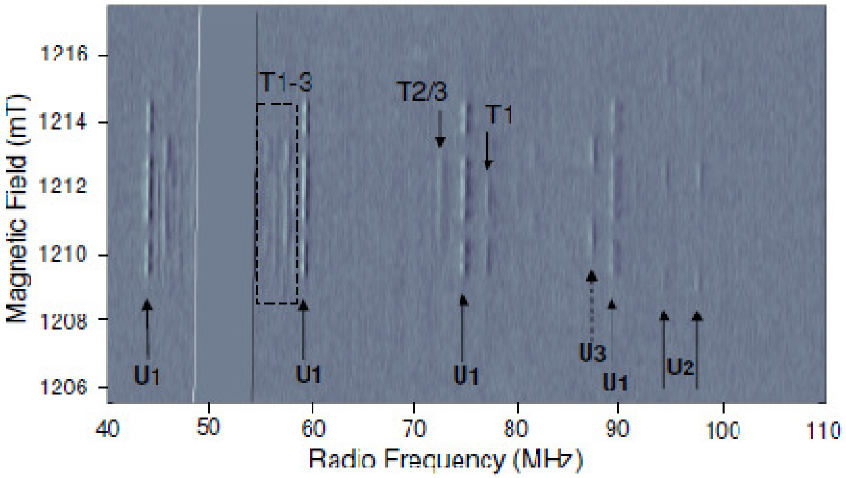
ENDOR in field-frequency space: orientation, species and quantum state selection, H. Vrielinck, F. Loncke, M. A. Tarpan, H. De Cooman, D. Zverev, F. Callens, *42nd Annual Meeting of the Electron Spin Resonance group of the Royal Society of Chemistry*, Norwich (United Kingdom), **19 - 23 April 2009**

Due to its specific detection method, via saturation of the EPR spectrum at a certain magnetic field position, ENDOR measurements are highly selective. Already in the late sixties Rist and Hyde recognized the possibilities of obtaining angular dependent information from powder specimens by recording the field-dependence of the ENDOR spectrum, by grace of the orientation selection principle.[1] However, also for single crystal samples it makes sense to record ENDOR spectra in the two-dimensional field-frequency space (FF-ENDOR). Next to orientation selectivity – when several symmetry-related orientations of the same paramagnetic species are simultaneously detected in the EPR spectrum – such measurements feature species selectivity and, for systems with S > ½ and/or I > ½, also quantum state selectivity. The former facilitates the interpretation of multi- composite EPR spectra, as illustrated in the figure below. Quantum state selectivity offers possibilities of determining the relative signs of spin Hamiltonian parameters, e.g. zero-field splitting and hyperfine, or hyperfine and quadrupole principal values. All these effects will be illustrated through recent examples in or research of radiation-induced radicals in sugars and high-spin transition ion or rare-earth doped fluoride crystals.



Q-band (33.97 GHz) Field-Frequency ENDOR spectrum of sucrose immediately after X-ray irradiation at room temperature. Transitions assigned to the stable (T1-3)[2] *and unstable (U1-3) radicals are labelled.*

References

1. GH Rist & JS Hyde; (1968) *J. Chem. Phys.* **49**, 2449-2450
2. H De Cooman, E Pauwels, H Vrielinck, A Dimitrova, N Yordanov, E Sagstuen, M Waroquier & F Callens, *Spectrochim. Acta A* **69**, 1372-1383