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Measurements of Resonance Frequency of Hydrogen Nucleus and Fluorine Nulceus by the Method of Nuclear Magnetic Resonance

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ABSTRACT

In this paper, the method of Nuclear Magnetic Resonance is used to measure the natural resonance frequency f_H for the hydrogen (^1H) nucleus and f_F for the fluorine (^9F) nucleus. The gyromagnetic ratio γ_N for ^1H nucleus and for ^9F nucleus are calculated from the experimental values of the natural resonance frequencies, f_H and f_F, and the NMR resonance frequency of the fluorine (^9F) nucleus. The analyses indicate that, comparing our results with those measured previously [1], the method used in this work is valid for medium external applied magnetic $\vec{B}_0$-field.

By the Normal Zeeman Effect, the energy levels of a nucleus with spin angular momentum $\vec{I}$ are split into $2I+1$ energy levels for each ground-state spin quantum number I in a magnetic field $\vec{B}$.

When a homogeneous magnetic field $\vec{B}_0$ is applied to a sample containing nucleus with $I=1/2$, the energy spacing between the adjacent splitting energy level is equal and can be shown to be $\triangle E = g_\ell \mu_N B_0 = \gamma_N B\hbar$, where γ_N is the gyromagnetic ratio of the nucleus and is defined as $\gamma_N = |\vec{\mu}_N| / |\vec{I}|$. Hence, as a proton with energy $\hbar\omega_0 = \triangle E$ bombards the nucleus, the proton will be totally absorbed and a resonance occurs. The resonance energy absorption will induce a transition of the nucleus from a lower energy level ($m=-1/2$) to a higher energy level ($m=1/2$).

This resonance can be observed and detected. The resonance frequency $f=\omega_0/2\pi$ can be measured by using a Marginal Oscillator which is connected to an oscilloscope. From the relation $\hbar\omega_0 = \gamma_N B\hbar$, the values of γ_N, γ_H and γ_F can also be calculated.

THEORY

A. Normal Zeeman Effect[2,3]

For an electron moving in a circular Bohr

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orbit around a fixed nucleus, we have a relation between its orbital magnetic dipole moment $\vec{\mu}_\ell$ and its orbital angular momentum $\vec{L}$ of the form: $\vec{\mu}_\ell = -\frac{g_\ell e}{2m_e}\vec{L} = -\frac{g_\ell \mu_b}{\hbar}\vec{L} = \gamma_e L$ (1)

where $\mu_b = \frac{e\hbar}{2m_e}$ is the Bohr magneton, g_ℓ is the orbital g-factor, and γ_e is the gyromagnetic ratio of the electron. Eq (1) also holds for an arbitrary rotating body with mass m and charge q (for example, a nucleus): $\vec{\mu}_\ell = g_\ell \frac{q}{2m}\vec{L}$.

Now, when the magnetic dipole moment $\vec{\mu}$ is placed in an external applied magnetic field $\vec{B}$, the torque $\vec{\tau}$ acting on the dipole to tend to align the dipole with the magnetic $\vec{B}$-field is given by $\vec{\tau} = \frac{d\vec{L}}{dt} = \vec{\mu}_\ell \times \vec{B}$

For a rotating electron around the fixed nucleus,

$\vec{\tau} = \frac{d\vec{L}}{dT} = -\frac{g_\ell \mu_b}{\hbar}\vec{L} \times \vec{B} = \frac{g_\ell \mu_b}{\hbar}\vec{B} \times \vec{L} = \vec{\omega} \times \vec{L}$

where $\vec{\omega} = \frac{g_\ell \mu_b}{\hbar}\vec{B}$ is the Larmor frequency. The potential energy of the electron corresponding to the orientation of $\vec{\mu}_\ell$ with respect to $\vec{B}$ is given by $E = -\vec{\mu}_\ell \cdot \vec{B} = \frac{g_\ell \mu_b}{\hbar}\vec{L} \cdot \vec{B}$ (2)

Because the orbital angular momentum $\vec{L}$ is quantized according to the rules: (i) the eigenvalues of L^2 are equal to $\ell(\ell+1)\hbar^2$, where ℓ is any nonnegative integer, $\ell = 0, 1, 2, \cdots, n$; (ii) the eigenvalues of L_z, z-component of $\vec{L}$, are equal to $m\hbar$, where the integer m lies between $-\ell$ and $+\ell$ for each given value of the integer ℓ, we see that, if we let the magnetic

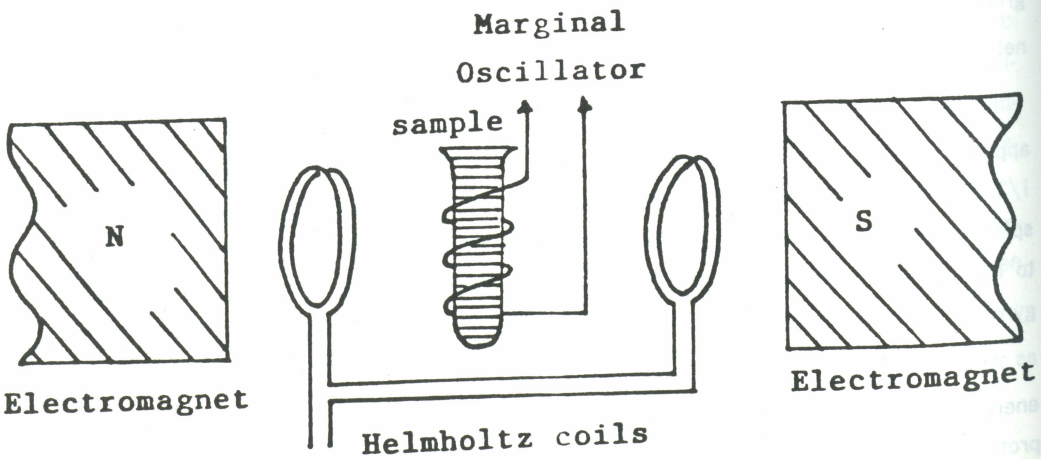

Fig. 1 Basic apparatus for a NMR experiment. The sample under investigation is placed in a uniform steady magnetic field $\vec{B}_0$ (norizontal) produced by the electromagnet and subjected to an oscillating magnetic field (vertical) produced by an RF coil which is connected to Marginal Osciallator (RF oscillator). A pickup coil (Helmholtz coils) registers an induced emf when the nuclear spins suddenly change direction.

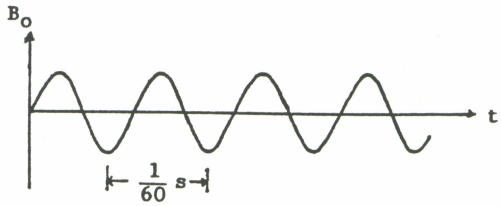

Fig. 2 The magnetic field on the sample will oscillate at the same frequency 60 Hz as the Helmholtz coils.

Fig. 3 The resonance condition is signaled by an enhanced attenuation of the radio waves passing through the sample.

field B in the z-direction, the potential energy of the dipole magnetic moment in an external applied magnetic field will be $E_m = \frac{g_\ell \mu_b}{\hbar} L_z B = g_\ell \mu_b m B = |\gamma_e| B m\hbar$ (3)

, where $m = -\ell, -\ell+1, \cdots, \ell-1, \ell$. This quantity E_m represents the additional energy acquired by the electron when the magnetic field is applied on it.

According to Eq(3), we see that the magnetic field will produce a discrete energy shift for each of $2\ell+1$ values of m in any n-orbital configuration. The energy spacing between adjacent energy levels can be found by taking the difference

$E_m = E_{m+1} - E_m = g_\ell \mu_b B = |\gamma_e| B\hbar$ (4)

This energy splitting in the energy levels is Normal Zeeman Effect. Obviously, this effect is due to the quantization of angular momentum $\vec{L}$ or the quantization of the dipole magnetic momentum $\vec{\mu}$ tof the electron.

B. Nuclear Magnetic Resonance (NMR) Phenomenon[4]

Similar to an orbital electron, a nucleus of angular momentum $\vec{I}$ possesses a magnetic dipole moment $\vec{m_N} = \gamma_N \vec{I}$, where $\gamma_N = |\vec{m_N}| / |\vec{I}|$, and $|\vec{I}| = I(I+1)\hbar$. Hence, the $(2I+1)$ degenerate nuclear spin energy levels are split by an amount of $\gamma_N B\hbar$ when the nucleus is in an applied magnetic field $\vec{B}$. (This is analogous to the Zeeman Effect.)

We see that, in the presence of magnetic field $\vec{B}$, when a photon with a proper energy $\hbar\omega_0 = \gamma_N B\hbar$ bombards the nucleus, a resonance absorption of energy occurs to excite transition between the split energy levels. This is NMR phenomenon. The resonant frequency of the nuclear magnetic resonance is determined by

$\omega_0 = \gamma_N B$ (5)

For proton NMR spectroscopy, in which the nuclei of the hydrogen atom is involved ($I = 1/2$), the resonance frequency is typically of order of 10 MHz for a magnetic field intensity of a few kilogauss, which lies within the range of radio frequencies[2].

C. Detection of NMR[1,4,5]

The basic apparatus for bringing about the resonance energy absorption is shown in Fig. 1. Both the small Helmholtz coils and the electromagnet provide the external magnetic field $\vec{B_0}$ which is applied directly on the sample. The large electromagnet has a main uniform magnetic field $\vec{B'_0}$ over the dimensions of the sample. But the samll Helmhotz coils provides a 60 Hz sweep field $\vec{B_0}$ oriented parallel to the main

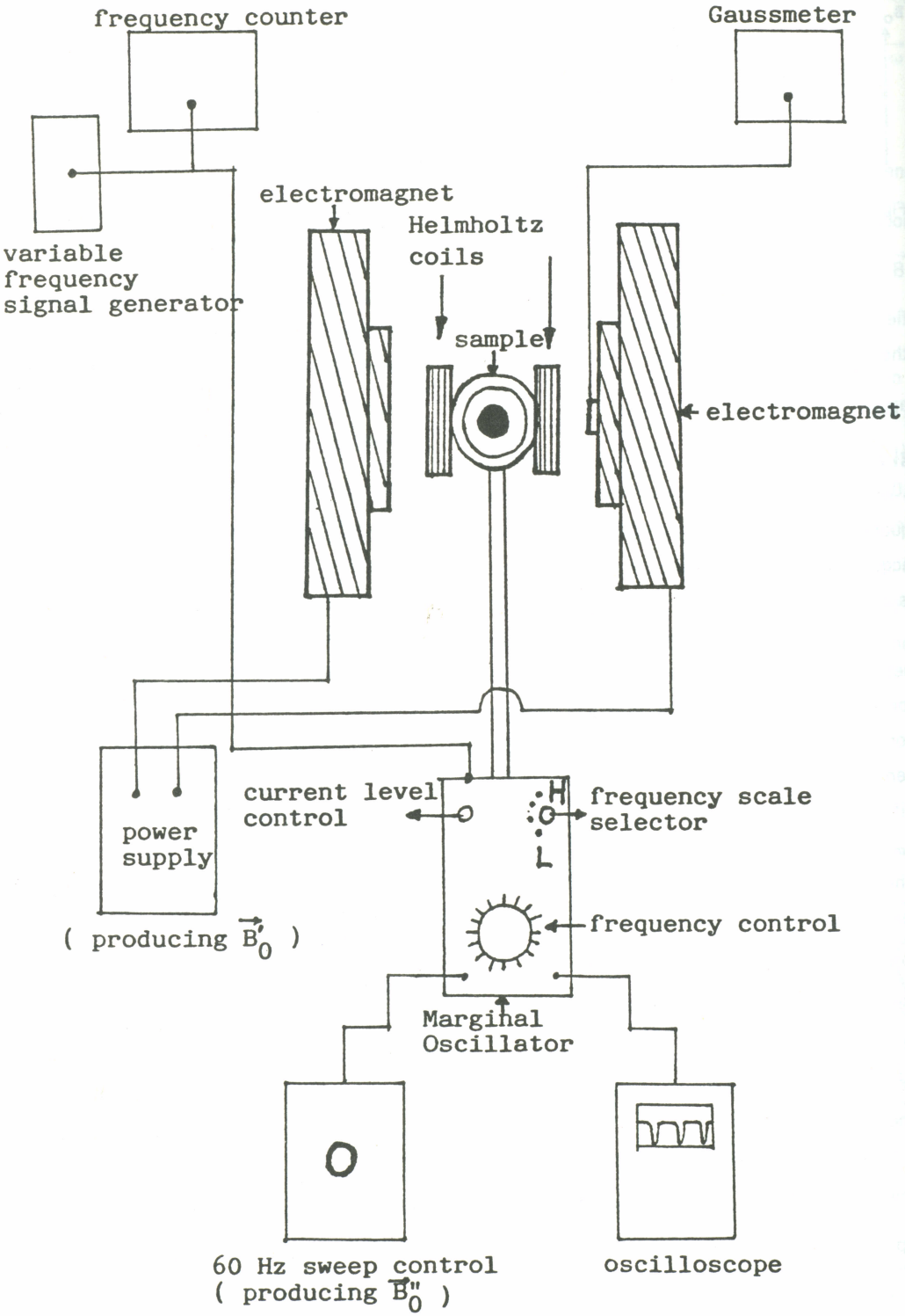

Fig. 4 Experimental apparatus set-up for measuring the natural resonance frequencies of the sample.

TABLE I The measured natural resonance frequencies of ^{1}H and ^{9}F nuclei for the corresponding external magnetic B_0-field producing NMR resonance absorption of energy.

	Sample (Nuceus)	Applied $\vec{B_0}$-field B_0 (kilogauss)	Dial setting of Marginal Oscillator	Measured natural Resonance Frequency f (KHz)
1	^{1}H	0.435	38.3	2726.7
	^{9}F	0.435	38.1	2734.7
2	^{1}H	0.531	58.8	1799.2
	^{9}F	0.531	52.7	2010.2
3	^{1}H	0.589	69.6	1980.4
	^{9}F	0.589	61.1	2171.1
4	^{1}H	0.685	87.6	3314.4
	^{9}F	0.685	79.8	3997.4

TABLE 2 Th resonant angular frequencies of ^{1}H nucleus for the corresponding external magnetic B_0-field producing NMR resonance absorption of energy.

	Applied $\vec{B_0}$-field B_0 (kilogauss)	Natural Resonance Frequency f_H (KHz)	$\omega_H = 2\pi f_H$ ($\times 10^6$ rad/sec)
1	0.435	2726.8	17.132
2	0.531	1799.2	11.305
3	0.589	1980.4	12.443
4	0.685	3314.4	20.825

TABLE 3 The resonant angular frequencies and the NMR frequencies of the ^{9}F nucleus for the corresponding external magnetic $\vec{B_0}$-field producing NMR resonance absorption of energy.

	Applied $\vec{B_0}$-field B_0 (kilogauss)	Natural Resonance Frequency f_F (KHz)	$\omega_F = 2\pi f_F$ ($\times 10^6$ rad/sec)	$f_{F,NMR} = 42.5759 \times f_F / f_H$ (MHz)
1	0.435	2734.70	17.183	42.7008
2	0.531	2010.20	12.630	47.5689
3	0.589	2171.10	13.641	46.6757
4	0.685	3997.40	25.116	51.3495

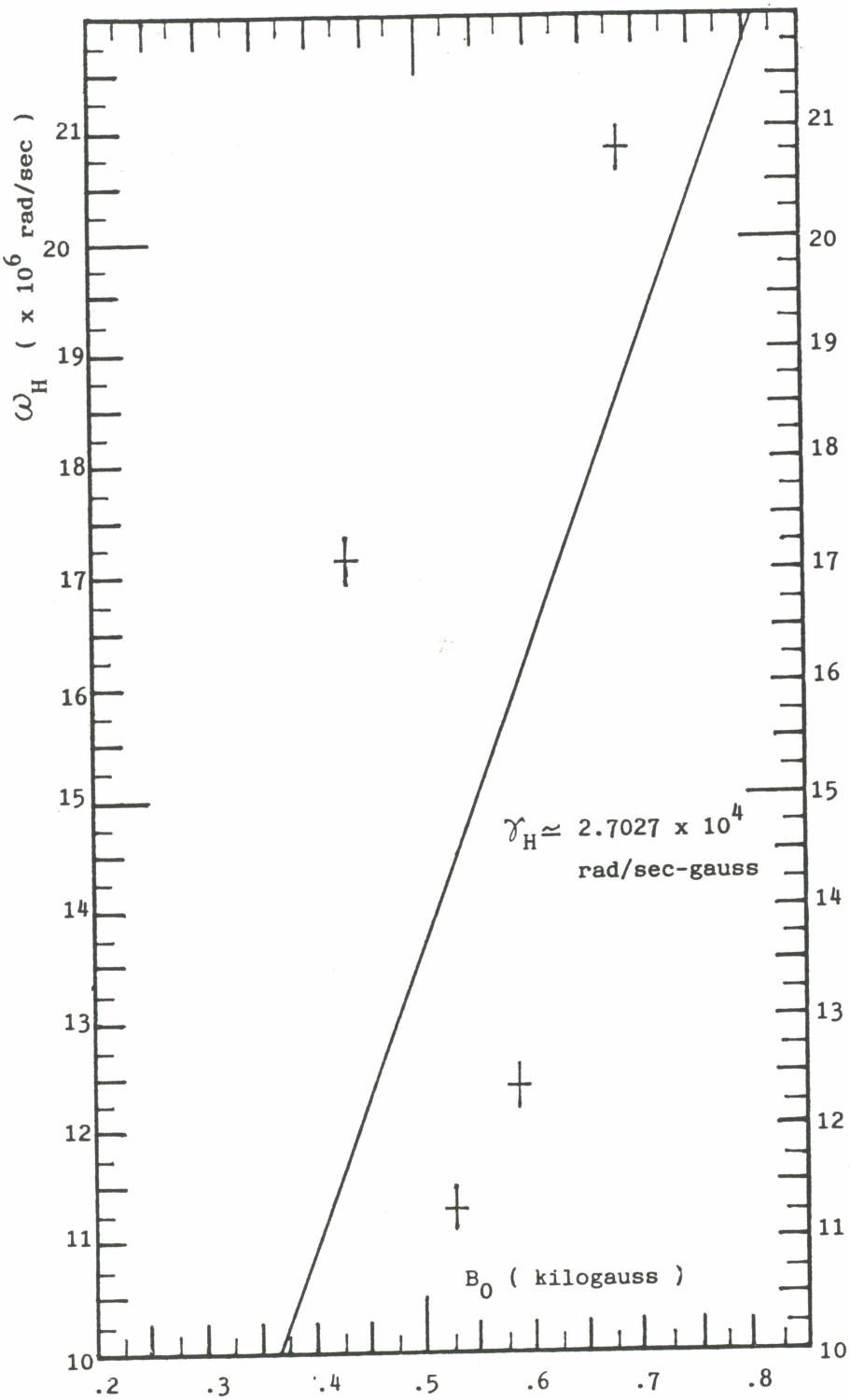

Fig. 5 ω_H vs. B_0 The linear relationship between ω_H and B_0 gives the gyromagnetic ratio γ_H of ^1H nucleus.

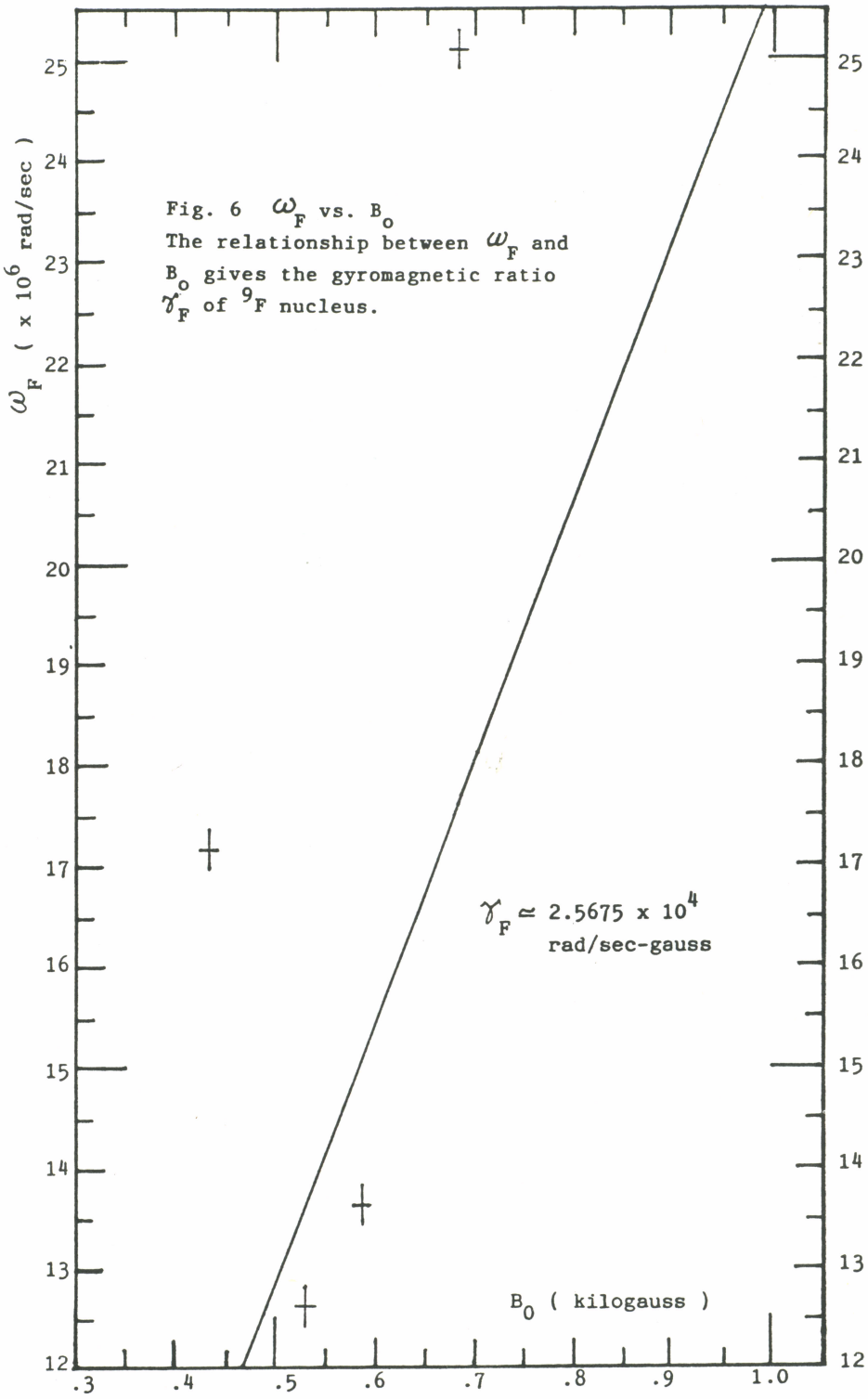

Fig. 6 ω_F vs. B_0 The linear relationship between ω_F and B_0 gives the gyromagnetic ratio γ_F of ^9F nucleus.

TABLE 4 The gyromagnetic ratio γ_H of ^1H nucleus and γ_F of ^9F nucleus for the corresponding external magnetic $\vec{B_0}$-field producing NMR resonance absorption of energy.

	B_0 (kilogauss)	f_H (KHZ)	$\gamma_H = \frac{2\pi f_H}{B_0}$ $(\frac{10^4 \text{ rad}}{\text{sec-gauss}})$	f_F (KHz)	$\gamma_F = \frac{2\pi f_F}{B_0}$ $(\frac{10^4 \text{ rad}}{\text{sec-gauss}})$	$f_{F,NMR} = 42.5759 \frac{f_F}{f_H}$ (MHz)	$\gamma_F = \frac{2\pi f_{F,NMR}}{10^4}$ $(\frac{10^4 \text{ rad}}{\text{sec-gauss}})$
1	0.435	2726.7	3.983	2734.70	3.950	42.7008	2.6829
2	0.531	1799.2	2.129	2010.20	2.379	47.5689	2.9888
3	0.589	1980.4	2.113	2171.10	2.316	46.6757	2.9327
4	0.685	3314.4	3.040	3997.40	3.667	51.3495	3.2263

$\vec{B_0}$ field. Therefore, $\vec{B_0}$ results in a modulation of the magnetic field $\vec{B}_0'$. Hence, the magnetic field $\vec{B_0}$ will have magnitude between $B_0' + B_0''$ and $B_0' - B_0''$, i.e., B_0 will oscillate sinusoidally at a frequency 60 Hz as shown in the Fig. 2.

The Marginal Oscillator, which acts as a driven oscillator, provides a driving magnetic field $\vec{B_1}$ on the sample by a small set of coils closely wrapped about the sample such that $\vec{B_1}$ is perpendicular to $\vec{B_0}$. The magnitude of $\vec{B_1}$ oscillates sinusoidally in the radiofrequency band.

When the radiofrequency is off resonance, the relative phase of the spin of the sample nucleus is random and no induced trasition occurs. However, when the radiofrequency matches the natural resonant frequency ω_0, all the precessing spins of the nuclei are brought into phase by the $\vec{B_1}$-field and an induction of transition occurs. The resonance absorption of magnetic energy by the sample at $\omega = \omega_0$ will cause the oscillations of $\vec{B_0}$ to cease. Thus, we will find a dip of $\vec{B_0}$-field in the radiofrequency level as shown in Fig. 3. This is the NMR resonance signal.

D. Determination of NMR Resonance Frequency[6,7]

Consider the samples of the proton (^1H nucleus) in liquid water, which is doped with $FeCl_3$, and the fluorine nucleus (^9F nucleus) in teflon.

Let ω_H = resonance angular frequency of proton

f_H = resonance frequency of proton

ω_F = resonance angular frequency of fluorine

f_F = resonance frequency of fluorine

For a fixed, arbitrary applied magnetic field $\vec{B_0}$, the resonance conditions for ^1H and ^9F nuclei are, according to Eq(5),

$$\omega_H = \gamma_H B_0 \tag{6}$$

, and $$\omega_F = \gamma_F B_0 \tag{7}$$

From Eq(6) and Eq(7), we have

$$\frac{\omega_H}{\gamma_H} = \frac{\omega_F}{\gamma_F} \tag{8}$$

, and $$\frac{f_H}{\gamma_H} = \frac{f_F}{\gamma_F} \tag{9}$$

When $B_0 = 10$ kilogauss, $\omega_H = \omega_{H,NMR}$, and $\omega_F = \omega_{F,NMR}$.

Thus, $$\gamma_H = \frac{\omega_{H,NMR}}{10 \text{ kilogauss}} \tag{10}$$

,and $$\gamma_F = \frac{\omega_{F,NMR}}{10 \text{ kilogauss}} \tag{11}$$

Therefore, Eq(8) becomes

$$\frac{\omega_H}{\omega_{H,NMR}} = \frac{\omega_F}{\omega_{F,NMR}} \qquad (12)$$

and Eq(9) becomes

$$\frac{f_H}{f_{H,NMR}} = \frac{f_F}{f_{F,NMR}} \qquad (13)$$

$f_{H,NMR}$ has been measured to be $f_{H,NMR} = 42.5759$ MHz[1]. So, we have

$$\frac{f_H}{42.5759\ \text{MHz}} = \frac{f_F}{f_{F,NMR}} \qquad (14)$$

As we find f_H and f_F experimentally, $f_{F,NMR}$ can be calculated by using Eq(14).

The previous measured value of γ_H was obtained from Eq(10).

$$\gamma_H = \frac{2\pi \times 42.5759 \times 10^6 \text{Hz}}{10 \times 10^3 \text{ gauss}}$$

$$= 2.673 \times 10^4 \text{ rad/gauss-sec}$$

Therefore, as soon as $f_{F,NMRF}$ is measured, the value of γ_F can be found by using Eq(11).

EXPERIMENTAL PROCEDURE

1. Place the sample of liquid water, which is doped with $FeCl_3$, on the sample position.
2. Connect all the equipments except the Variable Frequency Signal Generator and the Frequency Counter as shown in Fig. 4. We disconnect the Variable Frequency Signal Generator and the Frequency Counter so that there is no noise occuring on the oscilloscope.
3. Turn on the power supply to provide an arbitrary fixed magnetic field $\vec{B_0}$. Also, the Helmholtz coils are connected to the 60 Hz sweep oscillator to provide a uniform linearly oscillating magnetic field $\vec{B_0}$. Select the frequency scale on "LOW".
4. The frequency of Marginal Oscillator is varied until the oscilloscope screen shows equally spaced dips. These dips respresent a power drain from the Marginal Oscillator and show that the resonance occurs. Record the dial setting on the frequency control and the magnetic field strength on the Gaussmeter.
5. Trun off the power supply. Connect the Variable Frequency Signal Generator and Frequency Counter to Marginal Oscillator.
6. Trun on the Variable Frequency Signal Generator and Frequency Counter. Vary the output signal frequency until an oscillation occurs on the oscilloscope screen. This shows that this frequency matches the frequency of the Mrginal Oscillator, i.e., the resonance frequency. Record the frequency on the frequency counter. This is the value of f_H.
7. Turn off the Frequency Counter and the Variable Frequency Signal Generator and disconnect them from the Marginal Oscial-lator.
8. Replace the sample of liquid water by teflon on the sample position. Repeat the experiment at the same magnetic field strength B_0 to determine the measured dial setting and resonance frequency f_F.
9. Adjust B_0 to any other values. Repeat the experiment for three other trials.
10. From the measured values of B_0, f_H, and f_F, calculate γ_H, γ_F, and $f_{F,NMR}$.

CONCLUSION AND DISCUSSION

The field determining the frequency of the nuclear magnetic resonance is the field acting directly on the nucleus. The NMR resonance absorption of energy (see Fig. 3) is previously observed by fixing the frequency of the perturb-

ing radio-frequency (RF) field, and varying the applied magnetic field $\vec{B}_0$[7]. In our work, however, we tried to fix the magnetic field $\vec{B}_0$ and vary the radio-freuency until the resonance was observed. The results are shown in TABLE 1.

We calculate the values of γ_H and γ_F directly from the results in TABLE 2 and TABLE 3 for each $\vec{B}_0$-field producing NMR resonance absorption of energy. They are shown in TABLE 4. The accurate values of γ_H and γ_F can be obtained, however, by plotting ω_H vs. B_0 and $\omega_H$vs. B_0. They are shown in Fig. 5 and Fig. 6. According to Eq(6) or Eq(7), the slopes of the straight lines give $\gamma_H = 2.7027 \times 10^4$ rad/sec-gauss and $\gamma_F = 2.5675 \times 10^4$ rad/sec-gauss. Thus, we have $\frac{\gamma_F}{\gamma_H} = \frac{2.5675 \times 10^4 \text{ rad/sec-gauss}}{2.7027 \times 10^4 \text{ rad/sec-gauss}} = 0.9499$ as Eq(1) expected because $m_F > m_H$.

Since ^1H nucleus and ^9F nucleus have the same ground-state spin quantum number ($I = +1/2$), the theoretical value is given by [2,6]

$$\frac{\gamma_F}{\gamma_H} = \frac{\mu_F}{\mu_H} = \frac{2.6273}{2.7926} = 0.9408$$

The percentage error of our experimental result is given by

$$\frac{0.9499-0.9408}{0.9408} \times 100\% = 0.967\%$$

This low percentage error indicates that the method used in this work is reliable. But, this method is much better for the medium external magnetic B_0-field beacause noises, which were brought about on the oscilloscope due to the mechanical vibrations during varying the radio-frequency in our experiment to observe the resonance, affected our detection of NMR very much, especially for high $\vec{B}_0$-field and low resonance frequency (See Fig. 5 and Fig. 6).

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REFERENCES

1. A. C. Melissinos: "Experiments in Modern Physcs", Chapter 8 and Appendix (Rochester, New York, 1966)
2. Has C. Ohanian: "Modern Physics" (Prentice-Hill InC., Englewood Cliffs, New Jersey, 1987), pp382-385.
3. See any standard textbook of Quantum Physics. For example, R. Eisberg and R. Resnick: "Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles" 2nd Ed. (John-Willey & Sons, New York, 1985), pp364-370.
4. N. W. Ashcroft and N. D. Mermin: "Solid State Physics", (W. B. Saunders Company, Philadelphia, 1976), pp665-666.
5. J. R. Christman: "Fundamentals of Solid State Physics" (John-Willey & Sonns, New York, 1988) pp382-384, also has some basic discussions on NMR and its application.
6. C. Kittel: "Introduction to Solid State Physics", 6th Ed., (John-Willey & Sons Inc., New York 1986) pp 463-465.
7. It was measured by Adrian C. Melissionos. The values of γ_H and γ_F were 2.673×10^4

rad/sec-gauss and 2.515×10^4 rad/sec-gauss respectively. Thus $\gamma_F/\gamma_H=0.9408$. See the discussions in Ref. (1).

核磁共振法測定氫核及氟核之共振頻率

蔡文鋒

利用核磁共振的方法，氫核(質子)及氟核之自然共振頻率可以有效地被測定出來。以往藉由核磁共振方法測定原子核之自然廿振頻率均採用固定無線電頻率磁場(RADIO-FREQUENCY)，改變外加強大均勻磁場的方法。本實驗的結果顯示，當固定外加強大均勻磁場而改變無線電頻率磁場時，由所測得的氫核及氟核自然共振頻率來求得原子核之廻轉比率 γ_N(GYROMAGNETIC RATIO)也可以得到合理而精確的測量值。只是當外加磁場夠大時，由振盪而引起對共振頻率測定的影響必須避免。

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