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Abstract

The resonance absorption method has been applied to the measurement of the moments of C^{13} , F^{19} , Tl^{203} , and Tl^{205} in terms of the proton moment. The observed ratios of g-factor to that of the proton are as follows. C^{13} : $.25143 \pm .00005$; F^{19} : $.94077 \pm .0001$; Tl^{203} : $.571499 \pm .00005$; Tl^{205} : $.577135 \pm .00005$. By taking $5.5791 \pm .0016$ for the proton gyromagnetic ratio, the values of the moments in nuclear magnetons are: $\mu(C^{13}) = .7016 \pm .0004$; $\mu(F^{19}) = 2.626 \pm .001$; $\mu(Tl^{203}) = 1.612$; $\mu(Tl^{205}) = 1.628$. For the thallium isotopes, $\mu_{205}/\mu_{203} = 1.00986 \pm .00005$. The results for C^{13} and F^{19} are in close agreement with the molecular-beam values.

ON THE MAGNETIC MOMENTS OF C^{13} , F^{19} , Tl^{203} , AND Tl^{205}

1. Introduction

Since the first successful observations of nuclear magnetic resonances in macroscopic aggregates of matter,¹ the method has been applied to the precise measurement of a number of magnetic moments.²⁻¹² The method is based upon the detection of nuclear spin reorientations in a magnetic field induced by an applied radio-frequency field. In the absence of perturbing fields, the probability for such transitions will be a maximum when the quantum of energy of the radio-frequency field is equal to the energy difference between the equally spaced energy levels that a nucleus can occupy in a magnetic field, H . That is, when

$$h\nu = g\mu_0 H \quad (1)$$

where μ_0 is the nuclear magneton and g is the ratio of magnetic moment μ in units of μ_0 to angular momentum I in units of \hbar .

If an assemblage of nuclei in a magnetic field reaches the equilibrium Boltzmann distribution, transitions induced by an applied radio-frequency field will result in a net absorption of energy because the lower energy levels are more abundantly occupied. It is by this absorption of energy that the spin reorientations are detected.

2. Method and Apparatus

The sample containing the nuclei under investigation is placed in a uniform magnetic field. A small oscillating field perpendicular to the uniform field is supplied by a radio-frequency coil surrounding the sample. Under these conditions, a phenomenological theory developed by F. Bloch enables an explicit expression to be given for the r-f susceptibility of the coil when the passage through the resonance region, by varying the field or the frequency, is slow enough so that the rate of change of the component of nuclear magnetization in the field direction can be neglected.¹³

The susceptibility is complex, its real component representing a dispersion curve and its imaginary component, an absorption curve. If the amplitude of the oscillating field is sufficiently small, it does not contribute appreciably to the width of the resonance. Under these conditions, the maximum value of each component is of the order of

$\chi_0 (H/\Delta H)$ where ΔH is the separation in gauss of the half amplitude points of the absorption component and χ_0 is the static susceptibility of the nuclei given by the quantum generalization of Curie's law.*

Under experimental conditions, a half-width of about $\frac{1}{2}$ gauss in a field of 5000 gauss is achieved. The r-f susceptibility of the sample can then be greater than the static susceptibility by a factor of 10,000. It still, however, is only of the order of 10^{-5} at best. In order to keep ΔH small, and in fact limited by inhomogeneities in the applied field, it is necessary in general to work with liquid samples. In solids, neighboring nuclei are likely to be more nearly fixed and their magnetic fields will serve to increase the resonance width. In addition, if the nucleus has a spin greater than $\frac{1}{2}$, there may be quadrupole interactions which will further broaden the resonance.

The use of a bridge circuit suggests itself in the detection of small changes in the circuit parameters of a coil. We have constructed bridge circuits for this purpose similar in design to the type introduced by Purcell and his co-workers and described by them in detail.¹⁴ Such circuits are frequency sensitive, so that in searching for a resonance, it is the field which is varied rather than the frequency. Standard signal generators (General Radio Co. Types 805-C and 605-B) have been used to supply the bridge circuits. Communication receivers proved to have adequate sensitivity for use as detectors. The Hallicrafters SX-28 and the Signal Corps BC-348-N were employed.

A water-cooled electromagnet designed by F. Bitter has been used for most of the work. It has 8-inch diameter pole pieces and a $2\frac{1}{4}$ inch gap. It is energized by a bank of submarine storage batteries. As the current drawn from the batteries is considerably less than their rating, the field can be kept constant over long periods of time. Internal auxiliary coils are provided into which alternating current can be fed to modulate the field above and below its mean value.

The sample coils have for the most part been close wound with No. 33 enameled wire on hollow polystyrene forms $7/16$ inch in diameter. The volume occupied by such a coil for use in the range of 4.5 Mc/sec. is about $1\frac{1}{2}$ cc. and is correspondingly less for higher-frequency coils. The coils are mounted in a closed brass box which is attached to a positioning mechanism on the magnet so that it can be conveniently moved about in the field until the most homogeneous position is located.

A strong resonance may be observed directly on an oscilloscope connected to the audio output of the receiver. For this purpose, the magnetic field is modulated sinusoidally about the resonance value by applying 60-cycle current to the auxiliary coils of the magnet. A stationary pattern is observed when the oscilloscope sweep circuit is

* See, for example, Eq. (2) of Ref. 13.

synchronized to this frequency. Two resonances are observed on the screen as the resonance field is passed through twice during each cycle. The general features of the oscillations associated with the resonances under these conditions have been explained by considering transient solutions of Bloch's equations.¹⁵

To observe weak resonances, the oscilloscope is replaced by a narrow-band 30-cycle amplifier, as has been done by other investigators in this field. The resonance region is slowly traversed and at the same time, a small 30-cycle current is applied to the auxiliary coils of the magnet. A 30-cycle modulation of the r-f susceptibility change results, the amplitude of which is proportional to the slope of the resonance curve if the 30-cycle current is sufficiently small. A recording meter connected to the amplifier output enables a graphical record to be made of the resonance. One or the other components of the susceptibility change will be accentuated, depending upon the type of bridge balance.

3. Measurements

It is seen from Eq. (1) that the measurement of the resonant frequencies of two species of nuclei in the same magnetic field determines the ratio of their g-factors. In the experiments herein reported, the proton moment has been used as a reference moment. From its absolute value, one can then determine the absolute values of the moments measured in terms of it, taking into account values of I obtained from other experiments.

The great accuracy inherent in the resonance absorption method arises from the sharpness of the resonance that can be achieved. Whether or not the full accuracy of the method can be utilized in the comparison of moments is determined by the extent to which the assumption of identical fields at both kinds of nuclei is valid.

Factors preventing the field from being the same at the two types of nuclei when their resonant frequencies are measured can arise from the experimental arrangement and from the diamagnetism of the atomic electrons surrounding the nucleus.

The effect of the latter is to make the field at a nucleus slightly less than the applied field so that the observed gyromagnetic ratio is less than the actual one. A calculation by Lamb¹⁶ using the Fermi-Thomas model of the atom gives the expression

$$H'/H = 3.19 \times 10^{-5} Z^{4/3} \quad (2)$$

where H' is the reduction in field at the nucleus of an atom of atomic number Z in an applied field H . The dependency of the diamagnetic correction on Z as shown by Eq. (2) makes it of minor importance for the light nuclei. For the heavy nuclei, it becomes appreciable and in fact limits the accuracy with which values of their moments can be given.

The experimental arrangements for making these measurements have been of two types. Two coils can be placed in the magnetic field, each connected to a separate bridge circuit and containing one or the other of the two species of nuclei to be compared. An electronic switch permits the output of each radio receiver to be displayed as a separate trace on the oscilloscope. When the two sets of resonances are aligned, the frequencies are measured. If the coils are then interchanged and the measurements repeated, the effect of a possible difference in field at one coil as compared with the other can be eliminated by taking the geometric mean of the measurements.

An alternative procedure is to use one coil containing both types of nuclei. The frequency is varied so that first one resonance and then the other is obtained in the same field.

The next problem to consider is that of precisely locating the resonance. In the latter procedure outlined above, if the resonance is displayed on an oscilloscope, the amplitude of the modulating field is decreased while the resonance is kept centered on the trace by slight frequency readjustments. When the modulating field is reduced to the order of the resonance width, all that may be observed on the screen is a series of transient oscillations. By setting the frequency midway between the extreme points where the resonance appears, it is accurately located. The maximum possible error is limited to the amplitude of the modulating field which is but a few hundredths of a percent of the applied field. It will be recognized that provided the homogeneity in field can be maintained, the higher the applied field, the less the percentage error in locating the resonance.

If the resonance is too weak to be observed on the oscilloscope, a record of it can be made at a known frequency by using the narrow-band amplifier and recording meter. After it has been traced out, the reference proton resonance is obtained in the same magnet position. From a calibration of the sweep field, a correction can be made to take into account the small field difference separating the two resonances.

When the two sets of resonances are presented simultaneously on the oscilloscope, for a given amplitude of modulating field, it is again seen that the larger the applied field, the less consequential will be the error made in aligning the resonances. Ambiguity in telling

when the both sets of resonances are aligned can come about from marked differences in their appearance resulting from differences in relaxation times and magnetic moments. Studies of transient effects have shown that the appearance of the resonance may be delayed until the resonant field has been passed through.¹⁵ The delay may be sufficiently different for both sets of resonances so that if one aligns the right-hand resonances on each trace, the left-hand ones are distinctly misaligned. Such a case was encountered in the comparison of the proton and deuteron moments made in this laboratory and elsewhere.⁵⁻⁷ In these instances, use can be made of a symmetry property possessed by Bloch's equations which was pointed out by Jacobsohn and Wangness.¹⁵ They show that for a sinusoidal-field modulation and oscilloscope sweep centered at the resonance value, the observed trace resulting from the absorption component will be symmetrical about the center line while that from the dispersion component will be skew-symmetrical. Hence if bridge balance and frequencies are adjusted so that two symmetrical patterns appear, we know that the resonances are "aligned" regardless of differences in appearance or separation.

Frequencies have been measured by means of crystal-calibrated frequency meters, General Radio Co. Type 620-A and the Signal Corps BC-221-T. The error in measurement is of the order of .005 per cent to .01 per cent depending upon the dial setting. A short antenna attached to the frequency meter radiates sufficient power to enable the beat frequency between the meter and signal generator to be observed directly on the oscilloscope connected to the receiver output.

The particular conditions applying to each of the nuclei measured will next be considered.

3.1. Measurements on the Thallium Isotopes, Tl^{203} and Tl^{205} . The following values for the spins and magnetic moments of the two stable thallium isotopes, mass numbers 203 and 205, have been determined spectroscopically.¹⁷

$$I = \frac{1}{2}$$

$$\mu = 1.45 \qquad \mu_{205}/\mu_{203} = 1.00966 .$$

The relatively high gyromagnetic ratio and abundance of these isotopes indicated that their resonances could be searched for on the oscilloscope. This was consequently done during a period of time when the M.I.T. cyclotron magnet was available to us for experiments in resonance absorption.

Saturated solutions of the soluble acetate and later the formate were placed in a glass coil form 7/16 inch in diameter. Two coils,

$\frac{1}{2}$ inch long and separated by $\frac{1}{2}$ inch were wound on the form and connected to separate bridge circuits. One coil was intended for the observation of proton resonances in the solution. The coils were contained within a 6-inch diameter coil through which 30-cycle current was sent to modulate the field.

Two resonances separated by a one-percent field difference were observed for a field about 10 per cent less than that expected on the basis of the spectroscopic results. The stronger resonance occurred at the lower field and was attributed to Tl^{205} since it is 2.5 times as abundant as Tl^{203} .

The proton and thallium resonances were then displayed simultaneously on an oscilloscope, the frequency of the former being 30.5 Mc/sec. and that of the latter, in the vicinity of 17.5 Mc/sec. In this case, it was possible to line up the two resonances on one trace with the two on the other.

Measurements were first made on Tl^{205} , previously communicated,⁸ and subsequently on Tl^{203} . Although the signal-to-noise ratio of the latter resonances was poor, the accuracy of the measurements is not appreciably lowered thereby. The resonances can be clearly distinguished from the noise by their characteristic motion across the oscilloscope as the field is varied. The applied field being about 7000 gauss and the modulating field 7 gauss, as long as both sets of resonances were visible on the oscilloscope together, an accuracy of one part in 1000 is achieved without attempting to align them. As the resonances had a width of less than $\frac{1}{2}$ gauss, errors in aligning them could be kept below those involved in the frequency measurements.

The cyclotron magnetic field was sufficiently uniform over the distance between coils so that it was not necessary to repeat the measurements with the coil positions interchanged. When the proton-deuteron magnetic moment ratio was measured with the use of this magnet,⁷ no significant difference was noted when this interchange was made, even though an accuracy of almost one part in 100,000 was achieved.

Differences in phase shift in the audio stages of the two receivers were studied by observing the points on the oscilloscope trace where proton resonances entered and left as the field was varied so that the resonances occurred first in one coil and then the other. This error appeared to be under .01 per cent.

Six independent determinations of the ratio of resonant frequencies of Tl^{205} to the proton were made and five for Tl^{203} . The individual results are given in Table I. To make an allowance for possible errors of the type mentioned above, .01 per cent was taken for the probable error. The results are then

$$\nu_{\text{Tl}^{205}}/\nu_{\text{H}^1} = .577135 \pm .00005$$

$$\nu_{\text{Tl}^{203}}/\nu_{\text{H}^1} = .571499 \pm .00005 .$$

In considering the probable error to be associated with the ratio of the moments, possible systematic errors should cancel out and it would appear justifiable to add the probable errors obtained from the deviations in each set of measurements. Taking the ratio of the averages then gives

$$\mu_{205}/\mu_{203} = 1.00986 \pm .00005 .$$

Applying the diamagnetic correction as given by Eq. (2) and taking the proton gyromagnetic ratio to be $5.5791 \pm .0016^*$ give for the moments, in nuclear magnetons,

$$\mu (\text{Tl}^{205}) = 1.628$$

$$\mu (\text{Tl}^{203}) = 1.612 .$$

It is difficult to list any probable error in the above results. The diamagnetic correction amounts to 1 per cent of the values and there is no certain way of estimating the error in it.

The value of the ratio of the moments obtained in these measurements is .02 per cent higher than the spectroscopic value. The discrepancy is within the limit of error of the spectroscopic work so that no significance can be attached to it.

It is of interest to note that on the basis of their spectroscopic measurements, Schuler and Korsching¹⁷ concluded that the relation

$$\frac{M_{A+2}}{M_A} = \frac{\mu_{A+2}}{\mu_A}$$

appeared to hold for the isotopes of copper, rhenium, and thallium. M_A refers to the lighter isotope of mass number A and μ_A to its magnetic moment. The packing fraction of both the thallium isotopes is given to be $(2.9 \pm .5) \times 10^{-4}$ mass units.¹⁸ Their mass ratio is then their mass number ratio and is

* This is the molecular beam value given in Ref. 21. It has not been corrected to take into account recent work on the g-factor of the electron.

$$\frac{M_{A+2}}{M_A} = 1.00985 \pm .0001 .$$

The relation thus appears to hold very well for thallium. Pound¹⁰ has measured the moment ratio of the copper isotopes by the resonance method and finds $\mu_{65}/\mu_{63} = 1.0711 \pm .0002$, distinctly different from the mass ratio, 1.032. If the above relation represents a nuclear property which holds under certain conditions, possibly the higher spin of the copper isotopes (3/2) might prevent it from applying in their case.

The addition of copper sulphate solution to the thallium sample with the resulting concentration of about 10^{19} cupric ions per cc. enhanced the proton resonance but almost obliterated the thallium resonance. The apparently stronger interaction between the copper and thallium ions would indicate that their average distance of separation is less than that of the copper ions and the protons.

3.2 Measurements on C¹³. The availability of a sample of methyl iodide enriched in C¹³ prompted measurements to be made on it. Its gyromagnetic ratio had been measured previously by the molecular-beam resonance method.¹⁹ Its spin²⁰ is $\frac{1}{2}$. The molecular beam value of the moment is

$$\mu (C^{13}) = .701 \pm .002 .$$

The methyl iodide, which is a liquid, was contained in a sealed-off glass tube $\frac{1}{2}$ inch in diameter. The liquid filled the tube to a depth of $\frac{3}{4}$ inch; 56.7 per cent of the carbon atoms in the sample were stated to be C¹³. The tube was fitted into a polystyrene coil form.

A search, with the use of the recording meter, revealed a weak resonance in the expected vicinity. The resonance was attributed to C¹³ since there were no other nuclei in the sample which would give resonances in this region. The frequency was 4.5 Mc/sec. A second coil mounted in the same box was used to obtain a reference proton resonance in oil at 18 Mc/sec.

The C¹³ resonance was recorded at a known frequency by using a motor-driven variable resistor to vary a small current through auxiliary coils on the magnet. This sweep field had been previously calibrated by measuring the change in frequency required by a change in current to keep a resonance at the same point on the oscilloscope trace. The proton resonance was obtained in the same magnet position and located in a manner previously described by displaying it on the oscilloscope and reducing the amplitude of the modulating field to a very small value. The main magnet current was monitored by using a potentiometer circuit

with which a drift of a gauss could be easily detected. The field was corrected before each frequency measurement if a drift was noticeable.

The field difference separating the two resonances was about 10^{-3} of the applied field, so that an error of 10 per cent in the calibration of the sweep field would affect the results by only .01 per cent. The C^{13} resonance occupied about one gauss, while the applied field was 4200 gauss. The uncertainty in location of the exact resonance point is not believed to have exceeded .01 per cent. The results of seven independent determinations are given in Table I. A probable error of .02 per cent is considered to include the effects of possible errors. We then have for the ratio of resonant frequencies

$$\nu_{C^{13}}/\nu_{H^1} = .25143 \pm .00005 .$$

The diamagnetic correction in this instance increases the observed gyro-magnetic ratio by only .03 per cent, and hence does not leave the accuracy of the final result uncertain as in the case of thallium. The magnetic moment in nuclear magnetons is then

$$\mu (C^{13}) = .7016 \pm .0004 ,$$

most of the error arising from that in the proton moment. The value obtained is seen to be well within the limit of error of the molecular-beam result.

3.3. Measurements on F^{19} . The resonance absorption method was applied to the measurement of the moment of fluorine to see how the results would compare with the observed molecular-beam value

$$g (F^{19}) = 5.250 \pm .005 .$$

By taking into account its spin of $\frac{1}{2}$ and the diamagnetic correction of .06 per cent the molecular-beam value²¹ of its moment is

$$\mu (F^{19}) = 2.627 \pm .003.$$

Hydrofluoric acid was used as a sample. It does not affect polystyrene and was poured directly into the coil forms. The addition of small concentrations of manganese chloride or ferric chloride solutions to the acid enhanced the proton resonance but obscured that of fluorine, a behavior similar to that found in the case of thallium. Here, the greater effect of the paramagnetic ions on the fluorine might

be a result of their electrical attraction which would lower their average distance of separation.

Measurements on fluorine were first made by presenting both fluorine and proton resonances on an oscilloscope simultaneously as was done for thallium. The frequencies were in the vicinity of 4.5 Mc/sec., the field then being about 1000 gauss. As the modulating field was 10 gauss, the accuracy of the thallium measurements was not duplicated. The result obtained for the ratio of resonant frequencies was

$$\nu_{F^{19}}/\nu_{H^1} = .9407 \pm .0003 .$$

A subsequent series of measurements was made at a higher frequency, in the neighborhood of 19 Mc/sec. One sample coil was used. The field was kept constant and the frequency varied so that first one resonance was obtained and then the other. Slow field drifts, not exceeding one gauss, which sometimes occurred during the interval between measurements, were corrected. The resonances were displayed on the oscilloscope and located by reducing the modulating field until it was about .015 per cent of the applied field, and keeping them centered on the trace. Four independent determinations were made, the results being given in Table I. A probable error of .01 per cent is considered to include possible errors. The result is then

$$\nu_{F^{19}}/\nu_{H^1} = .94077 \pm .0001 .$$

Taking into account the diamagnetic correction gives for the moment, in nuclear magnetons,

$$\mu (F^{19}) = 2.626 \pm .001 ,$$

most of the error again arising from that in the proton moment. The value is in close agreement with the molecular-beam value.

Acknowledgment. The author is indebted to Professor F. Bitter for guiding the course of this research.

TABLE I. Ratio of Resonant Frequency to that of the Proton

Tl ²⁰⁵	1	.577129
	2	.577150
	3	.577111
	4	.577152
	5	.577112
	6	<u>.577155</u>
	average:	.577135
Tl ²⁰³	1	.571468
	2	.571526
	3	.571500
	4	.571503
	5	<u>.571498</u>
	average:	.571499
C ¹³	1	.251402
	2	.251423
	3	.251414
	4	.251443
	5	.251419
	6	.251467
	7	<u>.251459</u>
	average:	.251432
F ¹⁹	1	.940775
	2	.940767
	3	.940745
	4	<u>.940785</u>
	average:	.940768

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