NUCLEAR MAGNETIC RESONANCE ABSORPTION

By J. A. S. Smith, M.A., D.Phil.

(Dept. of Inorganic and Physical Chemistry, The University, Leeds)

I. Introduction

The first prediction of nuclear magnetic resonance absorption was made by Gorter ; [1] several early attempts to detect the phenomenon in the solid state failed,[1, 2] chiefly because of an unfortunate choice of compounds. However, the theoretical prediction provided a stimulus for work in other fields, and in 1938, the magnetic resonance method was applied to molecular beams,[3] and gave results of considerable importance.[4]

This Review is concerned with the effect in solids and liquids ; little further progress was made in this work until the close of the war. Great advances had then been made in the design of radiofrequency bridges and low noise-level amplifiers, and with this assistance Bloch,[5] and Bloembergen, Pound, and Purcell,[6] in 1946 were able to detect the phenomenon in the solid and in the liquid state.

In the past six years, these new methods have been used to study many problems of importance to chemistry. For example, they can provide information on inter-hydrogen atom distances in crystals, hindered rotation in the solid state, and the internal structure of liquids. In this Review, some of the more outstanding contributions of the subject to chemistry will be discussed, with special reference to the internal properties of crystals. Much promising work still at an early stage of development has been omitted ; in particular, we may mention recent studies of quadrupole effects, the splitting of the proton resonance line at low temperatures, and the fine structure of the liquid resonance line. More comprehensive reviews of these and other aspects of the subject are available.[5–11]

The novelty of the method in chemistry is that it is concerned essentially with the measurement of the magnetism of the atomic nucleus, rather than that of the electrons from which the well-known bulk properties of diamagnetism, paramagnetism, and ferromagnetism originate. It has been known for some time, notably from spectroscopic evidence, that many atomic nuclei have a magnetic moment, and that this is a consequence of the spin of the nucleus. As a rough analogy, it can be imagined that just as the spin of the negatively-charged electron gives rise to a magnetic moment, so the

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[1] Gorter, *Physica*, 1936, **3**, 995.

[2] Gorter and Broer, *ibid.*, 1942, **9**, 591.

[3] Rabi, Zacharias, Millman, and Kusch, *Phys. Review*, 1938, **53**, 318.

[4] Kusch, *Physica*, 1951, **17**, 339.

[5] Bloch, *Phys. Review*, 1946, **70**, 460.

[6] Bloembergen, Pound, and Purcell, *ibid.*, 1948, **73**, 679 (referred to as BPP in the text).

[7] Proceedings of the International Conference on Spectroscopy at Radiofrequencies, *Physica*, 1951, **17**, 169—484.

[8] Pake, *Amer. J. Physics*, 1950, **18**, 438, 473.

[9] Purcell, *Science*, 1948, **107**, 433.

[10] *Idem, Physica*, 1951, **17**, 282.

[11] Rollin, *Reports Progr. Physics*, 1948—1949, **12**, 22.

spin of a positively charged nucleus gives rise to a nuclear magnetic moment. This is a highly simplified model as may be realised from the fact that the neutron, which is uncharged, also has a magnetic moment. This analogy to the electronic magnetic moment extends to the equations defining the nuclear magnetic moment; a nucleus with a spin of I has a magnetic moment of magnitude

$$\mu = g\mu_n\sqrt{I(I+1)} \quad . \quad . \quad . \quad . \quad (1)$$

The quantity μ_n is the nuclear magneton,* and is defined by the equation

$$\mu_n = eh/4\pi Mc \quad . \quad . \quad . \quad . \quad (2)$$

g is the g-factor of the nucleus, and may be compared with the Landé g-factor for electronic spin; its value is accurately known for a number of nuclei.[12] The quantity equivalent to μ_n for the electron is the familiar Bohr magneton, $\mu_e = eh/4\pi mc$, and it will be seen that because of the difference in mass of the two particles, nuclear moments will be at least one thousand times smaller than electronic moments. The presence of nuclear magnets in any molecule gives rise to a nuclear paramagnetic bulk susceptibility defined through the equation

$$\chi_0 = Ng^2\mu_n{}^2I(I+1)/3kT \quad . \quad . \quad . \quad (3)$$

which is equivalent to the Curie equation for substances displaying normal paramagnetism. Because of the factor $\mu_n{}^2$ in equation (3), nuclear paramagnetic susceptibilities will be generally 10^6 times smaller than electronic paramagnetic susceptibilities and 10^3 to 10^4 times smaller than molecular diamagnetism; consequently, they would not be detected by the ordinary methods of measuring magnetic susceptibilities. Ideally, the magnitude could be found by measuring the magnetic susceptibility of a diamagnetic compound at very low temperatures. Diamagnetism is largely independent of temperature, but the relative contribution of the nuclear paramagnetism to the susceptibility is considerably increased when the temperature is very low. Such an effect has been detected in one case, by Lasarew and Shubnikow [13] in solid hydrogen in the range 1·76—4·22° K.

When a nuclear magnet of spin I is placed in a magnetic field H_0, the energy of the magnet in the field, which is given by the equation

$$W = \mu H_0 \cos\theta \quad . \quad . \quad . \quad . \quad (4)$$

where θ is the angle between μ and H_0, can assume $2I + 1$ values; *i.e.*, there are $2I + 1$ orientations of the nuclear spin with respect to the applied field. We shall be concerned mainly with hydrogen and fluorine nuclei for which $I = \frac{1}{2}$ (and the quadrupole moment is zero). In this case, the situation can be illustrated as in Fig. 1. Each nuclear moment has two components, one of magnitude $\pm\, g\mu_n/2$ parallel to the field, and the other of magnitude $g\mu_n/\sqrt{2}$ perpendicular to the field. The $\pm$ sign in front of the parallel components denotes the two possible nuclear magnetic energy

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[12] Mack, *Rev. Mod. Physics*, 1950, **22,** 64.

[13] Lasarew and Shuknikow, *Physikal. Z. Sowietunion*, 1937, **11,** 445.

* A complete list of the symbols used here is given in the Appendix (p. 305).

levels ($2I + 1 = 2$), one in which the component is parallel and the other in which it is antiparallel to the field, the latter having the higher energy. The actual moment, of a magnitude given by equation (1), is inclined at an angle to H_0 and precesses round the field vector. As a result of this magnetic quantisation, when a molecule containing hydrogen or fluorine atoms is placed in a magnetic field, apart from the rotational and vibrational transitions which occur in the ground electronic state, we also have the possibility of magnetic transitions between the two nuclear magnetic energy levels defined by their antiparallel components $g\mu_n/2$ and $-g\mu_n/2$. The Bohr frequency condition states that this difference in energy between the two levels is equivalent to a frequency ν given by

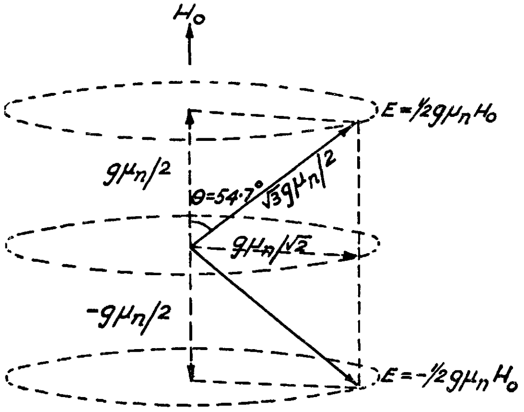

FIG. 1

$$h\nu = g\mu_n H_0 \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

For hydrogen nuclei in a field of strength 2350 gauss, this frequency is 10 megacycles per second [which is in the RF (radiofrequency) region], and should be the same for all hydrogen nuclei in whatever type of molecule they happen to reside, provided that the material is diamagnetic. For the ^{19}F nucleus g is 5·257, and for the deuterium nucleus 0·8574, so that at the same frequency fluorine resonance occurs at about 2500 gauss and deuterium resonance at about 15,300 gauss.

The precession of μ around H_0 will itself give rise to a magnetic field, which we may resolve into two components, a static component H_z along H_0 and a rotating component perpendicular to this. The precessional movement of the nuclear magnet about the applied field is familiar from Larmor's classical theorem ;[14] any magnet of moment μ in a field H_0 will precess around the direction of the field with an angular velocity given by

$$\omega h/2\pi = g\mu_n H_0 \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

The frequency of the rotating field produced by this precessing magnet at

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[14] The theorem is thoroughly discussed in Van Vleck, " Electric and Magnetic Susceptibilities ", p. 22 (Oxford Univ. Press, 1932).

right angles to H_0 is $\omega/2\pi$. If we superimpose on this system an *oscillatory* magnetic field, which we will call H_1, of the same periodicity and perpendicular to H_0, the precessing nucleus and the oscillatory field can exchange energy and the nuclear magnet can be made to " flop " between the parallel and the antiparallel states. Equation (6), which was derived classically, is entirely equivalent to equation (5), which was derived from the Bohr frequency condition. This system of a static field H_0 and an oscillatory field H_1, applied perpendicular to H_0, reproduces the essential conditions of the nuclear resonance experiment. The method is to measure the small change in the susceptibility of the material which occurs when an oscillatory field of the appropriate frequency is applied at right angles to the main field ; when equation (5) is satisfied, nuclear resonance occurs. It will be shown later that there are several processes which maintain a greater number of nuclei in the ground state than in the excited state. This was in fact assumed in writing equation (3), because this is an expression for the bulk susceptibility and so depends on the number of spins in each of the two nuclear magnetic energy levels. At resonance, the equilibrium distribution of the spins is disturbed, thereby altering the susceptibility. Transitions between proton Zeeman levels (so-called because of the analogy to the Zeeman splitting of electronic energy levels in magnetic fields) occur in the 4—40 Mc. region in fields of 1000—10,000 gauss, the usual range of practical values.

Simultaneously with the magnetic quantisation of the nuclear magnetic levels, all other types of magnetic moment possessed by the molecule will be similarly affected ; for example, if the molecule possesses an unpaired spin, the electronic magnetic moment will be quantised in the field with a frequency given by equation (5) with μ_n replaced by μ_e. Since the latter is 1000 times larger than the former, the frequency range over which resonance would be expected to occur is 4000—40,000 Mc., in the microwave region ; consequently, electronic magnetic resonance, or paramagnetic resonance, does not interfere in nuclear resonance experiments. It will be seen that there is an important distinction between the resonance methods of measuring the nuclear or electronic susceptibility and the more familiar methods of measuring the bulk susceptibility such as the Gouy magnetic balance. In the latter, the so-called static susceptibility χ_0 is obtained, denoting the magnetic properties of the molecules in a field of zero frequency. In the former, the situation is very similar to the measurement of the dielectric constant of materials in high-frequency electric fields. In both cases, we have the real components χ' which rotate in phase with the applied frequency, and the imaginary components χ'' which are 90° out of phase. Because of the phase difference between χ' and χ'', the susceptibility χ is a complex number and we must put

$$\chi = \chi' - i\chi'' \quad . \quad . \quad . \quad . \quad (7)$$

where $|\chi| = \sqrt{\chi'^2 + \chi''^2}$. If we are interested only in the energy absorbed by the system from the RF field, this can be shown [8] to be governed by χ'' ; the other component χ' governs the dispersion of the real susceptibility.

II. Methods of Measurement

One method of measuring χ'', the component giving rise to nuclear magnetic resonance absorption, follows directly from this discussion. The RF field is produced by passing, for example, a 10-Mc. signal through a small induction coil containing about one c.c. of the proton- or fluorine-rich liquid, and the coil is mounted with its cylindrical axis perpendicular to a homogeneous magnetic field of about 2350 gauss. The small inductance is made part of a twin-T RF bridge [15] which is so balanced that a very small change in the RF energy absorbed by the material inside the coil, with consequent change of susceptibility, suffices to throw the bridge off balance and allows a small signal to get through to a RF amplifier. The main magnetic field is not kept constant, but is made to oscillate, or " sweep ", over a range of field strength which is much larger than the region over which the nuclei of the liquid absorb. This is done by sending a low-frequency current through subsidiary coils attached to the magnet ; the frequency is known as the modulatory or sweep frequency and quite often falls in the 30—60 cps range. If the mean field is now brought to within a very small distance of the resonance field strength for the particular nucleus and frequency concerned, the modulation causes the field to sweep through resonance twice for each cycle of the sinusoidal modulatory sweep. If the amplified signal from the bridge is then applied across the Y-plates of a cathode-ray oscillograph and a tapping off the sweep to the X-plates, a stationary picture of the absorption line will be thrown on to the screen, provided that the RF bridge has been properly adjusted.

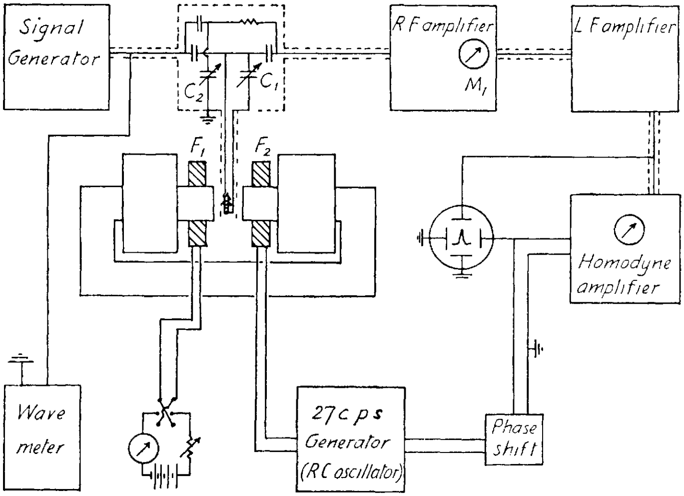

FIG. 2

Block diagram of the RF bridge method (reprinted, with permission, from Trans. Faraday Soc., 1951, **47**, 1264).

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[15] Tuttle, *Proc. Inst. Radio Eng.*, 1940, **28**, 23.

This is a general outline of the RF bridge method of Bloembergen, Purcell, and Pound [6] (generally abbreviated to BPP) and a block diagram of the apparatus is given in Fig. 2. Fig. 3 is a reproduction of the proton resonance line of water, a field of 3900 gauss being used with an inhomogeneity of about 0·1 gauss. (The term inhomogeneity refers to the variation of the main field over the volume of the sample.) It will be seen that the line has a definite width, denoting that the nuclei do not all absorb at the single frequency that equation (5) predicts. All gases and liquids have comparatively narrow absorption lines of this type and, in fact, in most liquids the lines are so narrow as to be governed entirely by the field inhomogeneity unless highly uniform fields are used. This is the case for the absorption line of water. The inhomogeneity of the field may cause the line to have a width of the order of 0·1 gauss, but the expected natural line width ($\Delta H_{\mathrm{m.sl.}}$) is about $3{\cdot}4 \times 10^{-5}$ gauss.[16] The line width $\Delta H_{\mathrm{m.sl.}}$ is the distance in gauss between the two points on the absorption curve where the slope has its maximum value. As a consequence, a small nuclear resonance coil containing, for example, water can be used in the form of a probe for measuring field strength and field inhomogeneity at various positions in the pole gap of a magnet.[17] Because of the sharpness of the resonance line in liquids and gases, the method has been widely employed in the measurement of nuclear magnetic moments. Two recent applications include the first accurate measurement [18] of the nuclear magnetic moment of ^{3}He, and a direct determination of the magnetic moment of the proton in nuclear magnetons.[19]

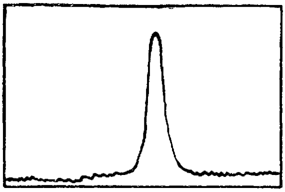

FIG. 3

The proton resonance absorption line of water.

Many solids, however, especially at low temperatures, give much broader lines, some 10—100 times wider than in liquids and showing marked fine structure. The signal in this case is correspondingly weaker and for very broad lines would be indistinguishable from the background of the line on the cathode-ray screen. This background, or " noise ", arises from thermal agitation of the atoms in the coil and the bridge, and the fluctuations generated in the first amplifying stage. The ratio of the signal strength to the noise is the factor which determines the sensitivity of the nuclear resonance apparatus, and an equation for the ratio in terms of the various constants of the circuits used and the materials studied has been derived by BPP.[6] A more sensitive method of recording broad lines is to use a modulatory sweep equivalent to a much smaller range of field strength than the line width. The signal then passes from the RF amplifier to a low-frequency amplifier of narrow band-width, which amplifies the sweep-frequency components of the signal, and thence to a homodyne rectifier which converts the signal to direct current, and a " lock-in " meter which is a device for

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[16] Torrey, *Phys. Review*, 1952, **85**, 365. [17] Gooden, *Nature*, 1950, **165**, 1014.

[18] Anderson, *Phys. Review*, 1949, **76**, 1460.

[19] Bloch and Jeffries, *ibid.*, 1950, **80**, 305.

reducing the relative contribution of noise to the experimental signal. It can then be shown that, as we move the main field through the range in which resonance occurs, the derivative of the line-shape is recorded on the meter,[8] and this is integrated to obtain the absorption line. This part of the apparatus is also drawn in Fig. 2.

Other methods of detecting nuclear resonance may be mentioned briefly. They fall into four groups. Instead of altering the field, the line can be traversed by varying the frequency and keeping the main field constant. This is a feature of the RF spectrometer designed by Pound and Knight.[20] The instrument is capable of the same degree of accuracy as the bridge method, and has the additional advantage that only the pure absorption line is recorded, so that the centre-points of the resonance line are accurately located. In the bridge method, both absorption and dispersion curves can be plotted according to the type of balance used, and a mixture of the two is obtained if the bridge is not properly adjusted. The second group contains methods using super-regenerative techniques.[21, 22] They provide little information on line-shapes and have been used mainly in measuring nuclear magnetic moments. Simultaneously with the development of the RF bridge method at Harvard, Bloch at Stanford was successfully applying a different technique to which he gave the name of nuclear induction.[5] The characteristic feature of the method is the use of a second coil round the substance to be measured which has its axis perpendicular both to the Zeeman field and to the RF field of the first coil. At the resonance frequency, there is a sudden change in the orientation of the nuclear moments, which induces an electromotive force in the second coil. The field is modulated as in the RF bridge method, and both the RF and the sweep-frequency components of the signal are amplified successively. The method has practically the same sensitivity as the RF bridge method and much the same range of application ; moreover, it can furnish the sign of a magnetic moment, which is governed by the orientation of the nuclear magnetic moment with respect to the electronic moment, and so has been much used in measuring nuclear moments.[23] The fourth group includes the pulse methods which have been developed recently by Hahn [24] and Torrey,[25] and have proved to be particularly useful in measuring the fine structure of the resonance line of some liquids.

III. Chemical Applications

The Relaxation Time.—The line width and the shape of the derivative and absorption lines are quantities of considerable interest to chemistry. In order to discuss their application, we must consider in very general terms the conclusions that can be drawn about the process of absorption from quantum mechanics. Previously, transitions between nuclear energy levels

[20] Pound and Knight, *Rev. Sci. Instr.*, 1950, **21**, 219.

[21] Roberts, *ibid.*, 1947, **18**, 845.

[22] Zimmerman and Williams, *Phys. Review*, 1949, **76**, 354.

[23] Proctor and Yu, *ibid.*, 1950, **77**, 716.

[24] Hahn, *ibid.*, 1950, **80**, 580.

[25] Torrey, *ibid.*, 1949, **76**, 461.

have been discussed as though they were caused only by interaction with the radiation field. However, at nuclear resonance frequencies, the processes of absorption and induced emission are effectively equal, which means that no set signal would be obtained in the nuclear resonance experiment. Clearly, since signals are obtained, there must be other processes which cause the nuclear spins to relax to a lower energy level; the magnetic energy of the spin in the applied field must be convertible into some other form of energy. There are several processes, such as spontaneous emission, and interaction with the thermal radiation field, which will provide a source of relaxation, but the lowest life-time which they predict for an excited state is about 10^3 years, whereas experiment shows that nuclear resonance life-times are of the order of seconds. We must therefore seek alternative relaxation mechanisms which will convert magnetic energy into thermal energy.

Nuclear spins are well shielded from deactivation mechanisms. They are affected only by other magnetic fields; and, in most molecules, the electrons which are capable of producing large magnetic fields as a result of their orbital and spin motion are paired off in the orbitals of the molecule, their magnetic effect in this case being very small. The situation may be compared (Purcell [9]) to the analogous case of the line width of spectral lines in ordinary spectroscopy. Here, in contrast, an atom or molecule can be deactivated by collision with another; this reduces the life-time of the excited state and as a result of the Heisenberg equation

$$\Delta E . \Delta t \simeq h/2\pi \quad . \quad . \quad . \quad . \quad (8)$$

a reduction in Δt, which represents the life-time of an excited state, increases the uncertainty in E, the energy of the level, and so broadens the spectral line. The analogy shows that in the case of nuclear resonance, the two problems of finding how an upper spin state loses its energy and how the resonance line is broadened are complementary. Any mechanism which supplies an effective deactivation of an excited spin level produces by equation (8) a contribution to the line-broadening. We shall frequently discuss line-broadening in terms of the relaxation times rather than the broadening of the energy levels.

Calculations have shown [5, 6] that two interactions are of predominant importance in determining the width of the proton resonance line. To anticipate the later discussion, the first arises from interaction of the precessing nucleus with oscillatory magnetic fields produced by molecular motion in the lattice, and the second from interaction with the oscillatory and static magnetic fields produced around it by neighbouring nuclei with a magnetic moment. The essential distinction between the two is that the first is the mechanism whereby magnetic energy of the nuclear spins of the material (or the spin system) can be converted into thermal energy of agitation of the molecules, whereas the second mechanism involves merely an exchange of energy between neighbouring spins, no energy entering or leaving the spin system.

The former effect clearly provides the alternative relaxation mechanism which we have previously shown to be necessary to obtain a net nuclear resonance signal. Its origin can be pictured in the following manner: random movement of the molecules causes the nuclear magnets embedded in them to undergo oscillations with a wide range of frequencies. This produces a corresponding range of oscillatory magnetic fields, and if this range overlaps the Larmor resonance frequency of the nucleus concerned, energy can pass from the spin system to the thermal energy of molecular agitation. In the solid state, this random motion of the molecules, which is taken generally to involve complete movement of the molecule or part of the molecule from one equilibrium position to another, must be distinguished in its effect on the second moment from the lattice vibrations which govern the specific heat of the solid (see p. 292). These are present in all crystals but their contribution to the relaxation time is considered to be negligibly small in nearly all compounds so far examined.[10] The spins of the compound can now be assumed to be in thermal equilibrium, which means that the spin state of the lowest energy is favoured. In other words, the theoretical transition probabilities must be weighted with Boltzmann factors, and this is found to give an excess number n_0 in the ground state of

$$n_0 = N\,|\,g\,|\,H_0\mu_n/kT \qquad . \quad . \quad . \quad . \quad (9)$$

where N is the total number of resonating nuclei. For hydrogen nuclei at 90° K in a field of 2500 gauss, the difference in distribution between the two levels is only about six per million nuclei, and yet it is the signal from this small number that the apparatus will detect. When the RF signal is applied, this equilibrium will be disturbed, and the actual excess number n between the lower and the upper state will depend on the rate at which the spins can relax. The rate at which n approaches n_0 when the RF field is removed is given by

$$n/n_0 = 1 - \mathrm{e}^{-t/T_1} \qquad . \quad . \quad . \quad . \quad (10)$$

where t is the time. The constant T_1 is known as the spin-lattice relaxation time and from equation (10) it can be defined as the time taken for a fraction 0·63 of the original excess number to relax to the ground state when the RF field is switched off.

One method of measuring T_1 for liquids is to increase the RF signal to the coil and simultaneously observe the maximum output on the " lock-in " meter; because of the finite relaxation time, saturation will set in at a certain point defined under certain conditions by the equation [5]

$$\gamma^2 H_1{}^2 T_1 T_2 = 1 \qquad . \quad . \quad . \quad . \quad (11)$$

in which T_2 is the relaxation time corresponding to the second mechanism, H_1 is the RF field, and γ the gyromagnetic ratio of the resonating nucleus (see Appendix). H_1 can be found by observing the saturation point in a substance of known T_1 and T_2, and equation (11) can then be used for finding T_1 in other materials, provided T_2 is known; in many liquids, T_2 is governed by the field inhomogeneity. The first measurement of T_1 for water was made by observing the nuclear resonance line under conditions in which saturation was occurring, and then photographing the rate at which the signal grew when the saturation condition was suddenly removed.[6] It must be noted that all measurements of the line-shape and line-width must be carried out at RF levels below the saturation limit, and so the value of T_1 is an important factor in determining whether or not a suitable nuclear resonance signal can be obtained from a compound. (Other methods can be used for measuring T_1.[8, 26, 27, 28]) The value of T_1 for pure water at 293° K is $2{\cdot}33 \pm 0{\cdot}07$ seconds[26] and for ammonium chloride at 90° K is about 100 seconds.[29]

If we put the last value in equation (8), the predicted line width is about 10^{-7} gauss. The experimental value is 23 gauss. The reason for the difference is that in many solids, the predominant relaxation mechanism is the second of the two which we have previously mentioned, that arising from neighbouring nuclear spins in the same or surrounding molecules. Any two nuclear magnetic dipoles whose moments are parallel and separated by a distance of r cm. will produce at each other a maximum magnetic field of approximately μ/r^3 gauss, which is 4·1 gauss for the two protons in a gaseous water molecule. The effective magnetic field at any point inside a diamagnetic crystal will be therefore that of the applied Zeeman field plus a second term which will depend on the distance of all neighbouring nuclei with magnetic moments from that point and the direction of their magnetic moments with respect to the applied field. It is this second term which gives rise to the line-broadening observed in ammonium chloride and many other proton- and fluorine-containing compounds. Alternatively, we can consider the effect in terms of relaxation times rather than line-broadening. From the Heisenberg uncertainty principle, the broadening will correspond to a relaxation time denoted by T_2 and known as the spin–spin relaxation time. There are two separate contributions to T_2, which we can picture in physical terms as follows. Any nucleus of moment μ precessing about the applied field H_0 will produce at a neighbouring nucleus a magnetic field which can be resolved into two components. The first is a static field along H_0 and if this has the value $\partial H_{\mathrm{st.}}$, it will spread the precessional frequency of the second nucleus by an amount

$$(h/2\pi)\partial\omega_{\mathrm{st.}} = g\mu_n\partial H_{\mathrm{st.}} \quad . \quad . \quad . \quad . \qquad (12)$$

This broadening of the magnetic energy levels corresponds to a relaxation time of $1/\partial\omega_{\mathrm{st.}}$ seconds. The second component will be an oscillatory component perpendicular to H_0 ; if the second nucleus has a component in the same direction and of the same frequency, energy can pass from one spin to the other (a process known as spin exchange) and the effective life-time of any spin state is thereby reduced. The sum of these two effects gives the spin–spin relaxation time T_2.

T_2 can be defined with respect to a quantity known as the mean-square frequency of the line and given the symbol $\langle\Delta\omega^2\rangle_{\mathrm{Av.}}$. Fig. 4 is a plot of an absorption line : the example chosen is in fact a Gaussian curve, such as

[26] Hahn, *Phys. Review*, 1949, **76**, 145.

[27] Pake and Gutowsky, *ibid.*, 1948, **74**, 979.

[28] Drain, *Proc. Phys. Soc.*, 1949, **62**, 301.

[29] Sachs, Turner, and Purcell, quoted by Purcell, *Physica*, 1951, **17**, 282.

is given, for example, by ammonium chloride at room temperature.[30] The quantity F(ν) is known as the line-shape function at the frequency ν and is a measure of the intensity of absorption at that particular frequency ; ν^* is the frequency at the centre of the line. $\langle\Delta\omega^2\rangle_{\text{Av.}}$ is then given by the equation

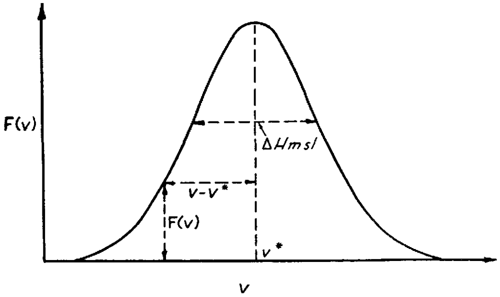

FIG. 4

A Gaussian absorption curve.

$$\langle\Delta\omega^2\rangle_{\text{Av.}} = \int_{-\infty}^{\infty} \mathrm{F}(\nu).(\nu - \nu^*)^2 \mathrm{d}\nu \quad . \quad . \quad . \quad (13)$$

The simplest method of treating T_2 is to define it with respect to $\langle\Delta\omega^2\rangle_{\text{Av.}}$ by the equation

$$1/(T_2) = \sqrt{\langle\Delta\omega^2\rangle_{\text{Av.}}} \quad . \quad . \quad . \quad . \quad (14)$$

Equation (14) strictly has meaning only if the line has the shape of a Gaussian curve ; otherwise, the equation defines a sort of mean value of T_2 which is still useful in drawing roughly quantitative conclusions. By using equation (6), equation (14) can be rewritten as

$$\langle\Delta\omega^2\rangle_{\text{Av.}} = \frac{1}{T_2^{\,2}} = \frac{g^2\mu_n^{\,2}}{(h/2\pi)^2}.\langle\Delta H^2\rangle_{\text{Av.}} \quad . \quad . \quad (15)$$

The quantity $\langle\Delta H^2\rangle_{\text{Av.}}$, in units of the gauss^2, is known as the second moment of the absorption line and is a very useful way of expressing the magnitude of the line-broadening. In the nuclear resonance experiment, the final recorder plots the derivative curve of the absorption line, and the latter is derived from the former by integration. The second moment of the absorption line is defined in the same way as the mean-square frequency, through the equation

$$\langle\Delta H^2\rangle_{\text{Av.}} = \int_{-\infty}^{\infty} \mathrm{F}(H).(H - H^*)^2 \mathrm{d}H \quad . \quad . \quad . \quad (16)$$

where F(H) is the line-shape function at any value of the field H, and H^* is the resonance field strength for an isolated nucleus, *i.e.*, the value of H at the centre of the absorption line. The second moment can therefore be derived directly from the experimental data by finding the total area under

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[30] Pake and Purcell, *Phys. Review*, 1948, **74**, 1184 ; erratum, *ibid.*, 1949, **75**, 534.

a plot of the function $F(H).(H - H^*)^2$ against H, although a method due to Pake and Purcell [30] using the derivative curve is more convenient in practice.

Ammonium Chloride.—One important application of the nuclear resonance method lies in the fact that, under certain conditions, the second moment of the absorption line bears a direct relationship to the distance between the resonating atoms. The reason is that T_2 depends on the size of the oscillatory magnetic fields perpendicular to H_0 produced by one nucleus at another, and these are very sensitive to the internuclear distance. If the resonating nuclei are hydrogen nuclei, we can therefore measure interproton distances in crystals, a fact of considerable importance to structure analysis. Now, in ammonium chloride at 90° K, T_2 is about 5×10^{-6} sec.[31] and T_1 is nearly 100 sec. Consequently, the broadening is due solely to T_2, and so depends on the interproton distances in the salt. The equation relating the second moment of a powdered crystal to the distance r_{jk} between resonating atoms has been calculated theoretically by Van Vleck,[32] and can be written as [31]

$$\langle \Delta H^2 \rangle_{\text{Av.}} = \frac{6}{5} I(I+1) N_s^{-1} g^2 \mu_n^2 \sum_{j>k} r_{jk}^{-6} + \frac{4}{15} \mu_n^2 N_s^{-1} \sum_{j,f} I_f(I_f+1) g_f^2 r_{jf}^{-6} \tag{17}$$

where the f subscripts refer to nuclei with magnetic moments other than the resonating nucleus which nevertheless contribute to the broadening. N_s represents the total number of resonating nuclei in the particular subgroup (*e.g.*, unit cell, molecular, or molecular complex) to which the broadening is attributed. It will be noticed that the second moment depends on r_{jk}^{-6}, illustrating the high sensitivity of the former to slight changes in the interproton distance. The two important conditions for equation (17) to hold are : (1) that the lattice must be rigid at the temperatures at which the experiment is carried out, or in more precise terms, the resonating nuclei must not have moved appreciably in a time comparable to T_2 ; and (2) that there must not be paramagnetic atoms present in greater atomic ratio to the resonating atoms than 10^{-6}. If this ratio is exceeded, the oscillatory magnetic fields which are produced by thermal agitation of the paramagnetic atoms or their low relaxation times will compete with the spin–spin interactions and so alter the second moment.[32] A further condition which we have assumed so far is that the resonating nuclei have no quadrupole moment ; this is necessarily true for nuclei of spin $\frac{1}{2}$.

These conditions are fulfilled for proton resonance in pure ammonium chloride at 90° K, and this compound will now be discussed in more detail. The derivative and absorption lines are shown in Fig. 5.[31] The distance between the two peaks on the derivative curve is 22 gauss, and the second-moment of the absorption line is $57{\cdot}0 \pm 3{\cdot}0$ gauss^2. For our sub-group, we take a single molecule of NH_4Cl for which $N_s = 4$. From equation (17),

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[31] Gutowsky, Kistiakowsky, Pake, and Purcell, *J. Chem. Phys.*, 1949, **17**, 972.

[32] Van Vleck, *Phys. Review*, 1948, **74**, 1168.

there will be three separate contributions to the second moment ; the first two arise from neighbouring hydrogen atoms in the same NH_4^+ ion and in neighbouring NH_4^+ ions, and the third from neighbouring Cl^- ions both isotopes of which have a magnetic moment. The last two contributions can be calculated from the known crystal structure of NH_4Cl at 88° K and prove to be very small. Subtraction of these values from the experimental second moment leaves 50·5 gauss^2 for the contribution of the NH_4^+ ion alone, which is consistent with an N–H bond distance of 1·025 ± 0·005 Å, in excellent agreement with the latest neutron-diffraction value [33] of 1·03 ± 0·02 Å.

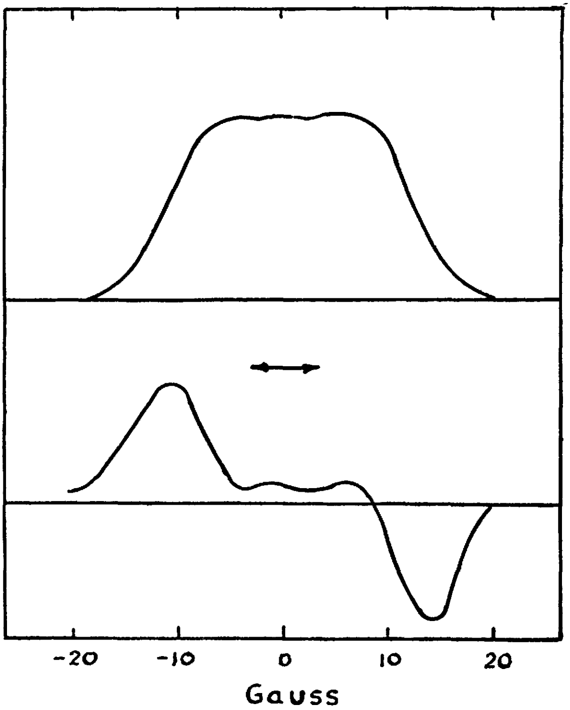

FIG. 5

Derivative and absorption lines of ammonium chloride at 90° K *(reprinted, with permission, from* J. Chem. Phys., 1949, **17**, 972).

Ammonium chloride is one of the most favourable cases studied in this way. The interproton distance is small, giving rise to a high second moment and a broad line ; T_1 has a sufficiently low value at 90° K to give a reasonable signal-to-noise ratio. Although there is an error of 10% in the second moment, this quantity depends on the sixth power of the interproton distance, and the corresponding error in the bond distance will therefore be a sixth of this. Consequently, the method is able to furnish in favourable

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[33] Levy and Peterson, *Phys. Review*, 1952, **86**, 766.

cases values of interproton distances as accurate as X-ray values for bonds involving heavier atoms. The most favourable cases occur in compounds, preferably of known crystal structure, in which most of the hydrogen atoms are in the form of XH_n groups as, for example, the CH_3 group in $CH_3{\cdot}CCl_3$, the H_2O molecule in hydrates, and the hydroxonium ion in perchloric acid monohydrate, provided that there are one or more convenient temperatures at which the lattice can be considered to be rigid and at which T_1 has a reasonable value. The method can then furnish considerable information on the disposition of the hydrogen atoms in a crystal and can be of valuable assistance in an X-ray analysis.

The Effect of Molecular Motion.—One drawback of the method is that a "rigid lattice" (see p. 290) is required. This condition is unlikely to hold for all temperatures up to the melting point of a solid, and it will certainly not hold in the liquid or the gaseous state. In particular, a number of solids, including ammonium chloride, are known to possess one or more transition points at which there may be abrupt changes in the crystal symmetry, the density, or the specific heat. These have in certain cases been associated with the onset of rotation or vibration of molecules or ions in the crystal.[34] If a molecule containing protons is free to rotate in all directions, the internuclear fields will be largely cancelled out and consequently the line-width and second moment will decrease.

The problem has been treated quantitatively by BPP, whose paper [6] gives a full account of the theory. A simple way of discussing the theory is to consider a system of two identical spins in a magnetic field H_0. The two spins can be located in either the same or adjacent molecules. The energy of this system depends on the angles made by the nuclear magnets $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ and by the vector joining the two moments $\boldsymbol{r}_{12}$ with the field H_0. The equation as derived classically is

$$W_{12} = \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 / r_{12}^3 - 3\boldsymbol{\mu}_1 \cdot \boldsymbol{r}_{12} \boldsymbol{\mu}_2 \cdot \boldsymbol{r}_{12} / r_{12}^5 \qquad . \quad . \quad (18)$$

The change in the orientation of $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ with time due to the influence of T_1 and T_2 gives rise to the line-broadening which has already been discussed. The random distribution of $\boldsymbol{r}_{12}$ in space, but *not* with time, is the effect we encounter in the powdered crystal. Suppose now that $\boldsymbol{r}_{12}$ varies with time, that is, the interproton vector oscillates or rotates with respect to the direction of the applied field. We can distinguish two types of motion. The first is the lattice vibrations of the crystal, which for the moment we omit from discussion. The second occurs in molecular crystals, *e.g.*, hydrates, in which the H_2O molecules can rotate over energy barriers ; because of the Boltzmann distribution of thermal energy, there will always be a small fraction of molecules at any temperature which will have sufficient energy to surmount such barriers. This type of motion is usually random. We also include in this group other types of motion which cause complete reorientation of a proton-containing group, such as quantum-mechanical tunnelling. Consider now what we can expect to happen as the temperature of the crystal rises. The frequency with which this orientation of $\boldsymbol{r}_{12}$ occurs will rise.

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[34] Staveley, *Quart. Reviews*, 1949, **3**, 65.

At a certain temperature, it will become comparable to the frequency of spin exchange, which is the reciprocal of T_2. Above this temperature, the two processes will compete in reorienting $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ but the former will rapidly overtake the latter as the temperature continues to rise. The spin-exchange process therefore becomes much less effective in inducing relaxation, causing T_2 to rise and so reducing the line width. It must be borne in mind that T_1 makes a negligible contribution to the line width at these temperatures and often we have to wait until the melting point before T_1 and T_2 approach each other in value. One important fact which has emerged from experiment is that the first type of motion, involving lattice vibrations, is generally much less effective than the second, involving reorientation of $\boldsymbol{r}_{12}$, and there are few, if any, crystals in which the former can be said to be the predominant relaxation mechanism.[10] However, the distinction we have drawn between lattice vibrations and group rotations is rather arbitrary. In particular, if the potential-energy curve of the rotation has a broad minimum, the group may undergo rotational oscillation with large amplitudes, *e.g.*, of the order of 30—45°, even at low temperatures. The second moment of the nuclear resonance line may then be reduced and the effect has been calculated for the two-spin group by Andrew.[35] In general, the reduction is smaller than that caused by rotation of the group ; a sudden change in the line width is more likely to be caused by group rotation than the lattice vibrations.

The calculations of BPP show that it is convenient to discuss the expected variation of T_1 and T_2 due to molecular motion in terms of a quantity τ_c, known as the correlation time, which can be considered to be the time in which a molecule is rotated to such an extent that the value of the second moment has altered by a detectable amount. Since the latter is governed by T_2, it follows directly from this definition that the line will begin to narrow when τ_c approaches T_2, and it will be recalled that this will break one of the conditions which determine the application of equation (17). Using statistical theory, BPP show that T_1 and T_2 can be written in terms of τ_c and that as τ_c varies, both quantities show the characteristic changes given in Fig. 6, which shows a plot of log T_1 and log T_2 against log τ_c. These variations are derived for a simplified model in which all interactions producing relaxation are assumed to have the same value of the correlation time. But τ_c, being a quantity referring directly to the freedom of movement of the molecule, will change with temperature. In general, it will decrease as the temperature rises, although its precise dependence may not be known *a priori*. In the case of liquids, BPP show that it is often directly proportional to the Debye relaxation time τ, which is the time taken for an assembly of polar molecules, originally oriented by an electric field, to assume a random distribution through Brownian movement when the field is removed. Since τ is inversely proportional to the temperature, τ_c in this case shows the same dependence. In solids, the precise form of the equation connecting τ_c and the temperature is not generally known, but the graphs in Fig. 6 can frequently be related to the variation of T_1 and T_2 with temperature. The forms of the curves for T_1 and T_2 show some of the characteristics

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[35] Andrew, *J. Chem. Phys.*, 1950, **18**, 607.

of these quantities which we have already mentioned. In particular, at high values of τ_c when $2\pi\nu\tau_c \gg 1$, *i.e.*, in an effectively rigid lattice (ν is the resonance frequency), T_2 tends to a constant value T_2'' which proves to be the value defined through equations (17) and (15). In this region, T_1 is directly proportional to τ_c and so rises as the temperature falls. At low values of τ_c, when $2\pi\nu\tau_c \ll 1$, *i.e.*, in liquids, T_1 is inversely proportional to τ_c and so rises as the temperature increases. The minimum which T_1 approaches when $2\pi\nu\tau_c$ tends to unity occurs theoretically at the point when τ_c equals $(\sqrt{2}\gamma H_0)^{-1}$. T_2 assumes the rigid lattice value when the correlation time is given by

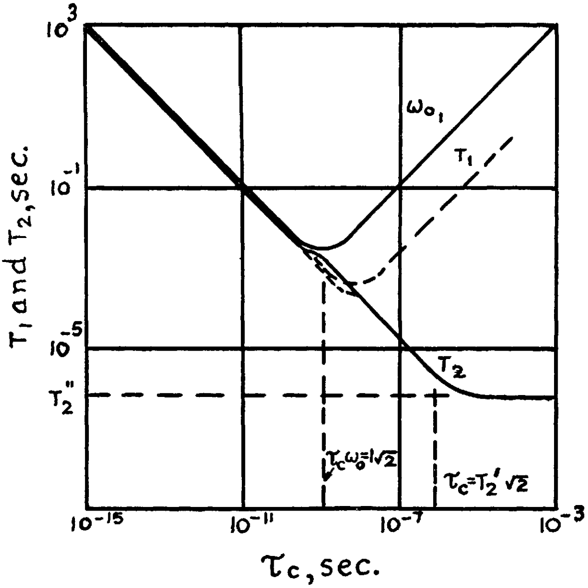

FIG. 6

Variation of T_1 and T_2 with τ_c (reproduced, with permission, from Phys. Review, 1948, **73**, 679).

$$\tau_c = (\sqrt{2}\gamma\Delta H_{\text{m.sl.}})^{-1} \qquad . \quad . \quad . \quad . \qquad (19)$$

Next, we must discuss how closely these relationships are obeyed in practice. We begin by resuming the discussion of ammonium chloride. There are measurements for this compound of T_1[29] and the line width $\Delta H_{\text{m.sl.}}$[36] covering the range 90—290° K. The plot of the line width is given in Fig. 7. At about 130° K, the line width of ammonium chloride decreases from 23 to 5 gauss over a temperature range of 16° ; above and below this temperature, it is nearly constant at 5 and 23 gauss, respectively. This rather sudden change in T_2 might not be expected from Fig. 6, and we have no precise way of predicting the variation of τ_c with temperature, except

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[36] Gutowsky and Pake, *J. Chem. Phys.*, 1948, **16**, 1164.

for some evidence from the variation of T_1, which is discussed later. Up to 130°, the line-width curve is horizontal, representing the rigid lattice part of Fig. 3, where $2\pi\nu\tau_c \gg 1$. The frequency of rotation of the NH_4^+ ion from one equilibrium position to another has meanwhile been slowly increasing and at 130° K reaches the critical value above which it begins to reduce the line width. This value is the reciprocal of T_2, which is 3×10^4 cps. It will be noticed that the limiting frequency is very small on the thermodynamic scale, where one is dealing with rotational and vibrational motions of frequencies greater than 10^{10} cps. Consequently, the changes in the line width need not necessarily correspond to or be related to any transition points or changes in the lattice constants, although they may be related to variations in the dielectric constant when we have polar molecules in the lattice.

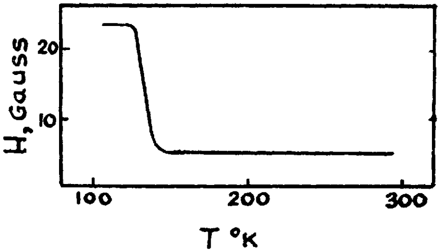

FIG. 7

$\Delta H_{m\,sl.}$–T *curve for ammonium chloride (reproduced, with permission, from* J. Chem. Phys., 1948, **16**, 1164).

Above the transition temperature of 130° K, it has been shown [29] that τ_c varies exponentially with temperature, and the results for ammonium chloride can be expressed to a very good approximation by the equation

$$\tau_c = (26 \times 10^{-14}) \exp 2370/RT \quad . \quad . \quad . \quad (20)$$

It has been suggested that the form of equation (20) shows that we are dealing with simple rotation over an energy barrier of a height of 2·37 kcal./mole, and similar equations have been proposed for τ_c in a number of other compounds, notably NH_4Br[29] and $CH_3{\cdot}CCl_3$.[37] If this picture is true, the fraction of NH_4^+ ions having sufficient energy to surmount an energy barrier of 2370 cal./mole is 10^{-8} at 138° K and 3×10^{-4} at room temperature. Free rotation of a fraction 10^{-8} of the NH_4^+ ions present is sufficient to reduce the line width by a factor of 5, which shows the extraordinary sensitivity of the nuclear resonance line to this form of motion.

This interpretation of the line-width transition may appear to conflict with the latest neutron-diffraction results for ammonium chloride,[33] which suggest that the second-order transition at − 30° C is of the order–disorder type. Below this temperature, the four hydrogen atoms of any one NH_4^+ ion occupy only four of the eight positions available for them in the lattice ; above, these eight positions are occupied at random.

A general picture of the situation has been given by Purcell.[10] Transitions from one set of positions to another will be proceeding at all temperatures, but the rate at which the ions reorient over the energy barrier hindering the process will rise with temperature. At 130° K, it reaches the critical

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[37] Gutowsky and Pake, *J. Chem. Phys.*, 1950, **18**, 162.

value above which it begins to reduce the line width. This value is the reciprocal of T_2 which is 3×10^4 cps. Above 130° K, the frequency rises still further until the molecule begins to spend an appreciable amount of its time in intermediate positions. The intermolecular forces will then begin to change, and eventually this will bring about a transition to a disordered lattice with a space-group of a higher symmetry, but with little further change in the line-width. The neutron-diffraction results also indicate that at room temperature the NH_4^+ ion as a whole is undergoing rotatory oscillation with a half-angle of about 11°, but this type of motion has not so far been shown to have a detectable effect on the line width.

The simple exponential form of equation (20) would not be expected if we were dealing with quantum-mechanical tunnelling through the energy barrier. Newman [38] has shown that this process might be occurring in potassium dihydrogen phosphate, in which τ_c is found to be almost independent of temperature over a certain range. Unfortunately it is not known to what extent paramagnetic impurities contribute to the result, and no precise calculation of the effect of quantum-mechanical tunnelling was made.

In liquids, the random thermal oscillations undergone by the molecules are called Brownian movement. This type of motion is very effective in inducing relaxation and gives rise to proton spin–lattice relaxation times of the order of seconds and values of T_2 ranging from 1 to 10^{-4} sec. Measurements on liquids have proved very useful in testing the BPP theory. For example, a plot of log T_1 against log η/T, where η is the viscosity, should be linear, and the agreement for glycerol and ethyl alcohol between − 35° and 60° C has been found to be quite satisfactory.[6] Among other interesting properties of the liquid resonance line, it has been found that the presence of paramagnetic ions slightly alters the value of the frequency at which resonance occurs,[39] and has a marked effect on T_1 and T_2 ; [6] for example, in 10^{-3}M-manganese sulphate solution, T_1 has dropped from 2·33 to 0·09 sec. This sensitivity has been used by Selwood and his collaborators [40] to determine the effective paramagnetic activity on supported oxide catalysts. As already noted, T_2 in a number of liquids is so small that it is completely masked by the field inhomogeneity ; however, it has been directly measured in a number of branched-chain hydrocarbons,[41] in which it shows an interesting dependence on the symmetry of the molecule. In highly homogeneous magnetic fields, the proton and fluorine resonance lines of some compounds are split into two or more peaks, and even in liquids showing single lines the exact frequency of the peak centre varies from compound to compound. This additional contribution to the line broadening is small in proton resonance lines but rather more important in fluorine lines ; for example, in fields of about 6365 gauss at a fixed frequency, the resonance field strength of ^1H and ^{19}F nuclei in a number of compounds has been found to vary

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[38] Newman, *J. Chem. Phys.*, 1950, **18**, 670.

[39] Gabillard and Soutif, *Compt. rend.*, 1951, **233**, 480.

[40] Selwood and Schroyer, *Discuss. Faraday Soc.*, 1950, **8**, 337.

[41] Clay, Bradford, and Strick, *J. Chem. Phys.*, 1951, **19**, 1429.

over a range of 0·12 and 3·98 gauss.[42] The phenomenon promises to give results of considerable interest, but the subject is developing rapidly and the reader is referred to refs. 24, 42, and 43 and recent issues of the *Physical Review.*

The Line Shape.—There is yet another aspect of the line which we have not discussed, and that is its shape. The simplest assumptions that can be made about the form of the absorption curve are [30] that it corresponds either to the familiar Gaussian distribution or to a Lorentzian distribution. The latter is characteristic of a damped oscillator, and is found in the pressure broadening of spectroscopic lines. In practice, few compounds show either of these simple line shapes ; the Gaussian form holds for ammonium chloride at 290° K, and the Lorentzian for polytetrafluoroethylene at the same temperature. The majority of proton resonance lines have shapes somewhere in between the two forms and it is generally impossible to calculate what line shape to expect.[30] The exceptions to this statement occur when the disposition of protons in the crystal is such that there are groups of resonating nuclei particularly close to each other and a considerable distance from any other sources of broadening, as for example, the H_2O molecule in certain hydrates, the CH_3 group in $CH_3{\cdot}CCl_3$, and the NH_4^+ ion in NH_4Cl. Since the second moment varies as the inverse sixth power of the interproton distance, these groups make by far the largest contribution to the broadening. In these cases, a rigorous quantum-mechanical calculation can be made of the line shape, which can then be compared with the experimental curve and second moment.

The three-spin group. The calculation of the line shape for the three-spin group of a CH_3 radical (which is assumed to be symmetrical) is carried out in three stages.[44] (1) First, the number and frequency of permitted transitions in the three-spin group are found quantum-mechanically ; these are nine in number. (2) Secondly, the effect of a random orientation of three-spin groups over 360° is calculated, in order to be able to apply the results to a powdered crystal ; this gives us a line shape with nine sharp maxima. (3) The broadening effect of neighbouring three-spin groups and foreign nuclei with magnetic moments is allowed for by applying a Gaussian broadening function to every fine-structure component of the curve in (2). That is, the final line-shape function $\mathrm{F}(H)$ at any value of the field H is found from the equation

$$\mathrm{F}(H) = \int_{-\infty}^{\infty} \mathrm{F}(H_0 - H^*).\mathrm{S}(H - H_0).\mathrm{d}H_0 \quad . \qquad . \quad (21)$$

where $\mathrm{F}(H_0 - H^*)$ is the line-shape function found in (2) and $\mathrm{S}(H - H_0)$ is a Gaussian broadening function proportional to $\exp - (H - H_0)^2$. The area under a plot of $\mathrm{F}(H_0 - H^*).\mathrm{S}(H - H_0)$ against H_0 gives the line-shape function at the field H. This process removes much of the fine structure of the curve and in $CH_3{\cdot}CCl_3$ leaves us with a triply-peaked absorption

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[42] Gutowsky and Hoffman, *J Chem. Phys.*, 1951, **19**, 1259.

[43] Ramsey and Purcell, *Phys. Review*, 1952, **85**, 143.

[44] Andrew and Bersohn, *J. Chem. Phys.*, 1950, **18**, 159 ; erratum, *ibid.*, 1952, **20**, 924.

curve, *i.e.*, a subsidiary maximum disposed symmetrically on either side of the central main maximum.

In the case of the two-spin system,[45] the final curve has two maxima symmetrically placed on either side of a central minimum. The calculations for the four-spin system are quoted by Purcell,[10] and the experimental curve for ammonium chloride at 90° K is flat-topped. The rigorous calculation of these line shapes requires considerable information about the structure of the crystal in order that a reasonable form for the Gaussian broadening function may be evaluated. Otherwise, the broadening effect of neighbouring nuclei has to be calculated by analogy with structures of similar compounds or by using van der Waals radii to determine the nearest distance of approach of the relevant groups.

The first three-spin system studied in this way was the CH_3 group in $CH_3 \cdot CCl_3$. The experimental line-shape and second moment were known,[31] and Andrew and Bersohn then showed [44] that by assuming a symmetrical CH_3 group with a tetrahedral value for the $\widehat{HCH}$ angle and a C–H bond length of 1·10 Å, the best fit to the experimental curve occurred when a Gaussian broadening function of second moment 2·1 gauss^2 was used. The two curves are superimposed in Fig. 8 ; the full line gives the experimental results and the broken line the calculated line-shape. There is a bad misfit at the sides of the curve which was attributed to the residual effects of the rotation of the CH_3 group, which reduces the line width from 28 to 3 gauss in the vicinity of 145° K.[46]. It has been shown [46] that if the experimental data on the variation of the line width with temperature are combined with the

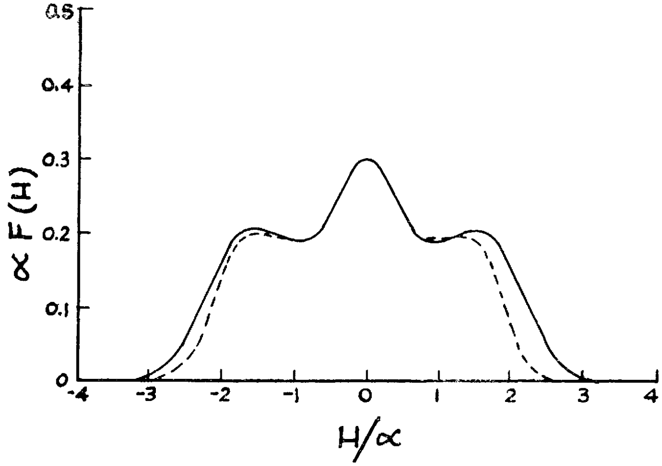

FIG. 8

The absorption line of $CH_3 \cdot CCl_3$ (*reproduced, with permission, from* J. Chem. Phys., 1950, **18**, 159).

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[45] Pake, *J. Chem. Phys.*, 1948, **16**, 327.

[46] Gutowsky and Pake, *ibid.*, 1950, **18**, 162.

BPP equations predicting the variation of τ_c with the former quantity,

$$\tau_c = (12 \times 10^{-13}) \exp 7000/RT \quad . \quad . \quad . \quad (22)$$

equation (22) can be derived. This suggests that the CH_3 group undergoes hindered rotation over an energy barrier of height 7000 cal.; when a fraction 10^{-11} of the molecules have sufficient energy to surmount the barrier, the motion begins to reduce the line width. The presence of residual low-frequency motion at low temperatures is supported by the gradual decrease of the dielectric constant down to 150° K.[47] The CH_3 group seems to be particularly prone to rotation of this sort, and at 90° K the critical fraction of rotating methyl groups required to narrow the line is exceeded in a number of compounds, notably C_2H_6, $CH_3{\cdot}CN$, CH_3I, $CH_3{\cdot}NO_2$, $HgMe_2$,[46] and C_6Me_6.[35]

Van Vleck's equation for the broadening in a rigid lattice can be modified to allow for the effect of hindered rotation or quantum-mechanical tunnelling; [46] the equation then includes a function depending on the angle between the axis of rotation of any one interproton distance r_{jk} and r_{jk} itself. In the three-spin system, it is found that when the axis of the motion is normal to the plane of the three spins, the intramolecular second moment (*i.e.*, the broadening contribution of any one three-spin group in isolation) should be one-fourth as great as that in the rigid lattice. The intermolecular broadening (*i.e.*, between neighbouring three-spin groups) will also be reduced, but not generally in the same ratio. However, the latter is usually small, and the effect of this type of motion is generally to reduce the total second moment by a factor of 4, as has been verified in $CH_3{\cdot}CN$ and NH_3, and more approximately in CH_3I, $CH_3{\cdot}NO_2$, and $HgMe_2$.[46] The low second moments of *o*-, *m*-, and *p*-xylene, mesitylene, and hexamethylbenzene at 95° K have also been explained by rotation or tunnelling of the CH_3 groups about the C–C side bonds.[35] Andrew and Bersohn [44] have also calculated the line shape to be expected for a symmetrical three-spin group which is rotating about the normal to its plane, and by comparing this with the experimental line shape, further confirmation of the proposed motion can be obtained. This analysis has been successfully carried out for $CH_3{\cdot}CN$ at 93° K,[44] in which the CH_3 group is found to be rotating round the C–C bond.

One three-spin group of great interest to chemistry is the hydroxonium ion, H_3O^+. It has been inferred for some time that this ion exists in a number of compounds in the solid state, and evidence from nuclear magnetic resonance absorption has confirmed many of these conclusions. The characteristic triply-peaked curve has been found in three hydrates of strong acids at 90° K, namely, HNO_3,H_2O,[48] $HClO_4,H_2O$,[48, 49] and $H_2PtCl_6,2H_2O$,[50] all of which give very similar absorption curves. For example, the outer maximum and the minimum of the absorption curves of HNO_3,H_2O fall at 13·4 and 9·3 gauss, those of $HClO_4,H_2O$ at 13·4 and 8·5 gauss, and

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[47] Turkevich and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 2468.

[48] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; erratum, 1952, **48**, 675.

[49] Kakiuchi, Shono, Komatsu, and Kigoshi, *J. Phys. Soc. Japan*, 1952, **7**, 108.

[50] Smith and Richards, *Trans. Faraday Soc.*, 1952, **48**, 307.

$H_2PtCl_6,2H_2O$ has a nearly horizontal inflection stretching from 8 to 13 gauss. The three second moments at 90° K are 30·4, 31·9, and 31·2 gauss^2 (each with an error of $\pm$ 5%). These values are reasonable for a rigid lattice of hydroxonium ions and NO_3^-, ClO_4^-, and $[PtCl_6^{--}]$ ions respectively. Furthermore, from the known crystal structure of HNO_3,H_2O,[51] the distance apart of neighbouring H_3O^+ ions can be calculated and so the line shape can be predicted. A value of 2·3 gauss^2 being used for the second moment of the Gaussian broadening function, the best theoretical fit to the experimental line shape is obtained for a symmetrical H_3O^+ ion with an interproton distance of 1·72 Å. This is illustrated in Fig. 9, where the full line is the calculated curve and the white and filled circles are two sets of experimental data from different specimens of HNO_3,H_2O. In $HClO_4,H_2O$, the temperature variation of the second moment [49] shows that the lattice has become rigid from the nuclear resonance point of view at 110° K and a calculation of the line shape at this temperature, reasonable van der Waals radii being assumed for the H_3O^+ and ClO_4^- ions, predicts an interproton distance of 1·70 Å. We can conclude that because of the closely-agreeing second moments and the similarity in line shapes (especially at the " tails " of the curves), the interproton distance is probably 1·72 $\pm$ 0·02 Å in all three compounds. However, this analysis requires some qualification. First, the calculations have been carried out hitherto for a symmetrical H_3O^+ ion only. Secondly, no reliable O–H bond length can be deduced because it is not possible to predict the $\widehat{HOH}$ angle precisely. The *X*-ray data have been interpreted in terms of a hydrate lattice,[51]* but if it is now considered to be $(H_3O^+)NO_3^-$ and if

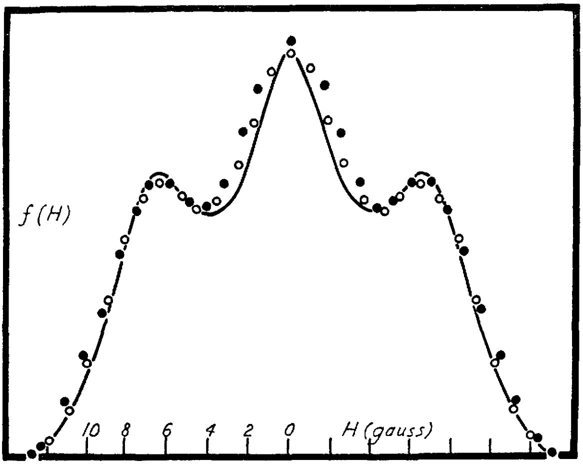

FIG. 9

The absorption curve of the H_3O^+ *ion in* HNO_3,H_2O (*reproduced, with permission, from* Trans. Faraday Soc., 1952, **48**, 675).

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[51] Luzzati, *Acta Cryst.*, 1951, **4**, 239.

* Later calculations of the *X*-ray data for $HNO_3,3H_2O$ have indicated the presence of an H_3O^+ ion ; see Luzzati, *Acta Cryst.*, 1953, **6**, 157.

the hydrogen atoms of the H_3O^+ ion are assumed to lie along the O···O directions, the results give a mean $\widehat{HOH}$ angle of 117°, which will agree with the nuclear resonance evidence if the O–H bond length is 1·01 Å, as compared with $r_0 = 0{\cdot}957$ Å and $\widehat{HOH} = 105° \; 3'$ in water vapour.[52]

The two-spin group. The line shape for the two-spin system of a water molecule has been calculated and compared with the experimental results for a single crystal of gypsum, $CaSO_4,2H_2O$, at room temperature.[45] As already mentioned, the theoretical line shape for a water molecule consists of two peaks symmetrically disposed about a central minimum. In a single crystal, the distance apart of the two peaks will depend on the angle between the line joining the two hydrogen atoms and the Zeeman field H_0. The crystal structure of gypsum [53] shows that, in any single crystal, there are in general two possible values for this angle and therefore for the peak separation. Consequently, when a single crystal is rotated in the field so that H_0 can take any direction in the (001) plane, the absorption curve consists of two superimposed double-peaked curves with different peak separations and so at certain orientations shows four peaks. The peaks merge and then resolve again as the direction of H_0 in the (001) plane changes, and these variations follow very satisfactorily the theoretical predictions for water molecules with an interproton distance of 1·58 Å. This value, in conjunction with a Gaussian broadening function of 2·37 gauss^2 deduced from the broadening of component lines in the resonance spectrum of the single crystal, was used to calculate the line-shape for the powdered crystal, and also provided a reasonable fit to the experimental results. As in the case of the H_3O^+ ion, no precise value of the O–H bond length is obtained because the $\widehat{HOH}$ angle is not known. If the hydrogen atoms of the water groups are assumed to lie along the O···O directions, which are hydrogen bonds of length 2·70 Å, the $\widehat{HOH}$ angle will then be 108°, consistent with an O–H bond length of 0·98 Å. A similar analysis of a single crystal of Li_2SO_4,H_2O[54] has given an interproton distance of 1·57 ± 0·02 Å.

Similar double-peaked absorption curves have been obtained [45] from powdered specimens of $KF,2H_2O$, $MgSO_4,7H_2O$, $ZnSO_4,7H_2O$, and $KAl(SO_4)_2,12H_2O$ at room temperature ; the separations of the maxima of the derivative curves all fell between 12·5 and 14·5 gauss. In borax, $Na_2B_4O_7,10H_2O$, however, the absorption curve was narrow with a single peak and a width ($\Delta H_{\mathrm{m\,sl.}}$) of 4·4 gauss. Ice just below 0° also shows a narrow line about 3·7 gauss wide ; [6] this broadens as the temperature is lowered, but the rigid lattice value is not reached until below 230° K. In ice, this behaviour would result from the type of motion that has been adduced to explain the residual entropy of ice,[55] that is, transition of a water molecule from one to another of the six positions it can assume in

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[52] Herzberg, " Infrared and Raman Spectra ", p. 489 (Van Nostrand, 1945).

[53] Wooster, *Z. Krist.*, 1936, **94**, 375.

[54] Soutif, Dreyfus, and Ayant, *Compt. rend.*, 1951, **233**, 395.

[55] Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2680.

the lattice, provided that the frequency of the motion is greater than 3×10^4 cps. When the frequency drops below this value, the line width rises to the rigid-lattice value. A similar explanation presumably holds for borax.

Nuclear Magnetic Resonance in More Complicated Molecules.—There are many compounds in which the hydrogen atoms are not all located in one of these two-, three-, or four-spin groups, as for example ammonium dihydrogen phosphate. In these cases, only a roughly quantitative prediction of the line shape can be made. In the example quoted above, the absorption curve obtained at 87° K,[38] given in Fig. 10, is explained most satisfactorily as resulting from the superposition of the broad flat-topped curve of a typical NH_4^+ ion, known from NH_4Cl, and the much sharper-peaked curve of an $H_2PO_4^-$ ion, known from KH_2PO_4. If the curve is divided in two, as shown by the dotted line, the areas of the upper and the lower portion are in the ratio of 0·57 ; since there are half as many hydrogen atoms in the acidic phosphate groups as there are in the NH_4^+ ion, the theoretical value should be 0·50. Because it is impossible to predict a very precise value of the intermolecular broadening without knowing something beforehand about the position of the hydrogen atoms, *i.e.*, the length of the O–H bond, whether or not the H atom lies on the O···O bond directions, and so on, no quantitative comparison of the theoretical and experimental absorption curves can be made, and this general drawback of the method becomes more serious as the number of chemically distinct hydrogen atoms in the molecule increases.

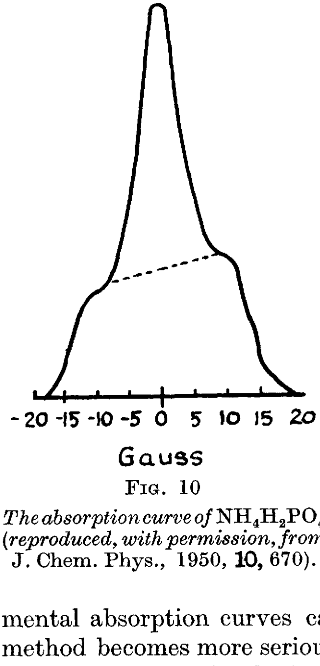

FIG. 10

The absorption curve of $NH_4H_2PO_4$ *(reproduced, with permission, from* J. Chem. Phys., 1950, **10**, 670).

A number of hydrates also fall in this category. Two in particular are oxalic acid dihydrate, for which there are the two possible structures $H_2C_2O_4,2H_2O$ and $(H_3O^+)_2C_2O_4^{--}$, and potassium pentaborate tetrahydrate, for which a hydroxonium structure $K^+(H_3O^+)_2(H_2B_5O_{10}^{---})$ has been proposed.[57] The nuclear resonance absorption spectrum of oxalic acid dihydrate at 90° K [48] is quite different in type from that of $(H_3O^+)_2(PtCl_6^{--})$ and has half the second moment of the latter. The absorption curve, illustrated in Fig. 11, could be obtained by superimposing two separate absorption curves, the first that of a water molecule of about the same dimensions as those in gypsum, and the second that of a more isolated single hydrogen atom. The single peak of the latter will obliterate the central minimum of the two-spin curve, giving a practically continuous absorption

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[56] (*a*) Ahmed and Cruickshank, (*b*) Cox, Dougill, and Jeffrey, (*c*) Jeffrey and Parry, *J.*, in the press.

[57] Zachariasen, *Z. Krist.*, 1937, **98**, 266.

curve. The results therefore support the hydrate structure $H_2C_2O_4,2H_2O$. This is in agreement with the most recent *X*-ray investigations,[56] which show that the dimensions and configuration of the oxalic acid molecule in the dihydrate are the same as in the α-anhydrous form (which must be $H_2C_2O_4$), in contrast to the non-planar oxalate ion in ammonium oxalate. A closely similar absorption curve is given by potassium pentaborate tetrahydrate,[50] which supports the structure $K^+(H_4B_5O_{10}^-),2H_2O$ for the compound. In contrast, a similar analysis of the monohydrates of sulphuric and selenic acid [48, 50] shows that the absorption curves and second moments are most satisfactorily explained in terms of hydroxonium compounds, so that in the solid state these substances should be formulated as

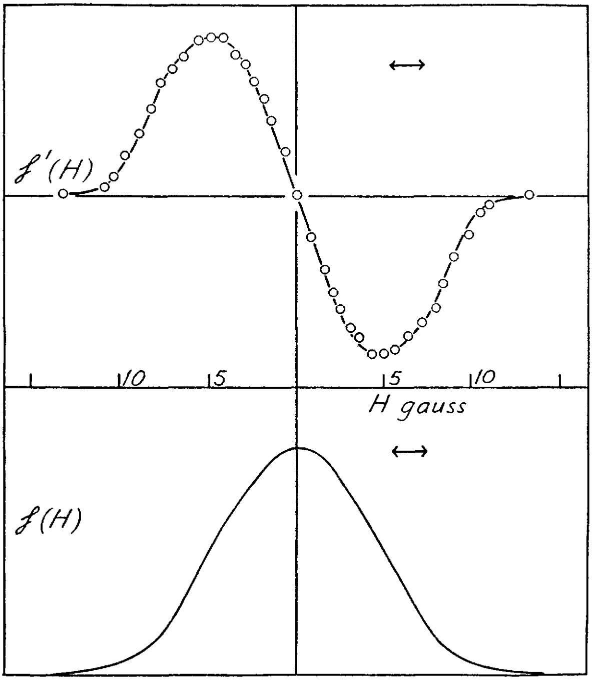

Fig. 11

The derivative and absorption curves of oxalic acid dihydrate (reproduced, with permission, from Trans. Faraday Soc., 1951, **47**, 1261).

$$(H_3O^+)(HSO_4^-) \text{ and } (H_3O^+)(HSeO_4^-)$$

although in the liquid state they appear to be incompletely ionised.

Many compounds, in which the hydrogen atoms occur in different groups and in which there is a large intermolecular broadening, give absorption lines which show little or no fine structure and cannot be calculated theoretically. In such cases, no precise interproton distances can be derived; but the second moment, the line width, and the spin-lattice relaxation time can furnish useful information on molecular motions in the crystal. Ideally, to make the most complete analysis of the solid which the method offers, all three quantities should be measured over a considerable range of temperature, but this has been carried out for comparatively few compounds. The measurement of the second moment involves a complete plot of the derivative line, and during the experiment the temperature must remain reasonably constant or the RF bridge will drift off balance and the second moment itself may change. Each line-scan has to be repeated at a number of fixed temperatures in a range from liquid-oxygen or -hydrogen temperatures to room temperature and perhaps higher. At each point, the compound must be left for a considerable time to reach equilibrium, and in view of the well-known tendency of many solids to show hysteresis in the vicinity of their transition temperatures, measurements must usually be taken in the direction of decreasing as well as increasing temperature. The materials must be carefully purified, especially if the impurity is liable to give a sharp resonance line at temperatures at which the compound under investigation gives a broad line. The sharply-peaked curve may then mask the slowly-varying background, and will also cause serious errors in T_1. It will also be recalled that T_1 is very susceptible to traces of paramagnetic impurity, especially when its value approaches the order of an hour or so.[10] Some inconsistencies in the published data may be attributed to neglect in making due allowance for these various factors.

A considerable amount of work has been done on the variation of some of the nuclear magnetic properties of various materials with temperature. A fairly complete study of benzene over a wide temperature range has been made; line-width data [35] show that molecular rotation, presumably in the molecular plane, begins to affect the line width at 100° K, and from the variation of T_1 from 85° K to 230° K, an energy-barrier for the rotation of 3800 cal. can be derived.[58] The results show that only a fraction, 10^{-7}, of the benzene molecules need be rotating in order to affect the line width. Many compounds have been investigated in order to discover any relationship between line-width transitions and second-order transitions, and what light the two processes may throw on each other. It has been previously emphasised that the two may be quite independent of each other. For example, this is so in methane, for which recent work,[59] correcting some earlier results,[60] has shown that there is no change in the line width at the specific-heat anomaly at 20·4° K, although there is an abrupt change in T_1. On the other hand, in Polythene [61] the line width changes over the range — 60° to — 20° C, and the density–temperature relationship also shows signs of a transition point at — 40° C.[62] Below — 60° C, the second moment is consistent with a zig-zag Polythene molecule in a rigid lattice, and both transition points then locate the region in which random motion of the polymer segments (involving either rotation or rotational oscillation) begins

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[58] Dr. E. R. Andrew and R. G. Eades, personal communication.

[59] Thomas, Alpert, and Torrey, *J. Chem. Phys.*, 1950, **18**, 1511.

[60] Alpert, *Phys. Review*, 1949, **75**, 398.

[61] Newman, *J. Chem. Phys.*, 1950, **18**, 1303.

[62] Hunter and Oakes, *Trans. Faraday Soc.*, 1945, **41**, 49.

to affect the macromolecular properties and the line width. Other polymers, including polytetrafluoroethylene,[30] natural rubber,[60] synthetic rubbers and polystyrene,[63] have also been examined, and the results have been of some assistance in interpreting the mechanisms involved in transitions.

Most of the work discussed in this Review is of recent development and it would be appropriate to conclude by summarising what has been achieved so far. Present experimental methods are sufficiently sensitive to record the nuclear resonance spectra of most nuclei with a magnetic moment in the solid, liquid, and in some cases the gaseous state. In the solid state, the crucial factor determining the sensitivity, the signal-to-noise ratio, depends very much on the values of T_1 and T_2, which in turn depend on the freedom of motion allowed to the nuclei in the lattice, their distance apart, and the concentration of paramagnetic atoms and lattice defects. These are therefore three subjects which can be studied by the method. From the first, we can derive considerable information on the low-frequency motions in certain crystals. From the second, we can in the most favourable cases determine bond lengths involving hydrogen atoms, as for example in ammonium chloride, or at least distinguish between two or more possible structures for a compound, as in the hydrates of some inorganic acids. In the liquid state, paramagnetic impurities also have a large effect on T_1, so the method has been used to measure the small surface concentration of paramagnetic atoms on supported oxide catalysts. Probably the most accurate method at present of measuring the strength and inhomogeneity of magnetic fields is to use the resonance line of a suitable liquid in conjunction with a frequency meter and oscilloscope.

The scope and usefulness of the method are still increasing. Recently it has been used to study electric quadrupole effects in the solid state, and the fine structure of the liquid resonance line has been shown to depend on the structure of the molecule so that, for example, the splitting of the fluorine resonance is different in IF_5 from that in IF_7. Recent experimental work has produced simple and robust apparatus for the detection of the effect, and new methods have been developed for increasing the sensitivity. The subject is now one of the most important new fields of physics to be developed since the war and for the part they played in its development, Professors Bloch and Purcell were jointly awarded the Nobel prize for physics in 1952. In its chemical applications, the future promises to be at least as interesting as the past seven years.

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APPENDIX

The Reviewer has conformed to the generally accepted usage of symbols in this field, despite the unfortunate clash with other important quantities.

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[63] Holroyd, Codrington, Mrowca, and Guth, *J. Appl. Phys.*, 1951, **22**, 696.

In particular, the capital letter T has been used with the subscripts 1 and 2 to represent the spin-lattice and spin-spin relaxation times. Magnetic field strength has been defined in units of the gauss. The other common symbols are given below in the order in which they occur in the text.

μ	The magnetic moment in absolute units. The so-called " magnetic moment " in the literature is generally the dimensionless number $\mu = gI$.
I	The nuclear spin quantum number (dimensionless).
g	The nuclear g-factor, or the ratio of the nuclear magnetic moment to the nuclear angular momentum (dimensionless).
μ_n	The nuclear magneton, $\boldsymbol{eh}/4\pi \boldsymbol{Mc}$, where $\boldsymbol{e}$ is the electronic charge, $\boldsymbol{h}$ Planck's constant, M the mass of the proton, and $\mathbf{c}$ the velocity of light.
μ_e	The Bohr magneton, $\boldsymbol{eh}/4\pi \boldsymbol{mc}$, where m is the mass of the electron.
H_0	The applied magnetic field, sometimes called the Zeeman field in the text.
RF	Radiofrequency.
cps	Cycles per second : 1 Mc. = 10^6 cycles per second.
ν	Frequency in cps.
ω	Angular velocity.
H_1	The applied RF field.
χ	The complex magnetic mass susceptibility, equal to $\chi' - i\chi''$ (dimensionless).
χ'	The real (in-phase, dispersive, or high-frequency) component of χ.
χ''	The imaginary (out-of-phase, or absorptive) component of χ.
χ_0	The static mass susceptibility.
$\Delta H_{\mathrm{m.sl.}}$	The separation (in gauss) of the two maxima of the derivative curve, *i.e.*, the two points of maximum slope, positive or negative, of the absorption curve.
T_1	The spin-lattice relaxation time.
T_2	The spin-spin relaxation time.
γ	The gyromagnetic ratio $ge/2Mc$, or the ratio of the angular Larmor frequency to the applied magnetic field.
$\langle \Delta\omega^2 \rangle_{\mathrm{Av.}}$	The mean-square frequency displacement of the absorption line.
$\langle \Delta H^2 \rangle_{\mathrm{Av.}}$	The second moment of the absorption line.
F(H)	The line-shape function at any value of the applied field H.
H^*	The resonance field strength at a fixed frequency of an isolated nucleus.
S($H-H_0$)	The Gaussian broadening function, of form exp $-(H-H_0)^2/2\beta^2$, where β is the second moment of the distribution.
N_s	The total number of resonating nuclei in the sub-group to which the line broadening is attributed.
r_{jk}	The internuclear distance between the j^{th} and the k^{th} nucleus.
τ_c	The correlation time.
τ	The Debye relaxation time for dielectric relaxation.