Developing a Terahertz-Frequency EPR Spectrometer

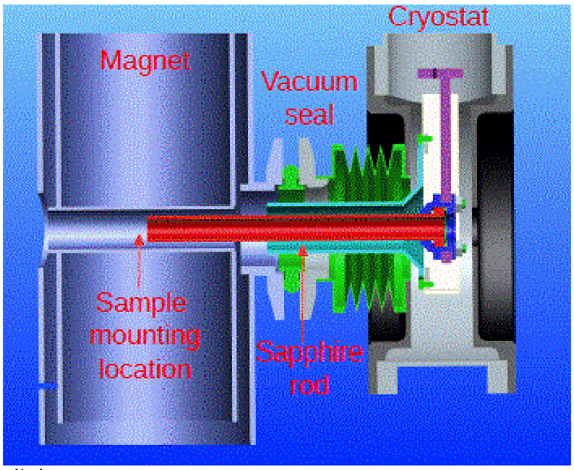
New type of THz-EPR spectrometer has been developed by combining a table top 30 T pulsed magnet and the single-shot detection-broadband THz radiation using spectral up-conversion technique. We have also investigated several new Ni and Co complexes by using the TESRA-IMR:ESR spectrometer installed at the Magnetism Division of IMR.

It has been recognized for a number of years that extending the frequency range of EPR spectrometers, that normally operate at microwave frequencies of 9.5 – 95 GHz, into the terahertz regime (1 THz = 1000 GHz) would have enormous benefits in terms of both spectral and temporal resolution. Recently, there has been a huge resurgence of interest in extending the frequency range of EPR spectroscopy, fuelled in-part by the advent of new terahertz radiation sources and detectors.

The aim of this proposal is to develop a compact laboratory-based EPR spectrometer that operates in the terahertz-frequency range and exploit its unique capabilities to probe next generation molecular magnetic materials. This will be achieved by combining an existing state-of-the-art laser-based terahertz time- domain spectrometer, developed by Dr Graham's group at the Photon Science Institute, with a portable high-field pulsed magnet developed by Prof Nojiri at the Institute of Materials Research.

Figure 1 (a) and (b) show the schematic view of the central part of the spectrometer and the photograph, respectively. The pulse magnet coil(not shown here) is set in the nitrogen bath with a vacuum-sealing pipe in the center. The THz- radiation goes through the central pipe. The sample is mounted on the sapphire cold finger pipe. The cold finger is attached to the He-gas flow type cryostat set side by side to the nitrogen bath. Temperature as low as several K is available with this setup. To adjust the shift of the sample by cooling, two cryostats are coupled by an adjustable bellow flange. Thanks to the short optical path, the adjustment can be done by a few supporting screws. The magnetic field up to 30 T is generated by the compact capacitor bank, which is developed and is assembled at IMR. The whole setup is easily mounted on the optical bench for its compactness. The capacitance, charging voltage and the storing energy of the bank are 8 mF, 2 kV and 16 kJ, respectively. The housing is 750X1100X1460 H and the weight is 350 kg. For the future upgrade, the voltage of the charger is set to 4 kV. The switching between the 2 kV and 4 kV modes can be made easily by the rearrangement of several solid busbars The extension of the capacitance can be made either by adding an extra capacitor box or by extending of the free-size Al-frame type housing.

(a)



(b)

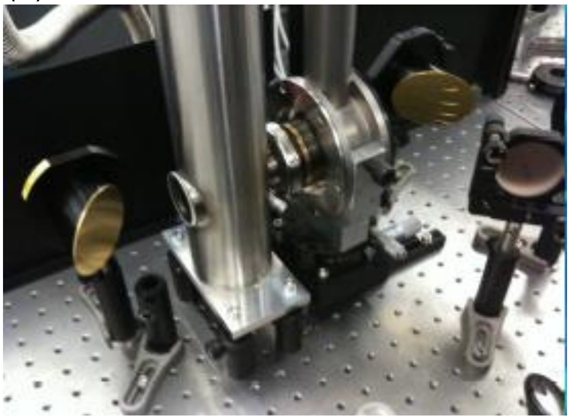


Fig.1(a) Schematic view of the nitrogen bath and the sample cryostat of the table top pulse magnet. Magnet coil is omitted.
Fig.1(b)Photo of the spectrometer setting on the optical bench.

The transmittance of the THz wave is measured between 0.1-3 THz. A sizable reduction of the transmission is found below 0.5 THz for the small opening angle of this system. A design to increase the angle to double that of the present system has been developed through the present collaboration and is now being commissioned. The key point of the upgrade is the use of a new nitrogen bath with the rectangular cross-section to minimize the optical path. It has the benefit to increase the nitrogen reservoir volume useful for longer operation time.

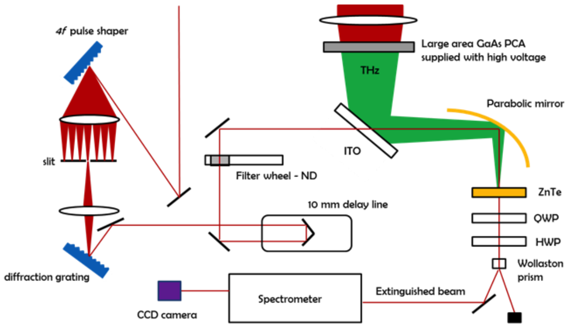
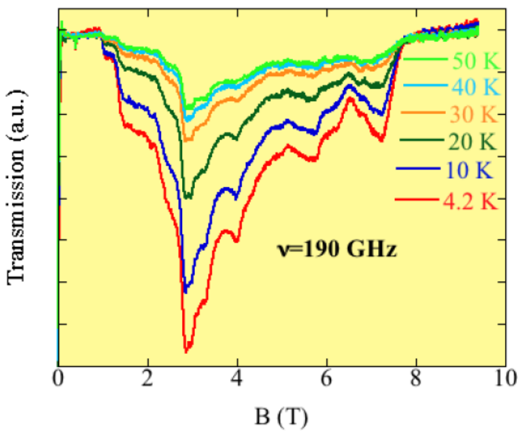


Fig. 2 Scheme of THz generation and detection.

(a)



(b)

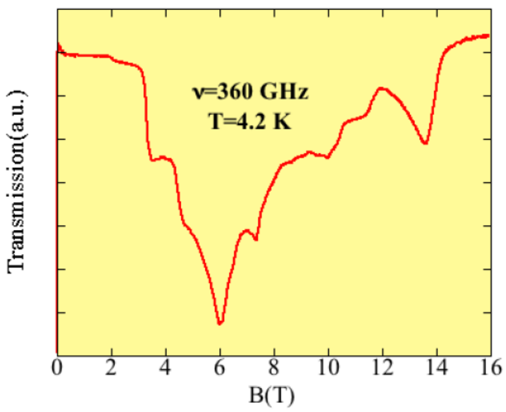


Fig. 3(a) Temperature dependence of EPR spectrum at 190 GHz measured by TESRA-IMR spectrometer. The broad multiple peaks are observed for the non- quenching orbital moment of Co ions.
Fig. 3(b) EPR spectrum at 360 GHz and at 4.2 K.

Figure 2 shows the schematic view of the single-shot broadband THz-generation scheme developed at Manchester University[1, 2]. The THz radiation spectrum can be measured as sidebands of the spectrum from a 100 fs amplifier with a central wavelength of 800 nm. A ZnTe crystal is used for up-conversion and the detection is made by using a single-grating spectrometer and CCD camera.

The THz spectrum has been obtained successfully by this scheme and the application for various materials is in progress.

We have also measured several Ni and Co based complexes at IMR. The purpose of this measurement is to compare the spectrum with THz-TDS and that of the conventional EPR.

Figure 3 (a) shows the temperature dependence of Co complex: [$Co_2(H_2O)$ $(piv)_4(Hpiv)_2$(3-methylpyridine)$_2$] measured at 190 GHz. In the spectrum, seven strong peaks are found with nearly constant spacing. The center of the peak is located at 2.8 T which is related to g~4.5. The large g-value is typical for Co ions with non-quenched orbital moment.

The EPR spectrum at 360 GHz is shown in Fig. 3(b). The separation of peaks becomes much clear for the high resolution. Such improvement of the resolution indicates the advantage of THz EPR to the microwave EPR.

The temperature dependence of the spectrum is monotonic and the intensity decreases with increasing temperature. This behavior indicates that the observed EPR is the transition from the ground state and/or from the low energy excited states.

In summary, we have developed a broadband THz EPR spectrometer by using a single-shot THz detection scheme and a table-top pulsed magnetic field generator. For the complementary research, several magnetic complexes have been investigated with the THz monochromatic frequency EPR spectrometer.

References

[1] D. A. Walsh, D. M. Graham *et al.* Optics Express 22, p. 12028 (2014).

[2] D.M. Graham *et al.*, IEEE DOI:10.1109/IRMMW-THz.2014.6956078

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