THE LOCATION OF HYDROGEN ATOMS IN CRYSTALS

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The structures of molecular crystals have been studied for many years by the powerful method of X-ray diffraction. The contribution of hydrogen atoms to the scattering pattern is, however, usually so small that the location of these atoms has been inferred from the positions of the heavy atoms, and determination of distance between hydrogen atoms has been out of the question.

Recently, the technique of measurement and the method of interpretation of X-ray patterns has permitted the location of hydrogen atoms with moderate accuracy, but the task is formidable.

Since the last war new methods have been used to find the positions of hydrogen atoms. The diffraction of electrons by crystals can now be used to determine crystal structures and the method has already proved itself capable of locating hydrogen atoms with an accuracy of 0·03—0·1Å. Neutron beams of high intensity can now be obtained from an atomic " pile " and the diffraction patterns obtained when such a beam is scattered by a crystal can be used to determine the positions of hydrogen and deuterium atoms.

Radiofrequency spectroscopy can now be used to study the positions of protons in crystals ; the method is restricted to relatively simple structures, but where it can be applied it is quick, the interpretation is easy, and the accuracy is as good as that of most diffraction methods.

In this Review, the principles of these methods are described and their applications are illustrated with typical examples. Radiofrequency spectroscopy, in so far as it can be applied to this problem, is discussed at greater length than the other methods, not because it is more important, but because the principles of the method are less familiar to most chemists than those of diffraction methods.

Diffraction Methods

Crystals constitute a three-dimensional diffraction grating and will scatter a beam of waves of suitable wavelength. The resulting diffraction pattern depends upon the wavelength of the beam of radiation and on the spatial distribution of the scattering elements in the crystal.

The process by which the detailed crystal structure is obtained from the diffraction pattern is beyond the scope of this Review ; a very clear account for the case of X-ray diffraction has been given by Jeffrey and Cruikshank.[1]

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[1] Jeffrey and Cruikshank, *Quart. Rev.*, 1953, **7**, 335.

It is not often possible to obtain the crystal structure directly from the diffraction patterns, but trial structures must be postulated and the intensities and positions of the maxima in the diffraction pattern, calculated from them, compared with experiment. When the correct structure has been found, there follows a series of successive refinements in which the atomic co-ordinates are adjusted to give closer and closer agreement between the calculated and observed diffraction patterns. This procedure is often a laborious and formidable task and the extent to which the refinements of the trial structure are carried depends on the amount of detail required.

***X*-Ray Diffraction.**—The scattering of *X*-rays arises primarily from their interaction with the extra-nuclear electrons of the atoms and the structure arrived at is a particular distribution of *electron density* in the crystal. This is often presented in the form of maps showing sections or projections of the crystal lattice with contours of equal electron density. The positions of the atoms are usually assumed to coincide with the regions of maximum electron density.

The electron density in the region of a hydrogen atom is extremely low and diffuse in comparison with that near other atoms. The hydrogen atom is associated with fewer electrons than any other, namely, only one, and even this is to some extent shared with the atom to which it is covalently bonded. If the link has appreciable ionic character, with the hydrogen atom the positive end of the dipole, there is virtually no maximum of electron density at the proton. The large amplitude of thermal vibration of the light hydrogen atom often makes the situation even less favourable. These considerations suggest that *X*-rays are unlikely to provide a sensitive method of locating hydrogen atoms. Indeed, hydrogen atoms are often omitted altogether from the calculations, although it is sometimes remarked that their inclusion in assumed positions improves significantly the agreement between the calculated and the observed patterns.

In spite of these difficulties, it is sometimes possible to locate hydrogen atoms if the most refined experiments and methods of interpretation are used. Intensities are re-measured with a Geiger counter instead of a photographic plate and much greater accuracy is achieved, although the measurements are long and laborious. These measurements are used to refine the model obtained from a conventional analysis, and finally a so-called difference synthesis is carried out. The distribution of electron density due to the heavy atoms only is calculated from the most refined model and in effect subtracted from the actual distribution of electron density obtained from the experimental results. Maps are then obtained of the variation of electron density due to the hydrogen atoms only.

Good examples of electron density maps for hydrogen atoms only, obtained by difference syntheses, are given by Penfold [2] in a description of *X*-ray studies on the structure of 2-pyridone. The positions of the hydrogen atoms are clearly defined and the estimated accuracy of the carbon–hydrogen and nitrogen–hydrogen bond lengths is ± 0·1 Å. Other examples of work

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[2] Penfold, *Acta Cryst.*, 1953, **6**, 591.

of this kind include the determination of the structures [3, 4] of B_4H_{10} and B_5H_{11}, in which the boron–hydrogen bond lengths are determined with an error of ± 0·04 to ± 0·1 Å. The positions of the hydrogen atoms in salicylic acid have been determined [5] with an accuracy of ± 0·1 Å, and in boric acid [6] the O–H distance has been found to be 0·88 Å, though the author says this must be too low. Fig. 1 shows a projection of the salicylic acid crystal, obtained by Cochran [5] by *X*-ray diffraction. The contours show the distribution of electron density due to the hydrogen atoms only, the contributions of the heavy atoms having been removed by carrying out a difference synthesis. The positions of the heavy atoms are shown by dots, and the arrangement of the hydrogen atoms can be seen from the contours. It is clear that the hydrogen atoms in the hydrogen bonds between the carboxyl groups lie nearer to one oxygen atom than to the other.

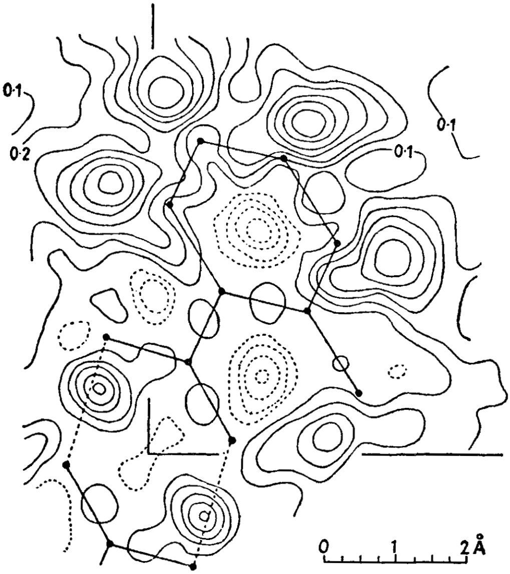

Fig. 1

The electron distribution in a single molecule of salicylic acid from which the contributions of carbon and oxygen atoms have been subtracted. Contours at every 0·1 eÅ^{-2}, *zero contours omitted, negative contours in broken line.* (*Reproduced by kind permission from Cochran.*[5])

Electron Diffraction.—The method of electron diffraction has been developed recently in Russia [7] and in Australia [8] for the study of crystal

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[3] Lipscomb, *J. Chim. phys.*, 1949, **46**, 252.

[4] *Idem*, *J. Chem. Phys.*, 1954, **22**, 614.

[5] Cochran, *Acta Cryst.*, 1953, **6**, 260.

[6] Zachariasen, *ibid.*, 1954, **7**, 305.

[7] Pinsker, *Trudy Institouta mineralnovo syria N.T.I.*, 1936, **109** ; *Uspekhi khim.*, 1939, **8** ; Pinsker, " Diffraction des électrons ", Editions de l'Académie des Sciences de l'U.R.S.S., 1949 ; Pinsker, *Travaux de l'Institut de Cristallographie*, Livraison 10, Communications au III Congrès International de Cristallographie, 1954, p. 91 ; Weinstein, *ibid.*, p. 115 ; Weinstein and Pinsker, *ibid.*, p. 145.

[8] Cowley, *Acta Cryst.*, 1953, **6**, 516.

structures. A highly collimated beam of electrons, accelerated through 50—70 kv, is diffracted by small, very thin single crystals or by oriented polycrystalline preparations. Although there are certain difficulties concerned with the theoretical interpretation of the diffraction patterns, it is often possible to carry out a full three-dimensional Fourier analysis in a manner analogous to that used in X-ray diffraction.[1]

The electron beam gives diffraction patterns by virtue of its wave properties, but because it consists of charged particles it interacts with regions of high electrostatic potential. Thus the contour maps obtained give the variation of electrostatic potential through the crystal instead of electron density as in the case of X-rays. The electrostatic potential in the crystal is determined by the distribution of the positively charged nuclei and of the electron clouds which surround them. The nuclei provide the points of maximum potential, and the more diffuse the electron distribution around the nucleus, the steeper will be the equipotential contours due to the positive nucleus. This is the opposite situation to that found for X-rays and it means that whereas the scattering factor of hydrogen for X-rays is about one-fifteenth of that of carbon, for electrons its scattering factor is only about one-fifth that of carbon. Any ionic character of the link to the hydrogen atom which draws the electrons from the proton into the bond will make the hydrogen atom more readily detected by electron scattering, whilst it is made more difficult by X-ray diffraction.

By taking advantage of this, Pinsker and Tatarinova [9] studied the crystal structure of paraffin and found the carbon–hydrogen distance to be 1·17 ± 0·05 Å. Cowley [10] has studied the structure of boric acid and finds the oxygen–hydrogen distance to be 1·00—1·05 Å (cf. Zachariasen [6]). Weinstein [7] studied the crystal structure of dioxopiperazine and was able to determine the carbon– and nitrogen–hydrogen distances with an error of approximately ± 0·03 Å, and Lobatchev [11] determined the structure of urotropine by electron diffraction and quotes the carbon–hydrogen distance as 1·17 ± 0·1 Å.

Neutron Diffraction.[12]—A beam of neutrons of momentum mv where m and v are respectively the mass and velocity of the neutrons, behaves as though it possesses wave properties of wavelength $\lambda = h/mv$. Neutron beams of wavelength about 1 Å are therefore diffracted by crystals and the patterns obtained can be used to derive information about the crystal structure.

Sufficiently intense neutron beams can only be obtained from an atomic pile ; a collimator is built into the pile and there emerges a beam of neutrons which have a range of velocities.[13] This collimated beam of neutrons is made nearly monochromatic by allowing it to be diffracted by a large crystal, and then collecting a narrow beam of the diffracted neutrons at

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[9] Pinsker and Tatarinova, *Acta Physicochim., U.R.S.S.*, 1936, **5**, 381.

[10] Cowley, *Acta Cryst.*, 1953, **6**, 516, 522, 846.

[11] Lobatchev, *Travaux de l'Institut de Cristallographie*, Livraison 10, p. 167.

[12] Bacon, " Neutron Diffraction ", Oxford Univ. Press, 1955.

[13] Bacon and Thewlis, *Proc. Roy. Soc.*, 1949, *A*, **196**, 50.

a suitable angle. The effective wavelength chosen is about 1·2 Å. The monochromatic neutron beam is then diffracted by the sample, which may be a powder or single crystal, and the diffraction pattern is measured. A boron trifluoride neutron-counter is used to measure the neutron intensity as a function of diffraction angle.

Neutron scattering by diamagnetic materials occurs mainly by interaction of the neutrons with the atomic nuclei in the crystal and the atomic scattering factors for neutrons vary only by a factor of about three over the Periodic Table, in striking contrast with the atomic scattering factors for X-rays which depend on the atomic number. This implies that the hydrogen atoms in a crystal contribute as effectively to the scattering pattern as most other elements and hence their positions can be determined with approximately equal accuracy. It happens that hydrogen atoms in molecules give rise to a very high proportion of incoherent scattering (this is due largely to the very different interactions which occur when the neutron and scattering proton have parallel nuclear spins as compared with when they have antiparallel spins) and whilst this is not a serious inconvenience for work with single crystals, it is usual to use deuterated materials for work on powdered samples, because deuterium atoms give a much weaker

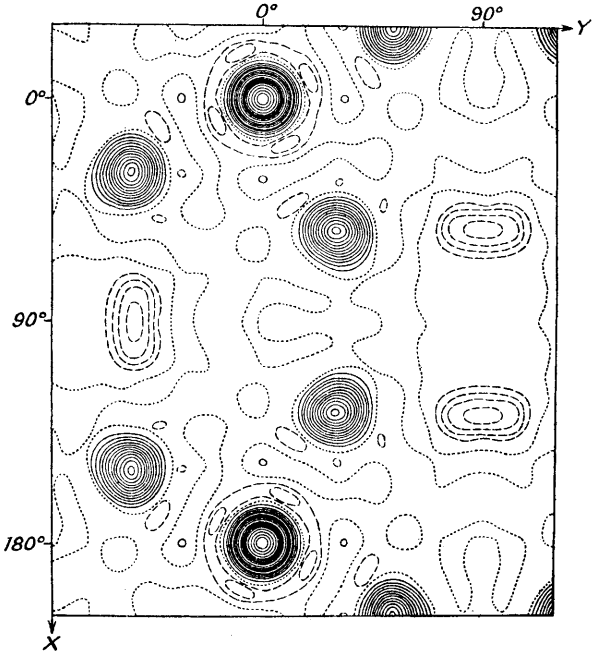

Fig. 2

Fourier synthesis of the neutron scattering density projected on the (001) *plane of* KH_2PO_4 *at room temperature. Continuous contours are positive, broken lines are negative, and zero contours are dotted. The elongated contours due to the hydrogen atoms in the hydrogen bond between the two oxygen atoms are clearly visible.* (*Reproduced by kind permission from Pease and Bacon.*[18a])

incoherent scattering than hydrogen atoms. However, although neutron diffraction appears to be ideally suited to the location of hydrogen atoms in crystals, various difficulties of interpretation, and the relatively low resolution at present available, require that an X-ray investigation of the crystal should be carried out first. The neutron-diffraction results can then be used to fill in the details not obtainable from the X-ray patterns. Measurements have so far been confined to relatively simple molecules. Peterson and Levy [14] studied a single crystal of heavy ice at – 50° c, and found the oxygen–deuterium bond length to be 1·01 Å with the DOD angle nearly tetrahedral ; they showed [15] from single crystal-measurements on potassium hydrogen difluoride that the proton was midway, ± 0·1 Å, between the fluorine atoms in the HF_2^- ion. The same authors [16] have determined the structure of ammonium chloride from single-crystal measurements and found the nitrogen–hydrogen distance to be 1·03 ± 0·02 Å, and they have also made a detailed study of all four phases of powdered deuteroammonium bromide.[17]

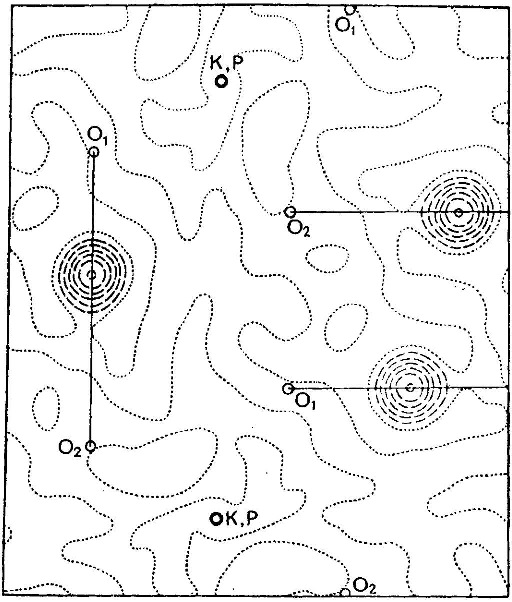

FIG. 3

Projection on (001) *of the density of neutron scattering due to hydrogen atoms in* KH_2PO_4 *at* – 180°. *The small circles mark the positions of the* K, P, *and* O *atoms, the contributions of which to the scattering pattern have been removed. The contours are as in Fig.* 2. *The ordered arrangement of the hydrogen atoms was maintained by applying an electric field to the crystal during the measurements.* (*Reproduced by kind permission from Pease and Bacon.*[18b])

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[14] Peterson and Levy, *Phys. Rev.*, 1953, **92,** 1082.
[15] *Idem, J. Chem. Phys.*, 1952, **20,** 704.
[16] *Idem, Phys. Rev.*, 1952, **86,** 766.
[17] Levy and Peterson, *J. Amer. Chem. Soc.*, 1953, **75,** 1536.

Measurements directed to the location of hydrogen atoms in hydrogen-bonded substances also include the study [18] by Pease and Bacon of potassium dihydrogen phosphate, KH_2PO_4. In this substance the hydrogen atom in the O–H–O hydrogen bond is considerably elongated along the O–O axis. Fig. 2 shows a projection of this crystal on the (001) plane and the contours of the hydrogen atoms lying between the two oxygen atoms show this asymmetry very clearly. The hydrogen atoms are indicated by the negative contours lying between the well-defined oxygen atoms. This elongation may be due to thermal vibrations of the hydrogen atom along the O–O axis or to a disordered arrangement of the hydrogen atoms among pairs of possible positions closer to one oxygen atom than to the other. If the latter is true, then the two positions cannot be further from the centre of the O–O line than $\pm$ 0·175 Å. Below $-$ 150° the crystal becomes ferroelectric and when an electric field is applied, the hydrogen atoms are then no longer elongated and lie asymmetrically between the oxygen atoms in an ordered arrangement. This is shown clearly in Fig. 3, which is projected on exactly the same plane as Fig. 2, although the contours represent the result of a difference synthesis in which the contributions of the heavy atoms have been removed, leaving only the contributions of the hydrogen atoms. The positions of the heavy atoms are shown by the small circles.

Spectroscopic Methods

Vibrational Spectra.—The atoms in a molecule can vibrate in a number of ways known as fundamental vibrational modes, and the frequencies of these vibrations are determined by the masses of the atoms and the forces between them. Most of these vibrational modes involve very complicated motions of all the atoms, and the particular values of the frequencies are often highly characteristic of a particular molecule. In certain cases, however, some of the modes of vibration are highly localised in the molecule and involve the motion of atoms in a particular group. These vibrations which are localised in a particular group within the molecule often occur at characteristic frequencies in all sorts of molecules which contain this particular grouping. These so-called "characteristic group frequencies" are very widely used for analysis and structural diagnosis.[19] The vibrational mode which involves the stretching vibration of an X–H bond is particularly characteristic of the X atom and its environment, because owing to the great difference in mass between X and H, the motion consists largely of the vibration of the hydrogen atom against the heavy X atom which remains nearly stationary. The masses of other atoms attached to X do not, therefore, have much effect on the vibration frequency of the X–H bond. The study of these characteristic frequencies in a crystal can therefore be used to decide to which atom a particular hydrogen atom is joined.

If the infrared radiation is polarised before it is allowed to fall on a single crystal, so that the electric vector of the radiation vibrates in only one direction with respect to the crystal axes, then those molecular vibrations

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[18] Pease and Bacon, (*a*) *Proc. Roy. Soc.*, 1953, *A*, **220**, 397 ; (*b*) *Nature*, 1954, **173**, 443.

[19] Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen, London, 1954.

which involve a change of dipole moment along this direction will absorb more strongly than those for which the change of dipole moment is perpendicular to the direction of polarisation of the radiation. This effect can be used to study the directions in which certain bonds point with respect to the crystal axes. For example, Ambrose and Elliott [20] have examined natural proteins and oriented films of synthetic polypeptides in this way. In the α-fibres, the nitrogen–hydrogen stretching vibration at 3300 cm.$^{-1}$ absorbs more strongly when the radiation is polarised along the fibre axis. This indicates that the nitrogen–hydrogen bond lies parallel to the polypeptide chain, in agreement with the folded-chain structures attributed to these substances. On the other hand, the β-fibres show strongest absorption of the nitrogen–hydrogen stretching frequency when the radiation is polarised at right angles to the fibre axis, indicating that the nitrogen–hydrogen bonds now lie perpendicular to the fibre axis, as required by an extended-chain structure.

Nuclear Resonance.—Nuclear resonance spectra [21] arise when transitions are induced by radiation among energy levels which become available to a nucleus when it is placed in a magnetic field. This branch of spectroscopy provides a useful method of locating hydrogen atoms in certain crystals for which the arrangement of hydrogen atoms is not too complicated.

The process which gives rise to a nuclear resonance spectrum will first be described and then the interactions which occur between nuclei will be discussed so far as they help in the location of hydrogen atoms.

Many atomic nuclei behave as though they possess a " spin ", *i.e.*, they have an angular momentum, p. It can be shown classically that a spinning uniform sphere of mass M and charge e has associated with it a magnetic moment $pe/2Mc$ which arises from the circulation of electric charge. For actual particles this is not quite true, and we write

$$\text{Actual magnetic moment} = \mu_a = g.pe/2Mc \quad . \quad . \quad (1)$$

where g is known as the nuclear g factor and must be obtained experimentally for each nucleus. The quantum theory requires that the angular momentum, p, of a particle must be given by

$$p = (\boldsymbol{h}/2\pi)\sqrt{[I(I+1)]} \quad . \quad . \quad . \quad . \quad (2)$$

where $\boldsymbol{h}$ is Planck's constant, and I is a " spin " quantum number which may have integral or half-integral values, and is a characteristic of the particle. Therefore, from equations (1) and (2),

$$\mu_a = g.\frac{e\boldsymbol{h}}{4\pi Mc}.\sqrt{[I(I+1)]} = g\mu_0\sqrt{[I(I+1)]} \quad . \quad . \quad (3)$$

where μ_0 is a unit of magnetic moment called the nuclear magneton. We may therefore regard the nucleus as a short bar magnet of moment given by equation (3).

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[20] Ambrose and Elliott, *Proc. Roy. Soc.*, 1951, *A*, **205,** 47 ; 1951, *A*, **208,** 75 ; 1951, *A*, **206,** 206 ; 1952, *A*, **211,** 490.

[21] Bloembergen, Purcell, and Pound, *Phys. Rev.*, 1948, **73,** 679 ; Bloch, *ibid.*, 1946, **70,** 460 ; Andrew, " Nuclear Magnetic Resonance ", Cambridge Univ. Press, 1955.

If this magnet is placed in a uniform magnetic field, H_0, it experiences a torque, like a compass needle, but on account of its spin angular momentum it precesses about the field H_0, just as a toy gyroscope, suspended on a vertical pivot, precesses about the Earth's gravitational field.

The potential energy of the nuclear magnet in the field H_0 clearly depends on its orientation in the field, and apart from an additive constant is given by

$$-H_0 \times \text{component of } \mu_a \text{ along } H_0 . \quad . \quad . \quad (4)$$

The quantum theory demands that this energy shall be quantised, and the condition is that the component of angular momentum in the direction of the field is $mh/2\pi$, where $m = I, I-1, I-2, \ldots 1, 0, -1, -2, \ldots -I$. Thus from equations (1), (2), and (3), the component of μ_a along the field, μ_m, is restricted to the values

$$mg\mu_0 = \mu_m\mu_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the potential energy of the nucleus in each of these levels must be, from equations (4) and (5),

$$U(m) = -H_0\mu_m\mu_0 = -H_0 mg\mu_0 \quad . \quad . \quad . \quad (6)$$

Since there are $(2I + 1)$ values of m, there are $(2I + 1)$ energy levels defined by equation (6), and each corresponds to a different orientation of the nuclear magnet in the field H_0. In each level the nucleus precesses about the field, maintaining the appropriate orientation which gives the allowed projection of p or μ_a along the field. In the case that $I = \frac{1}{2}$ (for example, for ^{1}H, ^{19}F, or ^{31}P nuclei) m can be $+\frac{1}{2}$ or $-\frac{1}{2}$, μ_a is $(g\mu_0\sqrt{3})/2$, and $\mu_m = +\frac{1}{2}g\mu_0$ or $-\frac{1}{2}g\mu_0$ (Fig. 4). The half-angle of precession is then $\cos^{-1}(\sqrt{3}/3)$ or $\cos^{-1}(-\sqrt{3}/3)$.

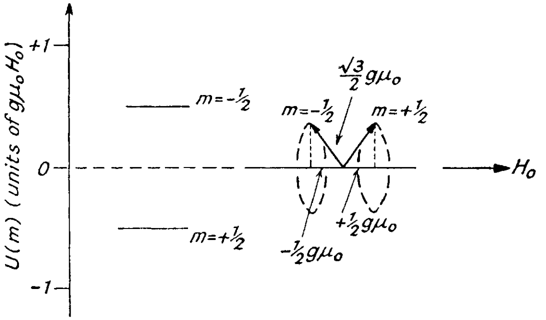

FIG. 4

Energy levels of a nucleus of spin $= \frac{1}{2}$ *in a field* H_0.

Clearly the maximum component of μ_a along the field is

$$\mu_0\mu_m(\text{max.}) = Ig\mu_0 = \mu\mu_0,$$

since I is the maximum value of m. The dimensionless quantity, μ, is what is usually called " the magnetic moment " of the nucleus.

If transitions are induced by radiation among these energy levels which become available to the nucleus in a magnetic field, then energy must be absorbed or emitted and the resulting spectrum is called the nuclear resonance spectrum. The frequency of radiation required to do this is such that $\Delta U = h\nu_0$, where ΔU is the separation of two adjacent energy levels, and ν_0 is the resonance frequency, since a selection rule applies which limits Δm to ± 1. Thus we have, from equations (6)

$$\begin{aligned} h\nu_0 = \Delta U_{m\rightarrow m+1} &= U(m) - U(m+1) = H_0 g\mu_0[m+1-m] \\ &= H_0 g\mu_0 = \mu\mu_0 H_0/I \quad . \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

This frequency, ν_0, turns out to be identical with the precession frequency of the nucleus in the field H_0 as given by Larmor's theorem, and a detailed classical calculation [21] of the interaction of the precessing nucleus with an oscillating magnetic field leads to the conclusion that the nucleus will be tipped from a given orientation by a radiation field rotating at the Larmor frequency in phase with the nuclear precession. Such a field is generated by electromagnetic radiation oscillating with its vector at right angles to H_0.

In a magnetic field of 10,000 gauss the radiation needed falls in the radiofrequency region of the spectrum. For example, for protons in a field of 10,000 gauss, ν_0 is about 42·6 Mc./sec.; for fluorine ν_0 is about 40·1 Mc./sec., and for nitrogen ν_0 is about 3·1 Mc./sec.

The transition probability is the same for $\Delta m = +1$ or -1, so that for net absorption of energy to occur the lower energy levels must be more populated than the upper ones. The levels are so closely spaced that this excess of population is very small. For example, for protons in a field of 10,000 gauss at room temperature, a Boltzman distribution would lead to an excess of population in the lower energy level of only 3 or 4 nuclei in every million, and it is on these that we must rely for our measurements!

The absorption spectrum can be measured by keeping the applied field H_0 constant and finding the frequency at which energy is absorbed, or, alternatively, by using a fixed frequency and varying the separation of the energy levels by altering the value of H_0. The spectrum can be plotted as intensity of absorption against frequency or against applied field strength, but for a given nucleus it is easy to convert one scale into the other by using equation (7).

For isolated nuclei, the absorption spectrum would be a single very sharp line at a frequency given by equation (7), but in a crystal the internuclear interactions modify this.

A nucleus of spin $I = \frac{1}{2}$ (for example, hydrogen) and moment $\mu\mu_0$ may occupy two orientations in a magnetic field H_0. This nucleus generates in its neighbourhood a weak local magnetic field of its own, $H_{\text{loc.}}$, which may be resolved into a static component in the direction of H_0 and a rotating component (arising from its precession about H_0) at right angles to H_0 (Fig. 5). The static component of the local field in the direction of H_0 is $\pm(\mu\mu_0/r^3)(3\cos^2\theta - 1)$ at a point distant r from the nucleus and of co-ordinate angle θ to the direction of H_0. The sign depends on the momentary orientation of the nucleus in H_0 (Fig. 5). If the nuclei are grouped in pairs at a distance r, each one will therefore find itself in a field

$$H_0 \pm (\mu\mu_0/r^3)(3\cos^2\theta - 1),$$

and a double absorption line would be expected with the doublet separation equal to $(2\mu\mu_0/r^3)(3\cos^2\theta - 1)$. The rotating component of the local field generated by one nucleus rotates at the Larmor frequency, which is itself nearly equal to the resonance frequency of a nearby nucleus because they are in closely similar fields H_0. Each nucleus of the pair will therefore experience a rotating field near the resonance frequency polarised at right angles to H_0. These are just the conditions required to induce transitions among the allowed energy levels. Two neighbouring nuclei which occupy adjacent energy levels could therefore exchange a quantum of energy through this interaction of the rotating components of their local fields, and simultaneously exchange energy levels and orientations in the field H_0. This so-called spin–spin interaction involves exchange of energy only among the nuclei and no energy is gained or lost by the surroundings. This spin exchange has the effect of limiting the life-time of a nucleus in a given energy level and leads, through the Heisenberg uncertainty principle, to a further magnetic interaction which gives a broadening about one-half of that caused by the static components of the local fields.[22] In the particular case of a pair of like nuclei the separation of the doublet is increased by this quantum mechanical effect to $(3\mu\mu_0/r^3)(3\cos^2\theta - 1)$. Of course, if the nuclei are unlike, so that their precession frequencies are different, the second broadening mechanism is negligible.

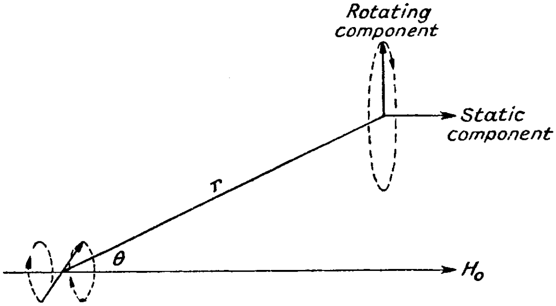

FIG. 5
Local fields generated by a precessing nucleus.

A crystal which contains protons grouped in pairs would therefore be expected to show a nuclear resonance spectrum which is a doublet, broadened to some extent by second-order interactions between relatively distant pairs of nuclei. The separation of the doublet depends on the distance between the adjacent nuclei and on the angle which the line joining them subtends to the field. The separation of the doublet therefore varies with the orientation of the crystal in the field. Pake [22] studied the proton resonance of a single crystal of gypsum as a function of crystal orientation in the magnetic field. The two water molecules have different orientations in the crystal, so two pairs of lines were observed, and from their separation and angular dependence it was possible to measure the H–H distances and the angles

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

they subtend to the crystal axes. Fig. 6 shows the absorption curves obtained for the proton resonance of a single crystal of gypsum, for various orientations of the applied magnetic field, H_0, in the (001) plane of the crystal. The angle between H_0 and the [100] direction is stated with each spectrum. At some settings, *e.g.*, 54°, the two pairs of lines due to the two distinguishable water molecules in the crystal are clearly separated, whereas at others they coalesce. Fig. 7 shows how the separation of the doublet

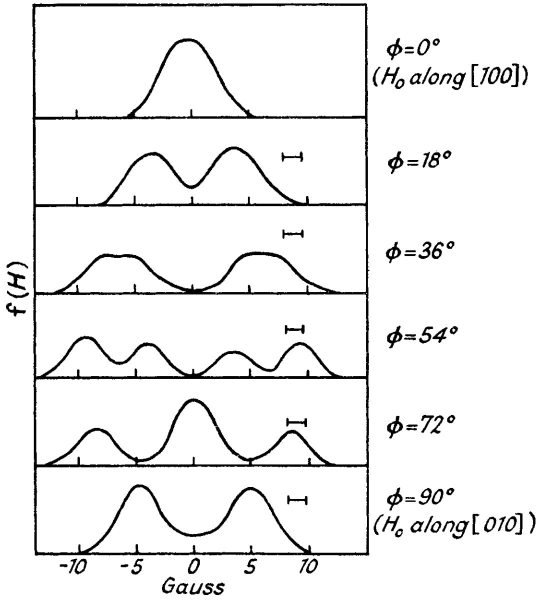

FIG. 6

Absorption curves of proton resonance in a single crystal of gypsum for various orientations of the crystal with respect to the magnetic field H_0. (*Reproduced by kind permission from Pake.*[22])

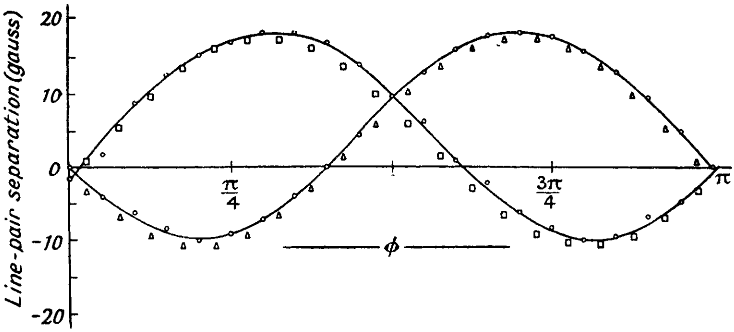

FIG. 7

Variation of the separation of the doublet peaks due to each water molecule in the unit cell of gypsum as a function of the angle ϕ *between* H_0 *and* [100]. (*Reproduced by kind permission from Pake.*[22])

peaks varies with the angle ϕ between H_0 and [100]. The two different water molecules in the unit cell give rise to two curves which differ only in phase. The circles are experimental points and the squares and triangles are calculated for an H–H distance of 1·58 Å. A simpler example is the study of the structure of urea by Andrew and Hyndman.[23] The crystal structure of urea was studied by X-ray methods [24] and the heavy atoms were located readily, but it was not possible to decide whether the planes of the amino-groups lay in the same plane as the rest of the urea molecule or at right angles to it. The two molecules of urea in each tetragonal unit cell are both arranged with the C=O bonds parallel to the tetragonal axis. If the crystal is placed in a magnetic field, H_0, with the tetragonal axis parallel to the field, it turns out that the proton pairs of the amino-groups are oriented at the same angle, θ, to the field, and on the basis of the planar model for the urea molecule θ would be $31° \pm 1\frac{1}{2}°$ whilst for the non-planar model θ would be 90°. By use of the value for r_{HH}, the H–H distance, of $1{\cdot}803 \pm 0{\cdot}015$ Å obtained from separate measurements of the second moment of the proton resonance (see below), the doublet separation $3\mu\mu_0 r^{-3}(3\cos^2\theta - 1)$ is $8{\cdot}7 \pm 0{\cdot}5$ gauss for the planar model ($\theta = 31°$) and 7·2 gauss for the non-planar model ($\theta = 90°$). The observed value of $8{\cdot}9 \pm 0{\cdot}2$ gauss confirms the planar model, and determines the orientation of the amino-groups in the crystal.

Further information can be obtained by making use of a relation due to Van Vleck.[25] For a crystal containing any arrangement of nuclei, the mean square-width or second moment of the nuclear resonance absorption line is given by the expression:

$$\langle \Delta H^2 \rangle_{\mathrm{AV}} = (3/2)I(I+1)g^2\mu_0{}^2.N^{-1}\sum_{j>k}[(3\cos^2\theta_{jk} - 1)^2 r_{jk}{}^{-6}]$$
$$+ (1/3)\mu_0{}^2.N^{-1}\sum_{j,f}[I_f(I_f+1)g_f{}^2(3\cos^2\theta_{jf} - 1)^2 r_{jf}{}^{-6}]$$

where N is the number of nuclei at resonance in the unit cell, θ_{jk} is the angle between the jk vector and the applied field H_0, I_f and g_f refer to nuclei of a different kind from those at resonance, and r_{jk} is the distance between the j-th and k-th nuclei.

The second moment or mean-square width of an absorption line can be obtained readily from the experimental measurements by numerical or graphical methods, since

$$\langle \Delta H^2 \rangle_{\mathrm{AV}} = \int_{-\infty}^{+\infty} \mathrm{f}(H).\Delta H^2.\mathrm{d}H \Big/ \int_{-\infty}^{+\infty} \mathrm{f}(H).\mathrm{d}H$$

where f(H) is the absorption line intensity as a function of H, and ΔH is the deviation from the centre of the symmetrical resonance line.

In the case of urea, Andrew and Hyndman [23] computed the expected

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[23] Andrew and Hyndman, *Discuss. Faraday Soc.*, 1955, **19**, 195.
[24] Vaughan and Donohue, *Acta Cryst.*, 1952, **5**, 530.
[25] Van Vleck, *Phys. Rev.*, 1948, **74**, 1168.

values of the second moment of the proton resonance for various values of r_{HH} and various orientations of the crystal in the field using the planar and the non-planar model. The variation of second moment with orientation in the field provided very convincing confirmation of the planar structure, and the value of the H–H distance was found from the experimental second moments to be 1·803 ± 0·015 Å, corresponding to an N–H distance of 1·046 ± 0·01 Å and an HNH angle of 119·1° ± 2°.

If a finely powdered solid is used instead of a single crystal, the absorption line obtained is an average resulting from superposition of the lines from all orientations of the crystal axes. The line shape can be calculated for a powder [22] with its protons grouped in pairs and is shown in Fig. 3. The broken line shows the shape calculated for nearest-neighbour interactions only. Relatively distant nuclei also exert a weak broadening effect, and this weak effect is usually assumed to have a gaussian form, exp $[-(\Delta H)^2/2\beta^2]$, where β^2 characterises the amount of this so-called intermolecular broadening.

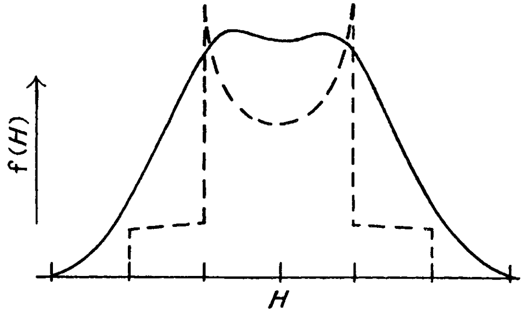

FIG. 8

Broken line : Absorption curve for an isolated pair of nuclei of $I = \frac{1}{2}$ (Pake [22]). Continuous line is obtained by applying a gaussian broadening function to the broken line to take account of intermolecular interactions.

In Fig. 8 the continuous line is the result of applying such a broadening function to the curve calculated from nearest-neighbour interactions only. Similar calculations can be made for other simple configurations of nuclei, and the line shape for powdered crystals with nuclei grouped in equilateral triangles is shown [26] in Fig. 9.

The second moment of the absorption line for a powdered sample can be calculated from equation (8) by replacing the terms in $(3\cos^2\theta - 1)^2$ by their average values over space. For a powder, the second moment then becomes

$$\langle \Delta H^2 \rangle_{\mathrm{AV}} = (6/5)I(I+1)g^2\mu_0^{\,2}.N^{-1}\sum_{j>k} r_{jk}^{-6} + (4/15)\mu_0^{\,2}N^{-1} \sum_{j,f}[I_f(I_f+1)g_f^{\,2}r_{jf}^{-6}] \quad . \quad . \quad . \quad (9)$$

The configurations of protons in the crystals of powdered substances

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[26] Andrew and Bersohn, *J. Chem. Phys.*, 1950, **18,** 159.

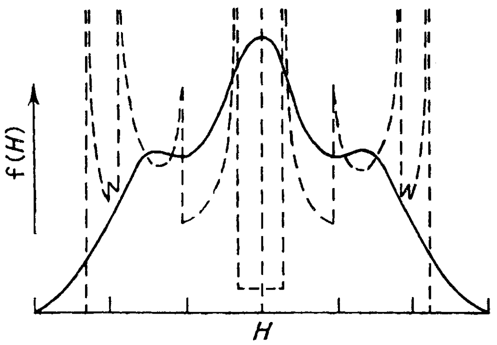

FIG. 9

Broken curve : Absorption curve for isolated triangles of nuclei of $I = \frac{1}{2}$ (*Andrew and Bersohn* [26]).

Continuous curve is obtained by applying a gaussian broadening function as in Fig. 8.

have been studied in this way for a variety of crystals. For example, the proton resonance spectrum of infusible white precipitate has been studied by Deeley and Richards.[27] This material is precipitated from mercuric

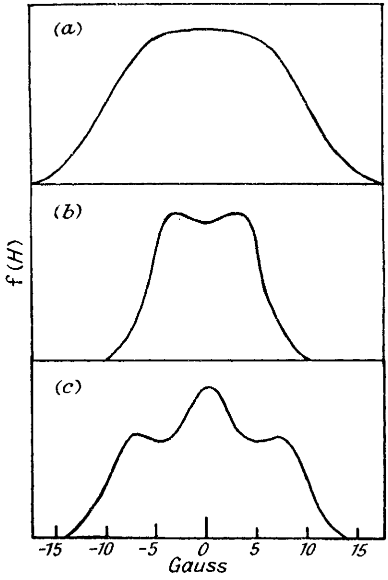

FIG. 10

Absorption curves expected for different structures :

(*a*) tetrahedral groups of nuclei (I)
(*b*) pairs of nuclei (II)
(*c*) triangles of nuclei (III).

(*Reproduced by kind permission from Deeley and Richards.*[27])

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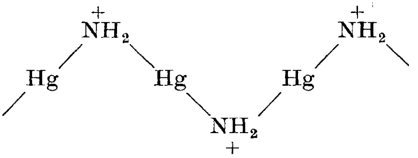
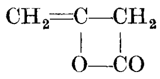
[27] Deeley and Richards, *J.*, 1954, 3697.

chloride solutions by ammonia under the right conditions, and various structures have been assigned to it. Rammelsberg [28] formulated it as NHg_2Cl,NH_4Cl (I), Franklin [29] as NH_2HgCl (II), and Britton and Wilson [30] and Glasson and Gregg [31] as $x HgO,(1 - x)HgCl_2,2NH_3$ (III). Lipscomb [32] interpreted *X*-ray diffraction patterns in terms of chains of mercury atoms and amino-groups, with chloride ions packed between the chains. In structure (I) the protons are grouped in tetrahedra, in (II) in pairs, and in (III) in equilateral triangles, and in Fig. 10 the calculated absorption curves for these three structures are drawn approximately to scale. The second moments of the proton resonances expected for the three structures are respectively about 50 gauss^2, 20 gauss^2, and 38 gauss^2. Experimental measurements gave curves which could be fitted closely to the pair structure (II), with a second moment of 18·6 gauss^2. From the second moment and quantitative comparison of the line width with theoretical curves, the hydrogen–hydrogen distance was found to be 1·688 Å. This distance corresponds to an N–H distance of 1·03 Å with a tetrahedral HNH angle as in the ammonium ion, and provides convincing confirmation of the chain structure (*A*). Similar experiments in which absorption line shapes have

(*A*)



(*B*)



been used to identify the configurations of hydrogen atoms in crystals have shown that nitric, sulphuric, perchloric, and chloroplatinic acid monohydrates crystallise as oxonium (H_3O^+) salts, but oxalic acid dihydrate does not ; [33] that hydrazine nitrate and sulphate contain the $N_2H_6^{++}$ ion, but the oxalate the $N_2H_5^+$ ion ; [34] that diketen crystallises [35] in the structure (*B*), and that the mono- and the di-hydrate of boron trifluoride crystallise as true hydrates and not as oxonium ions as has been suggested.[36]

If the positions of the heavy atoms in a crystal have been found by *X*-ray methods it is sometimes possible to use the second moment of the nuclear resonance spectrum to locate the hydrogen atoms, even when their configuration does not give a line with useful structure. This method is particularly applicable to problems in which only one parameter remains unknown. For example in an ionic crystal containing XH_4 ions, for which the positions of the X and other atoms are known, only the X–H distance remains to be determined if the ion is assumed to be tetrahedral. The second moment depends on the inverse sixth powers of the distances and

[28] Rammelsberg, *J. prakt. Chem.*, 1888, **38,** 558.
[29] Franklin, *J. Amer. Chem. Soc.*, 1907, **29,** 35.
[30] Britton and Wilson, *J.*, 1933, 601, 1045.
[31] Glasson and Gregg, *J.*, 1953, 1493.
[32] Lipscomb, *Acta Cryst.*, 1951, **4,** 266.
[33] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47,** 1261 ; 1952, **48,** 307.
[34] Pratt and Richards, *ibid.*, 1953, **49,** 744.
[35] Ford and Richards, *Discuss. Faraday Soc.*, 1955, **19,** 193.
[36] *Idem, J.,* **1956, 3870.**

so the major contribution to it comes from the H–H and X–H interactions within the ion, and a small proportion arises from *inter*-ionic effects. The X–H distances in the NH_4^+ ion,[37] the BH_4^- ion,[38] and the PH_4^+ ion [39] have been determined in this way and the method is best illustrated by a more detailed consideration of the work [37] on ammonium chloride. The second moment of the proton resonance at − 195° was found to be 49·5 ± 0·5 gauss^2. The crystal structure is cubic and the positions of the nitrogen and chlorine atoms are known. The intermolecular contribution to the second moment from interactions between hydrogen atoms in *different* ions are calculated from equation (9), an approximate value of the N–H distance of 1·04 Å being used, and found to be 6·5 gauss^2. The contribution of the ^{14}N and ^{35}Cl and ^{37}Cl atoms are now computed, and since their nuclear moments are small, this contribution is found to be only 0·1 gauss^2. When these two intermolecular broadening terms are subtracted from the total experimental value we are left with the contribution from intramolecular terms only, namely 42·9 gauss^2. A correction must now be applied which may be very important for symmetrical ions which are not very rigidly fixed in the lattice. Although the measurements are made at low temperatures the ammonium ion still undergoes a zero-point vibrational motion (*a*) of the hydrogen atoms with respect to themselves and to the nitrogen atom, and, more important, (*b*) of torsional oscillation of the ion as a whole in the force field which holds it in position in the crystal. Correction for (*a*) (Deeley and Richards [40]) is needed because the broadening of the lines depends on the mean value of r^3 and not on the cube of the mean value of r, and these are different for a vibrating bond. The correction is usually very small, however, and will be ignored here. Correction for (*b*) is needed because if the ion is rocking in some way in the crystal, this motion will to some extent reduce the local fields generated by neighbouring nuclei by an averaging effect, and the resultant reduction in the intramolecular contribution to the second moment can be calculated in terms of the amplitude of this zero-point rocking motion. For ammonium chloride, the frequency of this torsional motion is known from spectroscopic measurements [41] to be 390 cm.$^{-1}$ so that the amplitude can be calculated. This motion is found to have reduced the intramolecular second moment by the factor 0·913 so that the correct value should have been 47·0 gauss^2. By using this value and equation (9) the nitrogen–hydrogen distance is found to be 1·038 ± 0·004 Å.

If the nuclear resonance spectrum of more than one type of atom can be observed, then additional parameters can be obtained. In this way Deeley and Richards [40] measured the second moments of the proton and fluorine resonance spectra of hydrazine fluoride. The positions of the nitrogen and fluorine atoms are known from *X*-ray measurements, and this leaves two unknown parameters in the crystal structure, namely, the

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[37] Gutowsky, Pake, and Bersohn, *J. Chem. Phys.*, 1954, **22**, 643.
[38] Ford and Richards, *Discuss. Faraday Soc.*, 1955, **19**, 230.
[39] Pratt and Richards, *Trans. Faraday Soc.*, 1954, **50**, 670.
[40] Deeley and Richards, *ibid.*, p. 560.
[41] Wagner and Hornig, *J. Chem. Phys.*, 1950, **18**, 296, 305.

N–H distance and the H···F distance in the strong hydrogen bonds formed. The second moments of the proton and fluorine resonances provide the two necessary measured parameters and the N–H distance was found to be $1{\cdot}07_5$ Å (cf. the N–H distance in ammonium chloride) and the H···F distance to be $1{\cdot}54_2$ Å. The sum of these, 2·62 Å, is equal to the N···F distance found by *X*-ray methods and confirms that the hydrogen atom in this hydrogen bond lies along the N···F line.

If the crystal structure of the solid is not known, the intermolecular broadening can sometimes be estimated without a very serious loss of accuracy, but in certain cases a better method can be used which was devised by Andrew and Eades.[42] Experimental values of the proton second moment were obtained for benzene and for 1 : 3 : 5-trideuterobenzene. The deuteron has a much smaller magnetic moment than the proton and the substitution reduces the intra- and inter-molecular contributions by very different factors, both of which can be calculated. From the two measured second moments the inter- and intra-molecular contributions can be separately evaluated.

Conclusion

The merits of these methods for the location of hydrogen atoms may be summarised as follows.

X-*Ray diffraction.* Measurements with the most refined techniques must be used, and the experimental work may be considerable. The interpretation of the diffraction patterns must be carried out in the greatest possible detail and is usually a very lengthy and complicated operation. The accuracy is low, but the method can be applied to complicated structures, as well as to simple ones.

Electron diffraction. Measurements must be made on carefully prepared specimens of correct thickness. The protons make a more important contribution to the diffraction pattern than in the case of *X*-rays, so that better accuracy can be achieved with less elaborate methods of interpretation. Certain difficulties occur in the interpretation of the patterns in unfavourable cases, but the method is promising.

Neutron diffraction. The experiments are difficult to carry out and require expensive and elaborate equipment. Neutron-beam intensities at present available are low, so that the method has very limited resolving power. When used in conjunction with other diffraction methods, hydrogen atoms can be located with moderate accuracy, but this will undoubtedly be improved when more intense neutron sources become available.

Infrared spectra. Use of polarised radiation can give qualitative information about the positions of hydrogen atoms.

Nuclear resonance methods. The measurements are easy to perform and take only a few hours. The interpretation is relatively easy, but useful information can only be derived for rather simple structures. In cases where it can be applied the accuracy is good compared with that of the other methods.

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[42] Andrew and Eades, *Proc. Roy. Soc.*, 1953, *A*, **218**, 537.