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Pressure Shifts of the Hyperfine Structure of Atomic Nitrogen*†

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The hyperfine structure of atomic nitrogen in the $(2p)^3\,{}^4S_{3/2}$ electronic ground state has been investigated by the spin-exchange optical polarization method. The transmission of circularly polarized rubidium D_1 $(5\,{}^2P_{1/2} \leftrightarrow 5\,{}^2S_{1/2})$ resonance radiation through a flask containing rubidium vapor, a buffer gas, and atomic nitrogen was observed as a function of the frequency of an applied radio-frequency field. Measurements were made at pressures ranging from 10 to 65 mm Hg in neon, argon, helium, and molecular nitrogen buffer gases. The extrapolated zero-pressure frequency intervals and their corresponding pressure shifts, as determined by the method of least squares, are

Nitrogen isotope	Buffer gas	Transition	Pressure shift in cps/mm Hg	Zero pressure intercept in cps
N^{15}	Ne	$F=2 \leftrightarrow F=1$	1.6 ±0.21	29 290 917± 9
N^{15}	Ar	$F=2 \leftrightarrow F=1$	5.47±0.24	29 290 919± 9
N^{15}	He	$F=2 \leftrightarrow F=1$	0.87±0.15	29 290 910± 6
N^{14}	N_2	$F=\frac{5}{2} \leftrightarrow F=\frac{3}{2}$	4.12±0.54	26 127 340±21
N^{14}	He	$F=\frac{5}{2} \leftrightarrow F=\frac{3}{2}$	0.70±0.21	26 127 324± 9
N^{14}	He	$F=\frac{3}{2} \leftrightarrow F=\frac{1}{2}$	0.33±0.18	15 676 392± 6

Average values found for the hyperfine interaction constants are:

$$A(N^{14}) = +10\,450\,930 \pm 8 \text{ cps}$$
$$B(N^{14}) = +\qquad 1 \pm 5 \text{ cps}$$
$$A(N^{15}) = -14\,645\,457 \pm 5 \text{ cps}$$

The quoted errors are based on the dispersion of the various extrapolated values of the zero-pressure intervals. In terms of the statistical variation of the data this error is equivalent to three standard deviations of the mean.

The experimental pressure shifts are compared with a theory recently proposed by Adrian and an expression is derived for the Stark shift of the nitrogen hyperfine structure.

INTRODUCTION

THE ability of a buffer gas to reduce the Doppler contribution to the widths of certain radio-frequency transitions without producing detrimental pressure broadening has been understood for some time.[1] In such an environment high precision measurements on almost unperturbed atoms are possible. Previous measurements of the hyperfine transitions of S-state atoms have revealed a small dependence of the transition frequency upon the buffer gas pressure. Both the slope, commonly called the pressure shift, and the zero pressure intercept of a plot of apparent hyperfine transition frequency versus buffer gas pressure are of theoretical interest. Pressure shifts have been measured for hydrogen,[2] deuterium,[2] tritium,[2] sodium 23,[3] potassium 39,[4] rubidium 87,[5–7] cesium 133,[7,8] nitrogen 14,[9] and phosphorus 31.[10]

The ground state of the nitrogen atom is particularly interesting because the expected Russell-Saunders coupling of the configuration $(1s)^2(2s)^2(2p)^3$ into the ${}^4S_{3/2}$ atomic ground state would lead to no hyperfine structure.[11,12] Heald and Beringer,[13] however, found for N^{14} a magnetic dipole hyperfine interaction constant of 10.45±0.02 Mc/sec. The hyperfine interaction constants of both N^{14} and N^{15} have since been measured several times by the optical pumping spin-exchange

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† A preliminary account of this work has been given [R. H. Lambert and F. M. Pipkin, Bull. Am. Phys. Soc. **7**, 26 (1962)].

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§ Alfred P. Sloan Research Fellow, 1961–63.

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method.[9,14–19] All the presently reported experiments are consistent with the N^{14} quadrupole interaction constant being zero. Current attempts to understand the existence of the magnetic dipole interaction constant utilize either the configuration interaction approach[20,21] or the unrestricted Hartree-Fock method.[22–26] The latter approach removes the restriction that all electrons in a given orbit specified by quantum numbers n and l have the same radial wavefunction. Electrons in the $1s$ and $2s$ shells with spins parallel to the spin of the $2p$ electrons will have a different radial wave function than those with antiparallel spins because of the difference in exchange energy. This results in an unbalance of the net spin density at the nucleus, and, through the Fermi contact term, produces a hyperfine interaction. The contributions of the $1s$ and $2s$ shells are of opposite sign and large compared to the difference between them; consequently precise calculations are difficult. The single determinant unrestricted Hartree-Fock method predicts no quadrupole interaction. Holloway, Lüscher, and Novick have analysed the corrections to the $(2p)^3\ {}^4S$ ground state hyperfine levels resulting from second-order hyperfine interactions with the $(2p)^3\ {}^2D$ and the $(2p)^3\ {}^2P$ levels and due to the effects of spin-orbit and spin-spin coupling on the p^3 configuration. They find that the second-order hyperfine interactions produce an apparent quadrupole interaction for N^{14} of $B(14)=+2.0$ cps and that the mixing of the Russell-Saunders wave functions due to the spin-orbit and spin-spin interaction produces a true quadrupole interaction of $B(14)=-3.4\pm1.6$ cps. These two perturbations also produce small corrections to the magnetic hyperfine interaction constants. However, since the main source of the magnetic hyperfine interaction is not completely understood these calculated corrections cannot be tested experimentally at the present time.

Attempts to understand the pressure shifts have been made for the alkali atoms,[27–29] hydrogen,[30,31] and nitrogen.[32,33] The explanation proposed by Adrian[33] for the origin of the pressure shift of the nitrogen hyperfine structure assumes that the entire effect is due to the van der Waals interaction between the nitrogen atom and the buffer gas atom. The primary effect of this long range interaction is to promote one of the $2s$ electrons from the normal $(1s)^2\,(2s)^2\,(2p)^3$ configuration into a $(1s)^2\,(2s)\,(2p)^4$ configuration. This excitation process leaves in the $2s$ shell an electron with spin parallel to that of the normal $(2p)^3$ electrons and increases the spin density at the nucleus. This is equivalent to a positive pressure shift. Adrian predicts explicit values for the pressure shifts of the hyperfine structure of atomic nitrogen in helium, neon, argon, and molecular nitrogen buffer gases.

The work reported in this paper was undertaken primarily to determine the nitrogen pressure shifts. At the time this experiment was undertaken the only values for the pressure shifts were derived from paramagnetic resonance studies of the nitrogen atom in frozen gas matrices.[34] The interpretation of the matrix experiments is difficult because the precise geometry of the nitrogen site is not known. It is better to measure the pressure shifts by another method and use the matrix shifts to study the trapping sites. Secondary results of the experiments reported here are more precise values for the nitrogen hyperfine interaction constants.

METHOD AND APPARATUS

Since there exists a rather substantial literature concerning the use of optical pumping with spin ecxhange to determine the ground state hyperfine interaction constants of S-state atoms,[2,9,10,17,18,35] only a brief description of the method is presented here. Rubidium resonance radiation from an electrodeless discharge was circularly polarized, filtered to select the D_1 ($5\ {}^2P_{1/2}\rightarrow 5\ {}^2S_{1/2}$) line, and passed through a spherical absorption flask containing rubidium vapor, a buffer gas, and atomic nitrogen. The transmitted light was monitored with a 925 vacuum photocell. The atomic nitrogen was produced by a radio-frequency discharge which could either be pulsed or run continuously. The absorption of light by the rubidium vapor in the resonance flask polarized the rubidium. The spin exchange collisions between the polarized rubidium atoms and the atomic nitrogen polarized the nitrogen. Any change in the nitrogen polarization, such as was caused by the application of a radio-frequency field at the nitrogen hyperfine frequency, led to a change in the rubidium polarization, and to a decrease in the amount of light transmitted by the absorption flask.

Figure 1 is a schematic drawing of the optical pumping apparatus. With the exception of the frequency

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generating equipment, the main components of the apparatus have been described previously.[2,35] The 15-Mc/sec signal was generated by a General Radio 805 B Signal Generator. If allowed to run for some time prior to use this oscillator was stable to a few cycles/sec. The 26- and 29-Mc/sec frequencies were generated by multiplying up with a Gertsch AM-1 frequency meter a 1-Mc/sec signal derived from a National Company Atomichron. The resulting signal was amplified, modulated with a mercury relay at 18 cps and fed into a radio-frequency Helmholtz coil placed around the absorption flask with its axis perpendicular to the light beam. The frequencies were measured with a Northeastern frequency counter whose time base was derived from a 100-kc crystal oscillator maintained and monitored by J. A. Pierce of the Cruft Laboratory. The absorption flasks were 300-cc spherical bulbs provided with glass-covered tungsten electrodes. In each bulb there was approximately 1 g of rubidium, 1 mm Hg of spectroscopically pure nitrogen and an appropriate amount of buffer gas. The bulb pressures were measured with an oil manometer upon filling. The measured pressures were converted, using the ideal gas law, so as to give the correct pressure at 25°C. This 25°C temperature was within a few degrees the temperature at which the bulbs were filled.

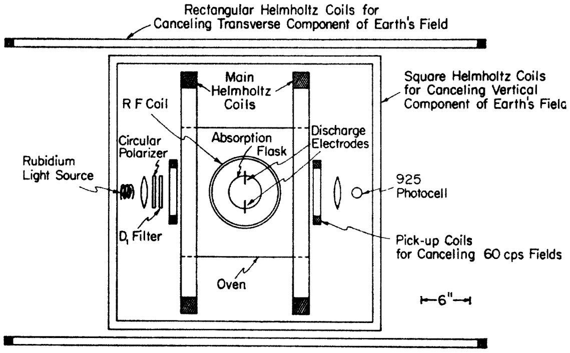

FIG. 1. A schematic diagram of the apparatus.

MEASUREMENTS AND RESULTS

The Hamiltonian describing the ground state of the nitrogen atom in an external magnetic field can be written in the form

$$\mathcal{H}=A\mathbf{I}\cdot\mathbf{J}+|g_J|\mu_0\mathbf{J}\cdot\mathbf{H}-g_I\mu_0\mathbf{I}\cdot\mathbf{H}+[B/2I(2I-1)J(2J-1)]\times[3(\mathbf{I}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}\cdot\mathbf{J})-\mathbf{I}^2\mathbf{J}^2]. \quad (1)$$

Here A is the magnetic dipole hyperfine interaction constant, B the quadrupole hyperfine interaction constant, and g_I and g_J are the nuclear and electronic gyromagnetic ratios, respectively. The nuclear spin, I, is 1 for N^{14} and $\frac{1}{2}$ for N^{15}; as a result B for N^{15} must be zero. The electronic angular momentum, J, is $\frac{3}{2}$ for atomic nitrogen in the $(2p)^3\,{}^4S_{3/2}$ ground electronic state. The energy levels for N^{14} and N^{15} are shown in Figs. 2 and 3, respectively.

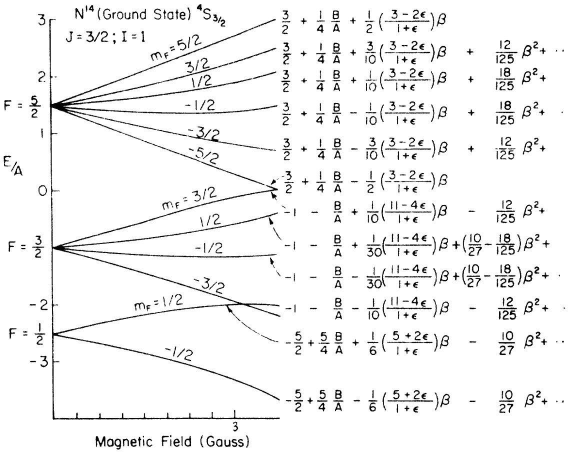

FIG. 2. The energy levels for N^{14} in a small magnetic field. Here $\beta=(|g_J|+g_I)\mu_0H/A$ and $\epsilon=g_I/|g_J|$. The expression for β given in the figure caption of Fig. 2 in reference 17 has an incorrect sign for g_I.

Since the spin exchange process populates states with a given m_F independently of F, no $\Delta m_F=0$ transitions were observable.[17] This made it necessary to make rapid measurements of pairs of $\Delta m_F=\pm1$ transitions which could be averaged to obtain the zero field hyperfine splittings. All of the $\Delta F=\pm1$, $\Delta m_F=\pm1$ hyperfine transitions of N^{14} and N^{15} can be divided into pairs, the sum of whose frequency depends only quadratically on the external magnetic field. Those pairs having the smallest linear dependence on the magnetic field were

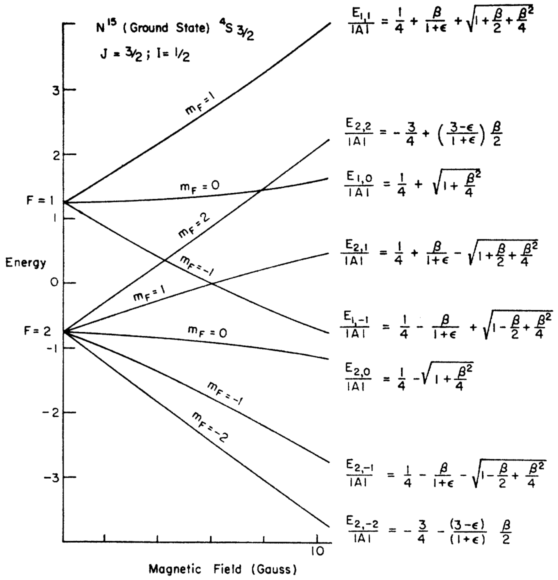

FIG. 3. The energy levels for N^{15} in a small magnetic field. Here $\beta=(|g_J|+g_I)\mu_0H/A$ and $\epsilon=g_I/|g_J|$. The expression for β given in the figure caption of Fig. 3 in reference 17 has an incorrect sign for g_I.

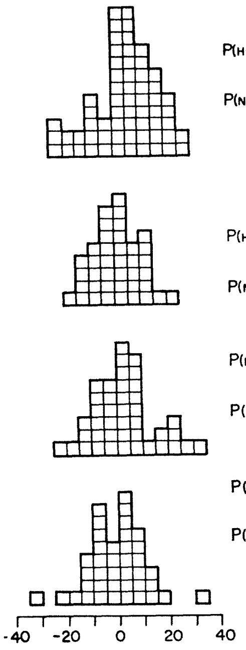

FIG. 4. A histogram of all the $(F=\frac{3}{2}\rightarrow F=\frac{1}{2})$ determinations made on the N^{14} in He bulbs. Each square represents one hyperfine determination in a 5 cps interval.

used for each isotope. They were the $(F=\frac{5}{2}, m_F=\pm\frac{5}{2}\leftrightarrow F=\frac{3}{2},\ m_F=\pm\frac{3}{2})$ and the $(F=\frac{3}{2},\ m_F=\pm\frac{3}{2}\leftrightarrow F=\frac{1}{2},\ m_F=\pm\frac{1}{2})$ transitions for N^{14} and the $(F=2, m_F=\pm 2\leftrightarrow F=1, m_F=\pm 1)$ transitions for N^{15}.

All the measurements were made in a field of approximately 0.15 G. In calculating the quadratic correction the difference of the frequency of the two transitions was used to determine the magnetic field. It was necessary in analyzing the data to expand the energy levels to fourth order in the external magnetic field. For reducing the data the g_J values of Heald and Beringer[13] and the g_I values of Anderson, Pipkin, and Baird[17] were used.

One determination of the hyperfine splitting consisted of two measurements of each of the pair of hyperfine transitions being used. The linewidth (full width at half maximum) ranged between 250 and 350 cps and depended critically upon the discharge conditions in the bulb. Approximately 180 cps (0.25 mG) of this width was due to magnetic field inhomogeneity. Measurements were made with the static magnetic field both parallel and antiparallel to the direction of the light beam. In a given experimental run, sets of ten determinations were made for each field direction. There was no clearly discernible dependence of the measured splittings on the field direction. Histograms of all the determinations for the N^{14} $(F=\frac{3}{2}\leftrightarrow F=\frac{1}{2})$ hyperfine interval in the helium bulbs are shown in Fig. 4. The results for the other buffer gases were similar. Several unsuccessful attempts were made to use a krypton buffer gas. The krypton severely decreased the rubidium polarization obtainable and made it difficult to measure the nitrogen transitions.[36]

TABLE I. The average frequencies for the N^{15} bulbs. One determination results from two measurements of each of the $(F=2,m_F=+2\leftrightarrow F=1,m_F=+1)$ and the $(F=2,m_F=-2\leftrightarrow F=1, m_F=-1)$ hyperfine transitions. The data were taken in sets of approximately ten determinations; the means and the standard deviations of the means are for the N determinations. The bulb pressures were measured at approximately 25°C and were corrected to that value using the ideal gas law. The measurements were made between 60 and 90°C.

Buffer gas	Pressure in mm Hg at 25°C	Number of determinations	$2A$—29 290 000 in cps
Neon	13.54±0.10	39	940.0±1.2
Neon	29.58±0.10	43	966.1±1.5
Neon	46.75±0.10	40	985.3±2.6
Neon	63.39±0.10	41	1022.5±2.2
Argon	11.48±0.10	39	977.1±3.1
Argon	25.37±0.10	40	1060.4±2.8
Argon	41.69±0.10	41	1153.1±1.7
Argon	63.56±0.10	40	1261.9±2.6
Helium	13.48±0.10	42	921.7±1.8
Helium	28.96±0.10	42	933.2±1.9
Helium	41.75±0.10	58	949.2±1.4
Helium	63.40±0.10	41	964.0±1.2

The average frequencies for the measurements of the nitrogen bulbs are summarized in Tables I and II and appear graphically in Figs. 5, 6, and 7. Table III summarizes the zero-pressure intercepts and pressure shifts calculated by fitting straight lines to the data by the method of least squares. The data have been corrected for the pressure shift due to the molecular nitrogen in the bulbs. It was assumed that the shifts for the different gases were additive. The final values for the zero field hyperfine splittings were obtained by weighting the zero pressure extrapolations of the various buffer gases inversely with the square of their errors and averaging. The errors quoted for the average hyperfine intervals are based upon the failure of the straight lines

TABLE II. The average frequencies for the N^{14} bulbs. One determination results from two measurements of each of the pair of hyperfine transitions being used. The data were taken in sets of between ten and twenty measurements. The reported values are the arithmetic means and their standard deviation. The bulb pressures were measured at approximately 25°C and were corrected to that value using the ideal gas law. The measurements were made between 60 and 90°C.

Buffer gas	Pressure in mm Hg at 25°C	Number of determinations	Observed frequency in cps
Nitrogen	13.13±0.10	20	26 127 393.8±2.9
Nitrogen	26.73±0.10	16	26 127 450.8±5.8
Nitrogen	58.39±0.10	10	26 127 580.6±3.3
Helium	10.99±0.10	39	26 127 336.2±2.4
Helium	23.21±0.10	35	26 127 333.5±2.4
Helium	37.21±0.10	39	26 127 348.2±2.5
Helium	54.02±0.10	47	26 127 363.9±2.0
Helium	10.99±0.10	40	15 676 391.6±1.8
Helium	23.21±0.10	41	15 676 405.5±1.8
Helium	37.21±0.10	40	15 676 404.3±1.4
Helium	54.02±0.10	62	15 676 408.5±1.6

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to intersect at zero pressure. In terms of the statistical variation of the data this error is equivalent to three standard deviations of the mean. The value obtained in this fashion for the N^{15} zero-field hyperfine frequency is

$$\nu(F=2\leftrightarrow F=1)=2|A|=29\,290\,914\pm10\text{ cps},\qquad(2)$$

and the corresponding hyperfine interaction constant is[37]

$$A(N^{15})=-14\,645\,457\pm5\text{ cps}.\qquad(3)$$

The zero-field hyperfine intervals for N^{14} are

$$\nu(F=\tfrac{5}{2}\leftrightarrow F=\tfrac{3}{2})=(\tfrac{5}{2})A+(5/4)B$$
$$=26\,127\,326\pm18\text{ cps},\qquad(4)$$

$$\nu(F=\tfrac{3}{2}\leftrightarrow F=\tfrac{1}{2})=(\tfrac{3}{2})A-(9/4)B$$
$$=15\,676\,392\pm12\text{ cps},\qquad(5)$$

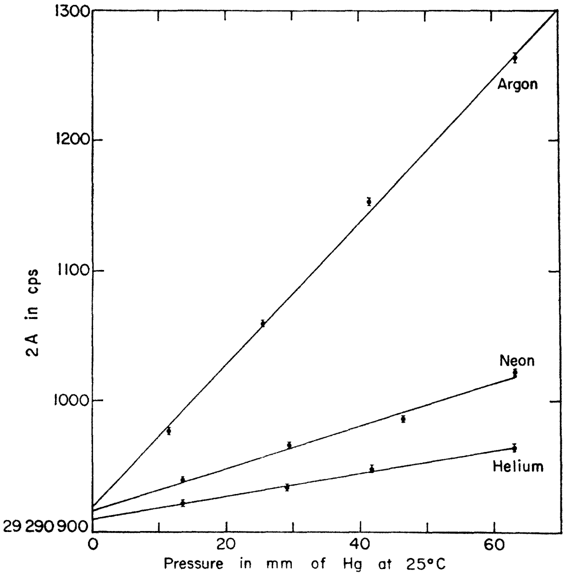

FIG. 5. A plot of the measured values of the $(F=2\rightarrow F=1)$ transition frequencies for N^{15} as a function of pressure for argon, neon, and helium buffer gases. The results of least-squares fits are given in Table III.

and the hyperfine interaction constants are

$$A(N^{14})=+10\,450\,930\pm8\text{ cps},\qquad(6)$$

$$B(N^{14})=+\qquad 1\pm5\text{ cps}.\qquad(7)$$

These results, when combined with the measured ratio of the nuclear moments for the nitrogen isotopes,[17,38,39] give for the $N^{14}-N^{15}$ hyperfine anomaly

$$\Delta=\frac{A(N^{14})}{A(N^{15})}\frac{g_I(N^{15})}{g_I(N^{14})}-1=(0.9986\pm0.0020)\times10^{-3}.\qquad(8)$$

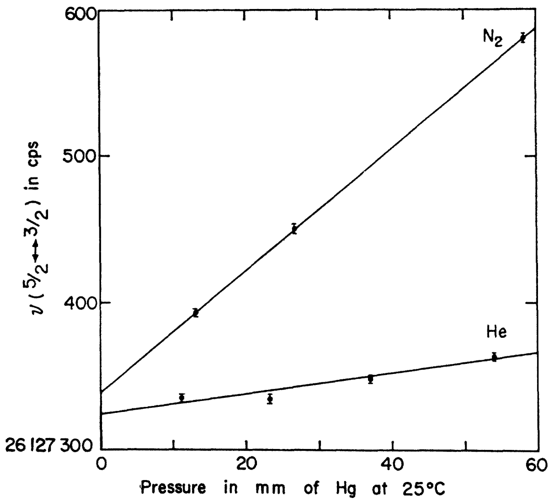

FIG. 6. A plot of the measured values of the $(F=\frac{5}{2}\rightarrow F=\frac{3}{2})$ hyperfine interval for N^{14} as a function of pressure for molecular nitrogen and helium buffer gases. The results of least squares fits are given in Table III.

DISCUSSION

The measured values for the N^{14} and N^{15} magnetic hyperfine interaction constants agree well with those recently reported by Holloway, Lüscher, and Novick.[9] The value for N^{15} disagrees with an earlier reported measurement by Anderson, Pipkin, and Baird,[17] The pressure shift for nitrogen in a molecular nitrogen buffer gas is in agreement with that of Holloway, Lüscher, and Novick. The value for the nitrogen 14 quadrupole interaction constant found in this experiment (1±5 cps) is in agreement with the experimental value reported by Holloway, Lüscher, and Novick (−5±20 cps) and with the theoretical value calculated by them (−1.4±1.6 cps).

The Adrian theory predicts that the pressure shifts at constant temperature should have the following dependence upon the characteristics of the buffer gas:

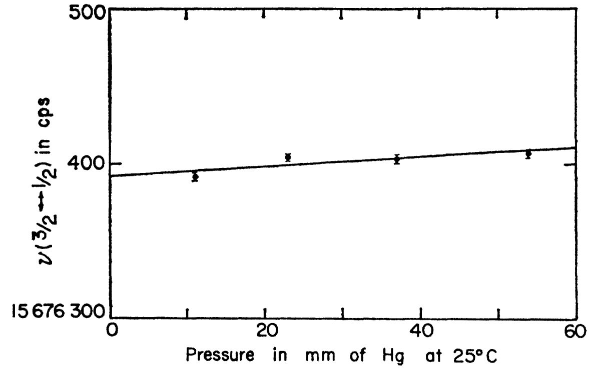

FIG. 7. A plot of the measured $(F=\frac{3}{2}\rightarrow F=\frac{1}{2})$ hyperfine interval for N^{14} in helium as a function of the buffer gas pressure. The result of a least-squares fit is given in Table III.

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[37] The signs were determined in reference 17.

[38] H. R. Brooker, P. J. Haigh, and T. A. Scott, Phys. Rev. 123, 2143 (1961).

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TABLE III. Values of the zero pressure intercepts and slopes of the frequency vs buffer gas pressure curves as determined by the method of least squares. Also included are the fractional pressure shifts, defined as $(1/A)dA/dP$. The errors in the slopes and intercepts were determined by the usual least squares methods, except that for purposes of determining the error of the zero-pressure intercepts and the slopes, the largest standard deviation of the mean points determining a line was taken to be common to all points of the line.

Nitrogen isotope	Buffer gas	Zero-pressure intercept in cps	Slope cps (mm Hg)$^{-1}$	Fractional pressure shift $\times 10^8$ in (mm Hg)$^{-1}$
N^{15}	Neon	29 290 917 ±3	1.60 ±0.07	5.46 ±0.24
N^{15}	Argon	29 290 919 ±3	5.47 ±0.08	18.67 ±0.24
N^{15}	Helium	29 290 910 ±2	0.87 ±0.05	2.97 ±0.17
N^{14}	Helium	26 127 324 ±3	0.70 ±0.07	2.68 ±0.27
N^{14}	Nitrogen	26 127 340 ±7	4.12 ±0.18	15.77 ±0.69
N^{14}	Helium	15 676 392 ±2	0.33 ±0.06	2.11 ±0.38

$$\frac{1}{A_{\mathrm{N}}}\frac{dA_{\mathrm{N}}}{dp}=\frac{8\pi}{kT}\left(\frac{e^2}{a_0}\frac{1}{E_{\mathrm{N}}}\right)\left(\frac{a_0}{\sigma}\right)^3\left(1+\frac{E_{\mathrm{N}}}{E_{\mathrm{N}}+E_M}\right)$$
$$\times\left(\frac{E_M}{E_{\mathrm{N}}+E_M}\right)\left[\frac{(s|z|z)}{a_0}\right]^2\frac{A_{\mathrm{N}2s}}{A_{\mathrm{N}}}I\left(\frac{kT}{\epsilon}\right)\alpha_M. \quad (9)$$

Here A_{N} is the hyperfine interaction constant for atomic nitrogen, p is the buffer gas pressure in dyn/cm^2, T is the absolute temperature, k is the Boltzmann constant, a_0 the Bohr radius, E_{N} is magnitude of the average excitation energy of the nitrogen atom when the $2s$ electron is promoted to the $2p$ shell, E_M is the magnitude of the ionization energy of the buffer gas atom or molecule, σ is the collision diameter for the two interacting systems, ϵ is the depth of the attractive potential well due to the van der Waals interaction, α_M is the polarizability of the buffer gas, $A_{\mathrm{N}2s}$ is the hyperfine interaction constant for a nitrogen $2s$ electron , $(s|z|z)$ is the matrix element for the excitation of a $2s$ electron into the $2p$ shell by a perturbation of the form z, and $I(kT/\epsilon)$ is a phase space integral which gives the fraction of the time the nitrogen atom and the buffer gas are interacting. This expression results from setting energy denominators equal to their average values and using completeness to sum those third-order perturbation terms involving both the van der Waals and the hyperfine interactions. Adrian evaluates $I(kT/\epsilon)$ and finds that it varies only from 0.50 to 0.46 in going from helium to argon. Table IV summarizes the fractional pressure shifts predicted by Adrian and the ones found in this experiment. Figure 8(a) shows a plot of the measured fractional pressure shifts vs the polarizability of the buffer gas; Fig. 8(b) shows a plot of the measured fractional pressure shifts vs the quantity

$$\left(\frac{a_0}{\sigma}\right)^3\left(1+\frac{E_{\mathrm{N}}}{E_{\mathrm{N}}+E_M}\right)\left(\frac{E_M}{E_{\mathrm{N}}+E_M}\right)\alpha_M. \quad (10)$$

For plotting this figure the values of σ and E_{N} were taken from Adrian's paper. The σ were $5.35a_0$, $5.51a_0$, $6.12a_0$, and $6.41a_0$ for helium, neon, argon, and molecular nitrogen buffer gases, respectively. Adrian obtained $0.402(e^2/a_0)$ for E_{N}. Table IV and Fig. 8 indicate that the Adrian theory gives the correct dependence on the buffer gas properties but that it overestimates the shift by a factor of 3.

Further information as to the origin of this discrepancy could be derived from a measurement of the Stark shift of the hyperfine interaction constant of atomic nitrogen. An external electric field will produce a quadratic Stark shift of the hyperfine structure in the same manner as the van der Waals interaction produces a pressure shift. The hyperfine Stark shift depends only on the properties of the nitrogen atom and does not depend upon the polarizability of the buffer gas atom or the details of the buffer gas-nitrogen atom interaction. Thus a measurement of the Stark shift of the nitrogen hyperfine interaction constant might indicate whether the failure of Adrian's theory was due to over simplification of the nitrogen atom wave functions or due to improper treatment of the buffer-gas-nitrogen atom interaction.

Adrian's formulas can easily be modified so as to give the expression for the Stark shift. If the interaction of the nitrogen atom with the electric field is written in the form

$$\mathcal{H}=eE\sum_{\mu=1}^{7}z_\mu, \quad (11)$$

where E is the electric field in statvolts/cm and z_μ is the z coordinate of the μth electron, then one need only replace the van der Waals interaction Hamiltonian in Adrian's paper [Eq. (2)] by Eq. (11). If this is done and the algebra is carried through, the following expression

TBALE IV. A comparison of the values for the pressure shift of the nitrogen hyperfine interaction constant calculated by Adrian and the measured values.

Buffer gas	$\frac{1}{A}\left(\frac{dA}{dp}\right)_{\mathrm{theo}}\times 10^8$ (mm Hg)$^{-1}$	$\frac{1}{A}\left(\frac{dA}{dp}\right)_{\mathrm{exp}}\times 10^8$ (mm Hg)$^{-1}$	$\frac{1}{A}\left(\frac{dA}{dp}\right)_{\mathrm{exp}}\Big/\frac{1}{A}\left(\frac{dA}{dp}\right)_{\mathrm{theo}}$
Helium	11	2.6±0.7	0.23±0.07
Neon	17	5.5±0.7	0.32±0.04
Argon	48	18.7±0.7	0.39±0.02
Nitrogen	46	15.8±2.0	0.34±0.04

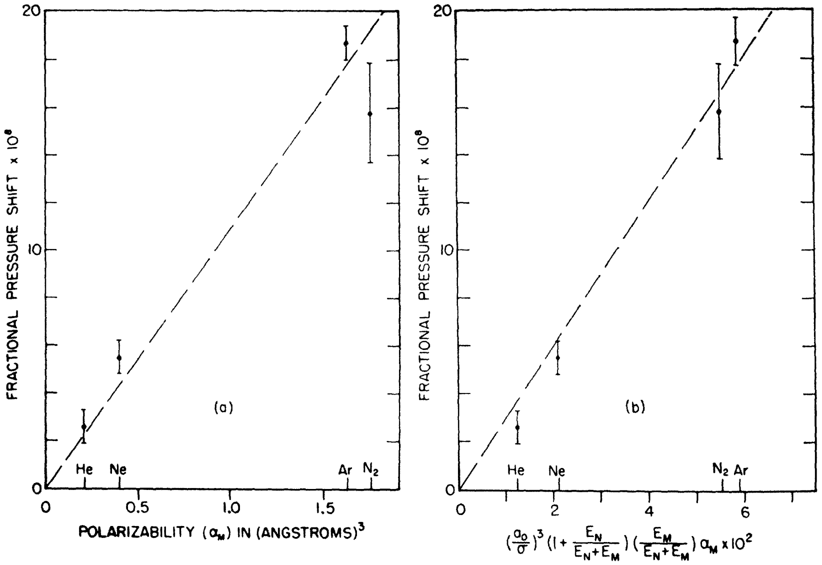

FIG 8 (a) A plot of the fractional pressure shifts $[(1/A)dA/dp]$ per mm Hg for nitrogen versus the polarizability of the buffer gas atom or molecule. (b) A plot of the fractional pressure shifts per mm Hg for nitrogen versus the function

$$\left(\frac{a_0}{\sigma}\right)^2\left(1+\frac{E_N}{E_N+E_M}\right)\left(\frac{E_M}{E_N+E_M}\right)\alpha_M.$$

is obtained for the hyperfine Stark shift:

$$\Delta A = -\frac{4}{3}\frac{e^2E^2}{(E_N)^2}(s|z|z)^2 A_{N2s}. \qquad (12)$$

If Adrian's values $(s|z|z)^2 = 0.607a_0^2$, $E_N = 0.402e^2/a_0$, and $A_{N^{14}2s} = 1510$ Mc/sec are inserted into Eq. (12), the hyperfine Stark shift for nitrogen-14 is

$$\Delta A(14) = 2.6\times 10^{-5}E^2 \text{ cps}. \qquad (13)$$

For a field of $E = 300$ statV/c

$$\Delta A(14) = 0.24 \text{ cps}. \qquad (14)$$

This shift is small but it should be measurable either by a refined optical pumping experiment or by a maser-type experiment[40] where atomic nitrogen is passed through an inhomogeneous magnetic field to select certain states, stored in a bulb whose walls have been coated so as not to relax the nitrogen, and then allowed to radiate into a tuned circuit and radio receiver.

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[40] D. Kleppner, H. M. Goldenberg, and N. F. Ramsey, Phys. Rev. **126**, 603 (1962).