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Pulsed EPR

In Parts I-III we considered continuous wave EPR: the absorption of a fixed microwave frequency is monitored as a function of a swept magnetic field. In pulsed EPR a fixed frequency, high power microwave pulse is applied at a constant magnetic field: the shorter the pulse length, the greater the excitation bandwidth. Fourier transform of the response of the sample gives a spectrum in the frequency domain. Free induction decay (FID) signals can be monitored, or further pulses applied to give rise to spin echoes which are the basis of many important techniques.

The effect of electromagnetic pulses on spins is treated well in NMR textbooks, and we recommend the following:

- "Spin Dynamics: Basics of Nuclear Magnetic Resonance", M.H. Levitt, John Wiley & Sons Ltd, 2005.

- "Modern NMR Spectroscopy: a Guide for Chemists", J. K. M. Saunders and B. K. Hunter, OUP 1993.

The Bruker website gives a good primer on the fundamentals of pulsed EPR and microwave pulse sequences:

- http://www.bruker-biospin.com/pulse.html

Helpful animations of spin echoes can be found in the following books:

- "Pulsed Electron Spin Resonance Spectroscopy: Basic Principles, Techniques, and Examples of Applications", A. Schweiger, Angew. Chem. Int. Ed. Engl. 1991, **30**, 265-292.
- "Electron Paramagnetic Resonance: A Practitioners Toolkit", M. Brustolon, E. Giamello (Eds) Wiley, Hoboken NJ, 2009.

The most comprehensive text is:

- "Principles of pulse electron paramagnetic resonance" A. Schweiger and G. Jeschke, OUP, 2001.

Because of the much shorter electron (cf. nuclear) spin relaxation times, much shorter pulse lengths are required in EPR than in NMR, and often it is necessary to measure at low temperatures (e.g. for transition ions). Moreover, the excitation bandwidth is rarely sufficient to excite the entire EPR spectrum. Nevertheless, pulsed EPR has developed into a range of robust and hugely powerful techniques, exploiting the advantages of time domain and multi-dimensional methods. Such experiments give access to information that is not accessible by c.w. methods, including information on weakly coupled nuclei, weakly coupled electron spins, and spin dynamics (relaxation).

Some of the most commonly used techniques include:

ESEEM: Electron Spin Echo Envelope Modulation

When a spin echo is generated by a multi-pulse sequence its amplitude decays (due to relaxation processes) as a function of the delay between pulses. Often, the echo decay is observed to be modulated: this is due to weak interactions with nuclear spins (and a breakdown of the $\Delta mI = 0$ selection rule). Analysis of this data identifies the nucleus and gives the weak hyperfine (and quadrupole) interactions which can then be used in, for example, a structural model.

2D correlation experiments based on the ESEEM effect exist: **HYSCORE (Hyperfine Sub-level Correlation Spectroscopy)** produces correlations between nuclear frequencies in the different electron spin manifolds (e.g. ms = +1/2 and -1/2). This aids assignment of spectra containing several overlapping signals.

ENDOR: Electron Nuclear Double Resonance

Pulsed ENDOR spectroscopy involves microwave and radiofrequency pulses. The electron spin echo is monitored as a function of a radiofrequency pulse which pumps the nuclear spin transition(s). This allows access to larger hyperfine interactions than ESEEM but which are still too small to resolve by c.w. EPR.

DEER/PELDOR: Double Electron-Electron Resonance/Pulsed Electron Double Resonance

DEER involves microwave pulses at two different frequencies. The modulation of an electron spin echo is monitored as a function of a second microwave pulse which, being at a different frequency, flips a different set of spins. The change in the second set of spins affects the field felt by the first set (which are giving rise to the spin echo). This allows the determination of the very weak dipolar interaction between remote electron spins to be determined. DEER is a hugely popular tool in biological and materials science applications, particularly when coupled with spin labelling techniques.

The advantages of performing pulsed EPR at different microwave frequencies have been discussed by Eaton and Eaton:

- “Frequency Dependence of pulsed EPR experiments”, S. S. Eaton and G. R. Eaton, Concepts in Magnetic Resonance, Part A, 2009, **34A**, 315-321.