Chapter 6

Electron-Electron Double Resonance

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Abstract: Electron Electron Double Resonance (ELDOR) consisting of a strongly saturating continuous wave (CW) pump microwave source and a nonsaturating observing source, can be used in a field swept display to monitor saturation-transfer mechanisms such as Heisenberg Exchange, nitrogen nuclear relaxation, and rotational diffusion. 2D pulse ELDOR techniques known as DEER or PELDOR using two separate microwave frequencies or a similar “2 + 1” technique using a single frequency have been configured for probing dipolar interactions up to 8 nm. Spin-echo ELDOR techniques have been developed to study slow motions in a wide range of biological problems. Two-dimensional Fourier transform techniques permit all combinations of pump and probe frequencies with nanosecond time resolution making it possible to study the microscopic orientations of a system. Multiquantum ELDOR techniques have been developed to measure the transfer of magnetization and not a reduction factor as measured in a field swept ELDOR.

1. INTRODUCTION

ELDOR is an acronym that stands for electron-electron double resonance, and requires two microwave frequencies within one resonator; one is called a “pump” microwave source and another is the observing microwave source. In the CW mode, the observing microwave frequency that monitors the change in EPR intensity of a line is fixed at a nonsaturating power level. The “pump” microwave source set at a strongly saturating power level irradiates a portion of the EPR spectrum either the same line or a matching line related by a hyperfine coupling, and the effect on the spectrum is monitored by the observing source. The effect observed is due to a transfer of saturation between spins irradiated by the pump source and those spins detected by the observing source. At short times, this is directly
related to the transition probability between the spectral positions. “Saturation transfer” means that the z component of the population difference at the observing frequency is no longer at the Boltzmann population difference. In the CW mode the ELDOR effect is measured by the ELDOR reduction factor $R$ given by

$$R = \frac{(\text{signal with pump off}) - (\text{signal with pump on})}{(\text{signal with pump off})}$$ (1)

In Figure 1, is given an eight level energy diagram showing the cross-relaxation pathways $W_x$, $W_x'$, and $W_x''$ that occur for a radical when there are two nonequivalent protons interacting with an unpaired electron. $W_n$ and $W_e$ are the lattice-induced nuclear spin-flip and electron-flip transitions probabilities, respectively. These transition probabilities are related to relaxation times by the following relations: $W_n = T_n^{-1}$, $W_e = T_e^{-1}$, $W_x = T_x^{-1}$, $W_x'' = (T_x'')^{-1}$. Applying a strong saturating pump source to the left most transition can be detected with a non-saturating observing source as a change in the right most line intensity. The change in intensity depends on the relative values of the cross-relaxation pathways $W_x$, $W_x'$, $W_x''$, $W_e$, $W_n$ and $W_e''$ whose magnitudes are dependent on a given relaxation or combination of relaxations. There are many mechanisms by which saturation of one line can be transferred to another line, resulting in both complexities in the ELDOR spectra and new tools to study mechanisms and their rates.

The theory of ELDOR was developed by Hyde et al. (1968) and Freed (1979, 1979a) who showed that a plot of $R^{-1}$ versus (pump power)$^{-1}$ is linear.