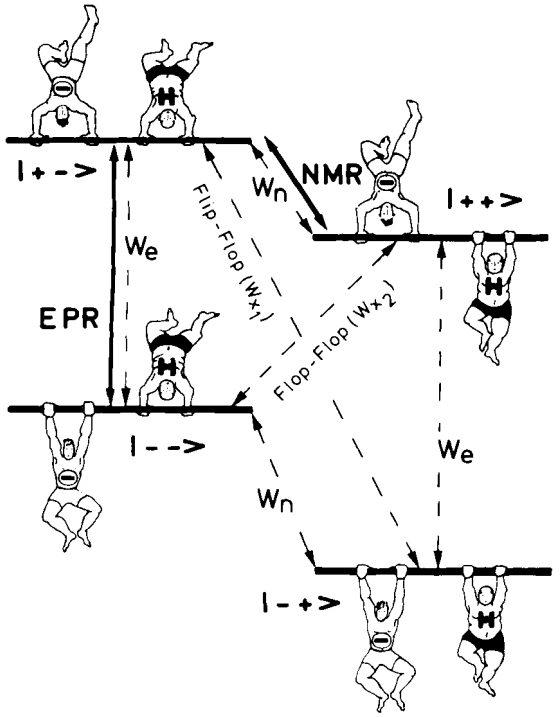
Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution

Application to Organic and Biological Chemistry



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B. Kirste and H. Kurreck, "Electron Nuclear Double Resonance (ENDOR) Investigations of Organic Doublet Radicals in the Nematic and Smectic Phase of Liquid Crystals," Appl. Spectrosc. 34, 305-310 (1980).Â Different types of organic doublet radicals have been investigated in isotropic, nematic, and smectic phases of liquid crystals by performing electron nuclear double resonance (ENDOR), general TRIPLE and special TRIPLE experiments. For this purpose phenalenyls (perinaphthenyls), galvinoxyl, tetra-*tert.*-butylcarbazolyl, and bis(biphenylenyl)propenyl radicals have been chosen including some partially deuterated and ^{13}C-labeled compounds. Anisotropic hyperfine interactions and deuterium quadrupole couplings could be determined. Electron nuclear double resonance (ENDOR) is a magnetic resonance technique for elucidating the molecular and electronic structure of paramagnetic species. The technique was first introduced to resolve interactions in electron paramagnetic resonance (EPR) spectra. It is currently practiced in a variety of modalities, mainly in the areas of biophysics and heterogeneous catalysis. 1H hyperfine (hf) coupling constants of semiquinone radical anions of 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, and 2-methyl-3-phytyl-1,4-naphthoquinone in frozen alcoholic solutions were measured using pulse Q-band electron nuclear double resonance spectroscopy. The resolved signals of the quinone protons as well as from hydrogen bond and solvent shell protons were analyzed and assigned.Â Density functional theory was used to calculate spin Hamiltonian parameters of the radical anions. Solvent molecules of the first solvent shell that provide hydrogen bonds to the quinones were included in the geometry optimization. The conductor-like screening model was employed to introduce additional effects of the solvent cage.