APPLICATIONS OF
NUCLEAR MAGNETIC RESONANCE
SPECTROSCOPY
IN ORGANIC CHEMISTRY

by

L. M. JACKMAN

FOREWORD

NUCLEAR magnetic resonance was first observed in bulk matter in 1945 by Purcell, Torrey and Pound at Harvard University, and Bloch, Hansen and Packard at Stanford University. The spectra were used to study nuclear properties, and the ways in which the nuclei would exchange energy with themselves and with their surroundings. Many fascinating experiments gave new insight into a variety of problems in physics including thermodynamics and subtle details about the properties of solids and liquids.

In 1948, nuclear resonance spectra were applied to the determination of distances between hydrogen atoms in some crystals and to the study of hindered molecular motion in solids. A number of chemical problems of this kind were then solved. In 1949 Knight described the so-called "chemical shifts" in metals, and in 1950 similar effects in chemical substances were described by Proctor and Yu, by Dickinson, by Lindström and by Thomas. Only one year later Arnold, Dharmatti and Packard showed that the hydrogen resonance of alcohol contained three lines, assignable to the CH_3, CH_2 and OH hydrogens. From this time it was clear that nuclear magnetic resonance, discovered only five years earlier, would be of considerable importance to organic chemists.

The methods of observing these high resolution nuclear magnetic resonance spectra have been developed with great rapidity and will, no doubt, receive considerable further refinement to improve the quality and reproducibility of the spectra. The method is already used extensively by chemists for structural determination, for studies of isomerism, reaction rates, molecular interaction and chemical equilibria.

The principles of the method and the interpretation of the results are usually rather simple, but the method can be used efficiently only with the aid of the many results and correlations already described in the literature.

This book is therefore very welcome and describes in a simple way how any organic chemist may understand some of the uses of this technique and interpret the spectra of his compounds.

Lincoln College,
Oxford.

Dr. R. E. RICHARDS, F.R.S.

EDITORIAL PREFACE

PRIOR to 1958, examples of the successful application of nuclear magnetic resonance (n.m.r.) to problems in structural organic chemistry were so few in number that organic chemistry departments could scarcely justify the purchase of expensive high resolution equipment. Now, less than two years later, departments which do not possess an n.m.r. spectrometer are at a considerable disadvantage relative to those where such facilities are available.

This new technique has many obvious, although not always unique, applications to the identification of functional groups. For example, the n.m.r. method can be used to demonstrate the presence or absence of a methyl ketone, a problem which can also be resolved by chemical methods, though with more effort and with the consumption of the compound under investigation. However, the real power of n.m.r. derives from its more subtle features. Thus chemical shift and spin-spin coupling data, when interwoven with the results of chemical experiments, may lead to a simplified solution of even complex structural problems. Indeed the method offers a new fascinating approach to work of this kind.

There are several problems which face the organic chemist who wishes to employ n.m.r. spectroscopy. Firstly he must acquire a working knowledge of the subject. In this respect his theoretical requirements will be of minor importance, but he will need to become familiar with the regions of absorption of protons in the more common organic chemical environments, and with the simpler concepts of spin-spin coupling. This book will satisfy these needs in an exemplary manner. Secondly, he will need to be aware of potential applications of the methods which lie outside his general experience. When such situations arise he will then be able to consult colleagues who are competent to tackle such tasks, for it would be quite unrealistic to expect the practising organic chemist to undertake the mathematical computations required for the analysis of certain complex spectra. The author of this book has carefully drawn attention to this situation and has wisely refrained from interspersing the text with mathematical equations which would render it incomprehensible to most of the intended readers.

It is indeed fortunate that Dr. L. M. Jackman, who has become an expert in n.m.r. spectroscopy, could be persuaded to write a clear and authoritative text suitable for organic chemists. The subject will obviously develop further in the next few years and the present volume is not the final word on progress in this field. Nevertheless, the applications of n.m.r. spectroscopy to organic chemistry are already so numerous and so important that an account of the subject at the present time is certainly justified. Dr. Jackman's book is warmly recommended to all organic chemists and to workers in other disciplines who are interested in any way in organic molecules.

Professor D. H. R. BARTON, F.R.S.

Imperial College of Science and Technology,
London.

PREFACE

NOWADAYS, the practice of pure organic chemistry requires the use of a number of physical methods, the fundamentals of which belong to the realms of chemical physics. Consequently, organic chemists have come to rely on standard treatises which provide simplified introductions to the theory of such methods, together with compilations of relevant data which can be used for the characterization of organic compounds and for the elucidation of molecular structure and stereochemistry. The most recent method to be adopted by the organic chemist is nuclear magnetic resonance spectroscopy and although the widespread use of this technique has only just commenced many workers are already alive to its considerable potential. For this reason there is a need for a text which provides a non-mathematical introduction to the theory and practice of n.m.r. and which provides such classified data as is at present available. In this book I have attempted to satisfy these needs. I have tried to keep the physical background to a minimum since physical concepts often constitute a "potential barrier" to the organic chemist. At the same time I consider that an understanding of the pertinent physical principles is vital if this powerful technique is to be used with maximum effect. Thus, I have tried to present these principles descriptively at the same time providing references for those readers who may wish to pursue the rigorously mathematical approach.

An unfortunate consequence of writing about n.m.r. at such an early stage in its development is that I have had to commit myself and my readers to one specific method of expressing the chemical shift of hydrogen, whereas in fact a number of systems are in current use and several committees are at present deliberating on such matters. The system I have used is that of τ-values introduced by G. V. D. Tiers. I have chosen the method of Tiers because I believe that its simplicity will appeal to organic chemists and because the values for a vast majority of protons in organic molecules lie between zero and ten and are thus readily committed to memory. If an alternative system is adopted by international agreement it must certainly be based on an internal reference so that the data in this book will be readily convertible to the new units.

I have drawn on the chemical literature up till May 1959 but as it appeared desirable to limit this book to its present length I have been able to quote only a few of the many examples of the application of n.m.r. in structural studies.

I consider that one of the principle features of this book is the summarized experimental data which it contains and I am therefore most happy to acknowledge my gratitude to Dr. G. V. D. Tiers of the Minnesota Mining and Manufacturing Co., and Dr. N. F. Chamberlain of the Humble Oil and Refining Company who provided me with their extensive compilations of unpublished data.

Although this book is comparatively short, the list of colleagues to whom I am indebted is long and I am glad of this opportunity to acknowledge their help.

July 1959   L. M. JACKMAN

Note added in proof. It is now conventional to present spectra with the field increasing from left to right. With the exception of Figs. 2·15, 5·4, 6·1, 6·2 and 6·16, spectra reproduced herein accord with this convention.

CONTENTS

CHAPTER 1

INTRODUCTION AND HISTORICAL REVIEW

1.1 DYNAMIC AND MAGNETIC PROPERTIES OF ATOMIC NUCLEI

APART from the use of atomic numbers and isotopic weights, the organic chemist has largely developed his subject without any special knowledge of the properties of atomic nuclei. The recent advent of nuclear magnetic resonance spectroscopy and, to a much lesser extent, microwave and pure quadrupole spectroscopy, has altered this state of affairs and organic chemists of the present generation have now to become acquainted with certain subjects hitherto the domain of the nuclear physicist and spectroscopist. Thus today a table of atomic weights of those elements commonly encountered by the organic chemist might usefully include other nuclear properties such as spin numbers, nuclear magnetic moments, and nuclear electric quadrupole moments. Of these additional nuclear properties the spin number, I, and the nuclear magnetic moment, μ, are of particular interest; the nuclear electric quadrupole moment, Q, will enter only occasionally into our discussions.

The nuclei of certain isotopes possess an intrinsic mechanical spin; that is they are associated with an angular momentum. The total angular momentum of a nucleus is given by $(h/2\pi).[I(I+1)]$ in which h is Plank's constant and I is the *nuclear spin* or *spin number* which may have the values $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ depending on the particular isotopic nucleus ($I = 0$ corresponds to a nucleus which does not possess a mechanical spin). Since atomic nuclei are also associated with an electric charge, mechanical spin gives rise to a magnetic field such that we may consider a spinning nucleus as a minute bar magnet the axis of which is coincident with the axis of spin.* The magnitude of this magnetic dipole is expressed as the nuclear magnetic moment, μ, which has a characteristic value for all isotopes for which I is greater than zero.

In a uniform magnetic field the angular momentum of a nucleus ($I > 0$) is quantized, the nucleus taking up one of $(2I+1)$ orientations with respect to the direction of the applied field. Each orientation corresponds to a characteristic potential energy of the nucleus equal to $\mu . H_0 . \cos \theta$ where H_0 is the strength of the applied field and the angle θ is the angle which the spin axis of the nucleus makes with the direction of the applied field. The importance of I and μ in our discussion is that they define the number and energies of the possible spin states which the nuclei of a given isotope can take up in a magnetic field of known strength. A transition of a nucleus from one spin state to an adjacent state may occur by the absorption or emission of an appropriate quantum of energy.

---

*The neutron has $I = \frac{1}{2}$ and possesses a magnetic moment even though it has no net charge. This apparent paradox is resolved in terms of Yukawa's dissociation theory in which it is assumed that the neutron, for a fraction of its life-time, is partially dissociated to a proton and negative meson, the magnetic moment of the latter being larger than, and of opposite sign to, that of the former.

Nuclei of isotopes for which $I > \frac{1}{2}$ are usually associated with an asymmetric charge distribution which constitutes an electric quadrupole. The magnitude of this quadrupole is expressed as the nuclear quadrupole moment Q.

Finally in this brief introduction to the properties of spinning nuclei we must consider the behaviour of a nucleus when subjected to a torque which tends to alter the spatial orientation of its axis of rotation. The general behaviour of a rotating body under the influence of a torque acting about an axis perpendicular to the axis of rotation is shown in Fig. 1.1. A torque of this nature does not affect
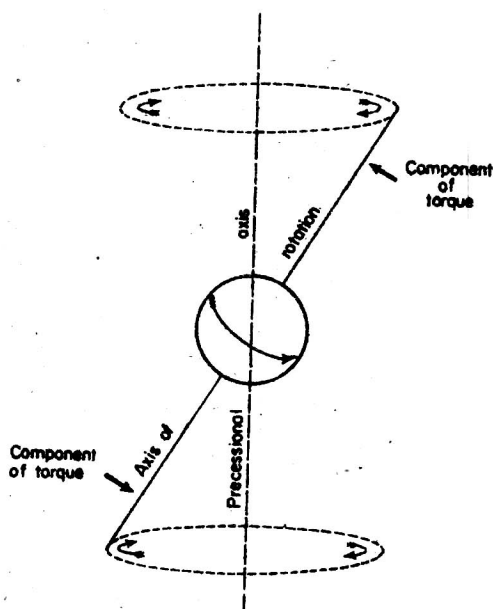
Fig. 1.1 Precessional motion of a rotating body.

the magnitude of the angular velocity of the body but causes the axis of rotation to alter continuously so that each pole of the axis sweeps out a circular path. The imposed motion is called precession* and familiar examples include the behaviour of toy gyroscopes and the precession of the equinoxes. A spinning nucleus will execute precessional motion under the influence of the torque imposed by a uniform magnetic field.

The properties discussed above are the basis of our subject. Now that we have defined them we can describe the sequence of events which has led to the discovery of one of the most powerful aids to organic chemistry and so acknowledge our debt to the physicist.

1.2 THE HISTORICAL BACKGROUND TO NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The concepts of nuclear spin and magnetic moment were developed at about the same time as the analogous properties of the electron. Uhlenbeck and Goudsmit[1]

*In accordance with common usage in the literature of nuclear magnetic resonance phenomena we shall employ the verb to *precess* although it does not appear in the O.E.D.

(1925), and Bechowsky and Urey[2] (1926), independently postulated the properties of angular momentum and magnetic moment of the electron in order to account for certain aspects of the fine structure of the atomic hydrogen spectrum. There had been prior suggestions that the electron possessed spin properties, and Pauli[3] in 1924 had even suggested that the hyperfine structure observed in atomic spectra could be explained if it were assumed that the *nuclei* of certain isotopes were associated with a magnetic moment. The idea of electron spin was rapidly accepted and it was not long before convincing experimental confirmation of nuclear spin and magnetic moment was forthcoming. Dennison[4] (1927) showed by heat capacity studies that hydrogen gas was composed of two molecular species (ortho- and para-hydrogen) which differed in the symmetry of their nuclear spin wave functions. Further evidence was obtained by Hund[5] from the rotational structure in the band spectra of homonuclear diatomic gases, and Pauli's original suggestion that nuclear magnetic moments were responsible for the hyperfine structure in the atomic spectra of pure isotopes also received experimental verification.[6]

Thus by the early 1930s the spins and magnetic moments of a number of isotopes had been determined and the following years saw further intensive research in this direction. This period also saw the development of two experimental techniques which ultimately pointed the way to nuclear magnetic resonance spectroscopy. The first of these was the extension by Estermann and Stern[7] of the original Stern–Gerlach experiment to a study of the magnetic deflection of atomic and molecular beams. The magnetic moment of the proton was first determined in this way. The second technique was introduced by Rabi and his co-workers[8] in 1939 and is called the molecular beam resonance technique. In the Estermann–Gerlach experiment a collimated beam of nuclei is split by an inhomogeneous magnetic field into components corresponding to the different spin states of the nuclei, i.e. to different values of I. Rabi's method involves a refocusing technique in which the deflected beam is subjected to a second inhomogeneous field which causes the nuclei to retrace the deflection caused by the first field. If during its passage through the two fields a nucleus changes its spatial orientation (i.e. if it undergoes a transition to another spin state) it will not be refocused, and the essential feature of the molecular beam resonance method is that it permits the detection of nuclear spin transitions. Normally, the number of nuclei which undergo transitions during the passage through the two fields is negligible. However, if prior to refocusing, the deflected beam is passed through a homogeneous magnetic field and simultaneously irradiated with electromagnetic radiation transitions between spin states will occur provided the frequency of the radiation corresponds to the energy difference between the spin states (p. 7). It transpires that for the strengths of the homogeneous field employed in these experiments the correct frequency lies in the radiofrequency region. The exact radiofrequency which will cause the efficiency of refocusing to fall to a minimum is a function of I, μ, and the strength of the homogeneous field, so that if I is known the value of μ can be determined.

We shall see in the next chapter that nuclear magnetic resonance spectroscopy involves the principles embodied in Rabi's method, the difference between the two techniques being of an experimental nature. In the latter method the absorption and emission of radiant energy is observed by virtue of its effect on the nuclei

whereas the former technique turns out to be a genuine spectroscopic method in as much as the absorption of electromagnetic energy is detected directly.

1.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY— PAST, PRESENT, AND FUTURE

Molecular beam resonance techniques were used in 1937 to determine the magnetic moment of the neutron[9] and were extended in 1938-1939 to atomic nuclei. The stage was thus set for the entry of nuclear magnetic resonance spectroscopy which was to be a simpler method applicable to all phases of matter. The first attempts directly to observe the absorption of electromagnetic radiation by matter were made by Gorter and Broer[10] in 1942. The substances examined were lithium chloride and potassium fluoride at low temperatures. These experiments were unsuccessful and although the correct reasons for their failure were advanced it was not until four years later that successful experiments were reported by two independent groups, namely Purcell, Torrey and Pound[11] at Harvard, and Bloch, Hansen, and Packard[12] at Stanford University. The impact of these experiments was immediate. For the first few years the method continued to be the province of the physicist and physical chemist and, although in this book we must perforce ignore much of this work, the discoveries and advances during this period make dramatic and exciting reading.[13]

Four or five years after the first successful nuclear magnetic resonance experiments there appeared several reports of a phenomenon which has since proved to be general and of the utmost significance to the organic chemist. It was found[14] that the characteristic absorption frequency of a nucleus in a magnetic field is dependent to a small but measurable extent on the molecular environment of the nucleus. In other words it was now apparent that nuclear magnetic resonance spectroscopy was not only a method for investigating nuclear parameters and certain physico-chemical problems but that it might possibly be useful in studies of molecular structure. The rapidity with which this possibility has become a reality can be gauged by the fact that this and other books dealing with the relation of nuclear magnetic resonance spectroscopy to molecular structure have been written within ten years of the original observations referred to above.

At the present time, nuclear magnetic resonance spectroscopy is finding wide application in organic chemistry although it would be incorrect to say that it is used as frequently as some other spectroscopic methods, for as yet many laboratories are without the necessary equipment. However, those workers who have both access to the method and the experience in interpreting the results cannot fail to agree that nuclear magnetic resonance spectroscopy is an extremely powerful technique.

What then does the future of the method hold for the organic chemist? At present the possibilities seem unlimited. Even if there were no further developments in experimental technique the utility of the method could not fail to increase as our experience extends over greater and greater numbers of organic compounds. Published data refer to less than two thousand compounds, a trifling number when we think of the vast number of spectra on which infrared correlation rules are based. However, on the experimental side great developments are conceivable. Improvements in magnet materials and in spin-decoupling methods (see next

chapter) could change the usefulness of the technique by an order of magnitude and thereby reduce the determination of the structures of many compounds to a very simple procedure.

REFERENCES

1. G. E. ULENBECK and S. GOUDSMIT, *Naturwiss.* 13, 953 (1925).
2. R. BICHOWSKY and H. C. UREY, *Proc. Natl. Acad. Sci.* 12, 80 (1926).
3. W. PAULI, *Naturwiss.* 12, 741 (1924).
4. D. M. DENNISON, *Proc. Roy. Soc.* A 115, 483 (1927).
5. F. HUND, *Z. Physik.* 42, 93 (1927).
6. S. TOLANSKY, *Hyperfine Structure in Line Spectra and Nuclear Spin*, 2nd ed., Methuen, London, 1948.
7. I. ESTERMANN and O. STERN, *Z. Physik.* 85, 170 (1933).
8. I. RABI, S. MILLMAN, P. KUSCH and J. R. ZACHARIAS, *Phys. Rev.* 55, 526 (1939); J. B. M. KELLOGG, I. RABI, N. F. RAMSEY and J. R. ZACHARIAS, *ibid.* 56, 728.
9. L. W. ALVAREZ and F. BLOCH, *ibid.* 57, 111 (1940).
10. C. J. GORTER and L. J. F. BROER, *Physica* 9, 591 (1942).
11. E. M. PURCELL, H. C. TORREY and R. V. POUND, *Phys. Rev.* 69, 37 (1946).
12. F. BLOCH, W. W. HANSEN and M. PACKARD, *ibid.* 127.
13. E. R. ANDREW, *Nuclear Magnetic Resonance*, Cambridge University Press, 1955.
14. H. S. GUTOWSKY and C. J. HOFFMAN, *J. Chem. Phys.* 19, 1259 (1951), and references given therein.

THE THEORY OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

ALTHOUGH the literature contains several detailed mathematical treatments of the theory of nuclear magnetic resonance which are based on microphysical[1,2] or macrophysical[2,3,4] concepts we will be content to develop the theory, as far as possible, in a purely descriptive manner by stating in words the results of the physicists' equations. In doing so we will no doubt lose the elements of exactness but as organic chemists we will gain tangible concepts of considerable utility, which would otherwise be lost to all but those possessing an adequate mathematical background.

2.1 NUCLEAR RESONANCE

The starting point of our discussion is a consideration of a bare nucleus, such as a proton, in a magnetic field of strength H_0. Later we will consider collections of nuclei. We will also add the extranuclear electrons and ultimately we will build the atoms into molecules but we must first consider the simple nucleus. We have already seen that certain nuclei possess two very important properties associated with spin angular momentum. These properties are the spin number I and the magnetic moment μ. We are only concerned with the nuclei of those elements for which these two quantities are not equal to zero. When such a nucleus is placed in a static uniform magnetic field H_0 it may take up one of $(2I+1)$ orientations which are characterized by energies dependent on the magnitudes of μ and H_0. If our bare nucleus is a proton, which has a spin number I equal to one half, we can liken it to a very tiny bar magnet. A large bar magnet is free to take up any possible orientation in the static field so that there are an infinite number of permissible energy states. Quantum mechanics tells us that the tiny proton magnet is restricted to just two possible orientations $[(2I+1) = 2]$, in the applied field and these can be considered to be a low energy or parallel orientation in which the magnet is aligned with the field and a high energy or anti-parallel orientation in which it is aligned against the field (i.e. with its N. pole nearest the N. pole of the static field). Since these two orientations correspond to two energy states it should be possible to induce transitions between them and the frequency, ν, of the electromagnetic radiation which will effect such transitions is given by the equation

$$h\nu = \frac{\mu\beta_N \cdot H_0}{I} \tag{1}$$

where β_N is a constant called the nuclear magneton. Equation (1) may be rewritten as (2)

$$\nu = \gamma \cdot H_0/2\pi \tag{2}$$

where γ is known as the gyromagnetic ratio. The absorption or emission of the

quantum of energy $h\nu$ causes the nuclear magnet to turn over or "flip" from one orientation to the other. For nuclei with spin numbers greater than $\frac{1}{2}$ there will be more than two possible orientations (3 for $I = 1$, 4 for $I = \frac{3}{2}$, etc.) and in each case a set of equally spaced energy levels results. Again electromagnetic radiation of appropriate frequency can cause transitions between the various levels with the proviso (i.e. selection rule) that only transitions between adjacent levels are allowed. Since the energy levels are equally spaced this selection rule requires that there is only one characteristic transition frequency for a given value of H_0. If we insert numerical values into our equation for ν we find that, for magnetic fields of the order of 10,000 gauss,* the characteristic frequencies lie in the radiofrequency region (ca. 10^7–10^8 c/s). Thus our first primitive picture of nuclear magnetic resonance spectroscopy may be summed up by stating that atomic nuclei of certain elements ($I > 0$) when placed in a strong magnetic field may absorb radiofrequency radiation.
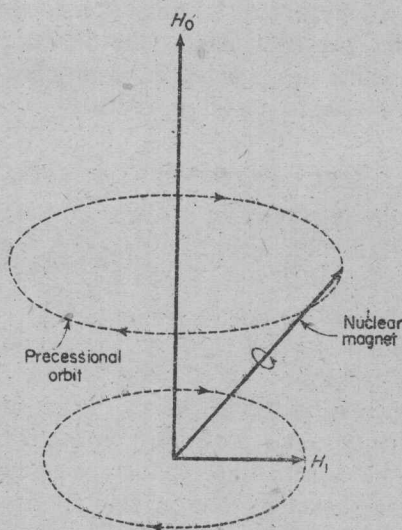

Fig. 2.1 The behaviour of a nuclear magnet in a magnetic field (in this figure the applied field, H_0, the rotating field, H_1, and the nuclear magnetic dipole are represented as vectors).

We shall now develop a classical picture of the absorption process which takes us a little further in our understanding of nuclear magnetic resonance and which provides a useful model for discussing the experimental procedure. Let us consider our spinning nucleus to be orientated at an angle θ to the direction of the applied field H_0 (Fig. 2.1). The main field acts on the nuclear magnet so as to decrease the angle θ. However, because the nucleus is spinning the net result is that the nuclear magnet is caused to precess about the main field axis. The angular velocity ω_0 of this precessional motion is given by equation (3).

$$\omega_0 = \gamma H_0 = 2\pi\nu \tag{3}$$

The precessional frequency ω_0 is directly proportional to H_0 and to the gyromagnetic

*The gauss is strictly speaking the unit of magnetic induction and the field strength should be measured in oersteds. In air the two units are almost equivalent and the former is commonly used.

ratio* and is exactly equal to the frequency of electromagnetic radiation which, on quantum mechanical grounds, we decided was necessary to induce a transition from one nuclear spin state to an adjacent level. We are now in the position to establish the exact character of the radiofrequency radiation necessary to do this. The act of turning over the nucleus from one orientation to another corresponds to an alteration of the angle θ. This can only be brought about by the application of a magnetic field H_1 in a direction at right angles to the main field H_0. Furthermore, if this new field H_1, is to be continuously effective it must rotate in a plane at right angles to the direction of H_0 in phase with the precessing nucleus. When these conditions are met the rotating magnetic field and the precessing nuclear magnet are said to be in resonance and absorption of energy by the latter can occur. The important point to be derived from the classical model at this stage is that in order to obtain a physically observable effect it is necessary to place the nucleus in a static field and then to subject it to electromagnetic radiation in such a way that the magnetic vector component of the radiation rotates with the appropriate angular velocity in a plane perpendicular to the direction of the static field. A discussion of the way in which this is achieved in practice is deferred to the next chapter which deals with the experimental procedure.

2.2 RELAXATION PROCESSES

We have now to enquire into the fate of the energy which has been absorbed by our nuclear magnet. Radiation theory tells us that the emission of energy in the form of electromagnetic radiation can take place either spontaneously or by a process stimulated by an electromagnetic field, and that the probability of occurrence of the latter process is exactly equal to the probability of absorption of energy from the field. Furthermore, the theory shows that the probability of spontaneous emission depends on the frequency of the emitted radiation in such a way that, at radiofrequencies, this probability is negligible. If we now consider a collection of nuclei of the same isotope which are equally divided between two adjacent spin states, we may conclude that the rate of absorption of energy by the lower state will exactly equal the rate of induced emission from the upper state and no observable effect is possible. The situation is saved by the fact that a collection of nuclei in a static magnetic field are not equally distributed between the various possible spin states but rather they take up a Boltzmann distribution with a very small but finite excess in favour of the lower levels. In other words the nuclei ($I = \frac{1}{2}$) all prefer to be aligned parallel to the main field (as they would be at equilibrium at 0°K) but because of their thermal motions the best that can be managed is a slight excess of parallel spins at any instant. Small though this excess is, it is sufficient to result in a net observable absorption of radiofrequency radiation since the probability of an upward transition (absorption) is now slightly greater than that of a downward transition (emission).

Let us anticipate the subject matter of the next chapter by assuming that we have a means of detecting the absorption of radiofrequency radiation. If now we irradiate the collection of nuclei ($I = \frac{1}{2}$) the rate of absorption is initially greater than the rate of emission because of the slight excess of nuclei in the lower energy

---

*We may note that ω_0 is *independent* of the angle θ.

state. As a result the original excess in the lower state steadily dwindles until the two states are equally populated. If we are observing an absorption signal we might find that this signal is strong when the radiofrequency radiation is first applied but that it gradually disappears. This type of behaviour is in fact sometimes observed in practice. More generally, however, the absorption peak or signal rapidly settles down to some finite value which is invariant with time. The reason for this behaviour is that induced emission is not the only mechanism by which a nucleus can return from the upper to the lower state. There exist various possibilities for radiationless transitions by means of which the nuclei can exchange energy with their environment and it can be shown[2] that such transitions are more likely to occur from an upper to a lower state than in the reverse direction. We therefore have the situation in which the applied radiofrequency field is trying to equalize the spin state equilibrium while radiationless transitions are counteracting this process. In the type of systems of interest to the organic chemist a steady state is usually reached such that the original Boltzmann excess of nuclei in the lower states is somewhat decreased but not to zero so that a net absorption can still be registered.

The various types of radiationless transitions, by means of which a nucleus in an upper spin state returns to a lower state, are called relaxation processes. Relaxation processes are of paramount importance in the theory of nuclear magnetic resonance for not only are they responsible for the establishment and maintenance of the absorption condition but they also control the lifetime expectancy of a given state. The uncertainty principle tells us that the "natural" width of a spectral line is proportional to the reciprocal of the average time the system spends in the excited state. In ultraviolet and infrared spectroscopy, the natural line width is seldom if ever, the limit of resolution. At radiofrequencies, however, it is quite possible to reach the natural line width and we shall therefore be very much concerned with the relaxation processes which determine this parameter.

We may divide relaxation processes into two categories namely spin–lattice relaxation and spin–spin relaxation. In the latter process a nucleus in its upper state transfers its energy to a neighbouring nucleus of the same isotope by a mutual exchange of spin. This relaxation process therefore does nothing to offset the equalizing of the spin state populations caused by radiofrequency absorption and is not directly responsible for maintaining the absorption condition. In spin–lattice relaxation the energy of the nuclear spin system is converted into thermal energy of the molecular system containing the magnetic nuclei, and is therefore directly responsible for maintaining the unequal distribution of spin states. Either or both processes may control the natural line width.

Spin–lattice relaxation is sometimes called longitudinal relaxation.[3] The term *lattice* requires definition. The magnetic nuclei are usually part of an assembly of molecules which constitute a sample under investigation and the entire molecular system is referred to as the lattice irrespective of the physical state of the sample. For the moment we will confine our attention to liquids and gases in which the atoms and molecules constituting the lattice will be undergoing random translational and rotational motion. Since some or all of these atoms and molecules contain the magnetic nuclei such motions will be associated with fluctuating magnetic fields. Now, any given magnetic nucleus will be precessing about the direction

of the applied field H_0 and at the same time it will experience the fluctuating magnetic fields associated with nearby lattice components. The fluctuating lattice fields can be regarded as being built up of a number of oscillating components (in the same way as any complicated wave-form may be built up from combinations of simple harmonic wave-forms) so that there will be a component which will just match the precessional frequency of the magnetic nuclei. In other words, the lattice motions, by virtue of the magnetic nuclei contained in the lattice, can from time to time generate in the neighbourhood of a nucleus in an excited spin state a field which, like the applied radiofrequency field H_1, is correctly oriented and phased to induce spin state transitions. In these circumstances a nucleus in an upper spin state can relax to the lower state and the energy lost is given to the lattice as extra translational or rotational energy. The same process is responsible for producing the Boltzmann excess of nuclei in lower states when the sample is first placed in the magnetic field. Since the exchange of energy between nuclei and lattice leaves the total energy of the sample unchanged it follows that the process must always operate so as to establish the most probable distribution of energy or, in other words, so as to establish the Boltzmann excess of nuclei in lower states.

The efficiency of spin–lattice relaxation can, like other exponential processes, be expressed in terms of a characteristic "relaxation" time T_1 which, in effect, is the half-life required for a perturbed system of nuclei to reach an equilibrium condition. A large value of T_1 indicates an inefficient relaxation process. The value of T_1 will depend on the gyromagnetic ratio (or ratios) of the nuclei in the lattice and on the nature and rapidity of the molecular motion which produce the fluctuating fields. Because of the great restriction of molecular motions in the crystal lattice, most highly purified solids exhibit very long spin–lattice relaxation times, often of the order of hours. For liquids and gases the value of T_1 is much less, being of the order of one second for many organic liquids. We shall presently discuss certain conditions under which T_1 falls to even lower values.

The term spin–spin relaxation, sometimes called transverse relaxation,[3] usually embraces two processes which result in the broadening of resonance lines. One of these processes is a true relaxation in that it shortens the life of a nucleus in any one spin state, whereas the other process broadens a resonance line by causing the effective static field to vary from nucleus to nucleus. Both effects are best understood from a consideration of the interaction of two precessing nuclear magnets in close proximity to one another. The field associated with a nuclear magnet which is precessing about the direction of the main field may be resolved into two components (Fig. 2.2). One component is static and parallel to the direction of the main field, H_0. The other component is rotating at the precessional frequency in a plane at right angles to the main field. The first component will be felt by a neighbouring nucleus as a small variation of the main field. As the individual nuclei in a system are not necessarily in the same environment, each may experience a slightly different local field due to neighbouring nuclei. Consequently, there will be a spread in the value of the resonance frequency which is, of course, proportional to the sum of the main field (H_0) and local fields. The resonance line will therefore be correspondingly broad. The rotating component at right angles to H_0 constitutes just the correct type of