

## Hyperfine Structure of Atomic Nitrogen\*

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The hyperfine structure of the ground state of  $N^{14}$  and  $N^{15}$  has been determined by optical pumping with spin exchange. A circulation system, which forced the nitrogen through an electrodeless rf discharge into the resonance bulb, provided a continuous source of atomic nitrogen. Optically-pumped cesium was used to polarize and analyze the nitrogen. The zero-field intervals extrapolated to zero pressure are  $N^{14}$ ,  $\nu(\frac{3}{2}-\frac{3}{2}) = 26\,127\,288 \pm 40$  cps;  $N^{14}$ ,  $\nu(\frac{3}{2}-\frac{1}{2}) = 15\,676\,390 \pm 40$  cps; and  $N^{15}$ ,  $\nu(2-1) = 29\,290\,902 \pm 40$  cps. The hyperfine constants are  $A^{14} = (+)10\,450\,925 \pm 20$  cps,  $B^{14} = (-)7 \pm 20$  cps, and  $A^{15} = (-)14\,645\,441 \pm 20$  cps. These results include small corrections for second-order hyperfine interactions. A pressure shift of  $+1.9 \pm 0.4$  cps/mm Hg of  $N_2$  was established for the  $N^{14}$  magnetic dipole interaction constant ( $A^{14}$ ). The hyperfine structure anomaly is  $\Delta = (A^{14}g_I^{15}/A^{15}g_I^{14}) - 1 = +(1.002 \pm 0.004) \times 10^{-3}$ . The effect of spin-orbit and spin-spin mixing of the  $4S$ ,  $3D$ , and  $2P$  states is discussed.

### I. INTRODUCTION

THE hyperfine structure of the ground state of atomic nitrogen has been the subject of recent theoretical and experimental studies.<sup>1-12</sup> The theoretical interest in this problem arises from the fact that the  $(1s)^2(2s)^2(2p)^3 4S_{3/2}$  ground state of nitrogen should not exhibit any hyperfine structure.<sup>13</sup> The  $(2p)$  valence electrons have a vanishing spin density at the nucleus, and the  $S$  symmetry precludes both an orbital magnetic interaction and an electric quadrupole interaction. Contrary to this prediction, Heald and Beringer<sup>6</sup> found a splitting in  $N^{14}$  corresponding to a magnetic dipole interaction constant  $A^{14} = 10.45 \pm 0.02$  Mc/sec. Abragam, Horowitz, and Pryce<sup>14</sup> suggested that this splitting may arise from the admixture of configurations with unpaired  $s$  electrons. Other authors have described this effect as an exchange polarization of the  $(1s)$  and  $(2s)$  core electrons by the unpaired  $(2p)$  valence electrons.<sup>1-5</sup>

The results of the most recent calculations of  $A^{14}$  are shown in Table I. Goodings<sup>3</sup> used an unrestricted Hartree-Fock method, in which electrons of the same  $n$  and  $l$  but different spin orientation are allowed to have different radial wave functions. His result is almost twice the experimental value. Das and Mukherjee<sup>4</sup> used a variational method to estimate the modification of the wave function resulting from core polarization. Bessis and co-workers<sup>5</sup> performed a configuration mixing calculation with a number of different approximate wave functions; the result listed in Table I was obtained with seven  $S$ -basis functions, with parameters chosen for minimum energy. While none of these results is in perfect agreement with the experimental value, it is clear that the theoretical description of the hfs is essentially correct. Presumably, better agreement will be obtained when more accurate wave functions become available.

Here, we report new precise values for the hyperfine intervals in  $N^{14}$  and  $N^{15}$ , as determined by optical pumping with spin exchange. We report the observation of a pressure shift in  $N^{14}$  and a new lower limit on the  $N^{14}$  quadrupole interaction.

### II. METHOD

Several experiments have been reported in which the hyperfine structure of atomic nitrogen was determined by optical pumping with spin-exchange.<sup>7-12</sup> In this method, optically oriented alkali atoms are used to polarize and analyze the nitrogen. The alkali vapor and a molecular nitrogen buffer gas are contained in a scattering cell that is irradiated with circularly polarized

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<sup>1</sup> T. P. Das and A. Mukherjee, *J. Chem. Phys.* **33**, 1808 (1960).

<sup>2</sup> S. M. Blinder, *Bull. Am. Phys. Soc.* **5**, 14 (1960).

<sup>3</sup> D. A. Goodings, *Phys. Rev.* **123**, 1706 (1961).

<sup>4</sup> N. Bessis-Mazloum, H. Lefebvre-Brion, and C. M. Moser, *Phys. Rev.* **124**, 1124 (1961).

<sup>5</sup> A. J. Freeman and R. E. Watson (to be published).

<sup>6</sup> M. A. Heald and R. Beringer, *Phys. Rev.* **96**, 645 (1954).

<sup>7</sup> W. W. Holloway, Jr. and R. Novick, *Phys. Rev. Letters* **1**, 367 (1958).

<sup>8</sup> N. Knable, W. W. Holloway, Jr., and R. Novick, *Bull. Am. Phys. Soc.* **4**, 259 (1959).

<sup>9</sup> L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., *Phys. Rev.* **116**, 87 (1959).

<sup>10</sup> W. W. Holloway, Jr. and E. Lüscher, *Nuovo cimento* **18**, 1296 (1960).

<sup>11</sup> W. W. Holloway, Jr., E. Lüscher, and R. Novick, *Bull. Am. Phys. Soc.* **7**, 26 (1962).

<sup>12</sup> R. H. Lambert and F. M. Pipkin, *Bull. Am. Phys. Soc.* **7**, 26 (1962).

<sup>13</sup> R. E. Trees, *Phys. Rev.* **92**, 308 (1953).

<sup>14</sup> A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A230**, 169 (1955).

TABLE I. Theoretical values for the  $N^{14}$  magnetic dipole interaction constant.

Author	$A^{14}$ (Mc/sec)
Goodings <sup>a</sup>	+20.2
Das and Mukherjee <sup>b</sup>	+ 7.3
Bessis <i>et al.</i> <sup>c</sup>	+11

<sup>a</sup> See reference 3.

<sup>b</sup> See reference 1.

<sup>c</sup> See reference 4.

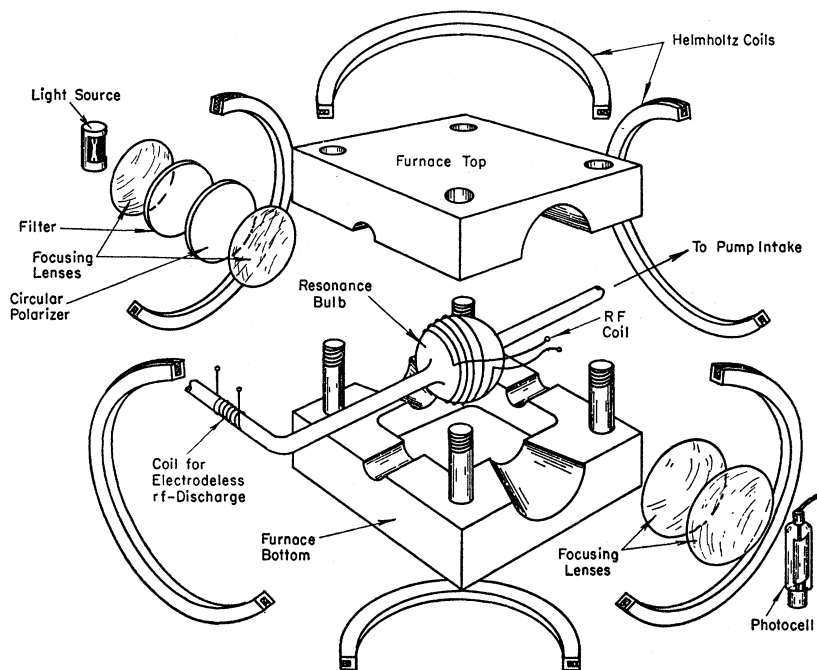


FIG. 1. Schematic diagram of the apparatus.

alkali resonance radiation. This radiation serves to orient the alkali atoms, and the opacity of the bulb provides a monitor of the resulting alkali polarization.<sup>15</sup> A small fraction of the molecular nitrogen is dissociated with a discharge. The nitrogen atoms become polarized through spin-exchange collisions with the oriented alkali. Magnetic resonance disorientation of the nitrogen is transferred to the alkali by spin-exchange and produces an observable decrease of the optical transmission of the bulb.<sup>16</sup> This method is extremely sensitive and is capable of high resolution.<sup>17</sup> The intrinsic linewidths, as determined by relaxation processes within the gas, are of the order of a few cycles per second.<sup>15</sup> In practice, magnetic field inhomogeneities produce a greater broadening.

In the previous experiments on nitrogen the atoms were produced periodically with a pulsed rf discharge within the resonance bulb.<sup>7-9</sup> The pulsed discharge caused a large electrical transient in the detector channel. The filter required to eliminate this transient distorted and shifted the apparent position of the atomic resonances. In the present experiment a continuous-flow technique is employed and the dissociation is produced continuously by an rf discharge in the flow line leading to the resonance bulb. The physical separation of the dissociator from the resonance bulb eliminates many of the possible systematic errors inherent in the pulse method.

<sup>15</sup> H. G. Dehmelt, *Phys. Rev.* **105**, 1487 (1957).

<sup>16</sup> H. G. Dehmelt, *Phys. Rev.* **109**, 381 (1958).

<sup>17</sup> The spin-exchange process is discussed in greater detail in reference 9.

### III. APPARATUS

A drawing of the experimental apparatus is shown in Fig. 1. The light source which provided the resonance radiation for the optical orientation of the cesium atoms was an Osram cesium spectral lamp. The vacuum jacket was removed so that a controllable flow of air could be passed over the interior bulb, in order to optimize the operating conditions. If the outer jacket was not removed, self-reversal in the lamp was so severe that resonances were not observable. The lamp was excited with a 10-Mc/sec radiofrequency oscillator. The radiation from the lamp passed through a Spectrolab<sup>18</sup> cesium interference filter peaked to transmit only the  $D_1$  (8944 Å) cesium line. This filtered light was circularly polarized with a Polaroid  $H$ -type linear polarizer and quarter wave plate and was focused on the resonance bulb with a series of lenses.

The resonance cell was a 250-cc spherical Pyrex flask with 10-mm Pyrex tubing projecting from either side to conduct circulating nitrogen gas through the bulb. Droplets of metallic cesium were deposited on the interior of the bulb. At the operating temperature of 50°C and a flow rate of about 1 liter per sec, this reservoir provided the optimum density of cesium atoms; with the flow shut off, the optimum temperature was somewhat lower. A buffer gas of molecular nitrogen at approximately 10–15 mm Hg pressure served to minimize the effects of disorientation by wall collisions. The light transmitted by the bulb was refocused by a series of lenses on a 917 RCA vacuum phototube. The

<sup>18</sup> Spectrolab, Inc., 7423 Varna Avenue, North Hollywood, California.

output of this phototube was displayed on an oscilloscope.

The disorienting rf field was applied to the bulb by a copper coil wrapped directly on the resonance cell. The axis of this rf coil was at an angle of approximately  $45^\circ$  to the optic axis (and hence the steady magnetic field), in order to provide components of the rotating fields appropriate for inducing both  $\pi$  transitions ( $\Delta F=0, \pm 1$ ;  $\Delta M_F = \pm 1$ ) and  $\sigma$ -hyperfine transitions ( $\Delta F = \pm 1$  and  $\Delta M_F = 0$ ). The dynamics of the spin exchange process are such that states with the same value of  $M_F$  and different values of  $F$  are equally populated.<sup>17</sup> Hence, the  $\sigma$  ( $\Delta F = \pm 1$ ;  $\Delta M_F = 0$ ) hyperfine transitions are unobservable.

In an effort to eliminate 60-cps stray magnetic fields, the cell was mounted in an aluminum-alloy furnace with walls  $1\frac{1}{2}$  in. thick. Unfortunately, a high-resistance joint in the shield prevented the full realization of the ac shielding possible with this design. In addition, a number of windings were provided on three mutually perpendicular sets of Helmholtz coils to (a) cancel the ambient magnetic field and its gradients, (b) provide a steady uniform field along the optic axis, (c) provide a Zeeman modulation field along the optical axis, and (d) provide a 60-cycle field of variable phase, amplitude, and direction to oppose the stray 60-cycle fields present in the laboratory.

In spite of these precautions, the resonance linewidths were limited to about 1 mœ by magnetic field inhomogeneities and fluctuations.

The currents to create the steady magnetic fields were supplied from wet-cell batteries, while the current for the modulation field was supplied by a Hewlett Packard model 202A low-frequency function generator. The output of this function generator also swept the oscilloscope, used to display the resonances. The rf disorienting field was supplied to the resonance bulb from a type 805C General Radio signal generator whose frequency was measured with a type 524B Hewlett Packard electronic counter. The frequency of the time-base oscillator, for the counter, was compared to the standard frequency broadcasts of the National Bureau of Standards *WWW* and was found to be stable and accurate to one part in  $10^7$ .

Even at the slow ( $\sim 4$  cps) repetition rates of the modulation field, the effects of time delays in the spin exchange process were observed. The resonance frequencies were determined with both increasing and decreasing fields so as to eliminate the shifts resulting from these delays.

Unfortunately, none of the observable hyperfine transitions are field independent at zero field, and we must resort to special means to obtain precise data. The  $\pi$  hyperfine transitions occur in pairs with equal and opposite linear but equal quadratic field dependence. The resonant frequency of each member of these pairs was determined in rapid succession. The average of the pair frequencies depends on the field only in



FIG. 2.  $N^{14}$  Zeeman resonances in the  $F=5/2$  and  $F=3/2$  states as observed in a field of 0.1 gauss.



FIG. 3. Quadratic splitting of the  $N^{14}$   $F=5/2$  Zeeman resonance into its five components in a field of 1.0 gauss.



FIG. 4. Single Zeeman component of the  $N^{14}$  hyperfine transition between the  $F=5/2$  and  $F=3/2$  states. The sweep time is 0.2 sec.

second order. These second-order Zeeman corrections were determined from the known magnetic moment of the  $N$  atom and the difference of the pair frequencies. This difference provides a direct measure of the magnetic field at the time of observation.

#### IV. EXPERIMENTAL RESULTS

All of the Zeeman transitions ( $\Delta F=0$  and  $\Delta M_F = \pm 1$ ) and all of the  $\pi$ -hyperfine transitions ( $\Delta F = \pm 1$  and  $\Delta M_F = \pm 1$ ) that would be expected for the ground state of  $N^{14}$  ( $J=3/2$  and  $I=1$ ) and  $N^{15}$  ( $J=3/2$  and  $I=1/2$ ) were observed. Typical Zeeman and hyperfine resonances are shown in Figs. 2, 3, and 4. The  $(5/2, \pm 5/2) - (3/2, \pm 3/2)$  transition in  $N^{14}$  was observed at several different pressures of the  $N_2$  buffer gas. The results obtained from this study are listed in Table II and are plotted in Fig. 5. The uncertainties listed in Table II are about two times the statistical probable error.

The straight line shown in Fig. 5 was determined by a least-squares fit to the data listed in Table II. The slope of this line and hence the pressure shift of the  $N^{14}$   $(5/2, \pm 5/2) - (3/2, \pm 3/2)$  interval ( $\nu_{5,3}$ ) is

$$d\nu_{5,3}/dP = +(4.7 \pm 1.0) \text{ cps/mm Hg.} \quad (1)$$

The uncertainty is about two times the probable error in the slope. From this result we find that the pressure shift of the  $N^{14}$  and  $N^{15}$  dipole interaction constants are:

$$\begin{aligned} dA^{14}/dP &= +(1.9 \pm 0.4) \text{ cps/mm Hg,} \\ d|A^{15}|/dP &= +(2.6 \pm 0.6) \text{ cps/mm Hg.} \end{aligned} \quad (2)$$

Here, we have assumed that the fractional pressure shift is the same in the two isotopes.

TABLE II. Zero-field hyperfine transition frequency for the  $(5/2, \pm 5/2) - (3/2, \pm 3/2)$  interval in  $N^{14}$  for several values of the  $N_2$  buffer gas pressure.

$N_2$ pressure (mm Hg)	Number of readings	Frequency (cps)
4.9	9	26 127 319±27
6.6	9	361±38
6.8	8	363±37
7.1	9	370±23
10.3	9	367±28
12.6	10	382±22
14.5	21	397±20
16.6	9	400±18
17.2	8	415±38
19.4	9	415±21
23.0	9	434±23
25.0	10	429±23

The values obtained for the zero field hyperfine intervals in  $N^{14}$  and  $N^{15}$  are given in Table III. The corrections to zero pressure were obtained from the results given in Eq. (2) above. The uncertainties in the uncorrected frequencies are about twice the probable error. The uncertainties in the corrected frequencies include an allowance for the uncertainty in the correction to zero pressure and an estimate of the possible shifts that may result from field distortions.

The zero-field intervals extrapolated to zero pressure are:

$$\begin{aligned} N^{14}, \nu(5/2-3/2) &= 26\,127\,288 \pm 40 \text{ cps}, \\ \nu(3/2-1/2) &= 15\,676\,390 \pm 40 \text{ cps}, \\ N^{15}, \nu(2-1) &= 29\,290\,902 \pm 40 \text{ cps}. \end{aligned} \quad (3)$$

The uncertainties in the values given in Eq. (3) are about the same as the uncertainties in the individual results listed in Table III. It was felt that a statistical reduction of the errors was unjustified. The 40-cps uncertainties are a few percent of the width of the narrowest resonances and are believed to represent the limit of reliability of the present results.

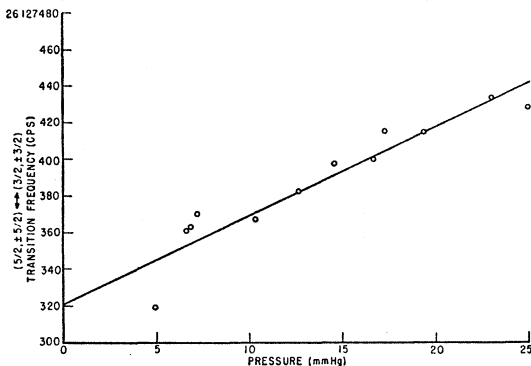


FIG. 5. Pressure dependence of the  $N^{14}$   $(5/2, \pm 5/2) \leftrightarrow (3/2, \pm 3/2)$  hyperfine transition frequency.

The hyperfine interaction constants obtained from the above results are<sup>19</sup>:

$$\begin{aligned} A^{14} &= (+)10\,450\,925 \pm 20 \text{ cps}, \\ B^{14} &= (-)7 \pm 20 \text{ cps}, \\ A^{15} &= (-)14\,645\,441 \pm 20 \text{ cps}. \end{aligned} \quad (4)$$

These constants contain small corrections for second-order hyperfine interactions with the metastable  $^2D$  and  $^2P$  levels. These corrections are evaluated in Sec. V. The values of  $A^{14}$  and  $B^{14}$  are consistent with previous determinations.<sup>7-9</sup> The value of  $A^{15}$  is consistent with the result obtained by Knable *et al.*,<sup>8</sup> but is significantly lower than the value obtained by Anderson and co-workers.<sup>9</sup> Using the results of Anderson, Baird, and Pipkin for the nuclear  $g$  factors,<sup>9</sup> we find that the  $N^{14} - N^{15}$  hyperfine structure anomaly is<sup>20</sup>

$$\Delta = (A^{14}gI^{15}/A^{15}gI^{14}) - 1 = +(1.002 \pm 0.004) \times 10^{-3}. \quad (5)$$

## V. SECOND-ORDER HYPERFINE INTERACTIONS

It is well known that the hyperfine operators have nonvanishing matrix elements connecting the various levels within a fine-structure multiplet. Here we will evaluate the energy shifts of the  $(2p)^3\ ^4S$  ground-state hyperfine levels resulting from second-order hyperfine interactions with the  $(2p)^3\ ^2D$  and  $(2p)^3\ ^2P$  levels. The most important result to be obtained from this calculation is the evaluation of the pseudo-quadrupole interaction in the  $^4S_{3/2}$  state of  $N^{14}$ . This is an apparent quadrupole interaction resulting from second-order dipole interactions with the other fine-structure levels. The observed quadrupole energy must be corrected for

TABLE III. Zero field hyperfine transition frequencies for  $N^{14}$  and  $N^{15}$ .

Isotope	Transition	Pressure (mm Hg)	Observed frequency (cps)	Transition frequency corrected to zero pressure (cps)	
$N^{14}$	$5/2, \pm 5/2; 3/2, \pm 3/2$	12.6	26 127 382±22	26 127 323±35	
		14.5	26 127 395±30	26 127 327±45	
		14.5	26 127 355±30	26 127 287±45	
		14.5	26 127 285±30	26 127 217±45	
	Average				26 127 288±40
	$3/2, \pm 3/2; 1/2, \pm 1/2$	14.5	15 676 426±30	15 676 385±40	
		12.6	15 676 433±30	15 676 397±40	
		12.0	15 676 432±30	15 676 398±40	
		14.5	15 676 420±30	15 676 379±40	
	Average				15 676 390±40
$N^{15}$	$2, \pm 2; 1, \pm 1$	8.7	29 290 960±30	29 290 914±40	
		10.2	29 290 964±30	29 290 910±40	
		10.6	29 290 972±30	29 290 916±40	
	$2, \pm 1; 1, 0$ $2, 0; 1, \pm 1$	8.7	29 290 941±30	29 290 897±40	
		10.6	29 290 930±30	29 290 875±40	
		Average			

<sup>19</sup> The negative ratio of  $A^{14}$  to  $B^{14}$  follows from the results given in Eq. 3. The negative ratio of  $A^{14}$  to  $A^{15}$  is obtained from the known signs of the nuclear moments. The absolute sign of  $A^{14}$  was determined in earlier work. See reference 9.

<sup>20</sup> Except for sign, this result agrees with that given in reference 9.

this effect before we can evaluate the true ground-state quadrupole coupling.

The dipole and quadrupole matrix elements are given by Trees<sup>13</sup> and Racah,<sup>21</sup> for a pure  $p^3$  configuration with  $LS$  coupling. In this representation there is only one nonvanishing quadrupole matrix element; this element connects the  $^2P$  and  $^2D$  states. The dipole operator has nonvanishing diagonal matrix elements in the  $^2P$  and  $^2D$  states and a single off-diagonal element connecting the  $^4S$  and  $^2D$  states. This last matrix element is the only one that gives rise to a second-order hyperfine interaction with the  $^4S$  ground state. The other matrix elements are effective only to the extent that the fine-structure levels are mixed by the spin-orbit and spin-spin interactions (see below). It is expected that the small modification to the configuration that is required to account for the existence of the hfs splitting of the  $^4S$  state will not seriously affect the value of the  $^4S-^2D$  magnetic dipole matrix element as given by Trees and by Racah. In any case, the second-order corrections arising from this matrix element are less than 20 cps and precise values are not required.

In the notation of Edmonds<sup>22</sup> the magnetic dipole matrix elements connecting the  $^4S_{3/2}$  ground state with the  $^2D$  states are

$$(IJ'F|H|IJF) = a[10]^{1/2}[I(I+1)(2I+1)]^{1/2} \\ \times (-1)^{I+J'+F+1} \begin{Bmatrix} F & J' & I \\ 1 & I & J \end{Bmatrix} (S'L'J'|\mathbf{X}^{(1)}|SLJ). \quad (6)$$

The single particle interaction constant,  $a$ , is given by<sup>13</sup>

$$a = \frac{Rc\alpha^2 a_0^3}{h} \left( \frac{m_e}{M_P} \right) g_I \langle 1/r^3 \rangle_{av}. \quad (7)$$

In the case of  $n$  equivalent electrons, the reduced matrix element of the tensor  $\mathbf{X}^{(1)}$  is

$$(l^n S'L'J'|\sum_{i=1}^n \mathbf{X}_i^{(1)}|l^n SLJ) \\ = [3(2J'+1)(2J+1)]^{1/2} \begin{Bmatrix} S' & L' & J' \\ S & L & J \\ 1 & 2 & 1 \end{Bmatrix} \\ \times (l|\mathbf{C}^{(2)}|l)(S'L'|\mathbf{V}^{(12)}|SL). \quad (8)$$

The tensors  $\mathbf{C}^{(2)}$  and  $\mathbf{V}^{(12)}$  have been evaluated and tabulated by Edmonds and Racah, respectively. The final values for the reduced matrix elements are<sup>21,22</sup>

$$(p^3 {}^4S_{3/2}|\mathbf{X}^{(1)}|p^3 {}^2D_{5/2}) = (6/5)(3/10)^{1/2}, \quad (9) \\ (p^3 {}^4S_{3/2}|\mathbf{X}^{(1)}|p^3 {}^2D_{3/2}) = -(2/5)(3/10)^{1/2}.$$

When we insert these reduced matrix elements into the

<sup>21</sup> G. Racah, Phys. Rev. **62**, 438 (1942); Phys. Rev. **63**, 367 (1943).

<sup>22</sup> A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

general expression given by Eq. (6), we obtain, for  $N^{14}$  ( $I=1$ ):

$$({}^4S_{3/2} \frac{5}{2} | H | {}^2D_{5/2} \frac{5}{2}) = + (126/125)^{1/2} a^{14}, \\ ({}^4S_{3/2} \frac{3}{2} | H | {}^2D_{5/2} \frac{3}{2}) = + (81/125)^{1/2} a^{14}, \\ ({}^4S_{3/2} \frac{5}{2} | H | {}^2D_{3/2} \frac{5}{2}) = + (9/125)^{1/2} a^{14}, \quad (10a) \\ ({}^4S_{3/2} \frac{3}{2} | H | {}^2D_{3/2} \frac{3}{2}) = - (4/125)^{1/2} a^{14}, \\ ({}^4S_{3/2} \frac{1}{2} | H | {}^2D_{3/2} \frac{1}{2}) = - (25/125)^{1/2} a^{14},$$

and for  $N^{15}$  ( $I=1/2$ ):

$$({}^4S_{3/2} 2 | H | {}^2D_{5/2} 2) = + (216/500)^{1/2} a^{15}, \\ ({}^4S_{3/2} 2 | H | {}^2D_{3/2} 2) = + (9/500)^{1/2} a^{15}, \quad (10b) \\ ({}^4S_{3/2} 1 | H | {}^2D_{3/2} 1) = - (25/500)^{1/2} a^{15}.$$

In order to evaluate  $a$ , we require an estimate of  $\langle 1/r^3 \rangle_{av}$ . Using a Hartree wave function,<sup>23</sup> we find

$$a_0^3 \langle 1/r^3 \rangle_{av} = 3.06. \quad (11)$$

With this value of  $\langle 1/r^3 \rangle_{av}$  the single-particle interaction constants become

$$a^{14} = +120 \text{ Mc/sec}, \quad a^{15} = -167 \text{ Mc/sec}. \quad (12)$$

The final expressions for the energy shifts in the ground-state hyperfine levels of  $N^{14}$  are

$$\delta E(F=5/2) = - \frac{135 (a^{14})^2}{125 \Delta E} = -26.5 \text{ cps}, \\ \delta E(F=3/2) = - \frac{85 (a^{14})^2}{125 \Delta E} = -16.7 \text{ cps}, \quad (13) \\ \delta E(F=1/2) = - \frac{25 (a^{14})^2}{125 \Delta E} = -4.9 \text{ cps}.$$

Here,  $\Delta E = E(^2D) - E(^4S) = 19,227 \text{ cm}^{-1}$ .

The corresponding shifts in  $N^{15}$  are

$$\delta E(F=1) = - \frac{1 (a^{15})^2}{20 \Delta E} = -2.4 \text{ cps}, \\ \delta E(F=2) = - \frac{9 (a^{15})^2}{20 \Delta E} = -21.8 \text{ cps}. \quad (14)$$

To correct the observed intervals for these second-order shifts, we must *increase* the  $N^{14}$  (5/2,3/2) and (3/2,1/2) intervals by 9.8 cps and 11.8 cps, respectively, and we must *decrease* the  $N^{15}$  (2,1) interval by 19.4 cps. The two isotopes behave differently because the  $N^{15}$  hfs is inverted while the  $N^{14}$  hfs is normal. The corresponding *corrections* to the hyperfine interaction constants are

$$\delta A^{14} = +4.9 \text{ cps}, \\ \delta B^{14} = -2.0 \text{ cps}, \quad (15) \\ \delta |A^{15}| = -9.7 \text{ cps}.$$

<sup>23</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

These corrections have been included in the results given in Eq. (4).

The final result for pseudo-quadrupole effect is that it contributes +2.0 cps to the apparent quadrupole interaction constant ( $B^{14}$ ) in  $N^{14}$ .

### VI. INTERMEDIATE COUPLING

Aller, Ufford and Van Vleck<sup>24</sup> have analyzed the effect of spin-orbit and spin-spin coupling on a  $p^3$  configuration. They show that in lowest order the ground-state wave function consists of the following mixture of the  $^4S_{3/2}$ ,  $^2D_{3/2}$ , and  $^2P_{3/2}$  Russell-Saunders states:

$$\Psi(^4S_{3/2}) = a'\Psi^0(^2P_{3/2}) + b'\Psi^0(^4S_{3/2}) + c'\Psi^0(^2D_{3/2}), \quad (16)$$

where,

$$a' = -\zeta/PS, \quad b' = 1, \quad c' = \frac{6\eta}{DS\sqrt{5}} + \frac{\zeta^2\sqrt{5}}{2(PS)(DS)}. \quad (17)$$

The superscript 0 indicates a pure Russell-Saunders state,  $\zeta$  and  $\eta$  are the spin-orbit and spin-spin interaction constants for a  $2p$  electron, and  $PS$  and  $DS$  represent the  $^2P-^4S$  and  $^2D-^4S$  energy intervals, respectively.

Even in the absence of core polarization this mixed state will exhibit a small magnetic dipole interaction. This arises from the diagonal dipole matrix elements in the  $^2D$  and  $^2P$  states and the off-diagonal dipole matrix element that connects the  $^2D$  and  $^4S$  states (see Sec. V). This mixing contribution is small compared to the theoretical value of the dipole interaction predicted on the basis of core polarization. At such time as precise core polarization calculations are performed, it will be necessary to allow for this mixing contribution before making a comparison with experiment. For completeness and for future reference, we have evaluated this mixing contribution to  $A^{14}$  and  $A^{15}$ .

Our main concern here is with the evaluation of the quadrupole interaction that arises from the breakdown of Russell-Saunders coupling. This interaction is proportional to the  $^2D-^2P$  off-diagonal quadrupole matrix element (see Sec. V). The core polarization that accounts for the dipole interaction is spherically symmetrical and does not produce a quadrupolar splitting.

By a straightforward application of the formulas given by Trees<sup>13</sup> and the results given in Sec. V, we can show that the mixing contribution to the dipole interaction constant, ( $A_m$ ), is

$$A_m(^4S_{3/2}) = (a')^2(8/15)a + (c')^2(16/25)a + 2(b'c')(2/5\sqrt{5})a, \quad (18)$$

where  $a$  is the single particle dipole interaction constant given in Eq. (12). The first two terms in Eq. (18) are very much smaller than the last term and can be neglected.

<sup>24</sup>L. H. Aller, C. W. Ufford, and J. H. Van Vleck, *Astrophys. J.* **109**, 42 (1949).

From the work of Trees<sup>13</sup> and of Racah<sup>21</sup> and in the notation of Edmonds,<sup>22</sup> the matrix elements of the quadrupole Hamiltonian are

$$\begin{aligned} & (I(S'L')J'F|H_Q|I(SL)JF) \\ &= (-1)^{I+J'+F+1} \frac{4}{3} \left[ \frac{(2I+3)!}{(2I-2)!} \right]^{1/2} \begin{Bmatrix} F & J' & I \\ 2 & I & J \end{Bmatrix} \\ & \times ((S'L')J' \parallel \sum_{i=1}^n b_i \mathbf{C}_i^{(2)} \parallel (SL)J) \end{aligned} \quad (19)$$

where the single-particle interaction constant,  $b$ , is given by<sup>13</sup>

$$b = \frac{3e^2Q}{16I(2I-1)\hbar} \langle 1/r^3 \rangle_{\text{av.}} \quad (20)$$

In the case of equivalent electrons the reduced matrix element becomes

$$\begin{aligned} & ((S'L')J' \parallel \sum_i^n b_i \mathbf{C}_i^{(2)} \parallel (SL)J) \\ &= b_i(l \parallel \mathbf{C}^{(2)} \parallel l) \delta_{S,S'} \times (-1)^{S+L+J} [(2J+1)(2J'+1)]^{1/2} \\ & \times \begin{Bmatrix} L' & J' & S \\ J & L & 2 \end{Bmatrix} (SL' \parallel \mathbf{U}^{(2)} \parallel SL). \end{aligned} \quad (21)$$

The matrix elements of  $\mathbf{U}^{(2)}$  are given by Racah<sup>21</sup> for a  $p^3$  configuration. In the case of interest, we obtain

$$\begin{aligned} & (I p^3 \ ^2P_{3/2} F | H_Q | I p^3 \ ^2D_{3/2} F) \\ &= (-1)^{I+F+3/2} (8/5) \begin{Bmatrix} F & 3/2 & I \\ 2 & I & 3/2 \end{Bmatrix} \left[ \frac{(2I+3)!}{(2I-2)!} \right]^{1/2}. \end{aligned} \quad (22)$$

The final matrix elements appropriate to  $N^{14}$  ( $I=1$ ) are

$$\begin{aligned} & (^2P_{3/2} \ ^{5/2} | H_Q | ^2D_{3/2} \ ^{5/2}) = (8/5\sqrt{5})b, \\ & (^2P_{3/2} \ ^{3/2} | H_Q | ^2D_{3/2} \ ^{3/2}) = -(32/5\sqrt{5})b, \\ & (^2P_{3/2} \ ^{1/2} | H_Q | ^2D_{3/2} \ ^{1/2}) = (40/5\sqrt{5})b. \end{aligned} \quad (23)$$

Since these matrix elements are diagonal in  $J$  we can express them in terms of an effective quadrupole interaction constant ( $B_{PD}$ ), where

$$B_{PD} = (32/5\sqrt{5})b. \quad (24)$$

The quadrupole interaction constant in the ground state resulting from mixing,  $B_m(^4S_{3/2})$ , is

$$B_m(^4S_{3/2}) = 2a'c'(32/5\sqrt{5})b. \quad (25)$$

In order to evaluate the mixing coefficients we must estimate  $\zeta$  and  $\eta$ . Using the interpolation procedure of Robinson and Shortley,<sup>25</sup> we find

$$\zeta = +70 \text{ cm}^{-1} \quad (26)$$

<sup>25</sup>H. A. Robinson and G. H. Shortley, *Phys. Rev.* **52**, 713 (1937).

for the  $2p$  electrons in nitrogen. It is reassuring to note that this result is consistent with the well-known formula<sup>26</sup>

$$\zeta = R\alpha^2 a_0^3 Z_i \langle 1/r^3 \rangle_{av}, \quad (27)$$

if we take  $Z_i = 3.1$  as given by Slater<sup>27</sup> and  $\langle 1/r^3 \rangle_{av}$  as given by Eq. (11).

Herzfeld<sup>28</sup> has evaluated  $\eta$  by fitting the formulas of Aller *et al.*<sup>24</sup> to the observations of Bowen.<sup>29</sup> He finds

$$\eta = +0.715 \text{ cm}^{-1}. \quad (28)$$

If we take  $Q = +(1.6 \pm 0.7) \times 10^{-26} \text{ cm}^2$ ,<sup>30</sup> and  $\langle 1/r^3 \rangle_{av}$  as given above, then the mixing contributions to  $A$  and  $B$  are

$$\begin{aligned} A_m^{14} &= +4700 \text{ cps}, \\ A_m^{15} &= -6500 \text{ cps}, \\ B_m^{14} &= -3.4 \pm 1.6 \text{ cps}. \end{aligned} \quad (29)$$

As anticipated, the mixing contribution to  $A$  is small compared to the contribution from core polarization. The value for  $B$  given by Eq. (29) is consistent with the experimental results.

## VII. DISCUSSION

The principal objective of this work was the precise determination of the hfs of atomic nitrogen for the purpose of revealing any quadrupole splitting that may exist in the  $4S_{3/2}$  ground state. In addition to studying this effect we have established the pressure dependence of the dipole interaction constant.

We have shown that the quadrupole coupling constant for  $N^{14}$  is

$$B^{14} = -7 \pm 20 \text{ cps}. \quad (30)$$

This result contains a 2 cps negative correction for the second-order dipole interaction with the  $(2p)^3 {}^2D$  state. The result given in Eq. (30) is consistent with the  $(-3.4)$  cps interaction that is expected for a pure  $(2p)^3$  configuration in intermediate coupling. The configuration mixing that accounts for the dipole coupling does not contribute to the quadrupole energy. There may be a small additional contribution to  $B^{14}$  from the  $(2p)^2(3p)$  configuration.<sup>31</sup> We have not attempted to estimate this effect, but our experimental result indicates that it cannot contribute more than 20 cps to the quadrupole constant.<sup>32</sup>

<sup>26</sup> C. Schwartz, Phys. Rev. **97**, 380 (1955).

<sup>27</sup> J. C. Slater, Phys. Rev. **36**, 57 (1930).

<sup>28</sup> C. M. Herzfeld, Phys. Rev. **107**, 1239 (1957).

<sup>29</sup> D. S. Bowen, Astrophys. J. **121**, 306 (1955).

<sup>30</sup> C. C. Lin, Phys. Rev. **119**, 1027 (1960).

<sup>31</sup> E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 198.

<sup>32</sup> The electrostatic mixing of the  $(2p)^3$  and  $(2p)^2(3p)$  configuration will not directly produce a quadrupole interaction. The various states of the  $(2p)^2(3p)$  configuration are nearly degenerate

Extensive studies have been made of the pressure shift of the hfs of alkali and hydrogen atoms in various buffer gases.<sup>33,34</sup> The most striking result of these studies is the observation that the pressure shift is positive for light buffer gases and negative for heavy ones. This has been explained by postulating that there are two competing effects that give rise to the shifts. Long-range van der Waals forces cause a mixing of the  $(s_0)$  ground state with excited ( $s^*$ ) states. Since these ( $s^*$ ) states exhibit a smaller hfs splitting than the  $(s_0)$  states, the van der Waals force produces a negative shift. In addition, there is a short-range exchange force that causes a compression of the wave function, an increase in the unpaired spin density at the nucleus and a positive pressure shift. The polarizability of the heavy gases is relatively large and the net shift in these gases is negative. The exchange forces dominate in the light gases and produce a positive shift. These effects have been treated by Adrian.<sup>35</sup>

In the case of nitrogen, the excited states that are mixed with the ground state by the van der Waals force have a larger hfs than the ground state. Thus both the van der Waals force and the exchange force produce positive pressure shifts. This is in agreement with our observations and those of Jen and co-workers<sup>36</sup> on trapped nitrogen atoms.

The nitrogen molecule is known to possess an electric quadrupole moment.<sup>37</sup> The fields associated with this moment also will mix the states of the nitrogen atom during a collision and will contribute to the positive pressure shift. *Note added in proof.* Adrian has recently analyzed the nitrogen hyperfine shifts and has shown that the shifts observed in both solid matrices and in buffer gases can be understood in terms of a van der Waals mixing of the  $(2s)$   $(2p)^4$  state with the normal  $(2s)^2(2p)^3$  state.<sup>38</sup>

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and may be strongly mixed by magnetic interactions of the type considered in Sec. V and VI. The electrostatic interaction of such mixed states with the ground state may produce a quadrupolar splitting of the ground state. [H. M. Foley (private communication)].

<sup>33</sup> M. Arditi and T. R. Carver, Phys. Rev. **112**, 449 (1958); E. C. Beaty and P. L. Bender, Phys. Rev. **112**, 450 (1958).

<sup>34</sup> L. W. Anderson and F. M. Pipkin, Phys. Rev. **120**, 1279 (1960).

<sup>35</sup> F. J. Adrian, J. Chem. Phys. **32**, 972 (1960).

<sup>36</sup> C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **112**, 1169 (1958).

<sup>37</sup> C. Greenhow and W. W. Smith, J. Chem. Phys. **19**, 1298 (1951).

<sup>38</sup> F. J. Adrian (private communication).