The University of Manitoba

THE DETERMINATION OF ELECTRON
DENSITIES BY PROTON MAGNETIC RESONANCE

by

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TO MY PARENTS

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ABSTRACT

Proton shifts relative to internal benzene of pyridine hydrochloride, hydrobromide and hydroiodide in methylene chloride, acetonitrile, nitromethane and formic acid are reported. A model involving a hydrogen bonded ion-pair between the pyridinium cation and the counterion is discussed. It is assumed that the counterion reduces considerably the π -electron polarization in the pyridinium ion calculated for the isolated ion by the VESCF method. If the electric fields arising from the π -electrons, the counterion, and from the positive charge in the $N-H^+$ sigma bond are taken into consideration, the observed order of the C-H proton shifts is predicted. The $N-H^+$ proton shifts are sensitive to the counterion, the solvent and traces of water. In formic acid the $N-H^+$ proton shifts of the hydrochloride and hydrobromide are characteristic of the solvent only. In these two cases the $N-H^+$ proton does not exchange rapidly and an $N^{14}-H^+$ coupling constant of 67.6 ± 0.5 c/s is found.

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Chapter I

INTRODUCTION

A - THE NUCLEAR MAGNET

Nuclear magnetic resonance is based on the fact that isotopes of the elements with non-zero spin possess a magnetic moment which is characteristic of the particular non-zero spin isotope.

A nucleus which has a magnetic moment and a spin angular momentum behaves as if it were a spinning bar magnet (1,2), a nuclear magnet. This magnetization may be said to originate from the circulation of mass and charge associated with the spinning of the nucleus about an arbitrary axis (3).

Nuclear angular momentum is given by

(1) $\underline{P} = \hbar \, \underline{I}$,

where $\underline{P}$ is the nuclear angular momentum vector

$\hbar = \dfrac{h}{2\pi}$; and h is Planck's constant,

$\underline{I}$ is the nuclear spin vector.

The magnetic moment vector $\underline{\mu}$ is written as

(2) $\underline{\mu} = \gamma \, (\hbar \, \underline{I}) = \gamma \, \underline{P}$

where γ is the magnetogyric ratio. The vector $\underline{\mu}$ is collinear with the vector $\underline{I}$.

Classically, for a proton, γ was calculated to be

(3) $\gamma = \dfrac{e}{2Mc}$

where e is the charge on the particle, M is the mass and c is the velocity of light. Experimentally, equation (3) was found to be incorrect, and is normally written as

$$(4) \qquad \gamma = \frac{ge}{2Mc}$$

where g is called the nuclear g factor (4,5), which is dimensionless and must be determined experimentally for each nucleus. Equation (2) then becomes

$$(5) \qquad \underline{\mu} = g \cdot \frac{e\hbar}{2Mc} \underline{I} \, .$$

According to the principles of quantum mechanics, the spin vector $\underline{I}$ has the magnitude $[I(I+1)]^{\frac{1}{2}}$ and consequently the nuclear angular momentum vector has the magnitude

$$P = \hbar \, [I(I+1)]^{\frac{1}{2}}.$$

The only measureable values of the spin I are given by m, the magnetic quantum number. $\underline{I}$, the spin vector, is found to be in one of $(2I + 1)$ states or orientations, and therefore m may take on any of the $(2I + 1)$ values

$$(6) \qquad m = - I, \ -(I-1), \ -(I-2), \ \dots \ (I-1), \ I.$$

Finally, we may write

$$
\begin{aligned}
\underline{\mu} &= \gamma \hbar \underline{I} \\
(7) \qquad &= g \cdot \frac{e\hbar}{2Mc} \underline{I} \\
&= g \mu_0 \underline{I}
\end{aligned}
$$

where μ_0 is the nuclear magneton

(8) $\mu_0 = \frac{e\hbar}{2Mc} = 5.050 \times 10^{-24}$ erg gauss^{-1}.

The structure of the atomic nucleus assumes that the spins of the protons and neutrons in the nucleus are paired, as are the spins of the electrons in an atom. Consequently, zero magnetic moments are obtained for nuclei with an even number of both protons and neutrons, since these have a net spin of zero (I = 0). Nuclei whose mass number is odd have half integral spin, while those of even mass number but odd charge number have an integral spin (6). Only nuclei for which I $\neq$ 0 may a nuclear magnetic resonance spectra be obtained. The proton falls into this category, but C^{12} and O^{16} do not. For this reason nuclear magnetic resonance is so valuable in the study of organic compounds, since one can study the proton spectra without interference from the latter nuclei.

B - INTERACTION OF NUCLEAR MAGNET WITH A MAGNETIC FIELD

In the absence of a magnetic field, the energy of the nuclear magnet is independent of its orientation. However, when nuclei with magnetic moments are placed in a uniform, external, magnetic field $\underline{Ho}$, this degeneracy is removed. The application of the external field causes a splitting into $(2I + 1)$ energy levels, known as the Zeeman splitting, corresponding to the $(2I + 1)$ values of m.

When the magnetic moment

$$\underline{\mu} = \gamma \underline{P}$$

is placed in a strong magnetic field $\underline{Ho}$, a torque, $\underline{L}$, is exerted on it such that

$$\underline{L} = \underline{\mu} \times \underline{Ho}.$$

The energy of the interaction is

(9a) $\quad E = - \underline{\mu} \cdot \underline{Ho}$

(9b) $\quad\quad = - \mu H_o \cos \theta$

where θ is the angle between the magnetic moment and the magnetic field vectors, and $\mu \cos \theta$ is the value of the component of $\underline{\mu}$ along $\underline{Ho}$, and may be written as μ_H. Therefore equation (9b) becomes

(10) $\quad E = - \mu_H Ho.$

According to equation (6), the only allowed values of the spin I are given by the (2I + 1) values of m, which correspond to a particular component of μ along Ho, or to the quantization of μ along Ho. Hence equation (7) may now be written as

(11) $\quad \mu_H = g \mu_o m$

where the values of m are those given in equation (6). Hence equation (10), which gives the (2I + 1) energy levels, becomes

(12) $\quad E = - mg \mu_o H_o.$

Since the selection rule for transitions of nuclei between energy levels is $\Delta m = \pm 1$, (7), then the energy difference between adjacent energy levels is given by

(13) $\quad \Delta E = g \mu_o H_o = \gamma \hbar H_o.$

For such a transition to take place, absorption of energy is required, and is given by the Bohr relation

(14) $\quad \Delta E = h \nu_o,$

where ν_o is the frequency of the electromagnetic radiation.

Equating equations (13) and (14), we obtain

(15) $\quad \nu_o = \dfrac{\gamma H_o}{2 \pi}.$

This is the fundamental relationship for the resonance condition in nuclear resonance.

When nuclei are placed in a magnetic field,
there is a Boltzmann distribution of the nuclei among
the various nuclear spin states. For a proton ($I = \frac{1}{2}$)
there are two such spin states (Fig. 1 and equation 12)(8).
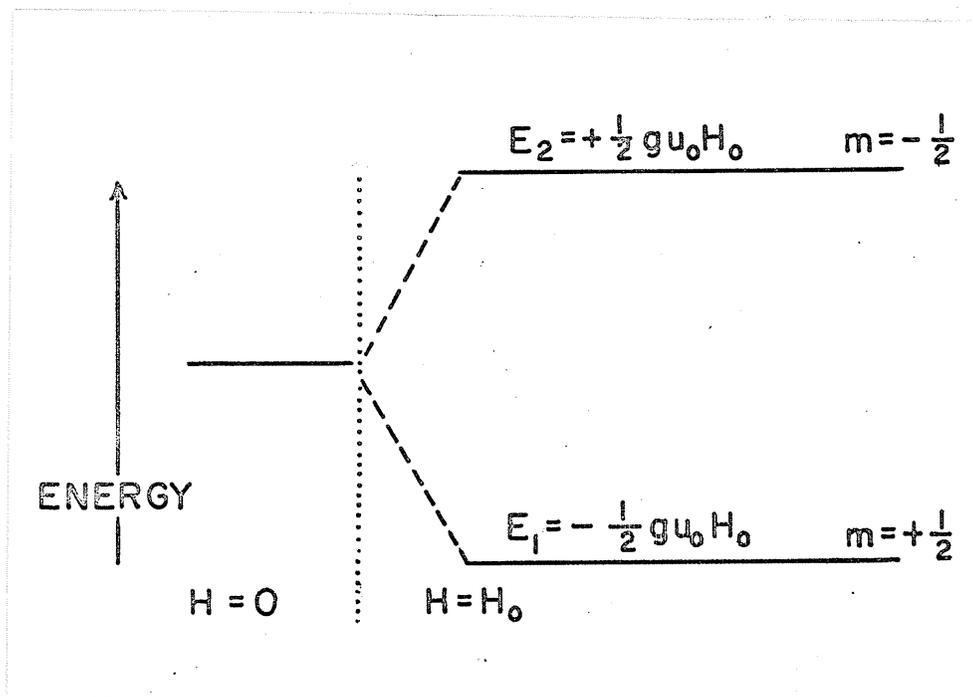
Figure 1: Energy levels for $I = \frac{1}{2}$.

When proton containing substances are placed
in a magnetic field, there is a distribution of the
protons between these two energy states, with a slight
excess in the lower. It is due to this slight excess
of nuclei in the lower state that the nuclear resonance
phenomenon is observed. When radiation of the right
frequency ν_o is used to excite protons from one level
to another so as to satisfy equation (15), a net
absorption of energy can occur, and the spectrum is

observed as an absorption of energy from the incident radiation.

For a bare proton, for $H_O = 10^4$ gauss, the resonance frequency is 42.577 megacycles, which is in the radio-frequency portion of the electromagnetic spectrum.

C - MAGNETIC RESONANCE

A spinning nucleus may be treated from a classical viewpoint. If a nucleus with a magnetic moment μ is placed in a magnetic field, the field exerts a torque upon μ, tending to align it with the field. This forces the vector μ to precess about the direction of the applied field (9,10). The rate of precession is given by the Larmor precession frequency (11,12).

$$(16) \quad \omega_o = \gamma H_o,$$

where ω_o is the angular frequency of precession, and γ is the magnetogyric ratio. This equation describes the precession of a nucleus in its particular energy level, as given by equation (12).

Since

$$(17) \quad \nu_o = \frac{\omega_o}{2\pi},$$

where ν_o is the frequency of precession, equation (16) becomes

$$(18) \quad \nu_o = \frac{\gamma H_o}{2\pi}$$

and is equivalent to equation (15). Consequently, the separation of the energy levels equals the Larmor precession frequency multiplied by $\hbar \omega_o$.

In the nuclear magnetic resonance experiment, transitions among the energy levels are induced by a small oscillating field H_1 applied to the sample perpendicular to H_o. This is achieved by passing radio-frequency current through a coil perpendicular to H_o. At resonance, when the applied radio-frequency equals the frequency of the nuclear Larmor precession, the torque acting on the nuclear magnetic moment vector due to H_1 causes the vector μ to tip over with respect to H_o (13). Consequently, transitions from a lower to an upper level are induced with absorption of a characteristic quantum of energy. This is the resonance condition for a single nucleus.

Resonance absorption may be observed by amplifying and rectifying the r. f. signal, since at resonance part of this radiation will be absorbed, causing a drop in the d.c. output. In actual practice, the applied radio-frequency is kept constant while the field is scanned. Descriptions of the nuclear magnetic resonance spectrometers are given in references (14) and (15).

Chapter II

THE CHEMICAL SHIFT

A - <u>INTRODUCTION</u>

Shortly after the discovery of the nuclear resonance phenomena, it was found that the resonance frequency for a particular nucleus may occur at a different value of the applied field, depending on the chemical environment of the particular nuclei. This effect arises because orbital electrons magnetically screen the nucleus so that the magnetic field at the nucleus differs slightly from the applied magnetic field. The difference in the resonance frequencies of a particular nucleus when it is located in different chemical environments is known as the chemical shift.

The chemical shift was first observed in metals, in 1949, when Knight (16) found discrepancies between the resonance frequencies of several metals as compared with their salts. In all cases it was found that the resonant frequencies were always higher for the metal than for the corresponding salt, for a constant value of the external, magnetic field. This shift was found to be directly proportional to the magnitude of the applied magnetic field, and was said to arise from the para-magnetic effect of the conduction electrons in the vicinity of the metal nuclei. Shortly afterwards, related effects were observed by Proctor and Yu (17) for the N^{14} nucleus. Two peaks were observed for NH_4NO_3. The first

peak corresponds to the N^{14} nucleus in the NH_4^+ ion and the second to the N^{14} nucleus in the NO_3^- ion. Dickinson (18) soon found the same effect for the F^{19} nucleus while for protons the chemical shift was first observed by Lindstrom (19) and Thomas (20). All of these effects were observed as the precision and resolution of the available spectrometers improved.

The chemical shift may therefore be said to arise from a secondary magnetic field which is produced by the circulation of electronic charge induced by H_o. The secondary field is proportional to, and acts in opposition to, the main magnetic field, thus decreasing the field as seen by the nucleus. Consequently, the field seen at the nucleus will be

$$(19) \qquad H_e = H_o (1 - \sigma),$$

where H_e is the "effective" field seen at the nucleus, H_o is the external magnetic field, and σ is the shielding parameter and depends on the electronic environment in the vicinity of the nucleus.

According to equation (19), it is obvious that the separation of signals between the two nuclei will be directly proportional to the field seen by the molecule, and to the difference between the screening constants of the two nuclei. Since the difference in shielding is a function of the applied field, the chemical shift is most often expressed in terms of a dimensionless parameter δ