SYMPOSIUM: WIDE-LINE NUCLEAR MAGNETIC RESONANCE (NMR)

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An Introduction to NMR[1]

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ABSTRACT

Nuclear magentic resonance (NMR) is a physical method for exploring the magnetic environment of the atomic nuclei of the atoms in a molecule. The substance is placed in a strong magnetic field and the nuclei take on an orientation with respect to this field. The reason for this is that the nuclei have angular momentum (spin) and, being charged, have magnetic moments like small compass needles. By subtle radio-frequency (r-f) techniques the nuclei are simply made to reorient (resonate) in this field. The reorientation involves a change of energy, which is supplied by the r-f quantum, $h\nu$. The frequency of resonance is therefore proportional to the reorientation energy and hence to the magnetic field in which the nucleus is found. As in other forms of spectroscopy, the width of the absorption line depends on a variety of factors. In solid samples, the fixed lattice positions of nearby nuclei and the contribution of some field by each nucleus to the others contributes to the line width. Also, due to thermal motion, quanta with the necessary energy for reorientation are naturally present in the sample materials so that the nuclei relax and thus contribute to line width. Therefore, the lifetime in each quantized state or orientation is limited and the energy of that state uncertain or broadened. Nuclei which are found in chemically different positions in the molecule experience different shielding by the diamagnetic cyclotron motion of the electrons of the molecule and thus give resonances at distinctly different frequencies, an extremely useful pheonomenon for the study of molecular structure. The apparatus for experimentation of this kind must obviously involve a large electromagnet with a very homogenous and stable magnetic field, a r-f transmitter and a receiver, an oscilloscope or chart recorder, and certain less obvious electronic instruments.

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INTRODUCTION

In familiar forms of spectroscopy, electromagnetic radiation is focused on a sample. When the frequency of the radiation corresponds to the energy difference between two atomic levels, energy is absorbed. The diminution of the transmitted radiation is a signal that such an energy difference has been found. However, in nuclear magnetic resonance (NMR), the sample material must be placed in a strong magnetic field. The energy differences one finds are caused by the reorientation in the magnetic field of the nuclei of the atoms composing the sample material. These energy differences are not so great as in optical spectroscopy, so that radio frequency (r-f) radiation must be employed.

Each chemical isotope has its own distinct frequency because each atomic species has one or more nuclear isotopes with unique magnetic properties. The strength of each signal is clearly an indication of relative amounts of each kind of atom. The width of the resonance line gives explicit information about the physical state of the sample,

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e.g., the more viscous, the broader the line. Other details, revealed by careful examination of the exact frequency of resonance or of the line shape, can give information about the chemical position of the atom in the molecule or about the kind of atoms which are neighbors to the species being observed.

A more detailed picture of NMR would include a description of the gyromagnetic properties of nuclei, the interaction of one nucleus with a magnetic field and the interaction among nuclei.

GYROMAGNETIC PROPERTIES OF ATOMIC NUCLEI

Chemists are well acquainted with two properties of the atomic nucleus, charge and mass. The properties of interest in NMR, however, are the spin and the magnetic moment. A nucleus with spin is literally spinning, and the magnitude of the spinning is measured by the angular momentum the nucleus possesses. Nuclear angular momentum is quantized, as are a great many things in the atomic scale of sizes. These quanta are integer and half integer multiples of $h/2\pi$ where h is Plank's constant and has the dimensions of angular momentum. The proton has an angular momentum of 1/2 $h/2\pi$, but we conventially say that it has a spin of 1/2. The isotope ${}^{12}_{6}C$, for example, has a spin of zero; ${}^{13}_{6}C$ has a spin of 1/2. ${}^{23}_{11}Na$ has a spin of 3/2, and ${}^{2}H$ a spin of 1. A nucleus composed of an even number of both neutrons and protons such as ${}^{12}_{6}C$, has no spin. Hence about one half of all the isotopes have no spin and, therefore, cannot be studied by NMR.

It is a familiar fact that a coil of wire carrying an electric current has a magnetic field around it. A nucleus with spin must, therefore, also have a magnetic field around it, since it is charged and turning. An element of charge is carried around as the nucleus turns, and thus it is, in a small way, an electric current going in a circle. The result is that nuclei with spin possess magnetic moments, i.e., they are surrounded by a pattern of magnetic fields which, at small distances from the nucleus, is the same as that which would surround a small bar magnet of the size of the nucleus. This field falls away rapidly as the distance from the nucleus increases. The strength of the nuclear magnetic moment μ is measured in units of the nuclear magnetron, a complicated unit the explicit definition of which is not important here. For a rough idea of the magnitude of nuclear magnetism, however, we observe that in nuclei which are several Angstroms apart in solids and liquids, one nucleus produces a magnetic field about one gauss in intensity at the position of another. One gauss is roughly the strength of the earth's magnetic field.

When nuclei orient themselves in a magnetic field and point, for example, in the direction of the field, the question is, what points in the direction of the field? After all, a nucleus resembles a round spinning ball which does not have one end painted red. A nucleus with spin turns about an axis which is also the axis of symmetry for the magnetic moment. It is the direction of this axis that we speak about. It is generally diagrammed as a small arrow which shows the direction of both the angular moment and magnetic moment. Which end of the axis the arrowhead is put on is governed by the classical definition of the direction of angular momentum.

ISOLATED NUCLEI IN A MAGNETIC FIELD

Pointing north is the familiar stable position of the compass needle. The equivalent of pointing south is, however, by quantum rules also a perfectly acceptable and stable position. Nuclei with spin 1/2 can point stably either in the direction of a magnetic field (symbol H) or opposite to it. Nuclei with spin greater than 1/2 may have stable intermediate positions.

The compass needle points north because it is energetically favorable for it to do so. It is the same with nuclei. There is an energy associated with each stable orientation. The applicable formula happens to be classical: the energy of a magnetic moment μ in a field of H is $E=-\mu H \cos\theta$, where θ is the angle between μ and H. The lowest energy state of a nucleus of spin 1/2 in a magnetic field H is $-\mu H$, when μ and H are parallel, or $\cos\theta=1$. The other permissible state, with μ opposed to H, has energy μH.

As mentioned in the introduction, NMR consists in radiating a sample of material, placed in a homogenous magnetic field with electromagnetic energy of a frequency ν such that the right energy is supplied to cause a transition from one state to the other. The formula for a particle of spin 1/2 is the following:

$$h\nu=2\mu H \qquad [1]$$

To find the frequency, we solve for ν, introducing 2π twice:

$$\nu = 1/2\pi\ [\mu/(1/2)\,(h/2\pi)]\,H \qquad [2]$$

The quantity in the square brackets can be recognised as the ratio of the magnetic moment to the angular momentum. It is called the gyromagnetic ratio and is unique for each isotope with spin.

NMR frequencies, for convenient laboratory magnetic fields of several kilogauss, lie in a region which is characterized by the expression "shortwaves," namely a few megahertz (MHz) to several hundred MHz. Hydrogen nuclei, for example, have a resonant frequency of 20 MHz for a laboratory field near 5000 gauss.

MANY NUCLEI IN A MAGNETIC FIELD

One may discuss the properties of an isolated nucleus because, practically, the nuclei are fairly isolated from each other. A nucleus feels the strong field imposed by the laboratory magnet, but feels a field of about one gauss from each of its nearest neighbors. Other nuclei are too far away to be important. The electrons are always paired, as is usual in chemical bonds. (An electron also has a spin of 1/2 and a rather large magnetic moment but, when paired, the electron magnetism disappears. In some substances there are unpaired electrons. One then can perform magnetic resonance with these and the technique is then called electron paramagnetic resonance.)

NMR spectroscopy shows that a sample of material, e.g., water, is simply a gas of protons, invisibly cushioned from one another. Slightly more than half of the many protons in the sample point along H, while the others point in the opposite direction. This is because the energy difference between the two orientations, $2\mu H$, is very small compared with the thermal kinetic energy KT, and, as usual, Boltzmann's law governs the statistical populations of quantum levels. When the sample is radiated by electromagnetic energy at the resonant frequency, there is a certain transition probability for reorientation which is the same for all the nuclei. As the radiation persists and the probability approaches unity, all the nuclei will have reoriented. But because there were more nuclei in the lower energy state, that is, parallel to the field, more energy is absorbed than reradiated. The magnitude and linewidth of this absorption is detected and presented on an oscilloscope or chart paper, the signal of NMR.

This signal, the line of spectroscopy, has certain features. Its intensity, all other things being equal, must evidently be a measure of the number of nuclei in the sample being observed. So an NMR spectrometer may serve to measure the quantity of hydrogen, and thus the oil in a kernel of corn. But how does one distinguish between the hydrogen of the oil and the hydrogen in the carbohydrates and proteins? The difference is that the oil is a liquid and the rest of the kernel is solid. In a solid sample, where the nuclei are fixed relative to each other, one nucleus produces a field on its neighbors which is unchanging. The field due to various neighbors may add or substract from the applied laboratory field, so that one proton resonates at one frequency, while another resonates at another. Since one proton produces a field about one gauss on a neighbor, one would expect, from a hydrogen-bearing organic solid, a line width of some gauss. In practice, it is near 10 gauss, a very broad line. In the oil, however, one proton moves its position with respect to another very rapidly, so rapidly, in fact, that the magnetic interactions between protons almost average out. The line is then very narrow, small fractions of a gauss. The NMR spectrometer may be adjusted to emphasize the narrow line, which then makes the instrument a selective indicator of oil, or more exactly, mobile hydrogen.

There are other sources for magnetism intrinsic in the sample. Electrons, in their molecular orbits, are charged particles in motion. When placed in a magnetic field, their motions are modified to produce a circulation about the direction of the field. This produces a small magnetic field which differs from point to point in the molecule. Using a liquid sample, such as oil, and a very homogenous magnet, the already narrow resonance line from the hydrogen will appear as many sharp lines, each characteristic of the position in the molecule where a proton is found. This particular kind of NMR spectroscopy is described as high resolution. It may be the most important analytical technique in organic chemistry today. Where, however, the NMR signal is composed of one or two broad lines, due either to using a magnet of modest homogeneity or because the sample is solid, one speaks of wideline or broadline NMR.

We must introduce a few other concepts before our understanding of NMR is sufficient to follow the other papers in this symposium.

The protons in the oil in the corn kernal do not remain forever in the stable orientation states described above. Indeed, a given proton always flips between the two states at irregular intervals; the average lifetime in either of the states is called the thermal relaxation time (T_1). A given proton P changes its orientation state because it is surrounded by other protons, each of which again carries a small magnetic field along with it, which move quickly and unpredictably as molecules slip by each other or change their own configuration. These fast motions generate at P magnetic fields which will happen to contain the resonant frequency (such as 20 MHz). The proton P cannot tell the difference between alternating magnetic fields genrated by the oscillator of the spectrometer or by motions of neighbors, so it reverses its orientation along H even without the spectrometer being turned on. The reorientation of one proton is sometimes coupled to the counter reorientation of another, but on the whole each flips independently and there are as many going in one direction at one instant as in the opposite direction.

T_1 is generally a measure of the time it takes for the "spin system" (to use the jargon of the NMR spectroscopist) to recover from any nonequilibrium distribution of spin orientations. T_1 is, therefore, the time which it takes for the nuclei to become oriented in the magnetic field when the sample is first placed within the probe. T_1 is generally a few seconds for protons in liquids, and longer in solids, since the motions are less dramatic. The practical consequence of thermal relaxation is not that one has to wait for the spin system to polarize before starting a measurement, but something quite different. When the NMR observation is made, the spin system is disturbed, e.g., there may be more nuclei in the upper energy state after observation. As a practical matter, the thermal relaxation process strives constantly to maintain the Boltzmann populations while the observing r-f fields strive constantly to upset them. This being the case, there is an optimum transmitter intensity such that the transition probability is equal to $1/T_1$. Thus, the population ratio is being restored at the same rate at which it is being destroyed. Weak r-f fields produce weak signals because few nuclei are being reversed; very strong r-f fields produce weak signals because they keep the populations essentially equal. This latter effect is called saturation. By setting the r-f amplitude optimally for nuclei with a certain T_1, a spectrometer may be used to examine selectively the resonances of the components of a mixture, for example, oil and water. Since T_1 is the average lifetime in a state, the narrowest line that can be observed (because of the Uncertainty Principle) is $1/T_1$. Therefore, lines as narrow as 1 Hz or narrower are observed in high resolution NMR. But there are situations, almost always in solids, where T_1 is long but the line is much wider than $1/T_1$. So we say that the line width is $1/T_2$. For liquid samples NMR lines often have this ideal linewidth, so that $T_2=T_1$. For our purposes, T_2 is a scientific measure of the inverse linewidth.

With a good qualitative idea of resonance itself, and of phenomena closely related to it, relaxation, saturation, etc., we are now prepared to understand the value of NMR to such research and analytical areas as molecular structure, analysis of mixtures, concentration of oil or water in foodstuffs, motion in solids, etc.

REFERENCES

1. Resource Letter, in "NMR and EPR, Selected Reprints," American Institute of Physics, New York, 1965.
2. Pake, G.E., Ibid.

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