Since div$j_{\mathrm{TOT}}=0$, one may write

$$j_{\mathrm{TOT}}=\frac{1}{W}\int_0^W\left(j_{\mathrm{COND}}+\epsilon\frac{\partial E}{\partial t}\right)dx, \tag{B.2}$$

where the second term in the parentheses is the displacement current density. Substituting Eq. (B.1), we find

$$j_{\mathrm{TOT}}=j\omega\epsilon v_{\mathrm{D}}/W+q\Phi(1-e^{-j\omega t_0})/(j\omega t_0), \tag{B.3}$$

where $t_0=W/u$ is the transit time of carriers through the depletion region, and v_{D} is the voltage across the depletion layer. From Eq. (B.3) the open-circuit voltage ($j_{\mathrm{TOT}}=0$) and the short-circuit current ($v_{\mathrm{D}}=0$) may be calculated.

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N^{14}-N^{15} Hyperfine Anomaly[*]

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The optical transmission of an optically oriented sodium vapor in spin-exchange equilibrium with atomic nitrogen has been used to measure the zero-field hyperfine splitting of N^{14} and N^{15}. The ground state of atomic nitrogen is $^4S_{3/2}$. For N^{14}, which has $I=1$,

$$\Delta\nu_{5/2\rightarrow 3/2}=26.12721\pm 0.00018 \text{ Mc/sec},$$
$$\Delta\nu_{3/2\rightarrow 1/2}=15.67646\pm 0.00012 \text{ Mc/sec}.$$

For N^{15}, which has $I=\frac{1}{2}$,

$$\Delta\nu=29.29136\pm 0.00016 \text{ Mc/sec}.$$

The nuclear moments of N^{14} and N^{15} have been remeasured by observing the effect of saturating the nitrogen resonance on the proton resonance in NH_4^+. The results were

$$g(14)/g(H^1)=0.072\,236\,95\pm 0.000\,000\,08,$$

and

$$g(15)/g(H^1)=-0.101\,330\,93\pm 0.000\,000\,08.$$

The $N^{14}-N^{15}$ hyperfine anomaly obtained by combining these measurements is

$$\Delta=\frac{A(15)/A(14)}{g(15)/g(14)}-1=0.000\,983\pm 0.000\,017.$$

A short discussion of the mechanism of spin-exchange collisions is given.

INTRODUCTION

The atomic ground state of nitrogen is $(1s)^2(2s)^2(2p)^3$, $^4S_{\frac{3}{2}}$. If there were no configuration mixing for this atom, there would be no nuclear hyperfine interaction or nuclear quadrupole interaction.[1,2] This can easily be seen since the total orbital angular momentum is zero so that the wave function is spherically symmetric and in the nonrelativistic approximation a p electron does not contribute to the Fermi contact interaction. Heald and Beringer[3] used the method of paramagnetic resonance absorption in a gas to make measurements on atomic N^{14} and found that the magnetic dipole hyperfine interaction constant was 10.45 ± 0.02 Mc/sec. They could detect no nuclear quadrupole interaction. Their large line width of 250 kc/sec, which was attributed to a combination of magnetic field inhomogeneity, Doppler broadening, and atom-atom interaction, made it difficult to determine the small magnetic dipole hyperfine interaction constant precisely. They showed that the g factor of the atomic ground state was the same as that of the free electron as would be expected for pure L-S coupling.

The discovery[4–7] that the hyperfine transitions of S-state atoms could be detected by using spin-exchange collisions with optically oriented sodium atoms has made it possible to measure the nitrogen hyperfine splitting more precisely. In this measurement the nitrogen resonance is observed by monitoring the transmission of circularly polarized resonance radiation through a bulb

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[*] This research was supported in part by Harvard University Funds, in part by a grant from the Research Corporation, and in part (J. C. B) by the Office of Naval Research.

[†] National Science Foundation predoctoral fellow 1958–59.

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containing sodium and nitrogen atoms in a buffer gas. When a radio-frequency field is applied so as to disorient the nitrogen, the spin-exchange collisions result in a change in the sodium polarization and consequently in the opacity of the bulb. The optical detection method makes it possible to measure the hyperfine splittings in a low magnetic field; the increased sensitivity of this method permits a reduction in the sample concentration, and the buffer gas reduces the Doppler broadening. Thus the hyperfine splittings of N^{14} and N^{15} can be measured with sufficient precision to determine the hyperfine anomaly. During the course of our experiment Holloway and Novick[8] reported a measurement of the hyperfine splittings in N^{14} using the optical orientation technique. We have previously given a preliminary report on the nitrogen measurements.[9]

It turned out that the ratio of the hyperfine splittings could be measured more precisely than the ratio of the nuclear gyromagnetic ratios was known.[10–12] Consequently the nuclear g factors were remeasured. This measurement was made by a double resonance technique. The proton resonance in NH_4^+ was monitored; the nitrogen resonance was then observed by noting the change in the proton resonance when a radio-frequency field was applied at the nitrogen resonant frequency.

In the first part of this paper the method of spin-exchange orientation as a tool for observing paramagnetic resonance is discussed, and the measurement of the N^{14} and N^{15} hyperfine splittings is described. The second part of the paper describes the double resonance measurement of the N^{14} and N^{15} nuclear gyromagnetic ratios.

MEASUREMENT OF THE N^{14} AND N^{15} HYPERFINE SPLITTINGS

A. The Method of Resonance Detection

The method for the detection of paramagnetic resonance through spin-exchange collisions works in the following fashion. A spherical bulb, containing a mixture of sodium vapor, a rare gas, and gaseous nitrogen, is illuminated with circularly polarized sodium resonance radiation, and the transmitted light is monitored with a photocell. The arrangement of the apparatus is shown in Fig. 1. The absorption of the circularly polarized light and its subsequent emission in a different state of polarization results in a net transfer of angular momentum to the sodium vapor, which becomes polarized with respect to an axis of quantization along the direction of propagation of the incident light beam. As the sodium becomes polarized, the vapor becomes less absorbing and the light incident upon the photocell increases. Equilibrium is reached when the amount of angular momentum absorbed from the light is equal to that lost from the sodium vapor through collisions with the rare gas and the walls. An intense radio-frequency discharge is used to dissociate some of the nitrogen molecules into atoms. The paramagnetic nitrogen atoms then collide with the polarized sodium and become polarized. In the steady state there is a net polarization of the nitrogen. If a radio-frequency magnetic field is then applied at the nitrogen frequency it will change the nitrogen polarization. Through spin-exchange collisions the sodium polarization is reduced, and consequently the resonance radiation transmitted by the cell decreases. Hence the light transmission can be used to detect the nitrogen paramagnetic resonance.

B. The Energy Levels of Atomic Nitrogen

Atomic nitrogen has a ${}^4S_{\frac{3}{2}}$ ground state. The Hamiltonian[13] for the nitrogen atom in a magnetic field is

$$\mathcal{H}=A\mathbf{I}\cdot\mathbf{J}-g_J\mu_0\mathbf{H}\cdot\mathbf{J}-g_I\mu_0\mathbf{H}\cdot\mathbf{I}+\frac{B}{2I(2I-1)J(2J-1)}[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}\mathbf{I}\cdot\mathbf{J}-\mathbf{I}^2\mathbf{J}^2],$$

where A is the magnetic hyperfine interaction constant, g_J is the atomic gyromagnetic ratio, g_I is the nuclear gyromagnetic ratio, B is the quadrupole interaction constant, $\mathbf{I}$ is the nuclear spin and $\mathbf{J}$ is the atomic angular momentum. Other terms which have the same transformation properties as the quadrupole interaction

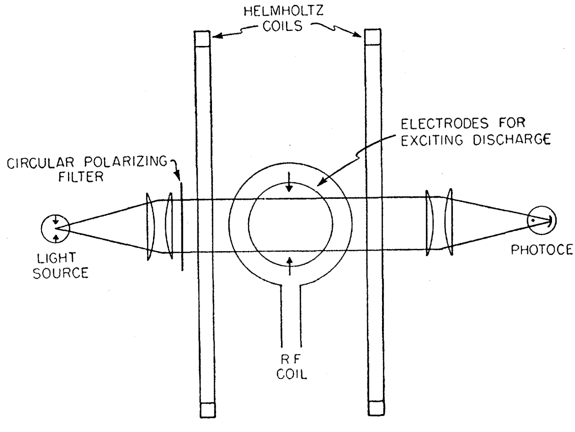

FIG. 1. A schematic representation of the optical pumping apparatus.

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[8] W. W. Holloway and R. Novick, Phys. Rev. Letters 1, 367 (1958).

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can occur if there are certain types of configuration mixing in the atomic state.[13] The quadrupole interaction is zero unless **I** and **J** are both one or greater. Thus the quadrupole interaction constant B is zero for N^{15} $(I=\frac{1}{2})$, but it is not necessarily zero for N^{14} $(I=1)$.

The ground state of N^{14}, which has a nuclear spin of one, contains three hyperfine states characterized in a low magnetic field by a total angular momentum $F=I+J=\frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. Each of these hyperfine states has its own characteristic g factor. The energy levels for N^{14} together with their g factors are shown in Fig. 2. Nitrogen-15 has a nuclear spin of $\frac{1}{2}$ and consequently in zero magnetic field there are two hyperfine states of total angular momentum $F=2$, 1. The energy levels of the ground state of N^{15} in a small external field are shown in Fig. 3.

C. The Spin-Exchange Process

In order to understand the factors which determine the amplitude of the signals and influence the observed line shape, it is necessary to investigate the systematics of the spin-exchange collisions. The spin-exchange cross sections are, also, of considerable interest themselves as they furnish another tool for the investigation of the forces between atoms. The large number of hyperfine states of the nitrogen and sodium atoms (8 for Na, 12 for N^{14}, and 8 for N^{15}) make it desirable to obtain some kind of simplification so that the results can be readily understood. In this section we shall present a qualitative picture of these effects.

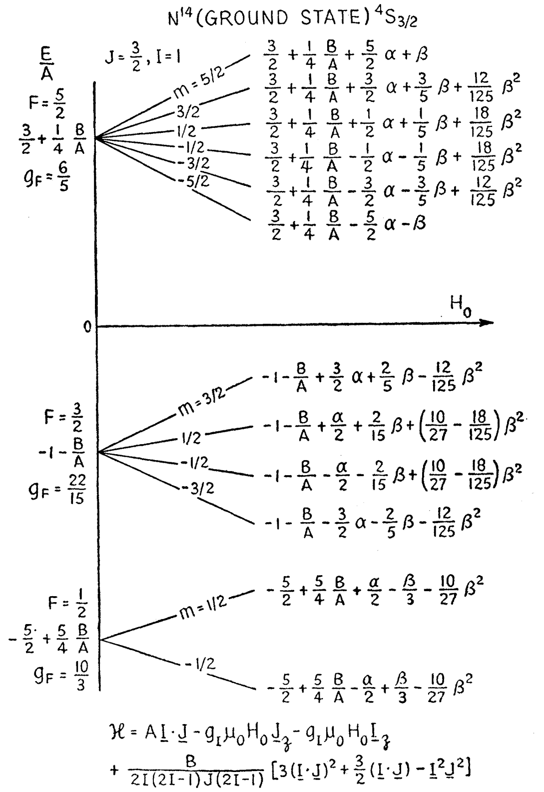

FIG. 2. The energy levels of the ground state of N^{14} in a low-magnetic field. E/A is plotted against H_0. $\alpha=|g_J|\mu_0H_0/A$; $\beta=-(|g_J|-g_I)\mu_0H_0/A$.

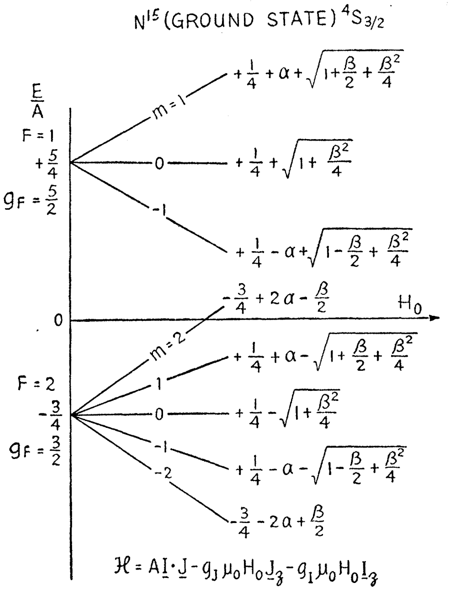

FIG. 3. The energy levels of the ground state of N^{15} in a low magnetic field. $E/|A|$ is plotted against H_0. $\alpha=|g_J|\mu_0H_0/|A|$; $\beta=(|g_J|-g_I)\mu_0H_0/|A|$.

To designate the state of an atom in a small external magnetic field the quantum numbers used are F, M_F, J, and I. Here F is the total angular momentum, M_F, is its projection on the magnetic field, I is the nuclear spin, and J is the total electronic angular momentum. Let the states of the nitrogen and sodium atoms before a collision be designated by the quantum numbers F_1, M_{F1}, $\frac{3}{2}$, I_1, and F_2, M_{F2}, $\frac{1}{2}$, I_2. The cross section for a collisional transition into the state F_1', $M_{F1'}$; F_2', $M_{F2'}$ will now be estimated. These transitions result principally from the dependence of the scattering cross section upon the relative orientations of the electronic angular momentum of the colliding sodium and nitrogen atoms. The interaction Hamiltonian for this system can be written as

$$\mathcal{H}_I=P_2V(r)+P_1K(r),$$

where P_2 and P_1 are the projection operators for the states of total electronic spin angular momentum 2 and 1, respectively. This Hamiltonian assumes that the scattering depends only upon whether the Na–N diatomic molecule enters a $^3\Sigma$ or a $^5\Sigma$ state. The potentials $K(r)$ for the $^3\Sigma$ state and $V(r)$ for the $^5\Sigma$ state can be determined from measurements of the vibrational spectrum of the diatomic molecule Na–N. The $^3\Sigma$ potential $K(r)$ is attractive, and the $^5\Sigma$ potential $V(r)$ is repulsive. In terms of the electronic spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$ for the nitrogen and sodium atoms respectively the projection operators are

$$P_1=(5+4\mathbf{S}_2\cdot\mathbf{S}_1)/8,$$

and

$$P_2=(3-4\mathbf{S}_1\cdot\mathbf{S}_2)/8.$$

To calculate the cross section a procedure similar to that used by Wittke and Dicke[14] and Purcell and Field[15] will be employed. Take a set of relative coordinates in which the sodium atom is at rest and the nitrogen atom is incident upon it with an energy E and impact parameter S. The spin wave function will be a mixture of that corresponding to the $^3\Sigma$ and $^5\Sigma$ states. During the collision the relative phase of these two parts of the wave function will change as they evolve with different energies. Thus after a collision the final wave function will be

$$\psi_f=(P_2+e^{i\varphi}P_1)\psi(F_1,M_{F1};F_2,M_{F2}),$$

where φ is the relative change in phase. This phase change will be assumed to be random and so ultimately an average over phases will be taken. In order to obtain the magnitude of the cross section, one must estimate the maximum impact parameter for which there will be a strong collision. It is reasonable to take this impact parameter as the one for which the particle will have zero velocity at the top of the centrifugal barrier for the $^3\Sigma$ potential. If this impact parameter is called S_0 then the spin-exchange cross section for the energy E will be

$$\sigma=\pi S_0^2|\langle F_1',M_{F1'};F_2',M_{F2'}|S|F_1,M_{F1};F_2,M_{F2}\rangle|^2,$$

where $S=P_2+P_1e^{i\varphi}$ is a unitary matrix and where an average over the phase is performed. For estimating this cross section it is convenient to use the Rydberg potential for diatomic molecules.[16] This potential is

$$K=-D_e[1+b(r-r_e)]e^{-b(r-r_e)},$$

where D_e is the dissociation energy, r_e the equilibrium radius, b is given in terms of the force constant k_e by $b=(k_e/D_e)^{\frac{1}{2}}$, and where r is the internuclear distance. The impact parameter S_0 can be found by requiring that the energy

$$E=(\mu/2)(\dot{r})^2+ES^2/r^2+K(r),$$

be such that the turning point $(\mu\dot{r}=0)$ occurs at the top of the centrifugal barrier for $S=S_0$. Thus it follows that

$$E=ES_0^2/r^2+K(r),$$

$$0=-2ES_0^2/r^3+dK/dr,$$

from which one can find S_0 by eliminating r. Using this method, the Purcell and Field[15] calculations for the spin-exchange cross section, which were made using the "best" hydrogen potential, can be reproduced for $T=100$°K and $T=300$°K to an accuracy of 10%.

There are two spin-exchange cross sections which are of interest in this experiment. They are the sodium-nitrogen cross section which produces the nitrogen polarization and the nitrogen-nitrogen cross section which can increase the line width of the nitrogen resonance by shortening the lifetime of the states. To calculate the nitrogen-sodium cross section an estimate must be made of the equilibrium distance r_e, the dissociation energy D_e, and the force constant k_e. The dissociation energy can be estimated from the chemical data on sodium and nitrogen bonds. This data suggests a value for D_e of between 1 and 4 ev. Pauling's rule for the sum of covalent radii gives a value for r_e of 2.28 A.[17,18] Badger's rule, which is an empirical relationship between the force constants and the internuclear distance of diatomic molecules, can be used to estimate k_e.[19] For diatomic molecules consisting of an element from row 1 and an element from row 2 of the periodic table, such as N−Na, Badger's rule is

$$k_e(r_e-0.94)^3=(0.535)^3,$$

where r_e is in A and k_e is in megadynes/cm. For $r_e=2.28$ A this gives $k_e=6.4\times10^4$ dynes/cm. For a particle with an average thermal energy of 400°K this gives the result that $\pi S_0^2=1.5\times10^{-14}$ cm^2 for $D_e=1$ ev and $\pi S_0^2=5.5\times10^{-14}$ cm^2 for $D_e=4$ ev.

A similar procedure can be used to estimate the nitrogen-nitrogen exchange cross section. In this case the situation is more complicated since when the two atoms collide they can form a $^1\Sigma$, $^3\Sigma$, $^5\Sigma$, or $^7\Sigma$ state. Of these the $^1\Sigma$ and $^3\Sigma$ states have strongly attractive potentials, the $^5\Sigma$ state has a slightly attractive potential, and the $^7\Sigma$ state has a repulsive potential. For the estimate of S_0 the potential for the $^1\Sigma$ state was used and the calculation of πS_0^2 was made in the same way as for the Na−N system. The empirical constants used were $D_e=9.756$ ev, $r_e=1.094$ A, and $k_e=2.293\times10^6$ dynes/cm. For thermal atoms at 400°K it was found that $\pi S_0^2=4.5\times10^{-15}$ cm^2. Although it seems improbable at a temperature as high as 400°K, it may be possible that the nitrogen-nitrogen spin exchange cross section may have been underestimated because the Van der Waals' forces have not been treated correctly.

In order to understand the exchange of populations in spin exchange, the case of nitrogen and sodium with no nuclear spins will be considered. It will be assumed that the relaxation times for the ground states of these two atoms is very long. If the populations of the various nitrogen states are denoted by $a_{\frac{3}{2}}$, $a_{\frac{1}{2}}$, $a_{-\frac{1}{2}}$, and $a_{-\frac{3}{2}}$ and the sodium by $b_{\frac{1}{2}}$ and $b_{-\frac{1}{2}}$ then the change in the

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[19] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

populations due to spin-exchange collisions is given by

$$
\begin{aligned}
da_{\frac{3}{2}}/dt&=\tfrac{1}{8}\pi S_0{}^2v[-3a_{\frac{3}{2}}b_{-\frac{1}{2}}+3a_{\frac{1}{2}}b_{\frac{1}{2}}],\\
da_{\frac{1}{2}}/dt&=\tfrac{1}{8}\pi S_0{}^2v[3a_{\frac{3}{2}}b_{-\frac{1}{2}}-3a_{\frac{1}{2}}b_{\frac{1}{2}}-4a_{\frac{1}{2}}b_{-\frac{1}{2}}+4a_{-\frac{1}{2}}b_{\frac{1}{2}}],\\
da_{-\frac{1}{2}}/dt&=\tfrac{1}{8}\pi S_0{}^2v[4a_{\frac{1}{2}}b_{-\frac{1}{2}}-4a_{-\frac{1}{2}}b_{\frac{1}{2}}-3a_{-\frac{1}{2}}b_{-\frac{1}{2}}+3a_{-\frac{3}{2}}b_{\frac{1}{2}}],\\
da_{-\frac{3}{2}}/dt&=\tfrac{1}{8}\pi S_0{}^2v[3a_{-\frac{1}{2}}b_{-\frac{1}{2}}-3a_{-\frac{3}{2}}b_{\frac{1}{2}}],\\
db_{\frac{1}{2}}/dt&=\tfrac{1}{8}\pi S_0{}^2v[-(3a_{\frac{1}{2}}+4a_{-\frac{1}{2}}+3a_{-\frac{3}{2}})b_{\frac{1}{2}}\\
&\qquad\qquad+(3a_{\frac{3}{2}}+4a_{\frac{1}{2}}+3a_{-\frac{1}{2}})b_{-\frac{1}{2}}],\\
db_{-\frac{1}{2}}/dt&=\tfrac{1}{8}\pi S_0{}^2v[(3a_{\frac{1}{2}}+4a_{-\frac{1}{2}}+3a_{-\frac{3}{2}})b_{\frac{1}{2}}\\
&\qquad\qquad-(3a_{\frac{3}{2}}+4a_{\frac{1}{2}}+3a_{-\frac{1}{2}})b_{-\frac{1}{2}}],\\
N_1&=a_{\frac{3}{2}}+a_{\frac{1}{2}}+a_{-\frac{1}{2}}+a_{-\frac{3}{2}},\\
N_2&=b_{\frac{1}{2}}+b_{-\frac{1}{2}},
\end{aligned}
$$

where $\pi S_0{}^2$ is the area related to the cross section for the Na–N system, where N_1 is the total number of N atoms, and where N_2 is the total number of Na atoms. Direct substitution into these equations shows that in the steady state the solution is given by

$$
\begin{gathered}
a_{\frac{3}{2}}:a_{\frac{1}{2}}:a_{-\frac{1}{2}}:a_{-\frac{3}{2}}=\alpha^3:\alpha^2:\alpha:1,\\
b_{\frac{1}{2}}:b_{-\frac{1}{2}}=\alpha:1.
\end{gathered}
$$

This solution suggests the general form of the steady-state solution for all spin-exchange problems. It is the most probable way in which two sets of particles can be arranged so that the number of particles in each set is a constant and so that the total z component of angular momentum is a constant. This implies that the density matrix for a system of Na and N in spin-exchange equilibrium is given by

$$
\rho=\frac{\exp[-(I_{1z}+S_{1z})\beta]\exp[-(I_{2z}+S_{2z})\beta]}{\mathrm{Tr}\{\exp[-(I_{1z}+S_{1z})\beta]\exp[-(I_{2z}+S_{2z})\beta]\}},
$$

where β is such that the total z component of angular momentum of the system is given by $\mathrm{Tr}[(I_{1z}+S_{1z}+I_{2z}+S_{2z})\rho]$. The parameter β might be called an angular momentum spin temperature. It has been shown by Hawkins[20] that for optical pumping by a sodium light source emitting equal amounts of D_1 and D_2 radiation with no reorientation in the excited states, the population of the sodium hyperfine states can be closely approximated by a density matrix of this form. In the case of reorientation in the excited state, the situation is more complicated.[21,22] The application of this theory to the experimental situation encountered will be discussed in the section on the experimental results. Figure 4 shows the relative populations of N^{14}, N^{15}, and Na^{23} in spin-exchange equilibrium.

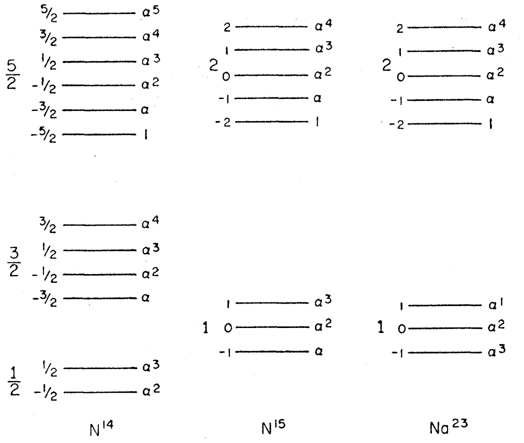

FIG. 4. The relative populations for N^{14}, N^{15}, and Na^{23} in spin-spin equilibrium. The parameter α must be determined from the total angular momentum of the ensemble. Note.—In lower column of Na^{23}, top and bottom rows, the numbers 1 and −1 should be reversed, to now read "−1—a^1, 0—a^2, 1—a^3."

D. The Optical Pumping Apparatus and Experimental Results

The physical arrangement of the apparatus used for the optical pumping experiment is shown in Fig. 1. A General Electric Na–I sodium lamp mounted in an oven produced the sodium resonance radiation. This light was then passed through a circular polarizing filter made by the Polaroid Corporation. The light subsequently passed through the absorption cell, which was mounted in another oven and was finally focused on a 929 photocell. The output of the photocell was sent to a Tektronix type 122 preamplifier and then to a Tektronix type 512 oscilloscope.

The absorption cell, which was a 500-cc spherical flask, contained a small amount of vacuum distilled sodium, 1 cm Hg of nitrogen, and 1 to 3 cm Hg of spectroscopically pure neon or argon. This bulb was provided with two uranium glass-covered tungsten leads. These leads were used to produce a 30-Mc/sec pulsed discharge in the bulb.

The oven containing the absorption cell was mounted at the center of a set of 32-inch-diameter Helmholtz coils. These coils were used to produce a magnetic field along the direction of the light beam. The axis of the apparatus was oriented so that it coincided with the horizontal component of the earth's field. Another set of coils was used to cancel the vertical component of the earth's field.

A ten-turn solenoid five inches in diameter was used to produce the radio-frequency field for inducing the transitions. The frequency source was a General Radio 805B oscillator. Frequency measurements were made with a Hewlett-Packard 524B frequency counter. For the measurement of the frequency the laboratory 100-kc/sec standard was used as a time base. This frequency is continuously checked with other standards

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[20] W. B. Hawkins, Phys. Rev. **98**, 478 (1955). See Table II.

[21] W. E. Bell and A. L. Bloom, Phys. Rev. **107**, 1559 (1957); H. G. Dehmelt, *ibid.* **105**, 1487 (1957).

[22] P. Bender, thesis (unpublished) Princeton University (1956). This thesis contains a calculation of the state populations for the case of reorientation in the excited state for the electron spin, but no reorientation of the nuclear spin. In this case the density matrix is almost that which we have found for spin-spin equilibrium.

and with an Atomichron made by National Company, and is stable to 1 part in 10^9.

The dc magnetic field was modulated at a 20-cps rate. This 20-cps frequency was phase locked to the 60-cps voltage in the room. At one point in each cycle the oscillator, which produced the discharge, was gated on for 3 msec. This produced an intense discharge in the bulb and dissociated some of the nitrogen molecules into atoms. A short time constant was used in the preamplifier to shorten the recovery from the overload produced by the discharge. During observations the temperature of the oven was always adjusted so as to maximize the signals. This generally corresponded to 50% absorption by the cell. The measurements were made by setting the signals at a fixed point on the oscilloscope and reading the frequency. Provisions were made so that the phase of the sweep could be changed by 180° to permit observation of the transitions with both increasing and decreasing magnetic fields.

The largest source of error in this experiment is due to the dependence of the line frequency observed in this fashion upon the direction of the modulation sweep relative to the orientation of the static magnetic field. This shift apparently arises from the population dependence of the various sublevels upon whether left or right circularly polarized light is used and upon the extra delay time in the observation produced by the spin exchange collision time. This type of asymmetry is frequently found in double resonance experiments.[23] Extensive investigations were made to arrive at a procedure which would yield results free from any systematic error. It was found that, if the measurements were made by averaging the two readings obtained with the modulation field both increasing and decreasing, the g-factors of the Zeeman transitions of atomic nitrogen could be measured consistently and agreed with the values calculated using Heald and Beringer's value for the g-factor of atomic nitrogen,

$$-g_J/g(\text{proton}) = 658.163 \pm 0.010.$$

Consequently, this method was adopted for making the measurements. In addition measurements were made with the static field both parallel and antiparallel to the direction of propagation of the light beam.

The source of line width in this experiment is not well understood. The apparent width of the signal as displayed on the oscilloscope is a combination of the true line width and the time necessary for the nitrogen to depolarize the sodium. Consequently it is difficult to determine the line width directly from the observed signals. The line width can, however, be estimated from the distribution of successive measurements. This gives a line width for the nitrogen signals of 2 kc/sec. This width is the same for all the observed transitions. If the populations of the nitrogen magnetic substates are assumed to be those expected for the most probable distribution for a system containing a given amount of angular momentum and if the line widths of the nitrogen are assumed to be the same for all transitions, then the relative amplitudes of the signals as displayed on the oscilloscope can be understood. In Table I the amplitudes of the transitions in N^{15} are listed together with the amplitudes calculated on the basis of this simple model. It is clear that the relative amplitudes of the pairs of hyperfine transitions with the same dependence on magnetic field (i.e., $F, M \rightarrow F+1, M+1$, and $F, M \rightarrow F+1, M-1$) are given by this analysis. However, the relative amplitudes for any pair of lines are not given with precision by this model.

TABLE I. The observed and predicted relative amplitudes for the $\Delta M = \pm 1$ transitions in N^{15}. The calculations labeled A were made assuming that the line width in frequency was the same for all lines. The calculations labeled B were made assuming that the line width was produced by an inhomogeneous magnetic field.

Transition	Observed amplitude	Calculated amplitude A	B
$(2,2) \rightarrow (2,1)$	1.1	1.2	1.2
$(2,1) \rightarrow (2,0)$	1.2	1.0	1.0
$(2,0) \rightarrow (2,-1)$	0.8	0.8	0.8
$(2,-1) \rightarrow (2,-2)$	0.6	0.7	0.6
$(1,1) \rightarrow (1,0)$	1.5	1.6	1.0
$(1,0) \rightarrow (1,-1)$	1.2	1.3	0.8
$(2,0) \rightarrow (1,-1)$	1.0	1.3	1.3
$(2,1) \rightarrow (1,0)$	1.15	1.0	1.6
$(2,2) \rightarrow (1,1)$	0.6	0.4	2.0
$(2,-2) \rightarrow (1,-1)$	0.33	0.2	1.0
$(2,-1) \rightarrow (1,0)$	0.88	0.8	1.3
$(2,0) \rightarrow (1,1)$	1.05	1.6	1.6

The sodium line width measured using the oscilloscope signal was 600 cycles/sec. It has been pointed out by Bloom[24] that a signal observed in this "fast passage" fashion cannot be easily interpreted in terms of the true line width. The sodium line width was not increased by more than 200 cycles/sec when the atomic nitrogen was present. From this and the exchange cross section an upper limit can be placed on the concentration of atomic nitrogen present. This is $N = 2\pi\delta\nu/v\sigma = 1.3 \times 10^{11}$ atoms/cc.

The line width of the nitrogen hyperfine transitions is approximately 2 kc/sec. If it is assumed that the nitrogen concentration is $N = 1.3 \times 10^{11}$ atoms/cc and that the spin-exchange cross section is indeed $\sigma = 4.5 \times 10^{-15}$ cm^2 then the nitrogen line width due to collisions between two nitrogen atoms is only $\delta\nu = 30$ cycles/sec. Thus some other mechanism must be responsible for broadening the line. It is felt that broadening due to magnetic field inhomogeneity is not the cause because if this were the case the lines which have the smallest dependence on magnetic field would be the narrowest, which is certainly not so. The most probable mechanism for explaining this line width is the collision of a nitrogen atom with a nitrogen molecule during which the atom is exchanged with one of the atoms making

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[23] J. Eisinger and G. Feher, Phys. Rev. **109**, 1172 (1958).

[24] A. Bloom, J. phys. radium **19**, 881 (1958).

up the molecule. This is an important mechanism for the para- to ortho-hydrogen conversion. Using the observed line width, a value for this cross section can be obtained:

$$\sigma=\frac{2\pi(\delta\nu)}{Nv}=\frac{(6.28)(2000)}{(0.33\times10^{18})(10^5)}=3.6\times10^{-19}\text{ cm}^2.$$

If it is assumed that the collision diameter of N_2 is 2 A, then this cross section can be used to calculate the potential barrier preventing this reaction. Thus $\sigma=(\pi/4)(2\text{ A})^2f$ where f is the fraction of the time a particle has a velocity large enough to overcome the potential barrier. This is assumed to be the same as the fraction of particles, in a Maxwell-Boltzmann distribution, having a velocity large enough to overcome this potential barrier. This value is $f=1.2\times10^{-3}$. This leads to the conclusion that the critical velocity for the reaction is $v_C=2.5\bar{v}$, where $\bar{v}$ is the average velocity of a thermal atom at $T=400$°K. This means that the potential barrier opposing the collision is

$$V\sim\tfrac{1}{2}mv_0^2=0.35\text{ ev}.$$

The component along the axis of the apparatus of the 60-cycle/sec stray magnetic field is 1 milligauss. This is $\frac{1}{5}$ the amplitude of the 20-cycle/sec modulation field. The stray field has high-frequency components which could broaden the line slightly, but its principal effect is to distort the observed line shape.

The following procedure was used in making the measurements of the hyperfine splittings. All of the observations were made in a field of approximately 0.07 gauss. Only the $\Delta F=\pm1$, $\Delta M=\pm1$ nitrogen π-transitions were observed. The measurements were made in sets of four, two with one phase of the modulation field and two with the modulation shifted by 180°. The sodium line was measured first as a calibration, then each of the hyperfine transitions in a given $F\rightarrow F\pm1$ multiplet were measured and then finally the sodium was measured again. In any given $F\rightarrow F\pm1$ set of lines there always occur pairs such that when their sum is taken there is only a quadratic dependence upon the external magnetic field. The data was analyzed by combining the lines in this manner. The second-order corrections were then computed from the measured value of the magnetic field and the value of the zero-field hyperfine splitting derived. A typical set of observed signals are shown in Figs. 5 and 6.

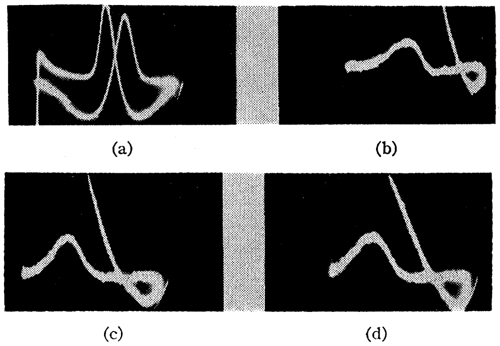
(a) (b) (c) (d)

FIG. 5. The hyperfine transitions in atomic nitrogen. (a) The Zeeman pattern in atomic sodium at a field of about 0.07 gauss. (b) The hyperfine transition $F=2$, $M_F=0\rightarrow F=1$, $M_F=-1$ in N^{15}. (c) The hyperfine transition $F=\frac{5}{2}$, $M_F=-\frac{1}{2}\rightarrow F=\frac{3}{2}$, $M_F=-\frac{3}{2}$ in N^{14}. (d) The hyperfine transition $F=\frac{3}{2}$, $M_F=-\frac{1}{2}\rightarrow F=\frac{1}{2}$, $M_F=\frac{1}{2}$ in N^{14}.

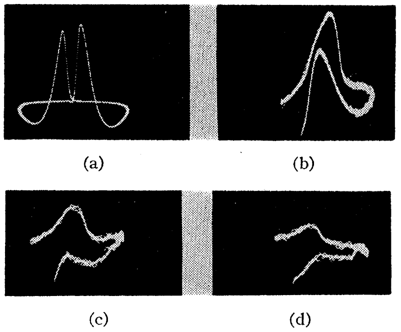
(a) (b) (c) (d)

FIG. 6. The Zeeman transitions in atomic N^{15}. (a) The Zeeman transitions in atomic sodium at a field of 0.07 gauss, without the radio-frequency discharge on. (b) The Zeeman transitions in the $F=2$ state of N^{15} at a field of 0.07 gauss. (c) The Zeeman transitions in the $F=1$ state of N^{15} at a field of 0.07 gauss. (d) The Zeeman transition $F=2$, $M_F=2\rightarrow F=2$, $M_F=1$ in N^{15} at a field of about 3 gauss.

For N^{15} there are three such pairs of transitions

$$\left.\begin{matrix}(2,0)\rightarrow(1,1)\\(2,0)\rightarrow(1,-1)\end{matrix}\right\},\quad \left.\begin{matrix}(2,1)\rightarrow(1,0)\\(2,-1)\rightarrow(1,0)\end{matrix}\right\},\quad \left.\begin{matrix}(2,2)\rightarrow(1,1)\\(2,-2)\rightarrow(1,-1)\end{matrix}\right\}.$$

For nitrogen N^{14} there are four such pairs in the $F=\frac{5}{2}\rightarrow\frac{3}{2}$ multiplet and two in the $F=\frac{1}{2}\rightarrow\frac{3}{2}$ multiplet.

The results of the measurements on the various lines in N^{14} are shown in Table II and those of N^{15} are shown in Table III. The errors quoted in these measurements are the standard deviations.

To see if there was any dependence of the transition frequency upon the pressure of the buffer gas, bulbs were prepared with neon pressures of 1 to 3 cm Hg and with the neon replaced by argon. The pressure shift was less than 10 cycles/mm Hg neon and there was no observable shift when the neon was replaced by argon. This result is reasonable. It has been shown that the Stark shift of the hyperfine transition in hydrogen, $\Delta(\mathcal{E})$, is proportional to the hyperfine separation,[25] i.e., $\Delta(\mathcal{E})=\mathcal{E}^2f\Delta\nu$, where f depends on the structure of the hydrogen atom. If it is assumed that the pressure shift is essentially a Stark type effect and that

$$\Delta(\mathcal{E})=\mathcal{E}^2f\Delta\nu,$$

where f is characteristic of a particular atom, holds

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[25] R. D. Haun and J. R. Zacharias, Phys. Rev. **107**, 107 (1957).

TABLE II. The values found for the zero-field hyperfine splittings in N^{14} using the different pairs of transitions. Only one set of transitions were measured for the $\frac{3}{2}\rightarrow\frac{1}{2}$ multiplet. The quoted errors are standard deviations.

$F=3/2\rightarrow 5/2$	$2(\Delta\nu)_{5/2\rightarrow 3/2}$ Mc/sec
$M_F=(-\frac{3}{2}\rightarrow -\frac{1}{2})+(\frac{3}{2}\rightarrow \frac{1}{2})$	52.254499 ± 0.000079
$(-\frac{1}{2}\rightarrow \frac{1}{2})+(\frac{1}{2}\rightarrow -\frac{1}{2})$	52.254454 ± 0.000101
$(\frac{1}{2}\rightarrow \frac{3}{2})+(-\frac{1}{2}\rightarrow -\frac{3}{2})$	52.254327 ± 0.000154
$(\frac{3}{2}\rightarrow \frac{5}{2})+(-\frac{3}{2}\rightarrow -\frac{5}{2})$	52.254395 ± 0.000145
$F=1/2\rightarrow 3/2$	$2(\Delta\nu)_{3/2\rightarrow 1/2}$ Mc/sec
$M_F=(\frac{1}{2}\rightarrow -\frac{1}{2})+(-\frac{1}{2}\rightarrow \frac{1}{2})$	31.352927 ± 0.00085

generally, then it would be expected that the pressure shift in nitrogen ($\Delta\nu=30$ Mc/sec) would be much less than for Cs ($\Delta\nu=9000$ Mc/sec). The observed shift in neon for Cs is about 600 cycles/mm Hg.[26,27] On this basis the nitrogen shift would only be approximately 2 cycles/mm Hg of neon.

To determine the sign of the hyperfine interaction constant, the nitrogen Zeeman patterns were studied in a high magnetic field. This experiment utilized the fact that if the circular polarization of the light is known then it is also known whether the states of positive m values are more populated than those of negative m values. To see this consider the case of N^{15}. If right circularly polarized light is incident upon the sample, so that only $\Delta M=-1$ transitions are induced, then the state with $F=1$, $M=-1$ will have a greater population than those with $F=1$, $M=0$ and $F=1$, $M=+1$. Hence the transition $(F=+1, M=-1)\rightarrow(F=1, M=0)$ will be more intense than the transition $(F=1, M=0)\rightarrow(F=1, M=1)$. If $A>0$ then the most intense transition will occur at a lower frequency than the weaker one and if $A<0$ the most intense transition will occur at a higher frequency than the weaker one. By examining the intensity of the various Zeeman patterns in a high field it was found that $A(15)<0$ and $A(14)>0$. This agrees with the signs expected for normal hydrogen-type hyperfine splitting with negative and positive nuclear magnetic moments in N^{15} and N^{14}, respectively.

The final values obtained for N^{14} are

$$\Delta\nu(14)_{\frac{5}{2}-\frac{3}{2}}=26.12721\pm 0.00018 \text{ Mc/sec},$$

$$\Delta\nu(14)_{\frac{3}{2}-\frac{1}{2}}=15.67646\pm 0.00012 \text{ Mc/sec}.$$

The quoted error is six probable errors. These two results can be used to determine the magnetic dipole and electric quadrupole interaction constants. The intervals are given by

$$\Delta\nu(14)_{\frac{5}{2}-\frac{3}{2}}=\tfrac{5}{2}A+5/4B,$$

$$\Delta\nu(14)_{\frac{3}{2}-\frac{1}{2}}=\tfrac{3}{2}A-9/4B.$$

When solved these equations give the following values for A and B:

$$A=+10.45091\pm 0.00007 \text{ Mc/sec},$$

$$B=-0.00005\pm 0.00008 \text{ Mc/sec}.$$

There is no statistically significant deviation from the interval rule. This value differs from the earlier reported value of Holloway and Novick.[8]

The value obtained for the N^{15} hyperfine splitting is

$$\Delta\nu(15)=29.29136\pm 0.00016 \text{ Mc/sec},$$

and the corresponding value of the magnetic dipole hyperfine constant is

$$A(15)=-14.64568\pm 0.00008 \text{ Mc/sec}.$$

NUCLEAR MOMENTS OF N^{14} AND N^{15}

A. Theory of the Experiment

Previous to this experiment, the nuclear magnetic moments of N^{14} and N^{15} were measured both by the molecular beam method[10,11] and by nuclear magnetic resonance.[12] The ratio of the two gyromagnetic ratios, $g(14)/g(15)$, was only known to one part in 10^4, however. For the remeasurement in this experiment it was decided to use a double resonance method. A complex, $(NH_4)^+$, was selected in which the N^{14} quadrupole interaction was small and in which the proton resonance satellites produced by the interaction with the nitrogen magnetic moment could be easily observed.[28,29] The nitrogen resonance was then detected by applying a radio-frequency field at the nitrogen frequency and observing the change in the structure of the proton resonance.

TABLE III. The values found for the zero-field hyperfine splitting of N^{15} using the different pairs of transitions. The quoted errors are standard deviations.

$F=1\rightarrow 2$	$2(\Delta\nu)$ Mc/sec
$m_F=(-1\rightarrow 0)+(1\rightarrow 0)$	58.583171 ± 0.000162
$(0\rightarrow 1)+(0\rightarrow -1)$	58.582455 ± 0.000146
$(1\rightarrow 2)+(-1\rightarrow -2)$	58.582557 ± 0.000131

For a species such as the $(N^{14}H_4)^+$ ion which contains two types of nuclei, whose gyromagnetic ratios are different, the nuclear magnetic resonance signal of one nucleus is split into a multiplet of lines by an interaction of the form $\mathcal{A}\mathbf{I}_1\cdot\mathbf{I}_2$ with the other nucleus.[30] This interaction is produced by the coupling of one nucleus to the other through the electron cloud.[31] The Hamiltonian for the NH_4^+ system is

$$\mathcal{H}=-\sum_{i=1}^{4} g_1\mu_n\mathbf{H}\cdot\mathbf{I}_{1i}-g_2\mu_n\mathbf{H}\cdot\mathbf{I}_2+\sum_{i=1}^{4}\mathcal{A}\mathbf{I}_{1i}\cdot\mathbf{I}_2, \quad (1)$$

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[26] M. Arditi and T. R. Carver, Phys. Rev. **112**, 449 (1958).

[27] Beaty, Bender, and Chi, Phys. Rev. **112**, 450 (1958).

[28] R. A. Ogg, Jr., and J. D. Ray, J. Chem. Phys. **26**, 1339 (1957).

[29] Schmidt, Brown, and Williams, J. Mol. Spectroscopy **2**, 539 (1958).

[30] Gutowsky, McCall, and Slichter, J. Chem. Phys. **21**, 279 (1953).

[31] N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).

where μ_n is the nuclear magneton, 1 refers to the proton, 2 to the nitrogen nucleus, and the summation is over the four equivalent protons. In a static magnetic field $\mathbf{H}=\mathrm{H}_0\hat{k}$ the energy levels of this Hamiltonian are

$$E(M_1,M_2)=-g_1\mu_nH_0M_1-g_2\mu_nH_0M_2+\mathcal{A}M_1M_2, \quad (2)$$

where

$$M_1=\sum_{i=1}^{4} M_{1_i}.$$

Throughout the discussion it will be convenient to use the effective total proton spin $\mathbf{I}_1=\sum_{i=1}^{4}\mathbf{I}_{i1}$. These energy levels are shown in Fig. 7. The allowed proton transitions ($\Delta M_1=\pm1$, $\Delta M_2=0$) occur at the frequencies

$$h\nu_1(M_2)=-g_1\mu_nH_0+\mathcal{A}M_2,$$

and the allowed nitrogen transitions ($\Delta M_1=0$, $\Delta M_2=\pm1$) occur at

$$h\nu_2(M_1)=-g_2\mu_nH_0+\mathcal{A}M_1.$$

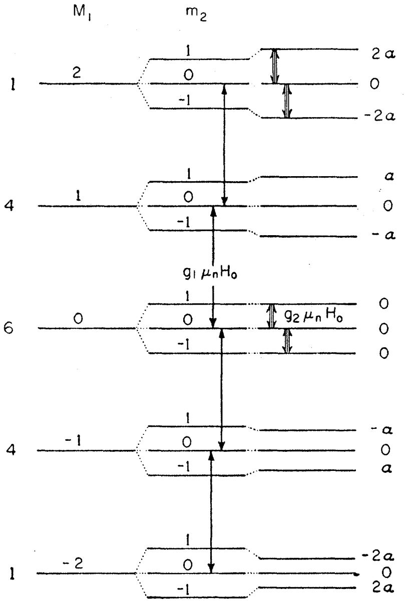

FIG. 7. The energy levels of $N^{14}H_4^+$. M_1 refers to the total z component of angular momentum of the protons and M_2 to the z component of spin of the nitrogen. The statistical weights of the levels are shown beside the levels.

For $(N^{14}H_4)^+$, $M_1=2, 1, 0, -1, -2$, and $M_2=1, 0, -1$. Thus the proton resonance is split into three equally spaced components and the nitrogen resonance into five equally spaced components. The pattern of lines which would be observed if resonance experiments were performed on the nitrogen and hydrogen separately are shown in Fig. 8.

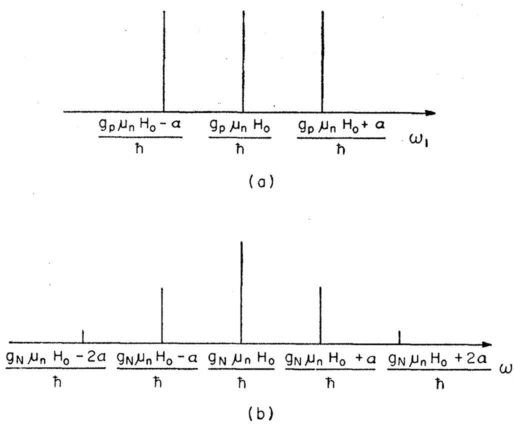

FIG. 8. The calculated positions of the resonance lines for $N^{14}H_4^+$. (a) The proton resonances. (b) The nitrogen resonances.

To obtain the relative effect upon the proton resonances of a second radio-frequency field applied at the various nitrogen frequencies assume that $\nu_1(1)$, $\nu_1(0)$, and $\nu_1(-1)$ are being observed simultaneously. If $\nu_2(M_1)$ is now applied to the sample, the populations in the states $(M_1, M_2=1)$, $(M_1, M_2=0)$, and $(M_1, M_2=-1)$ will be altered so that all three of the proton resonances are affected. The relative intensity of the effect of driving $\nu_2(M_1)$ on the proton signals is given by the number of states with the quantum number M_1 multiplied by the number of transitions going to a given sublevel (M_1,M_2). The results of this calculation are shown in Table IV. In Fig. 7 the situation corresponding to the observation of the transition $\nu_1(0)$ and the saturation of $\nu_2(2)$ and $\nu_2(0)$ is shown graphically.

To properly interpret the double resonance experiment it is necessary to find the energy levels for the case where the applied magnetic field has a large oscillating component. If the ineffective rotating component of the oscillating field is neglected, then the magnetic field is

$$\mathbf{H}=H_0\hat{k}+(H_1\cos\omega_1t+H_2\cos\omega_2t)\hat{\imath}+(H_1\sin\omega_1t+H_2\sin\omega_2t)\hat{\jmath}. \quad (3)$$

For this experiment $\mathrm{H}_2\gg\mathrm{H}_1$ and this problem is similar to one treated by Bloom and Schoolery.[32] The Schrödinger equation for this case is

$$i\hbar\partial\psi/\partial t=\mathcal{H}\psi=E\psi,$$

where the state of the system is assumed to be an energy eigenstate and where the Hamilton, $\mathcal{H}$, is given by Eq. (1) with the magnetic field given by Eq. (3).

TABLE IV. Calculated relative intensity of the effect upon the three equal proton resonance lines of applying a radio-frequency field at the nitrogen frequencies. $\nu_2(M_1)$ designates the nitrogen transition for which the total z components of the proton spin is M_1.

Nitrogen transition	$\nu_2(2)$	$\nu_2(1)$	$\nu_2(0)$	$\nu_2(-1)$	$\nu_2(-2)$
Intensity	1	8	12	8	1

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[32] A. L. Bloom and J. N. Schoolery, Phys. Rev. **97**, 1261 (1955).

TABLE V. Line positions computed for $(N^{14}H_4)^+$ for large H_2 field at the nitrogen resonance frequency ($\hbar\omega_2=g_2\mu_nH_0$). The calculations were made for the case where $g_2\mu_nH_2=\mathcal{A}$. $g_2\mu_n\Delta H$ has been neglected.

Transition $(M_1,M_2)\to(M_1',M_2')$				Position of line
2	$-1\to$	1	1	-3.6
-1	$1\to$	-2	1	-3.6
1	$-1\to$	0	1	-2.4
0	$1\to$	-1	-1	-2.4
2	$-1\to$	1	0	-2.2
-1	$0\to$	-2	1	-2.2
2	$0\to$	1	1	-1.4
-1	$-1\to$	-2	0	-1.4
1	$-1\to$	0	0	-1.4
0	$0\to$	-1	1	-1.4
1	$0\to$	0	1	-1.0
0	$1\to$	-1	0	-1.0
2	$-1\to$	1	-1	-0.8
-1	$-1\to$	-2	-1	-0.8
1	$-1\to$	0	-1	-0.4
M_1	$0\to$	M_1-1	0	0.0
1	$1\to$	0	1	$+0.4$
0	$1\to$	-1	1	$+0.4$
2	$1\to$	1	1	$+0.8$
-1	$1\to$	-2	1	$+0.8$
1	$0\to$	0	-1	$+1.0$
0	$-1\to$	-1	0	$+1.0$
2	$0\to$	1	-1	$+1.4$
-1	$1\to$	-2	0	$+1.4$
1	$1\to$	0	0	$+1.4$
0	$0\to$	-1	-1	$+1.4$
-1	$0\to$	-2	-1	$+2.2$
2	$1\to$	1	0	$+2.2$
0	$-1\to$	-1	1	$+2.4$
1	$1\to$	0	-1	$+2.4$
2	$1\to$	1	-1	$+3.6$
-1	$-1\to$	-2	1	$+3.6$

If the unitary transformation

$$u=\exp(i\boldsymbol{\omega}_2\cdot\mathbf{I}t),$$

where

$$\mathbf{I}=\mathbf{I}_1+\mathbf{I}_2;\quad \mathbf{I}_1=\sum_{i=1}^{4}\mathbf{I}_{1i},$$

and

$$\boldsymbol{\omega}_2=-\omega_2\hat{k},$$

is used to transform to a rotating coordinate system, the new Hamiltonian and wave function are given by

$$\mathcal{H}_R=\exp(i\boldsymbol{\omega}_2\cdot\mathbf{I}t)\mathcal{H}\exp(-i\boldsymbol{\omega}_2\cdot\mathbf{I}t),$$
$$\psi_R=\exp(i\boldsymbol{\omega}_2\cdot\mathbf{I}t)\psi.$$

This leads to

$$i\hbar\dot{\psi}_R=[-(g_1\mu_nH_0-\hbar\omega_2)I_{1z}-(g_2\mu_nH_0-\hbar\omega_2)I_{2z}+\mathcal{A}\mathbf{I}_1\cdot\mathbf{I}_2-g_1\mu_nH_2I_{1x}-g_2\mu_nH_2I_{2x}]\psi_R=(E+\hbar\omega_2I_z)\psi_R.$$

Hence the effective Hamiltonian in the rotating system is

$$\mathcal{H}'=-(g_1\mu_nH_0-\hbar\omega_2)I_{1z}-(g_2\mu_nH_0-\hbar\omega_2)I_{2z}+\mathcal{A}\mathbf{I}_1\cdot\mathbf{I}_2-g_1\mu_nH_2I_{1x}-g_2\mu_nH_2I_{2x}.$$

For the case where

$$\omega_2\sim g_2\mu_nH_0/\hbar,$$

the effective magnetic field seen by nucleus 1 is

$$(H_0-\hbar\omega_2/g_1\mu_n)\hat{k}+H_2\hat{\imath}.$$

The effective field seen by nucleus 2 is

$$(H_0-\hbar\omega_2/g_2\mu_n-\mathcal{A}M_1/g_2\mu_n)\hat{k}+H_2\hat{\imath}.$$

Here the interaction $\mathcal{A}\mathbf{I}_1\cdot\mathbf{I}_2$ has been regarded as producing an effective field at nucleus 2. Since the effect of H_2 on nucleus 1 is small, the eigenvalues of $\mathcal{H}'$ can approximately be written

$$E'=-(g_1\mu_nH_0-\hbar\omega_2)M_1-M_2[(g_2\mu_nH_0-\mathcal{A}M_1-\hbar\omega_2)^2+(g_2\mu_nH_2)^2]^{\frac{1}{2}},$$

where M_1 is the projection of I_1 along the z axis and M_2 is the projection of I_2 along the effective field at nucleus 2. This calculation neglects second order effects due to $\mathcal{A}\mathbf{I}_1\cdot\mathbf{I}_2$. The selection rule $\Delta M_1=\pm1$, $\Delta M_2=0$ does not hold in this case since the effective field of nucleus 2 changes when M_1 changes; consequently, a state with a given value of M_2 and one value of M_1 may not be orthogonal to a state with different values of M_2 and M_1. The energies of the various transitions are given by

$$\Delta E=E'(M_1,M_2)-E'(M_1',M_2')+\hbar\omega_2.$$

The approximate selection rule

$$\Delta M=\pm1,\quad \Delta M_2=0,\ \pm1,\ \pm2,$$

is valid if there are no double-quantum transitions. In order to calculate the observed pattern of signals ω_2 was assumed to be at resonance so that

$$\hbar\omega_2=g_2\mu_nH_0,$$

and H was written as $H_0+\Delta H$. The ΔH's for which the proton was at resonance so that

$$\Delta E=\hbar\omega_1$$

were then found. It was found that the best fit to the

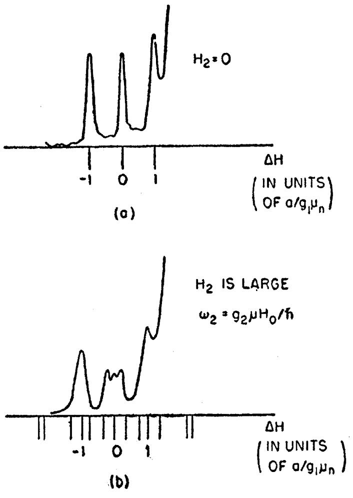

FIG. 9. (a) The theoretical positions at which the proton resonances should occur when $H_2=0$. The observed resonances are shown above the calculated ones. (b) The theoretical positions for the proton resonances when H_2 is large and $\hbar\omega_2=g_2\mu_nH_0$.

experimental data was obtained for a H_2 such that

$$g_2\mu_n H_2 \sim \mathcal{A}.$$

Table V shows the calculated positions of the transitions. Since $g_2 \ll g_1$, $g_2\mu_n\Delta H$ was neglected in constructing this table. Figure 9 shows the observable transitions for the case $H_2=0$ and the case H_2 large and such that $\hbar\omega_2=g_2\mu_n H_0$ together with the experimentally observed line patterns. No attempt was made to calculate the relative intensities of the lines.

B. The Experimental Results

A Varian Associates high-resolution spectrometer and electromagnet were used to observe the nuclear resonance. This was a standard spectrometer built to operate with the proton frequency at 40 Mc/sec. The spectrometer head was modified so that the transmitter coil could be driven both by a source at the proton frequency (40 Mc/sec) and by a source at the nitrogen frequencies (3 and 4 Mc/sec). Provisions were made to decouple the two sources but no effort was made to make the transmitter coil resonant at the nitrogen frequencies. A General Radio type 616D oscillator and a small power amplifier were used to produce the radio-frequency signals at the nitrogen frequencies. Although this oscillator was not stable enough to remain on the nitrogen resonance for long periods of time, sufficient accuracy was obtained by allowing the oscillator to drift through the nitrogen resonance frequency slowly as the temperature of the tank circuit changed. A Hewlett-Packard 524B frequency counter was used to measure the frequency of the nitrogen oscillator every 2 seconds. The proton's frequency was checked periodically. In this manner any drift of the main magnetic field could be corrected for.

The nuclear double resonance was performed in a saturated (17°C) solution of NH_4Cl in 3:1 H_2O-HCl. The NH_4^+ ion was selected because of the strength of the resonance signals and because it has a very small quadrupole interaction.[24] This made it possible for the spin-lattice relaxation times for N^{14}, which has a quadrupole moment, and for N^{15}, which has no quadrupole moment, to be approximately the same. Measurements were made in a sample containing both $N^{14}H_4^+$ and $N^{15}H_4^+$, so that their chemical environments were identical. A typical run through the resonance in $N^{14}H_4^+$ is shown in Fig. 10. The three proton resonances were observed to change radically as the nitrogen resonance was approached. Similar curves were obtained for $N^{15}H_4^+$. Only three resonances near $\hbar\omega_2=g_2\mu_n H_0$ were observed in this experiment. The ratio of their intensities was 5, 7, 5. The intensities were nearly those expected for the transitions

$$M_1=1,\ M_2=\pm1 \rightarrow M_1=1,\ M_2=0,$$
$$M_1=0,\ M_2=\pm1 \rightarrow M_1=0,\ M_2=0,$$
$$M_1=-1,\ M_2=\pm1 \rightarrow M_1=-1,\ M_2=0.$$

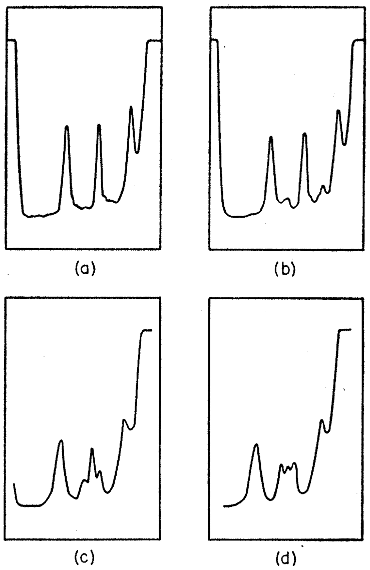

FIG. 10. A typical set of recorder traces of the proton resonances as the nitrogen resonance is approached. The large peak on the right is the proton resonance in water. The proton frequency was $\nu_1=39.999\,400\,0$ Mc/sec and the separation of the three resonances is 61.5 cycles per second. (a) $\nu_2=2.889506$ Mc/sec, (b) $\nu_2=2.889460$ Mc/sec, (c) $\nu_2=2.889447$ Mc/sec, (d) $\nu_2=2.889434$ Mc/sec.

Also, the separation of these resonances was the same as the separation of the proton resonances. Thus their identification was complete. The resonances corresponding to the transitions

$$M_1=\pm2,\ M_2=\pm1 \rightarrow M_1=\pm2,\ M_2=0,$$

were not observed. Their intensity should theoretically have been 0.6, which would have been only about $\frac{1}{3}$ the size of the noise and hence difficult to detect.

Five runs were made on both N^{15} and N^{14} in the same sample. The results are shown below. The errors quoted are six probable errors.

$$g(15)/g(14)=2\mu(15)/\mu(14)$$
$$=-1.402\,757\,6\pm0.000\,001\,5,$$
$$|g(14)/g(\mathrm{H}')|=0.072\,236\,947\pm0.000\,000\,080,$$
$$|g(15)/g(\mathrm{H}')|=0.101\,330\,930\pm0.000\,000\,080,$$
$$\mathcal{A}(15)=73.0\pm2.0\ \text{cps}.$$
$$\mathcal{A}(14)=51.0\pm2.0\ \text{cps}.$$

A large number of runs were made with the N^{14} and N^{15} in different samples and the results were identical with those obtained with the N^{14} and N^{15} in the same chemical environment. The spin-spin interaction constant $\mathcal{A}$ was measured from the splittings of both the nitrogen resonances and the splitting of the proton resonances.

The agreement of the observed line pattern with the expected results seems to be satisfactory in all respects except that the structure of the lines for $\hbar\omega_2=g_2\mu_n H_0$ is not fitted precisely by any value of H_2 assigned. The cause of this discrepancy is not known.

It is amusing to note that the nuclear moment of N^{15} is fitted quite well by a single odd proton in a $p_{\frac{1}{2}}$ state, and the moment of N^{14} is fitted by an odd proton in a $p_{\frac{1}{2}}$ state and an odd neutron in a $p_{\frac{1}{2}}$ state using *j-j* coupling. The single-particle theory gives

$$\mu(15) = -0.263\mu_n,$$

$$\mu(14) = 0.376\mu_n.$$

CONCLUSIONS

The values of the hyperfine intervals and the nuclear magnetic moments can be combined to give the hyperfine structure anomaly for N^1 $-$N^{15}. It is

$$\Delta = \frac{A(15)/A(14)}{g(15)/g(14)} - 1 = 0.000\,983 \pm 0.000\,017.$$

This is a surprisingly large anomaly since the configuration of atomic nitrogen is $(1s)^2(2s)^2(2p)^3$.

Goudsmit[1] has shown that the zero-field hyperfine splittings in an atom with a ${}^4S_{\frac{3}{2}}$ ground state should be zero so that the existence of such large hyperfine intervals implies some configuration mixing. The fact that there is no violation of the interval rule, the size of the hyperfine intervals, the observed sign of the hyperfine interaction constants $A(14)$ and $A(15)$, and the result that the electronic g factor of the nitrogen atom is the same as for the free electron suggest that the configurations which make up the ground state of the nitrogen atom are probably $(1s)(2s)^2(2p)^3(ns)$ and $(1s)^2(2s)(2p)^3(ms)$ as well as $(1s)^2(2s)^2(2p)^3$. This type of configuration mixing was suggested by Abragam, Horowitz, and Pryce to explain the hyperfine intervals observed in the paramagnetic resonance of S-state ions.[33]

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We would like to thank Professor R. V. Pound for his suggestions on how to measure the magnetic moments of N^{14} and N^{15}, for several discussions on the experiment, and for reading the manuscript. Also, we would like to thank Mr. Larry Donaldson for his aid in blowing the glass for the experiment.

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Radioactive Decay of Dy^{159}†

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Decay of Dy^{159} has been shown to feed three excited levels in Tb^{159}. Gamma rays with energies of 58 kev, 200 kev, 290 kev, and 350 kev have been observed and electron-capture branching ratios have been determined. Only L electron capture to the 350-kev level has been detected. The half-life of the 58-kev level in Tb^{159} has been shown to be less than 1×10^{-9} sec. The K conversion coefficient of the 58-kev gamma ray has been measured and found to be 5 ± 1.5. The disintegration energy of Dy^{159} has been shown to lie between 360 and 400 kev; the half-life was remeasured and found to be 144.4 ± 0.2 days.

INTRODUCTION

THE studies of Ketelle[1] and of Butement[2] indicated that Dy^{159} decayed by orbital electron capture to the ground state of Tb^{159}. The latter work established the mass assignment and an upper limit of 0.1% for decay by positron emission. Mihelich, Harmatz, and Handley[3] reported observations of L subshell conversion electrons which indicated that some decay occurred to the known 58-kev level of Tb^{159}. Several groups of experimenters[4,5] have reported Coulomb excitation studies which indicate the presence of levels in Tb^{159} at 58 kev and 136 kev. Precise values for the transition energies between the low-lying levels have been reported.[6] The energy difference between the first excited level and the ground state is 57.99 kev and the difference between the first and second excited states is 79.51 kev. There have been many studies of the beta decay of the 18-hr Gd^{159} to levels in Tb^{159}. The reports of Marty,[7] Ballini and Barloutaud,[8] and Malik, Nath, and Mandeville,[9] are the most complete and make reference to earlier work.

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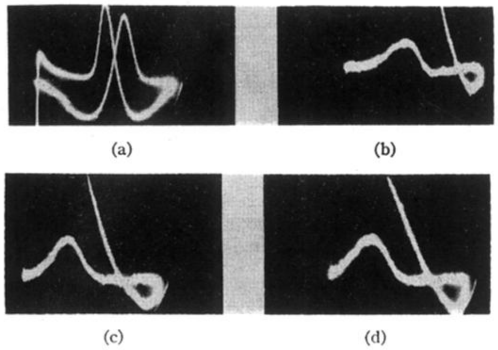
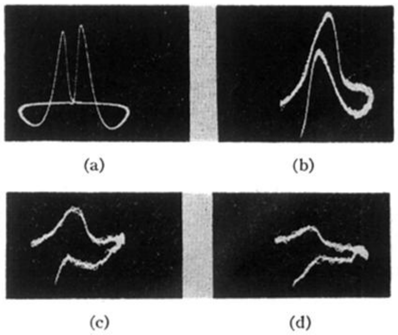


(a) (b)

(c) (d)

FIG. 5. The hyperfine transitions in atomic nitrogen. (a) The Zeeman pattern in atomic sodium at a field of about 0.07 gauss. (b) The hyperfine transition $F=2$, $M_F=0 \rightarrow F=1$, $M_F=-1$ in N^{15}. (c) The hyperfine transition $F=\frac{5}{2}$, $M_F=-\frac{1}{2} \rightarrow F=\frac{3}{2}$, $M_F=-\frac{3}{2}$ in N^{14}. (d) The hyperfine transition $F=\frac{3}{2}$, $M_F=-\frac{1}{2} \rightarrow F=\frac{1}{2}$, $M_F=\frac{1}{2}$ in N^{14}.


(a) (b)

(c) (d)

FIG. 6. The Zeeman transitions in atomic N^{15}. (a) The Zeeman transitions in atomic sodium at a field of 0.07 gauss, without the radio-frequency discharge on. (b) The Zeeman transitions in the $F=2$ state of N^{15} at a field of 0.07 gauss. (c) The Zeeman transitions in the $F=1$ state of N^{15} at a field of 0.07 gauss. (d) The Zeeman transition $F=2$, $M_F=2 \rightarrow F=2$, $M_F=1$ in N^{15} at a field of about 3 gauss.