

To resolve the hyperfine and quadrupole interactions between unpaired electron and nuclear spins which are not accessible with EPR or NMR, Feher introduced a double resonance technique [1] called Electron Nuclear Double Resonance (ENDOR). In the ENDOR experiment, an EPR transition, the so-called observer, is partially saturated, and a radio frequency field, the so-called pump, is swept in the region of the nuclear resonance transition. The change in the EPR signal is monitored over the rf frequency. The principle of ENDOR is shown for a $S=1/2$ and $I=1/2$ system in Figure 1. The bottom two spectra a and b correspond to $\nu_n > A/2$ and $A/2 > \nu_n$, respectively.

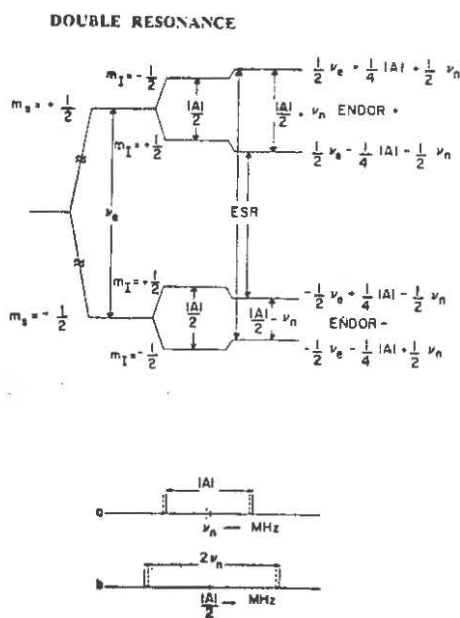


Figure 1

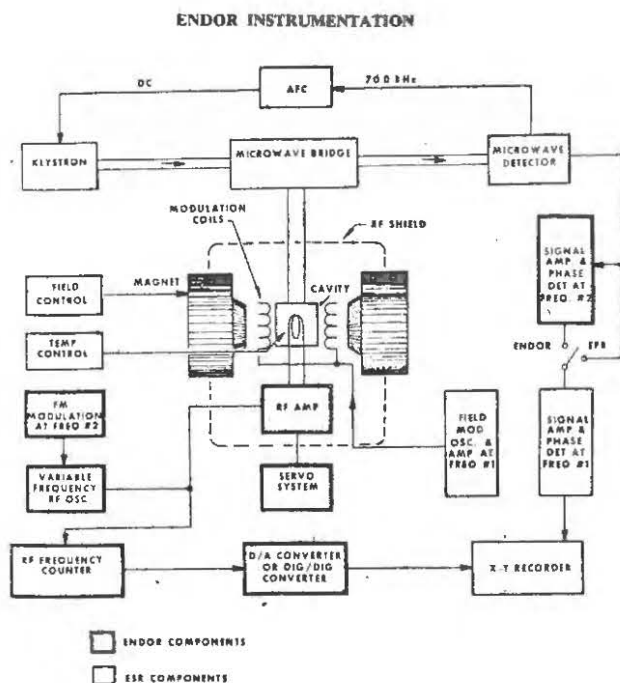


Figure 2

An ENDOR spectrometer is an EPR spectrometer with an extra rf system. The block diagram in Figure 2 shows the difference between these two spectrometers. In low power ENDOR spectrometer, the rf power is usually below 1W. On the other hand, the rf power employed by a high power spectrometer can range from 10W to 100W. In DOUBLE ENDOR, two independently tunable rf fields are mounted in the ENDOR cavity.

While solution ENDOR has been widely used to study organic free radicals, only one such study on transition metal complexes has so far been published [2]. It was found that the eight protons of chromyl ethyleneglyconate anion are equivalent with isotropic hyperfine coupling of 1.74 MHz. In addition, the authors studied the microwave, rf field and temperature dependence of the ENDOR

signal amplitude and line width. The majority of ENDOR experiments on transition metal complexes have been done on solids or glasses. In the first extensive ENDOR study of a transition metal complex, Rist and Hyde [3] applied ENDOR to Cu-8-hydroxyquinolate substituted into a single crystal and a powder of phthalimide. They successfully determined the hyperfine and quadrupole tensors by studying the angular dependence of the spectra. They found that it is possible to obtain single-crystal-like spectrum which corresponds to a restricted orientation, with powder or frozen glass samples. This orientation selection technique has now been generally adopted [4,5].

Of biological systems, hemoglobin (Hb) and myoglobin (Mb) have been the most extensively studied with the ENDOR technique [6]. It has been found that the two high frequency peaks of the proximal histidine nitrogen in Mb-F are about 0.5 MHz lower in frequency than the corresponding transitions in aquo-Mb. This shift is resulted from the trans effect upon the replacement of H₂O by F⁻. Recently, Hoffman applied ENDOR to the nitrogenase MoFe protein and found molybdenum to be correlated to the S=3/2 center [7].

ENDOR induced EPR (EI-EPR) is a convenient method to separate overlapping EPR signals from different radicals, molecular conformations or magnetic sites. In EI-EPR the external field B₀ is swept, and the NMR transition is saturated as a selector. Rudin and co-workers found that single-crystal-like EPR can be obtained with a powder sample by using the EI-EPR technique [8].

Two types of TRIPLE resonance (DOUBLE ENDOR) have been developed [9]. In the so-called "general" TRIPLE, the EPR transition and one of the NMR transitions are partially saturated. The intensity change in single ENDOR is observed while the second rf field is swept. Whereas, in "special" TRIPLE both rf fields are swept simultaneously and symmetrically with respect to the free nuclear resonance transition frequency. General TRIPLE is usually applied to determine the relative signs of hyperfine constants from different nuclei [10]. In special TRIPLE the spectrum amplitude is directly proportional to the number of the nuclei which have the same hyperfine constant. TRIPLE resonance has been used by several authors to study transition metal complexes. Kirste recently showed that TRIPLE resonance can be used to reduce a powder ENDOR spectrum to a single-crystal-like one [11].

In the last few years, ENDOR has shown rapid developments in the following aspects:

1. Increase in its resolution ability by using special rf sources.
2. Increase in its intensity by developing higher power rf frequency field.
3. Time-domain ENDOR.

The ENDOR technique, of course, is not restricted to transition metal complexes. A fast growing interest in double and multiple resonance is noticed in other fields such as radicals, radiation and polymer chemistry, solid state physics, etc. [12,13].

References

1. Feher, G., "Observation of Nuclear Resonances via the Electron Spin Resonance Line", Phys. Rev. 1956, 103, 834.
2. Plato, M.; Lubitz, W., "Examination of the Conditions for ENDOR-in-Solution Experiments on Transition Metal Complexes", J. Phys. Chem. 1982, 86, 149.
3. Rist, G.; Hyde, J., "Ligand ENDOR of Cu-8-hydroxyquinolinatate Substituted into Organic Single Crystals", J. Chem. Phys. 1969, 50, 4532.
4. Rist, G.; Hyde, J., "Ligand ENDOR of Metal Complexes in Powders", J. Chem. Phys. 1970, 52, 4633.
5. Schweiger, A.; Gunthard, Hs.H., "Single Crystal ESR and ENDOR of Bis-(Salicylaldoximate)Cu(II):Bis-(Salicylaldoximate)Ni(II): Copper, Nitrogen and Proton Hyperfine Data and Structure of the Internal H-Bond", Chem. Phys. 1978, 32, 35.
6. Scholes, C., etc., "Electron Nuclear Double Resonance from High- and Low-Spin Ferric Hemoglobins and Myoglobins", J. Am. Chem. Soc. 1979, 101, 1645.
7. Hoffman, B., "⁹⁵Mo and ¹H ENDOR Spectroscopy of the Nitrogenase MoFe Protein", J. Am. Chem. Soc. 1982, 104, 860.
8. Rudin, M.; Schweiger, A., "Proton ENDOR-Induced EPR with Large Magnetic Field Ranges. A New Application to Polycrystalline Sample", Chem. Phys. Lett. 1981, 80, 376.
9. Dorio, M.; Freed, J. "Multiple Electron Resonance Spectroscopy"; John Wiley and Sons: New York, 1979.
10. Cook, R.; Wiffen, D., "Relative Signs of Hyperfine Coupling Constants by a Double ENDOR Experiment", Proc. Phys. Soc. 1964, 84, 845.
11. Kirste, B.; Willigen, H., "ENDOR Study of Bis-(acetylacetonato)-copper(II) in Solid Solution", J. Phys. Chem. 1983, 87, 781.
12. Neverveen, K., "Resolution Enhancement in Electron Spin-Echo Spectroscopy by Means of the Maximum Entropy Method", Chem. Phys. Lett. 1981, 82, 443.
13. Wells, J., "ESR and ENDOR of Irradiated Solid of Biological Significance", Mag. Res. Rev. 1983, 8, 117.