INTRODUCTION TO MICROWAVE SPECTROSCOPY

TERENCE L. SQUIRES

A.M.Brit.I.R.E.

Assistant Editor R. & D. (Research and Development),
Fellow of the Physical Society, late Research Assistant
at the Research Unit in Radiobiology, Mount Vernon
Hospital, Northwood

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TO GRAHAM AND PATRICIA

Introduction

Spectroscopy is at least one hundred years old as a technique. It requires a source of electromagnetic energy which is filtered and focused and then passed through the substance under examination, the emergent energy then being observed and the absorption by the substance noted. From this information details of the structure and general nature of the sample can be deduced.

At first the energy source lay in the visible region of the electromagnetic spectrum but, about fifty years ago, analysis was extended to the regions in the spectrum on either side of the visible region, namely, the ultraviolet and infra-red regions. It is only lately, in the last twenty years, that work has been done seriously at much lower frequencies, that is in the microwave region of the spectrum. Since the energy exchanges are smaller as the frequency of the spectrometer source is reduced, in radio frequency spectrometry finer details of molecular structure can be studied than in other forms of spectroscopy. Radio frequency spectroscopy includes nuclear magnetic resonance, which uses radio frequencies in the v.h.f. (very high frequency) range—about 10 to 100 megacycles—and electron spin resonance, which uses radio frequency energy in the s.h.f. (super high frequency) range—around 10 000 megacycles. In both these frequency ranges a laboratory electromagnet, an indispensable part of the spectrometer, of very high field strength is necessary.

In nuclear magnetic resonance (n.m.r.) the nucleus of the molecule takes part in the phenomenon of absorption of radio frequency energy at a given magnetic field strength. In electron spin resonance (e.s.r.) it is the unpaired electron spinning around the molecule that takes part in the action. Because of the difference in mass between the two systems, the energy exchange is higher in electron spin resonance and so the radio frequency used is correspondingly higher.

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The frequency used in e.s.r. is in the gigacycles region (one gigacycle per second being equal to 1 000 megacycles per second), that is thousands of megacycles per second. The wavelength of such electromagnetic energy oscillations is so minute from the radio viewpoint as to earn the name of "microwave" and hence the title of the book, "An Introduction to Microwave Spectroscopy".

The use of microwave spectroscopy has so advanced that it has now become part of the examination syllabus of many university and technical college courses in chemical analysis and solid state physics, and before very long it may invade the courses for engineering students, especially those studying electronics.

Electron spin resonance has a wide range of applications, exceeding those of the longer established technique of nuclear magnetic resonance. Since e.s.r. occurs at s.h.f., that is in the microwave region, the instrumentation is more involved and is still in the experimental stage. It is, however, possible to obtain many of the microwave components from second-hand sources, and this makes it attractive to laboratory workers with limited budgets. The requirements of the magnet used in e.s.r. are not so exacting as those of magnets used in n.m.r., and this factor tempts many workers to build their own e.s.r. spectrometers.

In this book an attempt is made to introduce the reader to electron spin resonance techniques and to show some of the problems associated with the instrumentation.

This book has been written with the needs of several different types of reader in mind. Amongst them may be mentioned chemists and physicists taking up spectroscopy for the first time; undergraduates in science needing to fill in part of their syllabus; teachers of physical methods in chemistry and other lecturers in radiation studies, solid state physics, etc.; technicians called upon to help with construction and servicing of spectrometers; engineers who have the problem of designing the instrument and others who may have to prepare specifications for them; sales engineers who have to meet and talk with

scientists in this field. To all of these people the book is intended to be a first introduction. Mathematics have been kept to the minimum and wherever possible simple models have been used to illustrate difficult points.

Thanks are due to I. D. L. Ball, B.Sc., Deputy Editor of *R. & D.*, and to Dr. Paul Cook of the experimental radio-pathology unit at the Post-graduate Medical School, Hammersmith, for many helpful suggestions.

A New Spectrometer

Electron spin resonance (e.s.r.) is a relatively new technique which has provided the physicist, chemist and biologist with an exciting and powerful tool. Previous techniques in spectroscopy have used light, ultraviolet and infra-red sources. Control of these sources is well established, and the instruments used are reliable and relatively easy to operate, requiring only a few adjustments prior to use. With many years of design experience behind them, they can be made to operate with the same ease as a laboratory microscope, which needs only an occasional visit from a skilled technician to keep it in working order.

Building a Spectrometer

In e.s.r. analysis, the source of energy is lower in the electromagnetic spectrum, namely, the radio frequency end, and in consequence the instrumentation is complex. It is a highly skilled task to design and operate microwave apparatus despite the advances in the art over the last twenty years. Apart from microwave equipment an e.s.r. machine needs the services of a large homogeneous d.c. magnet, which demands a great deal of engineering skill to design.

Even those scientists who will only operate an e.s.r. equipment should be aware of the limitations of the apparatus, to avoid accepting erroneous or spurious results from the machine. Many of the components required to build a simple e.s.r. spectrometer can be purchased from surplus stores or secondhand. As a correspondent[1] to a well-known scientific journal has stressed, the best way to understand an e.s.r. spectrometer is to build one. The need to understand how the apparatus works before using it as a research tool is an aid to the scientist

and his assistants, and such knowledge is best obtained by actually building one.

Conditions for Absorption

If a small quantity of a chemical substance is placed at a point in space where there are two magnetic fields at right angles, then, providing that certain conditions are fulfilled, the phenomenon of e.s.r. will occur and can be recorded on suitable display equipment. The two magnetic fields are widely different: one is powerful (several thousand gauss) unidirectional and constant in value; the other (at right angles to the first) is very small (less than one gauss) and changes its direction and value at a super high frequency (s.h.f.). The latter field is often called the r.f. field or microwave field since the term s.h.f., although correct, is not in common use.

For any given chemical substance, if the value of the steady field and the frequency of the varying field have a fixed ratio to one another, then energy will be absorbed by the material from the s.h.f. field. This absorption, when recorded, provides information about the state of the molecules and atoms making up the chemical substance. Thus an analysis which tells us a great deal about the structure of the molecule is performed.

Chemical Analysis in Seconds

Free radicals, which can be produced from normal molecules by a number of agents including radiation, have lifetimes which vary from seconds to many years. How long they take to recombine is influenced by many factors; oxygen, for example, may accelerate the process. Temperature variations may also have some effect on the free radical concentration. With the e.s.r. spectrometer one is able to follow and record these changes and do in seconds an analysis which would take a chemist using other methods many hours. In fact, in some cases it would be impossible for the chemist to make an analysis at all, especially where recombination occurs within seconds. In some research applications the e.s.r. spectrometer is actually linked to the apparatus producing the radicals (a radiation

source) so that an instantaneous analysis can be carried out before the short-lived radicals reform again. Their actual recombination is then followed by the machine over a period of seconds and this fact recorded.

The technique of e.s.r. was discovered in 1945 by Zavoisky[2] and was later used to study radiation damage by Hutchinson[3] in 1949. Since then the number of applications has grown, and it is probable that many fundamental problems in physics, biology and chemistry, now of a speculative nature, will be solved by its use.

Instrumentation

The instrumentation used in e.s.r. and n.m.r. are similar. Both require d.c. magnetic field strengths of several thousand gauss to produce the phenomena of absorption of radio frequency energy, but whereas nuclear magnetic resonance is concerned with the magnetic properties of the *nucleus* of an atom, in electron spin resonance the interaction is with the *electron spins*.

Until the end of the book, e.s.r. only will be discussed since this is the most interesting technique from the instrument point of view. Later n.m.r. will be introduced and some simple apparatus for detecting n.m.r. described. Nuclear magnetic resonance apparatus can be used as a gauss-meter and is useful in calibrating the field strength of the large magnet (see chapter 7) required in r.f. spectroscopes.

Signals from Free Radicals

The chemistry of e.s.r. forms a subject on its own which is adequately dealt with by most of the standard textbooks[4] and scientific articles.[5] Engineers and technicians concerned with the design and construction of e.s.r. equipment will, however, need some chemical knowledge to understand the fundamental processes that go on during the absorption of radio frequency energy by the sample, which may be organic or inorganic matter, under investigation, and we shall start by giving a simplified account of this chemistry. Although e.s.r. is concerned with the

absorption effect in many types of molecule having an unpaired electron, it is simpler to start by considering the behaviour of a stable free radical, of which diphenyl picryl hydrazyl (d.p.p.h.) is a common example.

In talking about e.s.r. we shall concern ourselves with three items: a free radical, a large d.c. magnetic field, and a very weak radio frequency (s.h.f.) field. Then we shall go on to consider the production of all three and the relationships between them which causes the detectable energy changes which tell the analyst so much.

A Free Radical

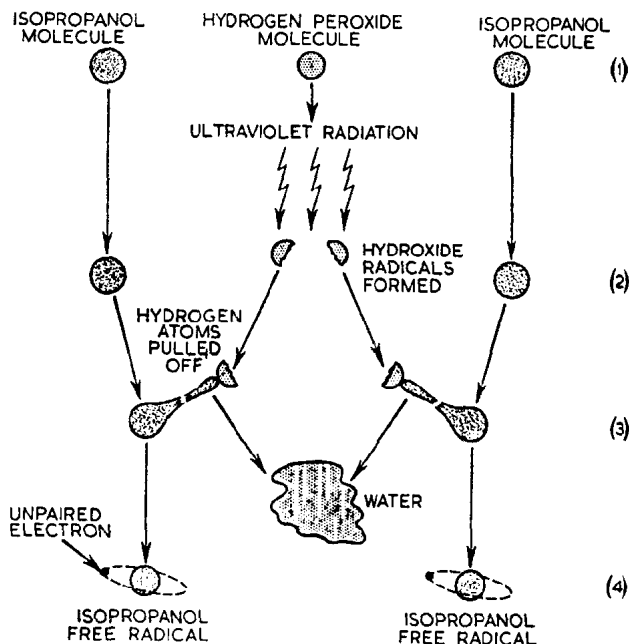The simplest radicals to understand are usually those organic

Fig. 1. The production of two free radicals ready to take part in e.s.r. action

radicals formed by breaking the chemical bonds in molecules by exposing them to a source of radiation. Free radicals produced in this way may recombine in time, although some may remain permanently defected. One permanent free radical is diphenyl picryl hydrazyl (d.p.p.h.), which is a highly soluble, dark-red crystalline substance used to demonstrate and check the working of many e.s.r. machines. A free radical can be formed when a covalent molecular bond is broken and an unpaired electron is left in orbit.

In Fig. 1 is shown how, when a mixture of isopropanol and hydrogen peroxide is exposed to an ultraviolet light, two free radicals are produced. The hydrogen peroxide, split into two hydroxide radicals, takes a hydrogen atom from the two isopropanol molecules. The result is two isopropanol radicals with unpaired electrons in orbit.

Electrical Behaviour of a Free Radical

A free radical with an unpaired electron in orbit behaves, electrically, in a most significant manner. The electron rotating around the rest of the molecule is equivalent to a current flowing in a complete turn of wire without resistance, and thus it produces a magnetic field which passes through its centre as shown in Fig. 2. This may be likened to the effect produced by a bar magnet with a N and S pole at opposite ends. Also as the electron is circling around the molecule it acts rather like a gyroscope, with the same reluctance to change the direction of its axis of spin. The bar magnet in our analogy would therefore be spinning around on its own longitudinal axis.

If a quantity of these free radicals are placed in a strong unidirectional and constant value magnetic field, H, some of the bar magnets will take up a position relative to the d.c. field as shown in Fig. 3. Since the bar magnet, M, is spinning around its own axis it is prevented from aligning itself with the line of force produced by the field, H, as it would if it were just a compass needle, for instance. Because of this spinning, the magnet will precess around an axis formed by the H field lines of force. This is similar to the effect which can be observed in

UNPAIRED ELECTRON
IN ORBIT

UNPAIRED ELECTRON
IN ORBIT

N   FIELD DUE TO
ELECTRON CURRENT

FREE RADICAL

(a)

S

(b)

N

M   EQUIVALENT
BAR MAGNET

BEHAVES IN THE LARGE EXTERNAL
MAGNETIC FIELD LIKE A GYROSCOPE
WOULD UNDER THE INFLUENCE OF GRAVITY

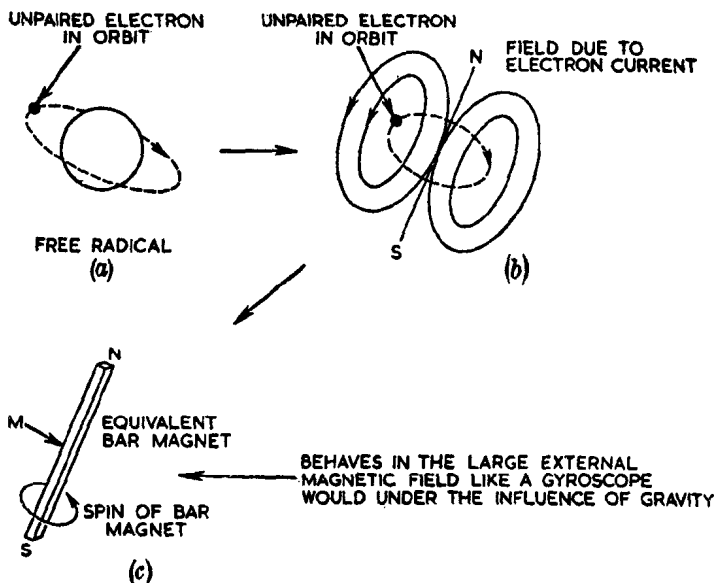SPIN OF BAR
MAGNET

S

(c)

Fig. 2. *How a free radical acts as a bar magnet with mass*

a spinning top as it begins to topple over due to the force of
gravity.
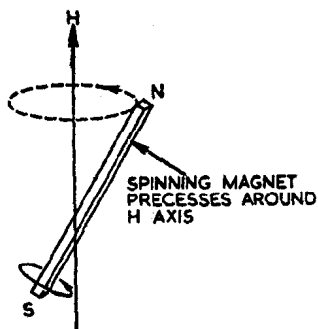
This effect alone cannot be detected, and before any infor-

H

N

SPINNING MAGNET
PRECESSES AROUND
H AXIS

S

Fig. 3. *The bar magnet in a strong field H*

mation can be obtained from the radical a second magnetic field is needed. Its value is considerably smaller than the first magnetic field and is applied at right angles to it. Whilst the first field is constant and unidirectional, the second alternates, changing both its direction and amplitude at a frequency which is of the order of several thousand million cycles per second. The result of this radio frequency field on the magnet, M, is
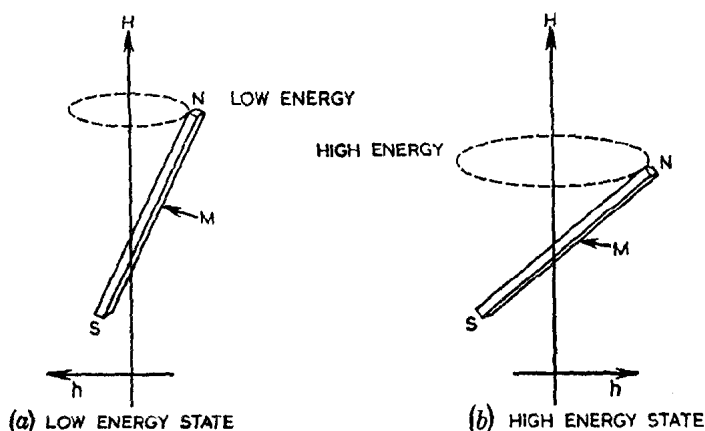

Fig. 4. Different energy levels caused by varying field H

shown in Fig. 4. When it is acting in one direction it makes M tip away from the axis of the H field (*b*), and when acting in the other direction it will tip the bar magnet so that it is more in line with the H field (*a*). In position (*b*) more energy is stored in M, the imaginary bar magnet, than in position (*a*).

This energy change can be illustrated by a commonplace example. In Fig. 5 a hand is shown lifting a beam against the force of gravity. When the beam is lifted away from gravity it has more energy stored in it than when it is allowed to drop nearer to the ground. Thus the beam can be moved back and forth between two energy levels, the difference in these levels being equal to the energy supplied by the hand.

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