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THz Electron Paramagnetic Resonance / THz Spectroscopy at BESSY II

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Abstract: The THz beamline at BESSY II employs high power broadband femto- to picosecond long THz pulses for magneto-optical THz and FIR studies. A newly designed set-up exploits the unique properties of ultrashort THz pulses generated by laser-energy modulation of electron bunches in the storage ring or alternatively from compressed electron bunches. Experiments from 0.15 to 5 THz ($\sim$ 5 – 150 cm^{-1}) may be conducted at a user station equipped with a fully evacuated high resolution FTIR spectrometer (0.0063 cm-1), lHe cooled bolometer detectors, a THz TDS set-up and different sample environments, including a superconducting high field magnet (+11 T - 11T) with variable temperature insert (1.5 K – 300 K), a sample cryostat and a THz attenuated total reflection chamber. Main applications are Frequency Domain Fourier transform THz-Electron Paramagnetic Resonance (FD-FT THz-EPR), THz-FTIR spectroscopy and optical pump - THz probe time domain spectroscopy (TDS), with sub-ps time resolution.

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1 THz beamline

Figure 1 depicts the general scheme of the THz beamline and the FD-FT THz-EPR user station. At the beamline coherent synchrotron radiation (CSR) is emitted by ultra-short electron bunches in low α mode (pulse length: < 10 ps, spectral range: 3 - 50 cm^{-1}, see insert in Fig. 1) or laser-energy modulated electron bunches in femto slicing mode (pulse length: 200 fs (rms), spectral range: 20 - 150 cm^{-1}) from the 2° dipole source (D112) at an acceptance of 60 mrad (h) x 15 mrad (v). CSR is than transmitted via a fully evacuated quasi-optical transmission line to the user station.
Figure 2 depicts a detailed layout of the experimental user station. In this set-up THz radiation extracted from the storage ring may be readily directed towards three different detection schemes:

- a FD-FT THz-EPR spectrometer (red and orange traces in Fig. 2)
- a slicing diagnostics stage (green trace in Fig. 2)
- a THz TDS pump probe set-up (blue trace in Fig. 2)

For FD-FT THz-EPR, the THz beam is transmitted by an evacuated low-loss quasi-optical transmission line and focused on the external radiation port of a high resolution FTIR-spectrometer (Bruker IFS 125, min. bandwidth: 0.0063 cm^{-1}), by off-axis parabolic mirrors. After passing through the spectrometer, the radiation again propagates through a vacuum-sealed quasi-optical beam line, which focuses the THz radiation onto the windows of a sweepable superconducting magnet (Oxford Spectromag). The split-coil magnet is equipped with four outer, wedged, z-cut quartz windows. In the standard configuration (Voigt geometry, red trace in Fig. 2) the external magnetic field is oriented perpendicular to the propagation direction of the radiation.

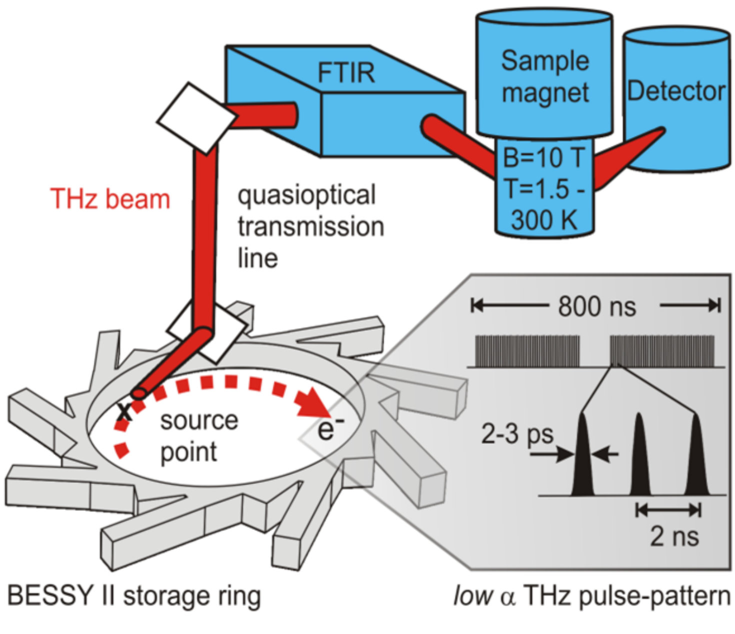

Figure 1: Schematic layout of the THz user station with the THz beam indicated in red. The insert shows the fill-pattern of the storage ring in low α mode.

In the magnet housing a variable temperature insert (VTI) equipped with additional four z-cut quartz windows is immersed. This configuration allows for measurements from T = 1.5 K to 300 K, at external magnetic fields between -11 and +11 T. The evacuated beam line incorporates a rotatable roof-top mirror, which acts as broad band polarization shifter. This device allows for orienting the magnetic component of the linearly polarized THz radiation parallel or perpendicular to the static magnetic field. Alternatively, the radiation may be guided through the second pair of magnet windows (Faraday

geometry, dotted trace in Fig. 3) or to an additional optical cryostat (T = 1.5 K - 300 K, orange trace in Fig. 2 Oxford Optistat,) inside the FTIR spectrometer. In all three configurations, highly sensitive detection may be achieved with either a liquid helium cooled Si-bolometers (IR labs, lHe cooled to 4.2 K or superfluid He cooled to 1.6 K)), an InSb bolometer (QMC, lHe cooled to 4.2 K) or a fast Schottky diode THz detector (ACST, RT; < 250 ps time resolution).
Alternatively, transient THz signals may be directly detected via a time domain spectroscopy (TDS) THz set-up. THz TDS allows for cross-correlation of THz pulses from the storage ring with the synchronized external fs-laser source (optical pump – THz probe).

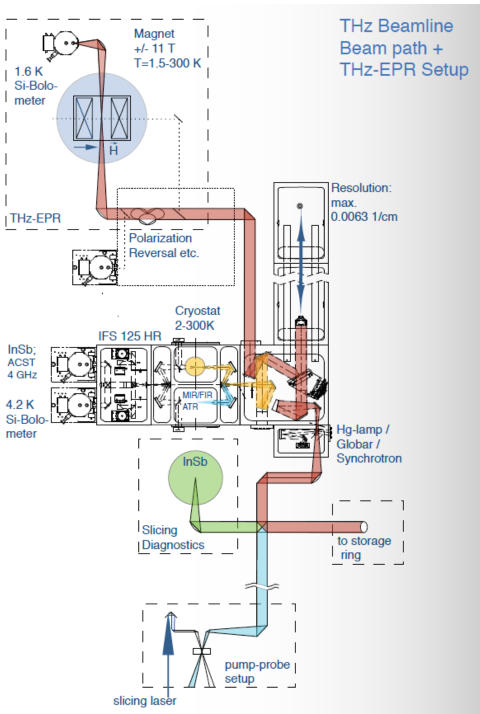

Figure 2: Optical layout of the FD-FT THz-EPR/THz spectroscopy user station. Red and orange: THz beam path of the FD-FT THz-EPR detection scheme through the sample magnet and through the sample cryostat, respectively, green: Slicing Diagnostics, blue: THz TDS pump-probe setup.

2 FD-FT THz-EPR

The dedicated FD-FT THz-EPR facility combines a broad range of excitation and detection schemes with extreme sample environments (in particular high magnetic fields and low temperatures). This combination renders FD-FT THz-EPR an ideal tool for studies in spin couplings (in particular zero field splittings and exchange interactions) of high spin transition metal and rare earth ions. Spin coupling energies are sensitive probes of the electronic structure and determine magnetic properties of compounds with unpaired electron spins. The latter are highly desired pieces of information, as high spin paramagnetic ions determine the function of many vital catalytic processes in proteins and synthetic complexes, as well as the properties of single molecule magnets. EPR is well established for studies in the magnetic structure-function relationship of materials containing unpaired electron spins. However, conventional single frequency EPR frequently fails in cases where spin transition energies exceed the quantum energy of the spectrometer (typically < 4 cm^{-1}). Recently, we have demonstrated that CSR based FD-FT THz-EPR (Schnegg et al., 2009), with very broad excitation frequency (3 cm^{-1} – 150 cm^{-1}) and magnetic field (-11 T - +11 T) ranges, provides a unique tool to overcome this restriction in a single spectrometer. FD-FT THz-EPR has been successfully applied to high spin ions in single molecule magnets (Dreiser et al., 2013, 2011; Pedersen et al., 2011; Pinkowicz et al., 2015) catalytic mononuclear integer high spin transition metal ion complexes (Forshaw et al., 2013; Nehrkorn, Schnegg, et al., 2015; Nehrkorn, Telser, et al., 2015) and very recently even in proteins (Nehrkorn et al., 2013). Recent science highlights include the determination zero field splitting parameters in met myoglobin and hemoglobin (Nehrkorn et al., 2013), the assignment of anisotropic exchange as source of the magnetic anisotropy in Mn trimer single molecule magnets (Dreiser et al., 2013; Pedersen et al., 2011) and the determination of spin ground state parities by polarization dependent FD-FT THz-EPR (Nehrkorn, Schnegg, et al., 2015).

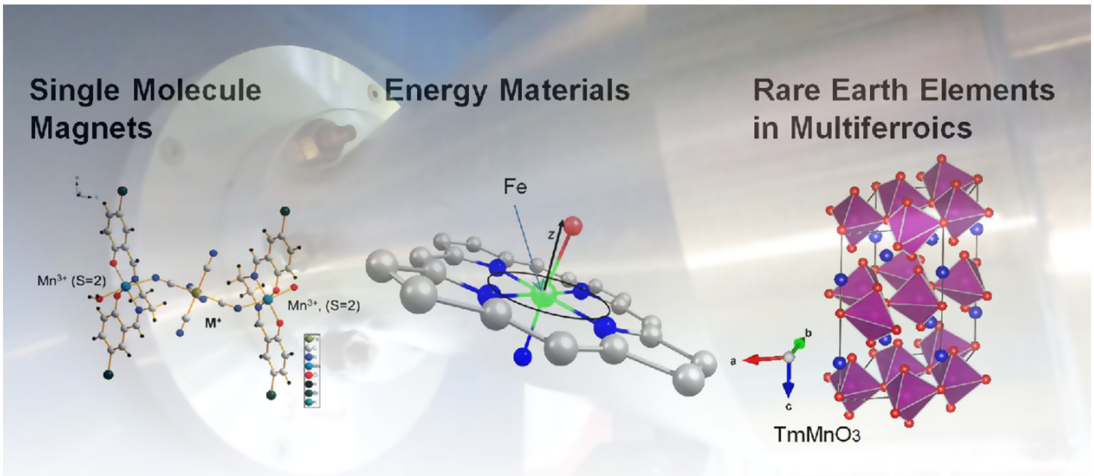

Figure 3: Examples for systems studied by FD-FT THz-EPR at BESSY II.

3 THz spectroscopy

Apart from paramagnetic and molecular systems, as illustrated by Fig.3, the setup extends conventional static high field FTIR spectroscopy in solids, powders and granular matter (Born et al., 2015; Vogel et al., 2015) to very low wavenumbers (3 cm^{-1}), which are only accessible at CSR sources at sufficient dynamic range. Moreover, the special time structure of THz emission in BESSY II's low alpha mode as well as from Laser-Energy Modulation (Slicing) allows for time-domain experiments revealing ultrafast (sub-ps) charge carrier and phonon dynamics in thin films also under very high magnetic fields. Here, the fs-slicing laser or it's harmonics (6 kHz) are used as an excitation laser while the THz pulse from the storage ring as transmitted or reflected from the sample is used a probe (Braggaglia et al., 2015).

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