Rapid Scan - the Revolution in EPR

Since 1995, the high level of sensitivity in Continuous Wave EPR (CW-EPR) has technologically reached its maximum. Recently a new method of acquiring the EPR signal, Rapid Scan EPR (RS-EPR), has been pioneered by the Eaton research lab at the University of Denver. RS-EPR is a revolutionary technique that improves the signal to noise ratio and significantly decreases the acquisition time (down to milliseconds).

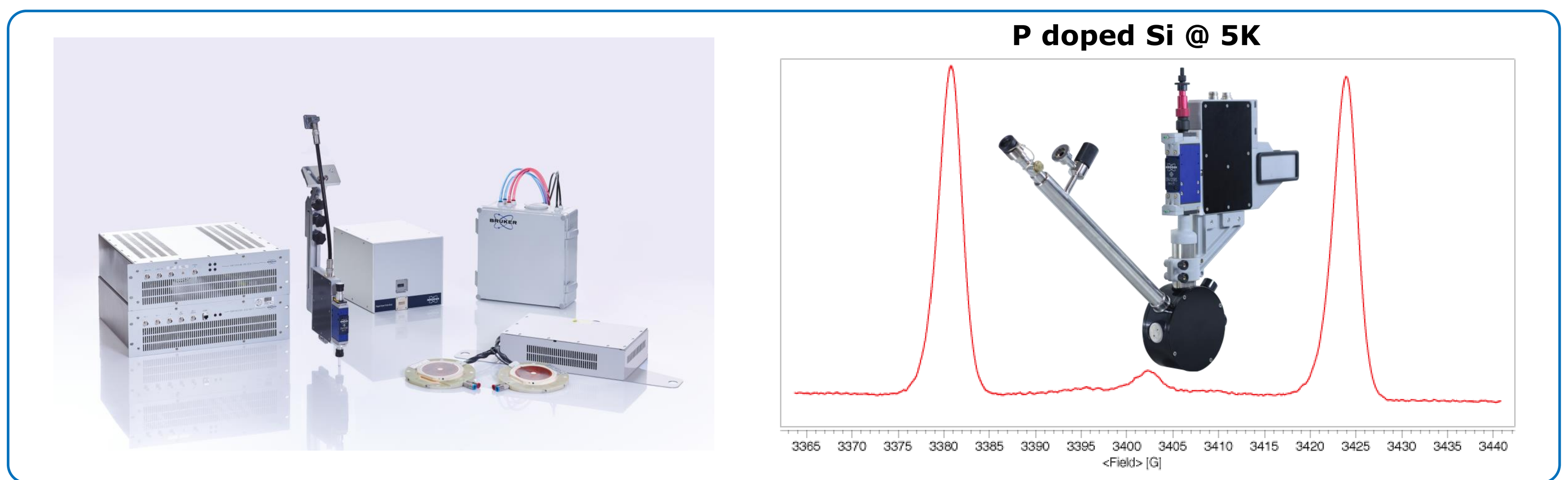

Fig. 1: Overview of the Rapid-Scan accessory (Left), consisting of acquisition unit, driver unit, resonator, front-end, cooling unit and Rapid-Scan coils including capacitors for tuning. Combability of the Rapid-Scan resonator with helium and nitrogen variable temperature systems (Right). The Rapid-Scan spectrum of P doped Si was acquired at 5 K.

The main difference between CW-EPR and RS-EPR is the size of the modulation amplitude and the sweep rate of the magnetic field. In RS-EPR the modulation amplitude is much larger than the EPR linewidth and the field is swept a million times faster (10 MG/s).

Continuous Wave EPR	Rapid-Scan EPR
Phase sensitive lock-in detection	Direct detection
Derivative line shape	Absorption line shape
Modulation amplitude << line width	Scan width >> line width
Slow scan, G/sec	Rapid scan, 10 MG/sec
Unlimited sweep width	Sweep width ≤ 200 G per segment

Advantages in Rapid Scan EPR

The main advantage of RS-EPR comes from the later onset of signal saturation allowing higher microwave powers to be used. This increases the signal amplitude relative to CW-EPR leading to a higher signal-to-noise ratio.

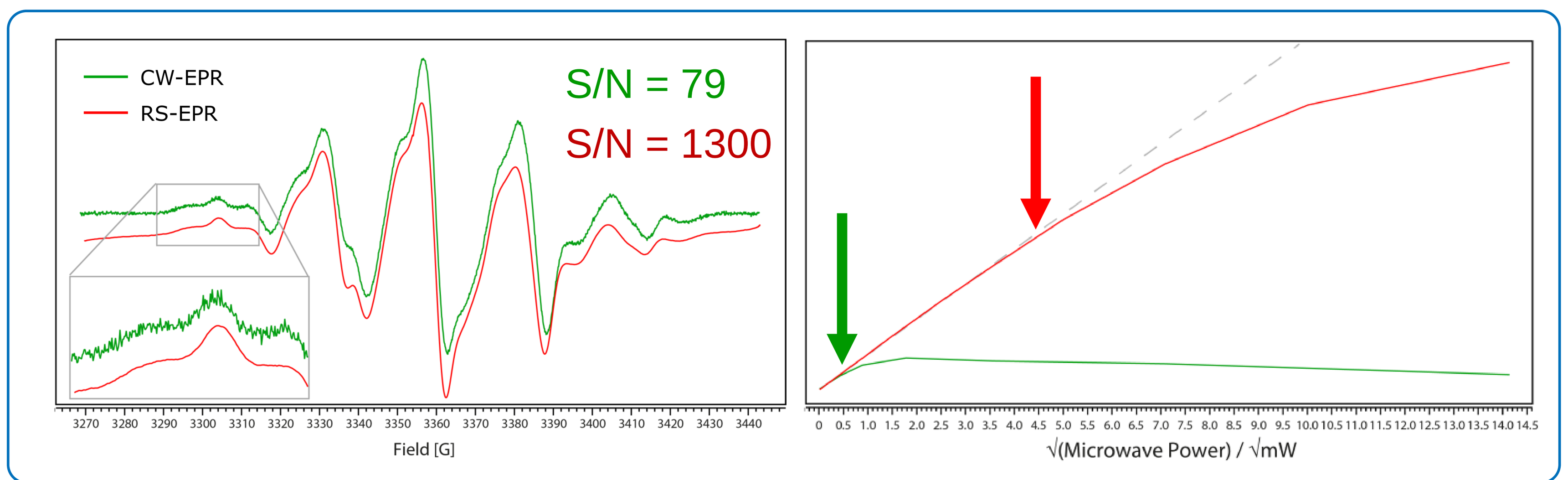

Fig. 2: Comparison of RS- and CW-EPR for irradiated alanine. RS- and CW-EPR spectra (Left) were obtained with a microwave power of 0.2 (CW) and 20 mW (RS), respectively. An identical sweep time (21 s) and modulation amplitude (5 G, pseudo-modulation for RS) were used. Saturation curves (Right) show the different saturation behavior of Alanine for RS- and CW-EPR.

The short acquisition time in RS-EPR allows extensive signal averaging and very high time resolution. Compared to CW-EPR, RS-EPR delivers higher signal to noise in the same total experimental time.

The Rapid-Scan resonator can be critically coupled for Q-factors in the range of 500-6000. Although higher Q-factors give a better S/N, lowering the Q-factor is required for the highest field resolution. In this case the bandwidth of the narrowest signal needs to be smaller than the resonator bandwidth.

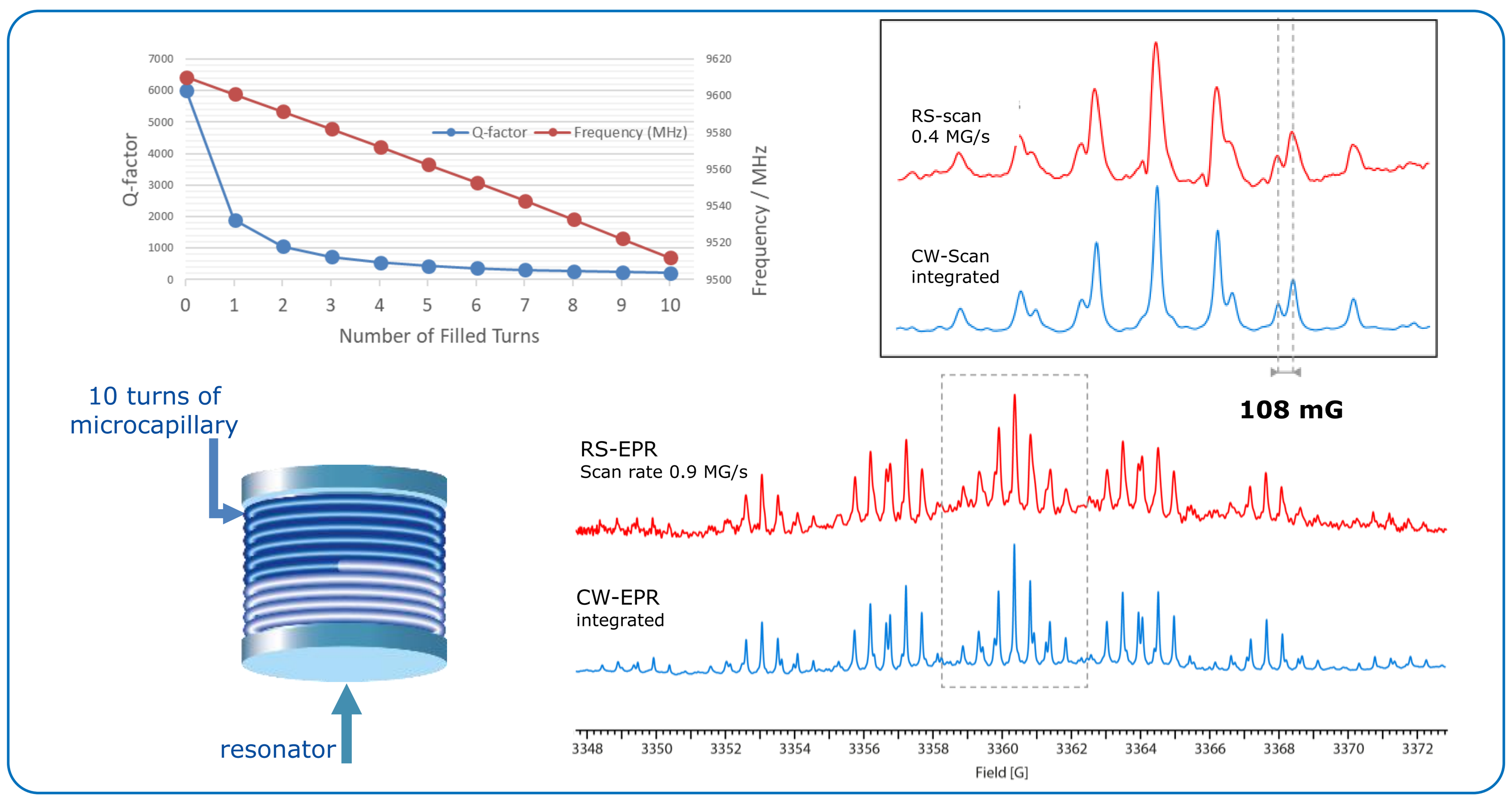

Fig. 3: Variable Q-factors at critical coupling as function of filled microcapillary turns (Left). Rapid-Scan and CW-EPR spectra (Right) of perylene obtained with a Q of 300 and a scan width of 30 G (0.9 MG/s at 10 kHz). The inset shows Rapid-Scan spectra that were acquired with a smaller scan rate.

Full spectrum kinetic measured in field vs delay experiment. With sweep times as low as 10 microseconds, short lived EPR species are observed, and their changes are followed with unprecedented time resolution.

RS Spin Trapping: full spectrum of 70 G in 10 ms!

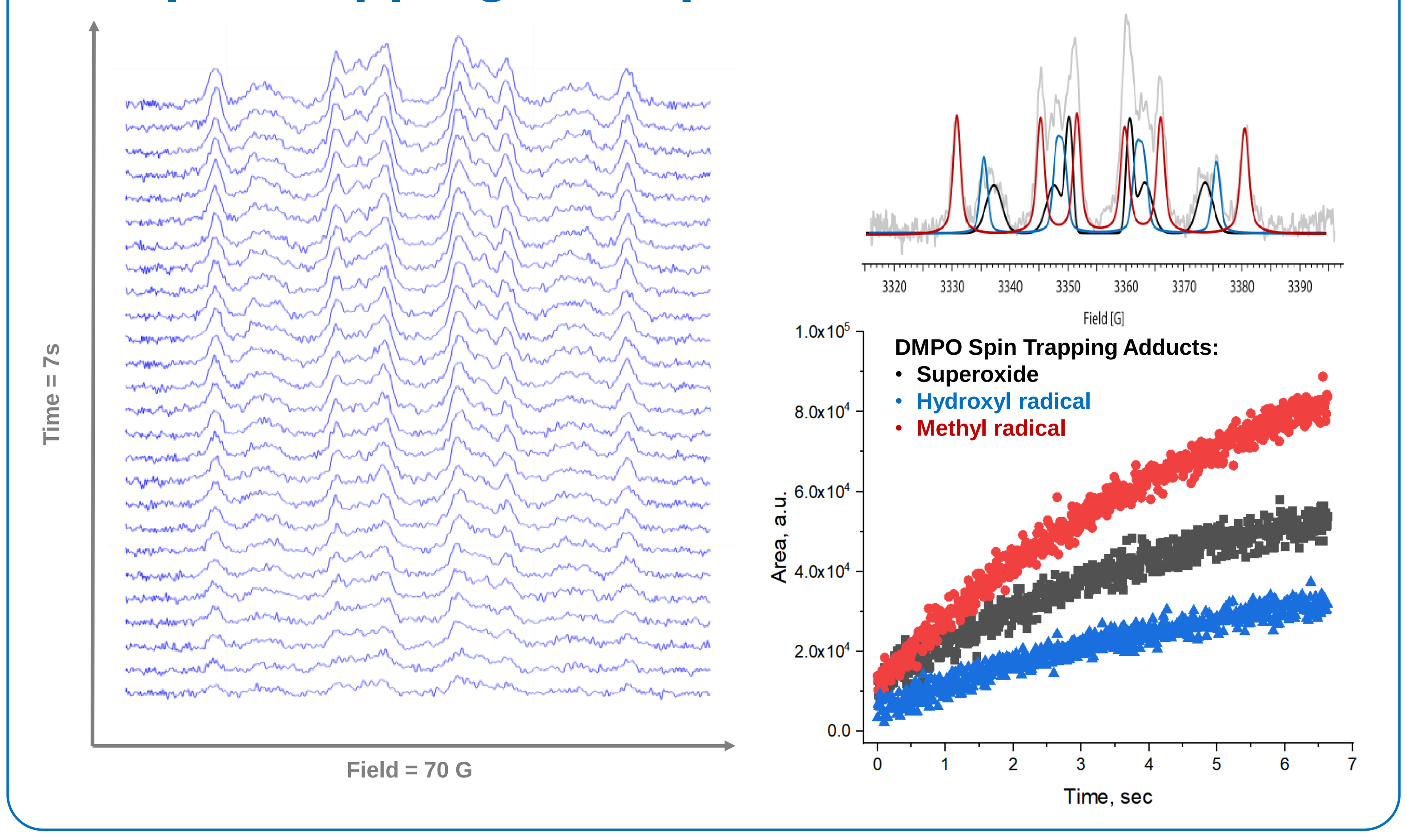

Fig. 4: Spin trapping experiment of a photoinduced reaction on nano particles of TiO_2. Total experimental time: 7 s. Time resolution: 10 ms. Number of time slices: 670. (Left) Selected time slices. (Right) Quantification of the spin trapping adducts using SpinFit and SpinCount.

Summary

- Impressive Signal-to-Noise gain vs CW-EPR
- Reaction monitoring with unprecedented time resolution
- Low temperature compatible (4K -300K)