

Figure 3.82 Local magnetic field at the electron, B_1 , due to a nearby nucleus. (Courtesy of Bruker Corporation.)

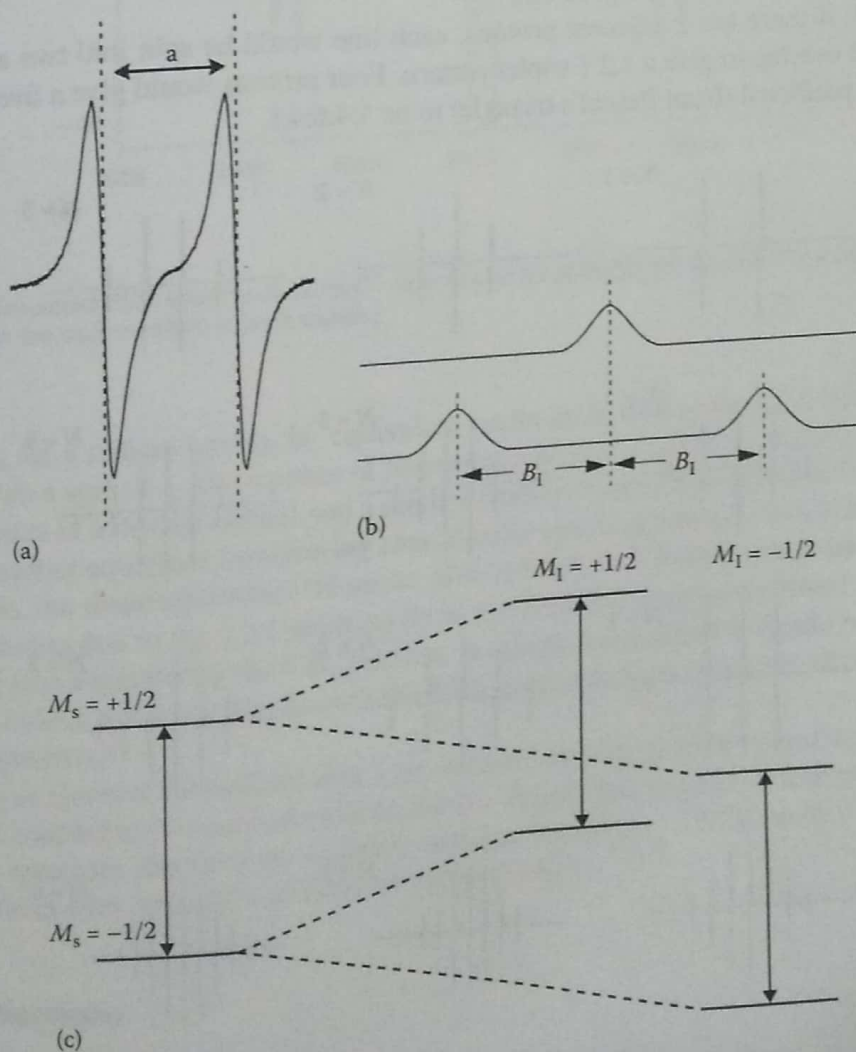


Figure 3.83 (a) Hyperfine splitting of an ESR signal by neighboring nuclei. The distance a is the hyperfine coupling constant. (b) Splitting of the ESR signal due to the local magnetic field of a nearby nucleus. (Courtesy of Bruker Corporation.) (c) Energy levels resulting from splitting by a single spin $1/2$ nucleus. (From Ebsworth, E. et al., *Structural Methods in Inorganic Chemistry*, CRC Press, Boca Raton, FL, 1987. Used with permission.)

The magnetic moment of a nearby nucleus produces a magnetic field, B_1 , at the electron, which may oppose or add to the magnetic field from the instrument magnet. When B_1 adds to the magnetic field, the field for resonance is lowered by the amount B_1 ; when B_1 opposes the magnetic field, the field for resonance is raised by an amount B_1 . For a spin $1/2$ nucleus, such as the proton, the single ESR signal splits into two signals, each B_1 away from the original signal, as seen in Figure 3.83b.

Hyperfine interactions follow the same selection rules as NMR. For isotopes with $I = 0$ (atomic number and mass number both even), no EPR or NMR spectra are seen. For isotopes with odd atomic number and even mass number, the value for I will be an integer, such as ^{14}N with $I = 1$. For isotopes with odd mass numbers, I values will be fractional, such as ^1H , $I = 1/2$.

For one adjacent nucleus with spin $= I$, the number of lines seen in the ESR spectrum is $2I + 1$. (This equation should be compared with the NMR equivalent). For N nuclei, the number of lines $= 2NI + 1$. For example, an adjacent nitrogen atom, $I = 1$, would give a three line ESR spectrum, while Mn, $I = 5/2$, would give a six line spectrum. Figure 3.84a shows the simulated spectra expected from N adjacent nuclei with spin $= 1/2$. The intensity patterns follow the binomial distribution (Pascal's triangle) as in NMR. Figure 3.84b shows similar spectral patterns for $I = 1$, but the relative intensities differ. For hyperfine coupling to 1N atom, for example, the pattern would be 1:1:1, 2N atoms, 1:2:3:2:1, 3N atoms, 1:3:6:7:6:3:1, and so on.

As in NMR, if there are 2 adjacent protons, each line would be split into two additional lines and these would overlap to give a 1:2:1 triplet pattern. Four protons would give a five line spectrum with intensities predicted (from Pascal's triangle) to be 1:4:6:4:1.

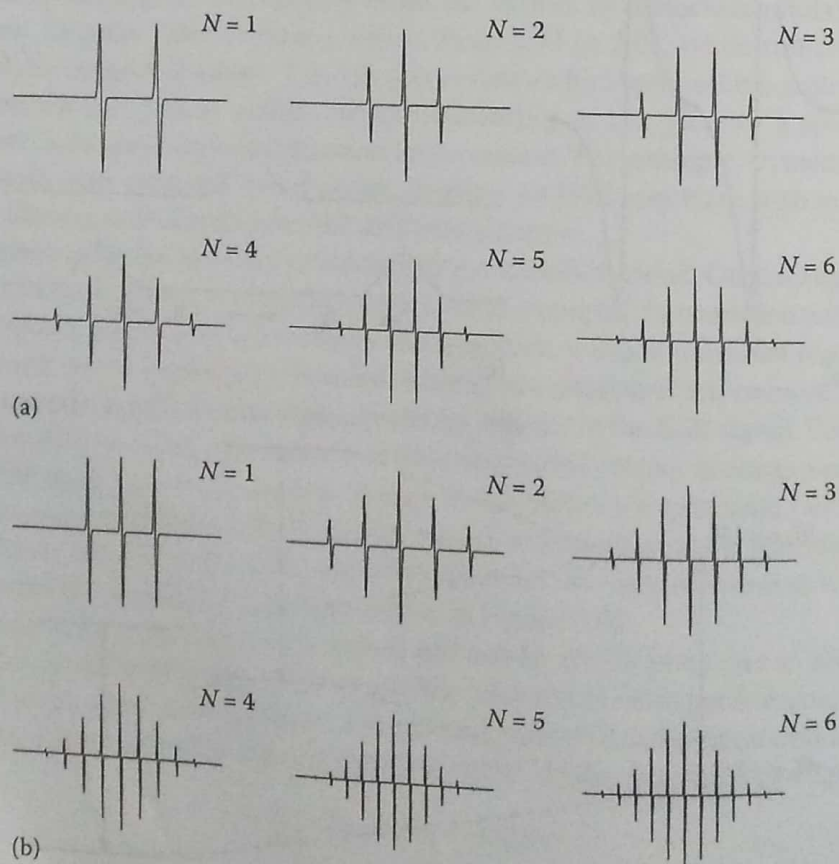


Figure 3.84 (a) Spectral patterns expected for N interacting nuclei with $I = 1/2$. (b) Spectral patterns expected for N interacting nuclei with $I = 1$.

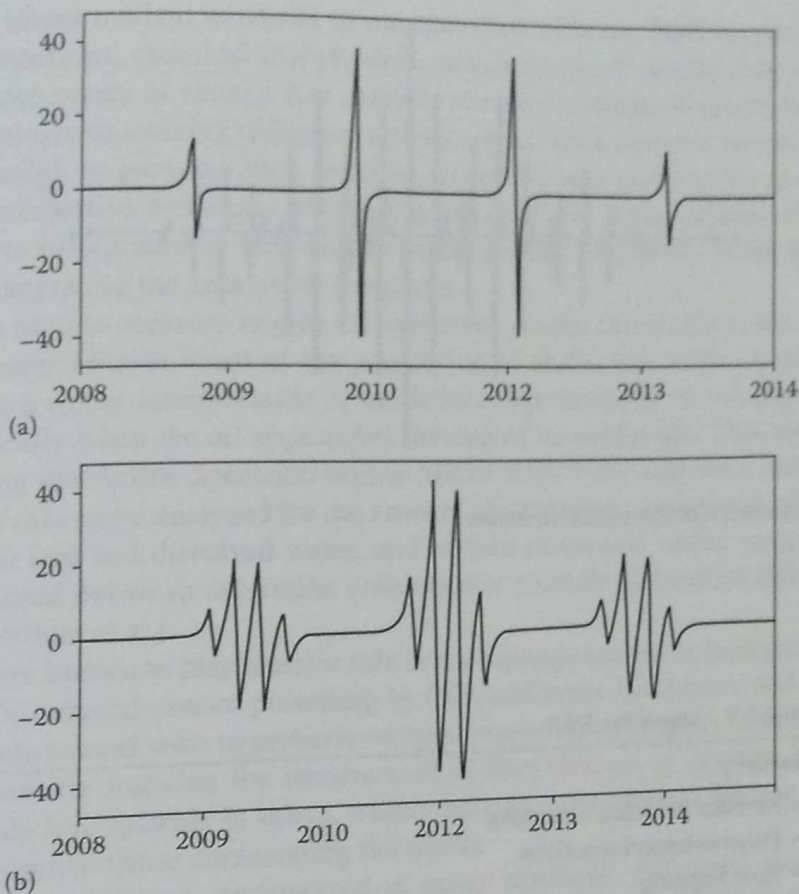


Figure 3.85 Simulated ESR spectra of (a) $\text{H}_3\text{C}^\bullet$ radical and (b) $(\text{CH}_3\text{O})\text{CH}_2^\bullet$ radical. (The unpaired electron is on the carbon atom in both cases.)

In general, for a radical having M_1 equivalent nuclei each with a spin of I_1 and a group of M_2 nuclei, each with a spin of I_2 , the number of lines expected is $N = (2M_1I_1 + 1)(2M_2I_2 + 1)$. The simulated ESR spectra of a methyl radical and a methoxymethyl radical are shown in Figure 3.85.

From the earlier equations (and having seen similar splitting patterns in NMR), it is clear that in Figure 3.85a, the three equivalent ^1H nuclei give $2(3)(1/2) + 1$ lines in a 1:3:3:1 ratio; (b) shows a triplet of quartets due to the 1:2:1 splitting from the 2 methyl protons followed by each of these lines splitting into a quartet by the CH_3 protons. A question the student should be able to answer from having studied NMR is "why doesn't the ESR spectrum show a quartet of triplets instead of the triplet of quartets?"

If we have an electron delocalized over a six-membered ring, as in the pyrazine anion, $\text{C}_4\text{H}_4\text{N}_2^-$, the electron is coupled to two equivalent N atoms ($I = 1$) and then couples to four equivalent protons ($I = 1/2$). The spectrum should show a quintet with intensities of 1:2:3:2:1, with each of those lines split into a quintet with intensities of 1:4:6:4:1 (Figure 3.86).

3.12.4 Applications

ESR is used in chemistry, biochemistry, biology, archaeology, geology, and physics to detect, identify, and study free radicals and paramagnetic compounds and materials. Table 3.7 summarizes some of the uses for ESR.

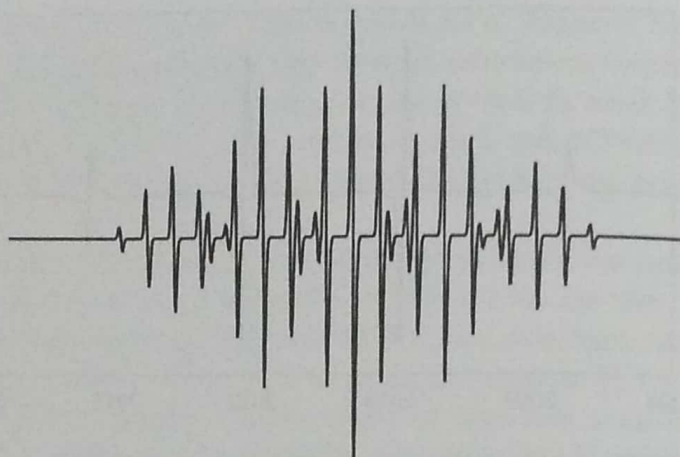


Figure 3.86 ESR spectrum of the pyrazine anion.

Table 3.7 Uses for ESR

Chemistry

- Kinetics of radical reactions
- Polymerization reactions
- Spin trapping
- Organometallic compounds
- Catalysis
- Petroleum research
- Oxidation and reduction processes

Physics

- Measurement of magnetic susceptibility
- Transition metal, lanthanide, actinide ions
- Conduction electrons in semiconductors, conductors
- Defects in crystals (e.g., color centers in alkali halides)
- Optical detection of MR, excited states
- Crystal fields in single crystals

Biology and medicine

- Spin-label and spin-probe techniques
- Spin trapping
- Free radicals in living tissue and fluids
- Antioxidants, radical scavengers
- Oximetry
- Enzyme reactions
- Photosynthesis
- Structure of metalloprotein active sites
- Photochemical generation of radicals
- NO in biological systems

Source: Courtesy of Dr. Ralph T. Weber, Bruker BioSpin, Bruker Corporation.

It is the only direct method available to measure free radicals. ESR is used to study both the radicals and the reactions, chemical and physical, which create or modify free radicals. Examples of reactions that can create or change free radicals are electrochemical reactions, exposure to UV radiation, and exposure to ionizing radiation, among others. ESR samples can be liquid, such as oil, blood, or saliva, solid, or gaseous, such as measurement of soot particulates in air. ESR is both a qualitative and quantitative technique, measuring the type and concentration of free radicals in a sample. Qualitative information is obtained from the g value of a peak, while quantitative results are obtained by integrating the area under the peaks.

ESR has been used to measure engine oil oxidation. As the oil oxidizes, the free radical signal increases in intensity. Measurement of the population of stable free radicals generated by breakdown of the oil is a direct measurement of oxidation. The intensity of the organic radical signal increases dramatically when the oil approaches the end of its useful life. This application has been demonstrated using the Active Spectrum online Micro-ESR™ for real-time monitoring of engine oil. Many types of oil can be analyzed for the amount of oxidation, the amount of soot in the oil, the percentage of both free and dissolved water, and certain metal and sulfur compounds. Crude oils also can be monitored online to determine both organic radicals and metals like vanadium (as the vanadyl radical) (White et al.).

Free radicals are known to play a major role in the damage caused to biological systems by ionizing radiation, UV-induced cancer, poisoning by CCl_4 and some herbicides, and in oxygen toxicity in premature infants treated with hyperbaric oxygen (www.niehs.nih.gov). ESR is used by medical and biological scientists studying the involvement of free radicals in disease. For example, EPR can be used to study free radicals in saliva, which can cause periodontal disease (the inflammation and/or loss of connective tissue surrounding the teeth).

In biochemistry, metal ions are involved in many reactions. All metal atoms with unpaired electrons (paramagnetic ions) can theoretically be studied by ESR, but the experimental conditions vary widely. Atoms with important paramagnetic states that can be measured by ESR include Cu, Fe, Mn, Gd, and V, among others. Oxidation state and coordination can be determined in proteins, for example.

Radiation damage over time creates free radicals in materials. In the case of teeth, free radicals in tooth enamel have been measured to date teeth in archaeology studies and to evaluate exposure of people to ionizing radiation after several major nuclear reactor leaks. Radiation dosimetry and analysis of irradiated foods, gamma-irradiated polymers, and other solids such as ceramics, bone, and coal are common applications of ESR.