HIPER High Sensitivity Pulsed EPR

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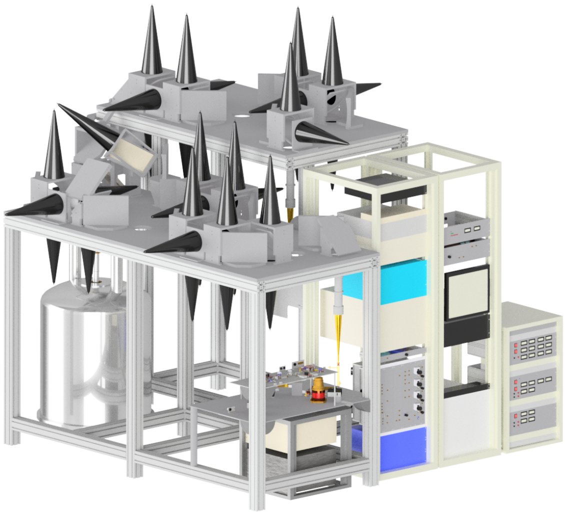
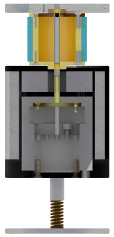
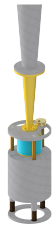
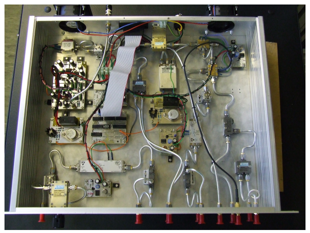
The HIPER System

The HIPER W-band pulsed EPR spectrometer was developed over 30 person-years under the UK Basic Technology Initiative. It combines state-of-the-art concentration sensitivity, state-of-the-art dead-time, with very high spectral and temporal resolution for pulsed EPR measurements. The instrument software makes it easy to set-up complex pulse sequences with precise frequency, phase, amplitude and magnetic field settings, and combines it with fully phase coherent detection and easy sample handling. The instrument can be operated from 5 K to 300 K, and operates in two working modes: low power mode with a 1 W amplifier, and high power mode with a 1 kW amplifier at 94 GHz. This is the highest mm-wave frequency where kW amplifiers are available.









Main Features

1 kW peak power levels at 94 GHz
< 6 ns $\pi/2$ pulses
5 W average power
High power handling components
Very low level system reflections
Very high transmitter isolation >100 dB
Very high detector isolation >60 dB
Wideband low loss optics

Effective dead-time ~ 20 ns
1 GHz excitation bandwidth (at kW power levels)
1 GHz instantaneous detection bandwidth
Low system noise figure

HIPER – Key Features

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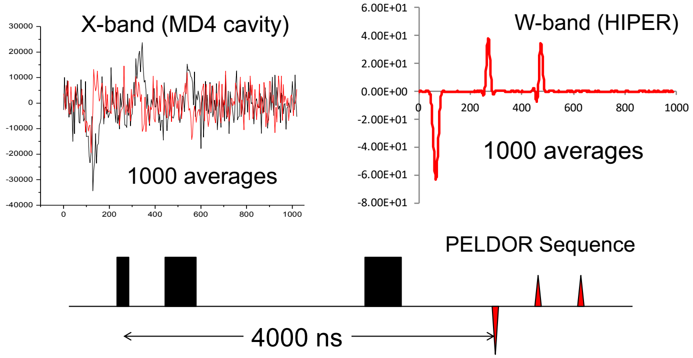
High Concentration Sensitivity

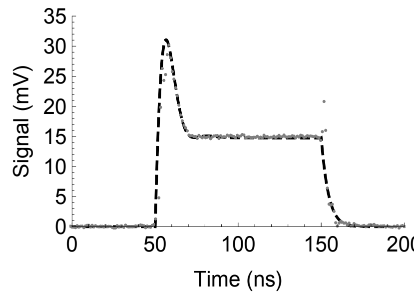
The combination of high frequency (94 GHz) and high power (kW) operation, with carefully designed sample holders allows the HIPER spectrometer to have extremely high concentration sensitivity. Using HIPER, measurements can be made in a few minutes, which would normally take 24 hours at X-band (10 GHz) using a modern commercial pulsed kW spectrometer



Refocussed spin echo (+ 2 Hahn echos) of 1 μM TEMPO in water glycerol at 50K under conditions typical of a PELDOR measurement. Same fractional number of spins excited.

Low Dead-time

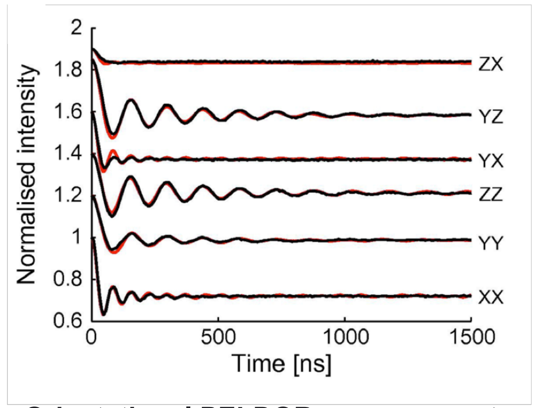
The instrument uses advanced quasi-optical, detection and switching techniques (developed in-house) to reduce system dead-time. Isolation between transmitted power and detected signal is so high that large EPR signals can be easily monitored *during* a kW pulse. For lower level signals an effective dead-time of ~ 20 ns is typically achieved.



Transient measurement of 20 mM TEMPO in hexane at room temperature *during* a kW pulse. The data shows both experiment and fit assuming an effective T_1 = 20 ns and T_2= 4 ns.

High Instantaneous Bandwidth

Broadband electronics and quasi-optical instrumentation allows frequencies to be selected over a 1 GHz bandwidth. This allows orientatonal selective PELDOR measurements on nitroxide spin labeled systems, broadband Gd PELDOR (without artefacts) and broadband EDNMR.



Orientational PELDOR measurements on a bis-nitroxide model system in o-terphenyl. This highly constrained data set, obtained over 500 MHz bandwidths allows both distance and orientational distributions to be derived.

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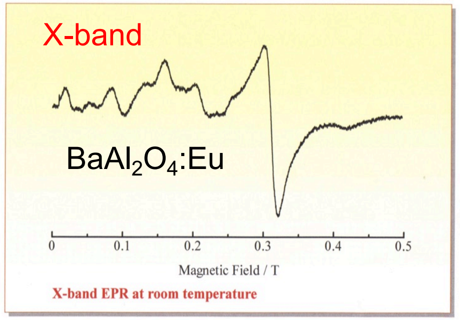
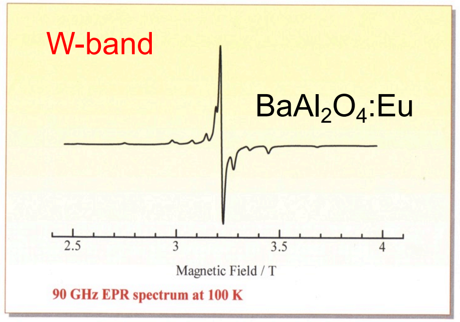
Advantages of high field EPR

Advantages of High Field EPR using HIPER

- Higher g-factor resolution (e.g. for better fingerprinting, better sensitivity to fast dynamics and orientational effects. Nitroxide spectra become fully orientationally resolved at W-band).
- Higher concentration sensitivity (e.g. for in-cell PELDOR measurements)
- Better time resolution and lower deadtime (e.g. FID detection)
- Larger excitation and detection bandwidths (for distance measurements with metal centers)
- Better resolution for detecting hyperfine coupled low γ nuclei
- Large zero-field splitting systems are better resolved or simplified
- Simplification of spectra due to reduction of 2^{nd} order effects (e.g. Gd)
- More favourable relaxation times for certain metal centres



X-band EPR at room temperature



90 GHz EPR spectrum at 100 K

Cw spectra of Eu doped phosphorescent system.

At X-band the zero-field splitting is comparable to the Zeeman splitting causing mixing of the states and the spectra becomes difficult to interpret.

At W-band the zero-field splitting is small compared to the Zeeman splitting and the spectra is easy to interpret