determine T_1 of SMM, the magnetic susceptibility of a macroscopic sample is usually measured by AC SQUID magnetometry. Another direct method is pulsed EPR spectroscopy, which requires diamagnetically diluted samples.

T-jump spectroscopy can be used as an alternative to SQUID magnetometry and pulsed EPR. This is a type of time-resolved (TR) EPR spectroscopy that records the change in microwave (MW) absorption caused by pulse heating of a sample. The sign and shape of the resulting signal reflect the difference in the EPR signals of the spin system before and after the external stimulus. The use of far infrared radiation (30-60 cm^{-1}) does not cause photochemical reactions, but heat the sample, initiating spin dynamics.

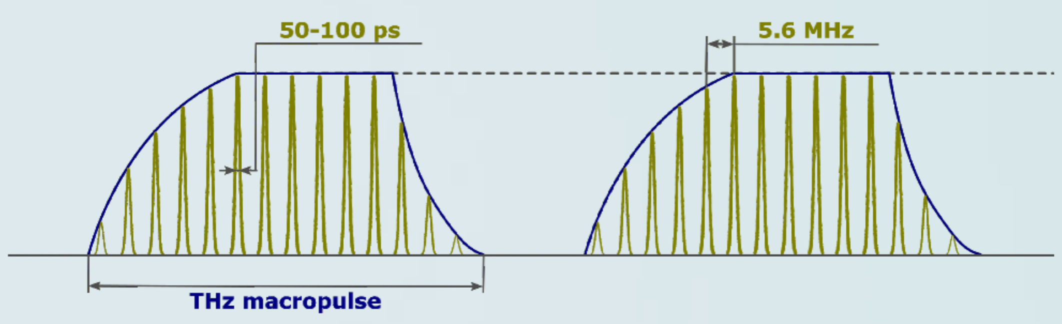
Materials & Methods

Novosibirsk Free Electron Laser

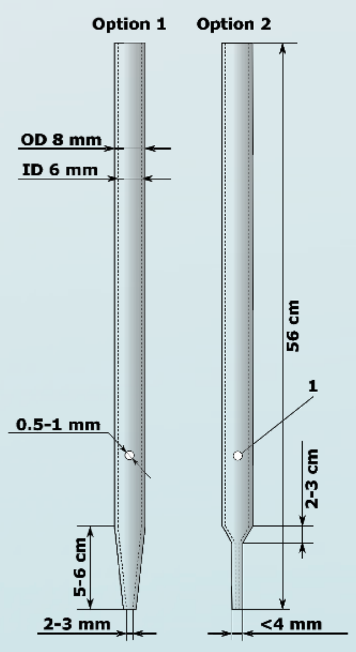


Main assemblies of the NovoFEL facility and their spacial layout.

In the continuous mode, the radiation of NovoFEL consists of a periodic train of pulses with duration of several tens of picoseconds. The pulse mode allows generating THz macropulses of various durations containing a sequence of individual pulses.



Schematic view of NovoFEL radiation macropulses. The length of the individual THz pulse and their repetition rate are shown for the first FEL.



THz radiation is transmitted to the sample using a special hollow metal/dielectric waveguide. The transmission coefficient of the waveguides is about 0.65 (4.4 dB/m) at 45.5 cm^{-1}. THz radiation with a wavenumber of 76.9 cm^{-1} was used in the experiments. To ensure maximum sensitivity to T_1 of the sample, the macropulse duration was 30 µs at 4.5 Hz repetition rate.

Simulations

The spin dynamics were calculated in the Tilted Rotating Frame for the Hamiltonian (1) using the Liouville von Neumann equation (2).

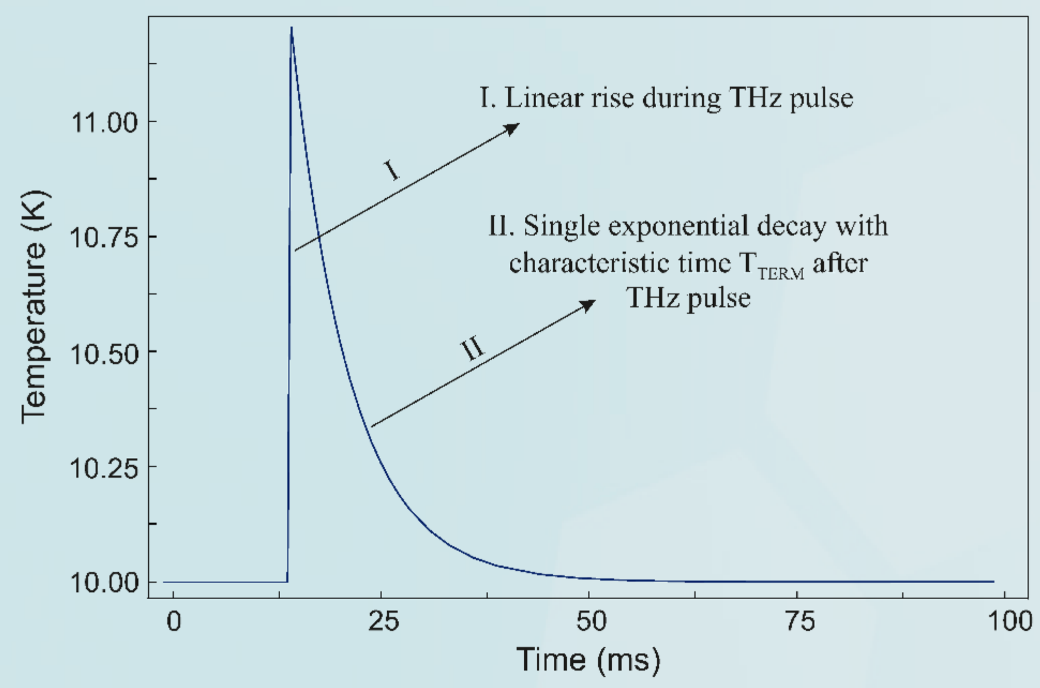
$$\hat{H}_R = \beta B_1 g_1 (\vec{k}_1, \vec{S}) \quad (1)$$

$$\frac{d\vec{\rho}}{dt} = -i\hat{\hat{L}}\vec{\rho}, \quad (2)$$

where $\hat{\hat{L}} = -\hat{H}_R \otimes \hat{1} + \hat{1} \otimes \hat{H}_R^{+} + i\hat{\hat{R}}$

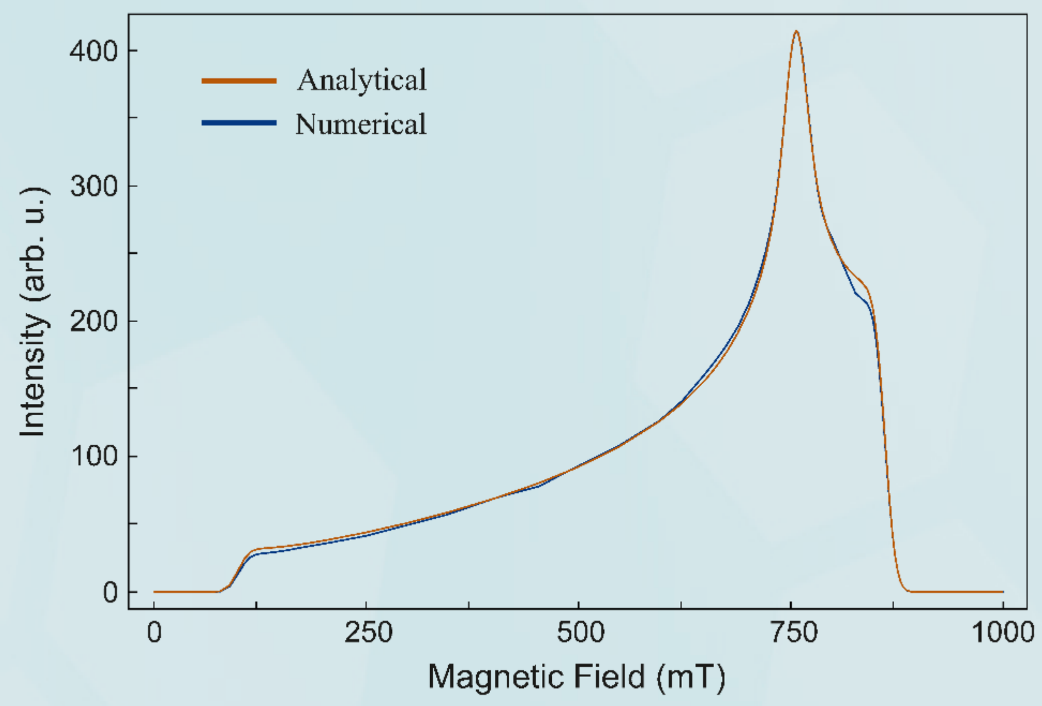
$\hat{\hat{R}}$ is the relaxation superoperator phenomenologically determined by the relaxation times T_1 and T_2. A spin system with effective spin $^1/_2$ was considered in the calculations.

The equilibrium density matrix depends on the temperature, which changes during the experiment: (i) linearly during THz pulse and (ii) exponentially after the end of the pusle.



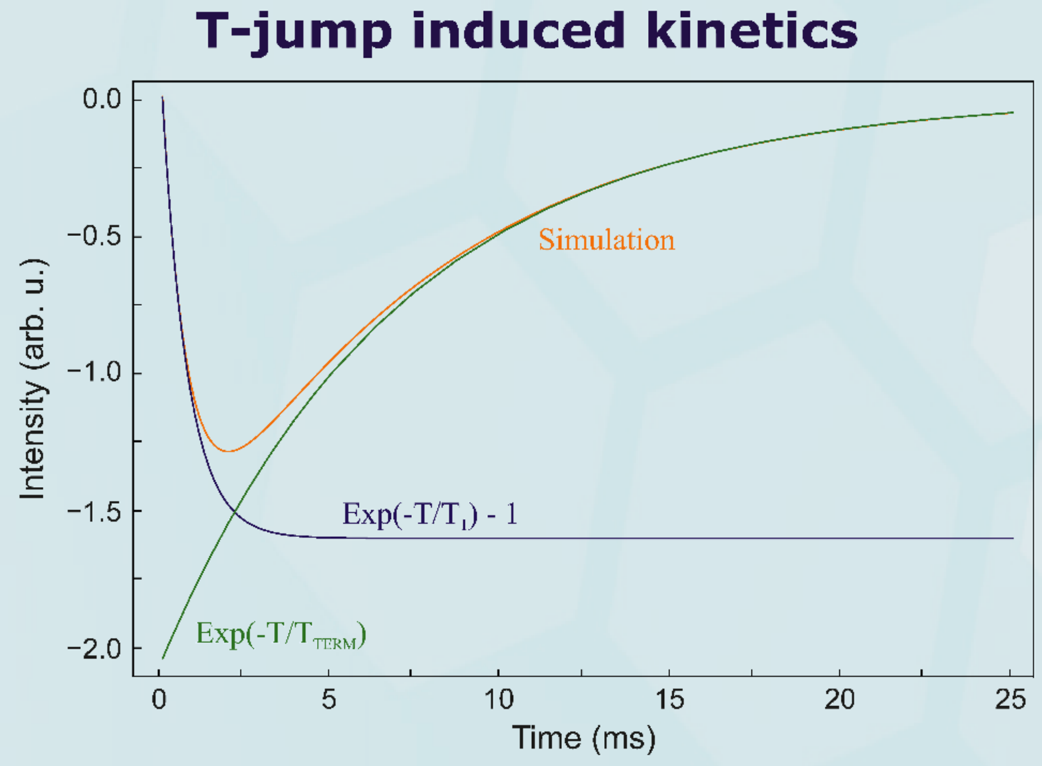
Typical temperature dependence on time during the experiment.

T-jump induced powder spectrum



Comparison of the calculated EPR signal induced by T-jump and analytical calculation of the lineshape for the model system with effective spin $^1/_2$. The numerical simulation was performed for 400,000 random orientations. The inhomogeneous linewidth was 10 mT. The spectrometer frequency was 9.75 GHz.

T-jump induced kinetics

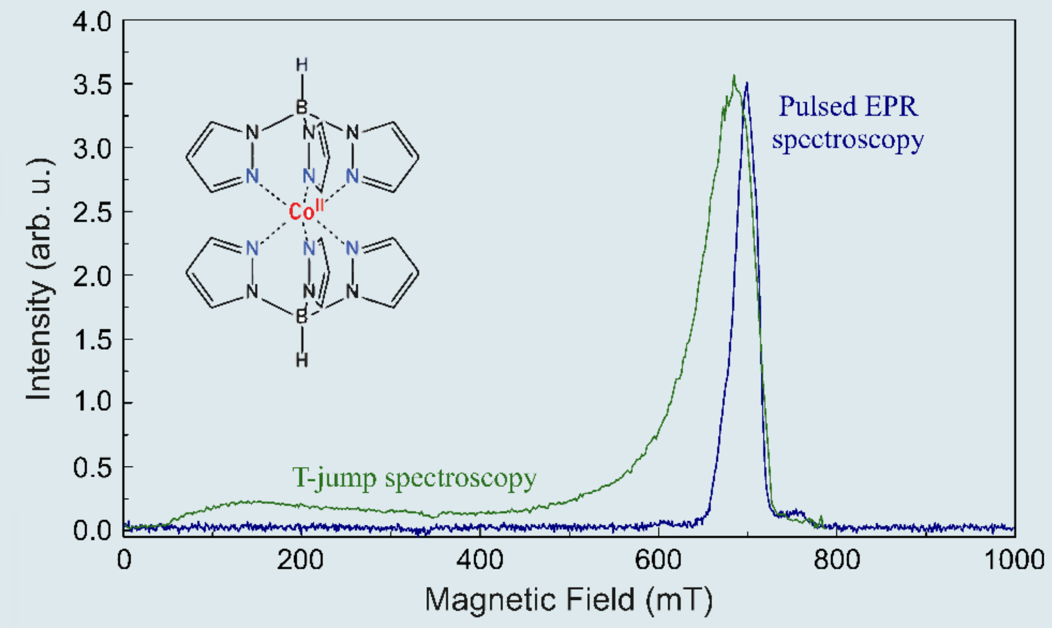


Comparison of the kinetics traces obtained from the numerical simulation (orange) with exponential thermal relaxation with a characteristic time of 7 ms (exp(-T/T_{TERM}), green) and exponential T_1 relaxation with a characteristic time of 750 µs (exp(-T/T_1) - 1, dark blue).

[1] Julia programming language: https://julialang.org/
[2] Veber S.L. et al., X-band EPR setup with THz light excitation of Novosibirsk Free Electron Laser: Goals, means, useful extras // 10.1016/j.jmr.2018.01.009
[3] Kulipanov G.N. et al., Novosibirsk Free Electron Laser - Facility Description and Recent Experiments // 10.1109/TTHZ.2015.2453121

Results

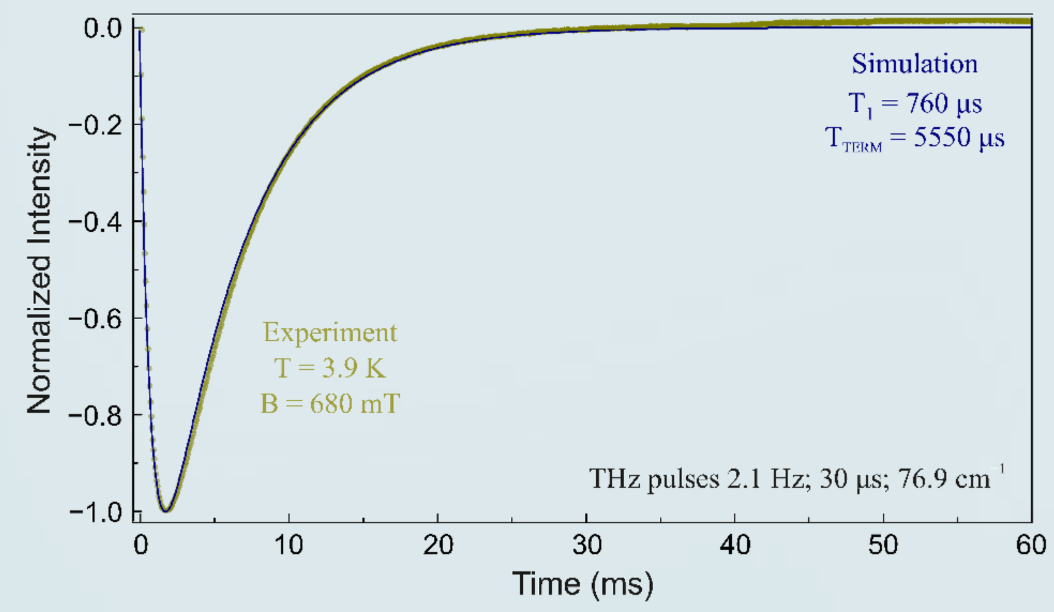
Pulsed EPR and temperature jump spectroscopy reveal the orientation dependence of both T_1 and T_2.



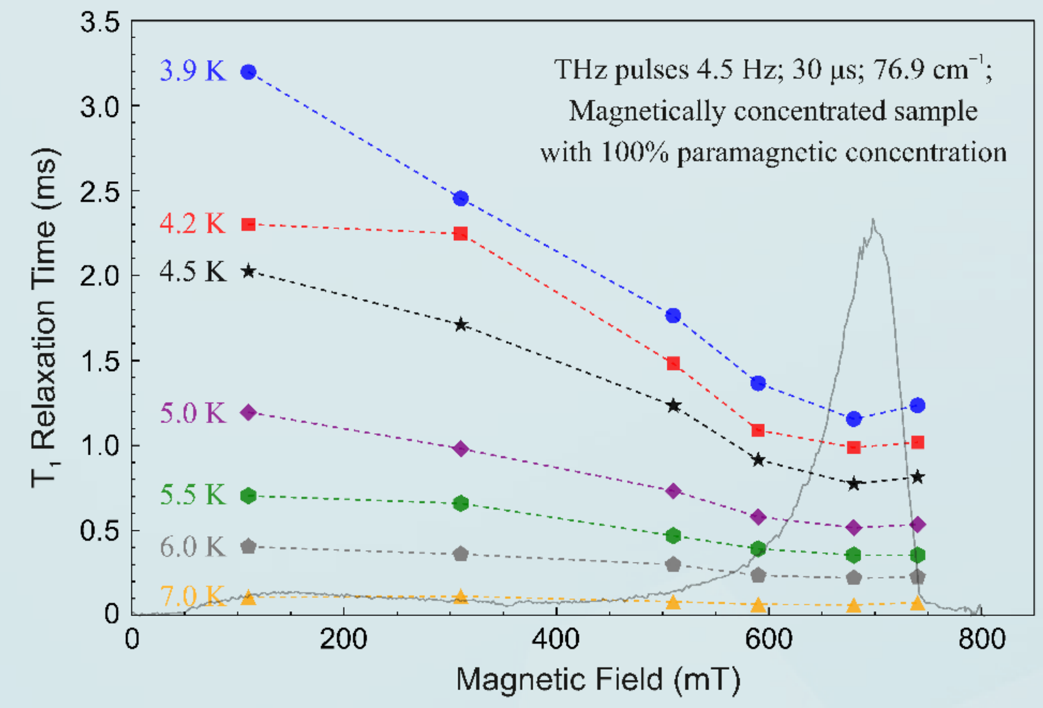
Comparison of spectra of bis[tris(pyrazolyl)borate] cobalt(II) with 1% concentration of paramagnetic ions at 4.2 K.

T_1 of magnetically undiluted sample

The T_1 orientation dependence of magnetically concentrated samples can be obtained from the leading edge of the T-jump induced kinetics.



Least square fitting of the experimental data obtained by T-jump spectroscopy by the proposed numerical model.



Orientation and temperature dependencies of T_1 relaxation time of bis[tris(pyrazolyl)borate] cobalt(II) measured by T-jump spectroscopy under pulsed heating by THz irradiation.

Conclusions

Herein, we propose a numerical approach for modeling spin dynamics under continuous MW irradiation and a T-jump induced by pulsed THz radiation and exemplify it with results obtained for cobalt(II) bis[tris(pyrazolyl)borate] with 100% cobalt(II) ion content. Numerical modeling is based on solving the Liouville von Neumann equation in the Julia programming language [1]. The T_1 values were determined over a wide temperature range at several magnetic field positions of the powder spectrum. T-jump experiments were carried out at the EPR spectroscopy endstation [2] utilizing pulsed THz radiation of the NovoFEL [3].

Poster #054

Thank you for your attention