

Juan A. McMillan¹
 Instituto de Fisica de
 San Carlos de Bariloche
 Bariloche, Rio Negro, Argentina

Electron Paramagnetic Resonance of Free Radicals

Among the many techniques of investigation that have been developed during the last decade, electron paramagnetic resonance (EPR) is one of the most significant for chemists. It is expected to play a role comparable to that played by optical spectroscopy during the first half of this century. It has already proved to be particularly fruitful in two fields: the study of the electronic configuration of the transition metal ions in relation to the crystalline field, and the study of the products of irradiation of matter, especially free radicals and color centers. For example, EPR studies made on iron(II) and iron(III) complexes suggested hypotheses for the mechanism of transport of oxygen by haemoglobin; also, studies on irradiated plastics have led to the explanation that their improved mechanical properties are due to cross-linking between their molecular chains.

This article will not attempt in the limited space available to duplicate the details of the pertinent theory (1, 2, 5, 7). Rather it will attempt to suggest the importance of the phenomenon as a means of understanding some of the chemistry of free radicals, particularly their stabilization and recombinations.

Electron Paramagnetic Resonance is based on the fact that atoms, ions, molecules, or molecular fragments which have an odd number of electrons exhibit characteristic magnetic properties. Of the $2n + 1$ electrons in such units, the magnetic moments of n electrons are compensated by the other n paired electrons; the remaining unpaired electron has its magnetic moment uncompensated and the molecule itself has therefore a magnetic moment other than zero. For the sake of simplicity, we shall assume that the magnetic moment of the electron is mainly (if not only) due to its spin. This is not too restrictive an assumption in the case of free radicals, since the great majority of them have been found to fit into this category. In the absence of a magnetic field, these magnetic dipoles point at random, and hence all the unpaired electrons have the same energy E_0 (Fig. 1). A further assumption has been made in the foregoing statement: there is no coupling between the spins of neighboring molecules; or, in the language of physicists, there is no spin-spin interaction. This is again almost true in the case of free radicals produced by irradiation, since their dilution in the parent substance is a thousand-fold or more, and neighboring spins are then sufficiently far apart to involve no appreciable interaction. If a magnetic

field is applied, the electron dipoles line up parallel and antiparallel to the magnetic field as a result of a competitive process between thermal motion (that tends to keep the orientation random) and magnetic interaction (that tends to line up all the dipoles parallel). The new energy levels will therefore be, as shown in Figure 1:

$$E_1 = E_0 + \frac{1}{2}g\beta H \text{ for antiparallel alignment, and}$$

$$E_2 = E_0 - \frac{1}{2}g\beta H \text{ for parallel alignment,}$$

where $\pm 1/2$ stands for the quantized spin along the direction of the magnetic field, g is the Zeemann coupling factor (also known as Lande spectroscopic splitting factor or more simply as the g -factor), β is the Bohr magneton, and H the intensity of the magnetic field. The ratio of populations N_1 and N_2 of both levels is a function of the temperature and of the difference $E_1 - E_2$ according to the equation:

$$\frac{N_1}{N_2} = e^{-(E_1 - E_2)/kT}$$

where k is the Boltzmann constant and T the absolute temperature. Since the net magnetization of the sample is proportional to $N_1 - N_2$, it follows that it will increase with decreasing temperature and will tend to vanish at sufficiently high temperature. This is the behavior known as the Curie law of paramagnetic substances, whose first approximation is

$$\chi = C/T + \chi_0$$

where χ is the magnetic susceptibility per unit mass, χ_0 the diamagnetic contribution to the susceptibility, and C is a constant, characteristic of the substance, that depends on the number of unpaired electrons and their g -values. The value of g in the case of a free electron (paramagnetism due to spin only) is 2.0023.

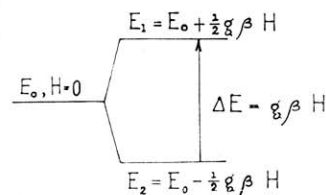


Figure 1. Levels of an unpaired electron in the presence of a magnetic field.

The small departure from 2.0000 is due to a quantum electro-dynamical correction. The magnetic moment of the electron is, therefore, approximately β . However, larger departures from 2.0000 are observed, due to variable contributions of the orbital angular momentum of the electron to the total magnetic moment of the

This article is based on lectures delivered by the author for High School and College Teachers' Summer Institutes supported by the National Science Foundation, under the 1960 Visiting Foreign Staff Project.

¹ Present address: Argonne National Laboratory, Argonne, Illinois.

molecule. The knowledge of the actual value of the g -factor is therefore of main importance, this being one of the objectives of EPR. It should be noted that g is often anisotropic, i.e., its value depends on the orientation of the radical, and therefore is a tensor quantity. In these cases, measurements on single crystals are necessary. Returning to the scheme of levels shown in Figure 1, irradiation of the samples by photons of an energy precisely equal to the difference $E_1 - E_2$ will cause electrons in E_2 to absorb energy and be raised to level E_1 . This is a typical process of resonance, since absorption of photons of either higher or lower energy cannot occur. The promotion of electrons from E_2 to E_1 is counterbalanced by their interaction with the lattice, through which they return to the lower level. This allows a steady absorption to take place. Measurement of the frequency ν of the photons and of the magnetic field H will suffice to determine the actual value of g , since the condition of resonance states

$$h\nu = E_1 - E_2 = g\beta H$$

where h is the Planck constant. Each value of g , therefore, determines the value of the ratio ν/H . Replacing the actual figures for the constants, one finds for example that using magnetic fields of the order of 3000 oersted, the frequency should be of the order of 9 kiloMegacycles/second for an approximate value of g equal to 2. This frequency corresponds to a wavelength of 3 cm (in the microwave region). Since microwave sources can be tuned only to within a very narrow range of frequencies, usually of the order of a few percent, it is much more satisfactory to work at constant frequency and make observations while varying H . The equipment for microwave production, developed for World War II radar, operated at 9 and 23 kMc/sec. Accordingly, most of the EPR results have been obtained at these frequencies. Commercially available equipments operate in 9 kMc/second (X-band). Lower frequencies, that could be obtained with simpler electronic circuits, are not always advisable because the signal-to-noise ratio decreases with decreasing frequency, and the consequent lower magnetic field would no longer be much higher than the magnetic fields due to surrounding nuclear magnetic moments, so that an electron spin would not line up in the direction of the applied magnetic field.

Several types of equipment, as well as the typical operation, have been described elsewhere (2, 5); the author refers the reader to the literature cited at the end of this article for further information on the subject. Essentially, the variation of the absorption of microwave energy by the sample as a function of the magnetic field is measured by conventional devices. Depending on how elaborate the equipment is, the measured effect can be either the absorption of energy or the variation of the absorption with time as a function of the magnetic field. Figure 2 shows typical curves in three cases.

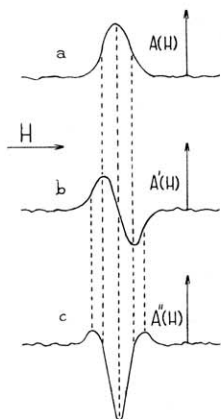


Figure 2. Curves of the absorption of microwave power, its first and second derivatives as a function of the magnetic field H .

Hyperfine Structure

In the foregoing, we have considered only the interaction of the electron with the applied magnetic field leading in general to a well defined frequency of resonance. Rather incidentally, when discussing the choice of lower frequencies, the magnetic field due to neighboring nuclei's magnetic moments was mentioned. Now we will discuss their influence in the observed spectra, which produces a further splitting of levels known as hyperfine splitting, and whose study is the second objective of EPR.

Let us consider first a nucleus of spin $1/2$. In the absence of a magnetic field, these spins (or magnetic dipoles) will point at random. If a magnetic field is applied, these nuclei will line up parallel and antiparallel to the magnetic field, just as in the case of the electron spins. However, since the difference between the nuclear magnetic energy levels is less by several orders of magnitude, the population of both states will not be affected by temperature to the same extent as in the case of electrons. At temperatures above a few thousandths of a degree Kelvin, therefore, the population of both nuclear levels will be, for practical purposes, equal. Consequently, if the unpaired electron is near one of these nuclei, because of the chemical composition of the molecule, for example, the probabilities will be equal for the electron experiencing a magnetic field higher than the applied one (due to the field of a parallel nucleus) or lower (due to an antiparallel one). Each electron level will therefore split into two, as shown in Figure 3a. Since the frequency of resonance of nuclei is very different, nuclei will not be promoted from one state to the other, so that permitted transitions of the electron will occur with constant orientation of the nuclei ($\Delta s = 0$). Accordingly, transitions simultaneously involving electron and nucleus are forbidden, and therefore not observed. Interaction with a nucleus of spin $1/2$, then, splits the spectrum of an unpaired electron into two lines (Fig. 3a). If the spin of the nucleus is 1, there will be three positions for the nuclei with the components of the spin, oriented with respect

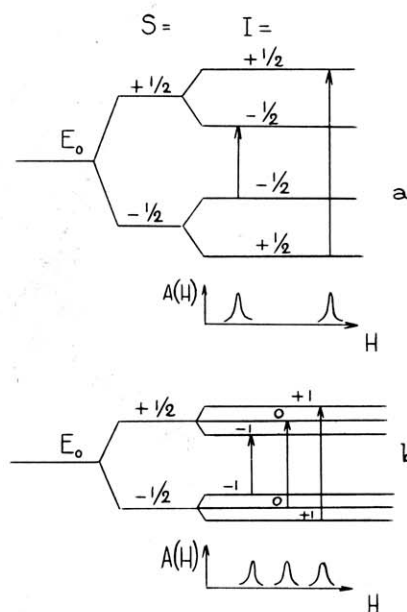
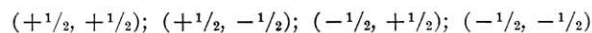


Figure 3. Interaction with a nucleus of (a) spin $1/2$, and (b) spin 1.

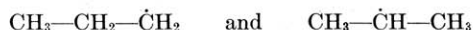
to the direction of the magnetic field, equal to 1, 0, and -1 . As shown by Figure 3b, this leads to three lines in the spectrum since transition will be made only with $\Delta s = 0$. In general, if I is the spin of the nucleus, the hyperfine structure of the spectrum will show $(2I + 1)$ lines. Use is often made of this fact in the study of free radicals, since isotopic substitution of different spin nuclei of the same element often leads to information on the location of the unpaired electron in the molecule. Incidentally, this type of interaction, depending not only on the spin but also on the actual value of the nuclear magnetic moment, often permits an accurate evaluation of these characteristic constants. The hyperfine interaction is sometimes anisotropic, as is the g -tensor; in these cases, a study on single crystals should be made. Considerations of anisotropic interaction are, however, out of the scope of this article. In the following, we shall restrict our discussion to the cases of isotropic splitting.

Interaction with Several Nuclei; Spectra of Free Radicals

There is a tremendous variety of organic compounds of carbon and hydrogen, with and without oxygen. This latter element has zero magnetic moment (with the exception of ^{17}O which is very dilute in natural oxygen) so irradiation of organic compounds produces free radicals which have spectra whose hyperfine structure is due to interaction with protons ($I = 1/2$). If interaction occurs with two equivalent protons, there will be four configurations for the nuclei;



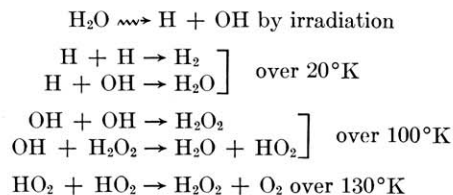
Of these four, the second and third are equivalent. There will actually be, then, three configurations, in the ratio of probability of occurrence 1:2:1, and the spectrum of such a species will exhibit three lines in the same ratio of intensities. Interaction with three protons will give four lines with intensity ratio 1:3:3:1, and so forth. In general, interaction with n protons will give rise to $(n + 1)$ lines, with a distribution of intensities determined by the coefficients of Newton's binomial. In saturated hydrocarbon radicals, the only protons that are equivalent are those bound to the element which also bears the unpaired electron and are near chemical neighbors. For example, irradiation of propanol would be expected to produce the two radicals:



The former would produce a five-line spectrum, the

latter an eight-line spectrum. The experimental evidence shows that a spectrum of eight lines in the ratio of intensities 1:7:21:35:35:21:7:1 is obtained. This suggests that irradiation produces as the more stable free radical, one having the unpaired electron in the middle carbon (7).

Studies on the rate of disappearance of the spectra at different temperatures also provide information in regard to the recombination and eventual appearance of secondary radicals. Studies made, for example, on ice, irradiated and measured at low temperatures, suggest the following reactions (8):



In the case of free radicals, the results will, in general, aim at providing information on: location and magnetic parameters of the unpaired electron in the radical, identification of radicals, and kinetics of recombination.

It should be noted, however, that electron paramagnetic resonance is neither the sole research technique in this field nor the most important. Much information can be obtained by means of less involved techniques, such as optical, infrared, and ultraviolet spectroscopy and most of the common physico-chemical measurements. Electron paramagnetic resonance helps decide between species suggested by more readily available methods; it is essentially a high sensitivity technique.

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