

was so poor that only a broad peak at 9.0 eV and shoulders at 9.5 and 10.3 eV were distinguishable. There is a steep rise at 11.2 eV which, similar to the case of krypton, is some 0.9 eV below the ionization threshold.

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## Paramagnetic-Resonance Spectrum of Metastable ( $^2D$ ) Atomic Nitrogen\*

H. E. RADFORD† AND K. M. EVENSON

*National Bureau of Standards, Boulder, Colorado 80302*

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The paramagnetic-resonance spectrum of free metastable ( $^2D$ ) nitrogen atoms has been observed in the flowing products of an electric discharge in nitrogen-helium gas mixtures. An analysis of the Zeeman effect and hyperfine structure yields the following values for the atomic  $g$  factors and radial integrals:  $g_J(^2D_{5/2}) = 1.20036 \pm 0.00001$ ;  $g_J(^2D_{3/2}) = 0.79949 \pm 0.00002$ ;  $\langle r_i^{-3} \rangle = (20.21 \pm 0.02) \times 10^{24} \text{ cm}^{-3}$ ;  $\langle r_s^{-3} \rangle = (22.22 \pm 0.02) \times 10^{24} \text{ cm}^{-3}$ . The  $^2D$  fine-structure separation is found to be  $-8.69 \pm 0.02 \text{ cm}^{-1}$ . Evidence is found of a small electric-quadrupole hyperfine-structure interaction.

#### INTRODUCTION

RECENT work at this laboratory has shown it possible to detect paramagnetic-resonance absorption by metastable ( $^2D$ ) nitrogen atoms in a mixture of nitrogen and helium gas that has passed through an electric discharge.<sup>1</sup> The spectrum is interesting because it shows well-developed anisotropic hyperfine structure, a type of hyperfine structure which the familiar spectrum<sup>2,3</sup> of ground-state ( $^4S$ ) atomic nitrogen does not have, and also because it provides an alternative technique of studying the formation and decay of metastable nitrogen atoms, a technique with some potential advantages over those of optical<sup>4,5</sup> and mass<sup>6</sup> spectrometry. As first observed, the absorption lines were weak and broad, and subsequent efforts have been made to intensify and sharpen the  $^2D$  spectrum, and to detect the corresponding spectrum of the metastable  $^2P$  term. These efforts have not succeeded, and the present report is limited, therefore, to an analysis of the hyperfine structure and Zeeman effect of the  $^2D$  term, based on precise measurements of spectra like that of Fig. 1, which is reprinted here from the earlier report.

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† Permanent address: National Bureau of Standards, Washington, D. C. 20234.

<sup>1</sup> K. M. Evenson and H. E. Radford, *Phys. Rev. Letters* **15**, 916 (1965).

<sup>2</sup> M. A. Heald and R. Beringer, *Phys. Rev.* **96**, 645 (1954).

<sup>3</sup> K. M. Evenson and D. S. Burch, *J. Chem. Phys.* **45**, 2450 (1966).

<sup>4</sup> J. F. Noxon, *J. Chem. Phys.* **36**, 926 (1962).

<sup>5</sup> Y. Tanaka, A. S. Jursa, F. J. LeBlanc, and E. C. Y. Inn, *J. Planet. Space Sci.* **1**, 7 (1959).

<sup>6</sup> S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **37**, 1662 (1962).

#### EXPERIMENT

A double modulation (100-kHz and 100-Hz) X-band electron-paramagnetic-resonance (EPR) spectrometer was used to measure the spectra. In order to obtain the desired accuracy of one part in  $10^5$ , each  $^2D_{3/2}$  line was traced 2 to 6 times with a 1-sec time constant, and each  $^2D_{5/2}$  line was traced 6 to 12 times with a 3-sec time constant.

A standard frequency counter accurate to one part in  $10^8$  and a transfer oscillator were used to measure the klystron frequency. The same counter was used to measure (to about one part in  $10^6$ ) the resonant frequency of the nuclear-magnetic-resonance (NMR) magnetic-field probe, which contained a cylindrical sample of mineral oil 2 mm in diameter and 10 mm long. A small correction, typically  $0.3 \pm 0.01 \text{ G}$  at 5500 G and  $1.0 \pm 0.3 \text{ G}$  at 8300 G, was made for the difference between the magnetic field at the center of the EPR cavity and the NMR-probe position. The difference was due partly to the field inhomogeneity of the electromagnet and partly to a paramagnetic impurity in the material from which the EPR cavity was constructed. The klystron frequency was locked to the cavity resonance, and was monitored continuously during the recording of each EPR line; the uncertainty in measuring this frequency was one part in  $10^6$ , due to small drifts of the klystron frequency during the sweeping of each line. The largest inaccuracy in the measurements was in determining the exact center of each line; in the weakest of the lines a single scan yielded the line center to about 3 parts in  $10^5$ . However, 10 or more

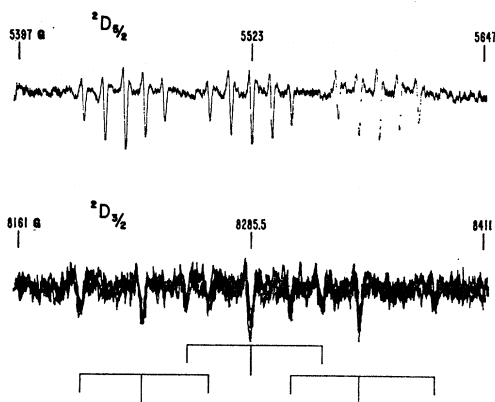


FIG. 1. Tracings of the EPR spectra of the metastable  $^2D$  levels of atomic nitrogen, as observed, taken in a helium-nitrogen afterglow. The upper trace shows the  $^2D_{5/2}$  spectrum and the lower trace, the  $^2D_{3/2}$  spectrum. The microwave frequency was 9.280 GHz. The 250-G scans were made in 50 min with a 10-sec time constant.

scans were made on these weaker lines to achieve an accuracy of better than one part in  $10^5$ .

Nitrogen and helium entered the EPR cavity through the same gas handling system, electric discharge, and high-speed nozzle as that used in the earlier measurements.<sup>1</sup> The partial pressures were 0.1 Torr of nitrogen and 3.4 Torr of helium; the impurity levels listed as typical by the manufacturer were 25 ppm in the nitrogen and less than 20 ppm in the helium. High gas purity was necessary, as was shown by the loss of all EPR signals when a 1-m length of plastic hose was substituted for the copper tubing normally used in the low-pressure line between the gas tanks and the nozzle.

The EPR linewidths were  $2.7 \pm 0.4$  MHz in the  $^2D_{5/2}$  spectrum, and  $3.1 \pm 0.5$  MHz in the  $^2D_{3/2}$  spectrum. They were not found to change over a pressure variation of about a factor of 3; however, accurate measurements could not be made because the signal weakened rapidly as the total pressure was changed to either side of 3.5 Torr.

### ANALYSIS

The  $^2D$  term of nitrogen lies  $19223 \text{ cm}^{-1}$  (2 eV) above the ground  $^4S$  term; it has two fine-structure levels,  $^2D_{3/2}$  and  $^2D_{5/2}$ , separated by  $8 \text{ cm}^{-1}$ , the  $^2D_{3/2}$  level being higher.<sup>7</sup> The Lande  $g$  factors are  $6/5$  for  $^2D_{5/2}$  and  $4/5$  for  $^2D_{3/2}$ , and this puts the X-band paramagnetic-resonance spectra of the two levels at magnetic-field strengths of roughly 5500 and 8300 G, respectively, as shown by Fig. 1. A pictorial explanation of the line-splitting patterns is given by Fig. 2, which shows the energy-level structure in detail. The magnetic-dipole-hyperfine-structure interaction splits each spectrum into  $2I+1=3$  groups of lines, each group containing

<sup>7</sup> C. E. Moore, *Atomic Energy Levels* (U. S. Government Printing Office, Washington, D. C., 1949), Vol. I, Natl. Bur. Std. Circ. No. 467, p. 32.

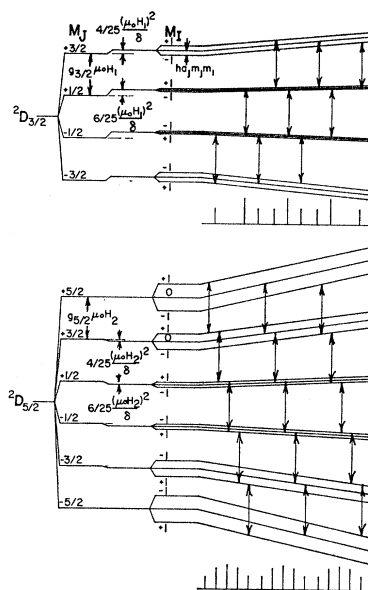


FIG. 2. Zeeman energy-level diagram of the  $^2D$  state of atomic nitrogen.

$2J$  (5 for  $^2D_{5/2}$ , 3 for  $^2D_{3/2}$ ) individual lines. The splittings within each group of lines are caused mostly by the quadratic Zeeman effect, which is large because of the close fine-structure spacing. This close level spacing makes the Zeeman effect fairly complicated (an "incipient Paschen-Back effect"), and requires, as a first step in the analysis, an accurate solution of the Zeeman effect. The hyperfine structure may then be evaluated by perturbation theory, using as zero-order functions the calculated Zeeman wave functions. The resultant Zeeman hyperfine energies can be represented by a summation, the terms of which are discussed separately in the following sections. The over-all level of accuracy sought in the analysis is  $\pm 0.1$  MHz, to match the accuracy of the experimental results.

### ZEEMAN EFFECT

The  $^2D$  term is well isolated in energy, and it is only necessary to diagonalize the perturbation matrix of the spin orbit and Zeeman operator,

$$H_1 = \zeta \mathbf{L} \cdot \mathbf{S} + \mu_0 (g_l \mathbf{L} + g_s \mathbf{S} + g_I \mathbf{I}) \cdot \mathbf{H}, \quad (1)$$

within the  $^2D$  term itself. The matrix is  $2 \times 2$ , and has the exact solution<sup>8</sup> (good for any  $L$  doublet)

$$W_1 = -\frac{\delta}{2(2L+1)} + (g_I m_J + g_I m_I) \mu_0 H \pm \frac{1}{2} \delta (1 + 2\alpha x + x^2)^{1/2}, \quad (2)$$

<sup>8</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1959), p. 153. Our Eq. (1) is a condensation of Condon and Shortley's Eqs. (12a) and (12b), with changes in notation, and is analogous to the Breit-Rabi equation for hyperfine structure.

where

$$\begin{aligned} x &= (g_s - g_l)\mu_0 H / \delta, \\ \alpha &= 2m_J / (2L + 1), \end{aligned}$$

and  $\delta$  represents the fine-structure interval, positive or negative according to whether the fine structure is regular or inverted. The upper sign before the square root in (2) is used for the  $J = L + \frac{1}{2}$  level, the lower sign for the  $J = L - \frac{1}{2}$  level. These identifications are only approximate, for the magnetic field mixes the two  $J$  levels, giving field-dependent wave functions of the form

$$\Psi(^2L, m_J, x) = C_1 \psi(J = L - \frac{1}{2}, m_J) + C_2 \psi(J = L + \frac{1}{2}, m_J), \quad (3)$$

where

$$\begin{aligned} C_1 &= \frac{1}{2} \frac{1 + [\alpha + (1 - \alpha^2)^{1/2}]x \mp (1 + 2\alpha x + x^2)^{1/2}}{[1 + 2\alpha x + x^2 \mp x((1 - \alpha^2)(1 + 2\alpha x + x^2))^{1/2}]^{1/2}}, \\ C_2 &= -\frac{1}{2} \frac{1 + [\alpha - (1 - \alpha^2)^{1/2}]x \pm (1 + 2\alpha x + x^2)^{1/2}}{[1 + 2\alpha x + x^2 \mp x((1 - \alpha^2)(1 + 2\alpha x + x^2))^{1/2}]^{1/2}}. \end{aligned}$$

The upper signs again go with the  $J = L + \frac{1}{2}$  level, the lower signs with the  $J = L - \frac{1}{2}$  level, as may be verified by setting  $x = 0$  in these formulas.

The actual values of the field parameter  $x$  for the  $^2D$  nitrogen spectrum do not exceed 0.05, and Eqs. (2) and (3) are more convenient to use in power-series expansions. The Zeeman energies are given correctly to better than 0.1 MHz by an expansion of (2) to fourth order in  $x$ . An expansion of the wave functions (3) to second order in  $x$  is required for the hyperfine-structure calculation of the next section.

The linear term of the Zeeman energy expansion, when written in the form  $(g_J m_J + g_I m_I)\mu_0 H$ , defines the atomic  $g$  factor  $g_J$  which is the main point of contact between theory and experiment for the Zeeman effect. The  $g$  factors for the two levels of a spin doublet are, according to (2),

$$g_J = g_l \pm (g_s - g_l) / (2L + 1), \quad (4)$$

but this formula is subject to correction for deviations from  $L$ - $S$  coupling and for relativistic effects,<sup>9</sup> both of which are disregarded by (2). The correction to the  $^2D$   $g$  factors for deviation from  $L$ - $S$  coupling, caused by the spin-orbit interaction within the ground electron configuration, may be computed from perturbation theory. The result is

$$\begin{aligned} \Delta g(^2D_{5/2}) &= 0, \\ \Delta g(^2D_{3/2}) &= 2\zeta^2 / 3 (E_D - E_P)^2, \end{aligned} \quad (5)$$

where  $E_D - E_P$  is the energy separation of the metastable  $^2D$  and  $^2P$  terms, 9609  $\text{cm}^{-1}$ , and  $\zeta$  is the spin-orbit parameter. The latter has been estimated<sup>10</sup> by

<sup>9</sup> V. H. Hughes, in *Recent Research in Molecular Beams*, edited by I. Esterman (Academic Press Inc., New York, 1959).

extrapolation from neighboring configurations to be 69  $\text{cm}^{-1}$ , giving  $\Delta g(^2D_{3/2}) = 3 \times 10^{-5}$ . The method of computing relativistic  $g$ -factor corrections is known,<sup>9</sup> but an accurate calculation is beyond the scope of this paper.

## HYPERFINE STRUCTURE

The expectation values of the magnetic-dipole hyperfine-structure operator

$$H_2 = 2g_I \mu_0 \mu_N \mathbf{I} \cdot \left[ \sum \frac{\mathbf{I}_i}{r_i^3} - \frac{\mathbf{s}_i}{r_i^3} + 3 \frac{\mathbf{s}_i \cdot \mathbf{r}_i}{r_i^5} \mathbf{r}_i + \frac{8\pi}{3} \delta(r_i) \mathbf{s}_i \right], \quad (6)$$

calculated with the field-dependent wave functions (3) are, to second order in the field parameter  $x$ ,

$$\begin{aligned} W_2^{(1)} &= h \left[ \frac{1}{2} (1 \pm 1) a_J + \frac{1}{2} (1 \mp 1) a_{J-1} \right] m_I m_J \\ &\quad \mp \frac{1}{2} h a_{J, J-1} m_I (2L + 1) (1 - \alpha^2) x \\ &\quad \pm h (a_{J, J-1} - a_J + a_{J-1}) m_I m_J (1 - \alpha^2) x^2, \end{aligned} \quad (7)$$

insofar as they depend on  $m_I$ ,  $m_J$ , and  $x$ . The upper signs again go with  $J = L + \frac{1}{2}$  and the lower with  $J = L - \frac{1}{2}$ . The coupling constants  $a_J$ ,  $a_{J-1}$ , and  $a_{J, J-1}$  may be computed from (6) and appropriate combinations of one-electron wave functions, or from the equivalent operator of Harvey<sup>11</sup> [his Eq. (12)] and the Wigner coefficients<sup>12</sup> of the  $L$ - $S$  multiplet. The results for the  $^2D$  levels are

$$\begin{aligned} h a_{5/2} &= 2g_I \mu_0 \mu_N [4 \langle r_i^{-3} \rangle / 5 + 4 \langle r_s^{-3} \rangle / 25 + 8\pi \psi^2(0) / 15], \\ h a_{3/2} &= 2g_I \mu_0 \mu_N [6 \langle r_i^{-3} \rangle / 5 - 14 \langle r_s^{-3} \rangle / 25 - 8\pi \psi^2(0) / 15], \\ h a_{5/2, 3/2} &= 2g_I \mu_0 \mu_N [\langle r_i^{-3} \rangle / 5 + 7 \langle r_s^{-3} \rangle / 50 - 8\pi \psi^2(0) / 15]. \end{aligned} \quad (8)$$

These formulas account for the possibility of polarization effects on both the core and valence electrons of the atom, as recent studies of the hyperfine structure of  $O^{17}$  and  $F^{19}$  by Bessis *et al.*<sup>13</sup> and Harvey<sup>11</sup> have shown to be necessary. This is done by allowing the radial integral  $\langle r^{-3} \rangle$  to take differing values for the spin and orbital contributions to the anisotropic hyperfine structure, as well as by the more usual method of introducing an isotropic  $[\psi^2(0)]$  term even though the zero-order electron configuration has no unpaired  $s$  electrons. The validity of this "three-parameter analysis" of hyperfine structure is supported by theory, but it has been verified experimentally only on one atom,  $O^{17}$ , where the existence of four measured coupling constants allows a redundant determination of the three parameters. It will be evident in the next section that the nitrogen hyperfine structure provides a further, but somewhat

<sup>10</sup> C. W. Ufford and R. M. Gilmour, *Astrophys. J.* **111**, 580 (1950).

<sup>11</sup> J. S. M. Harvey, *Proc. Roy. Soc. (London)* **A285**, 581 (1965).

<sup>12</sup> Reference 8, p. 75.

<sup>13</sup> N. Bessis, H. Lefebvre-Brion, and C. M. Moser, *Phys. Rev.* **128**, 213 (1962); **130**, 1441 (1963).

less rigorous, verification of the three-parameter analysis.

The perturbation calculation of magnetic-dipole hyperfine structure must be carried to third order to reach terms smaller than 0.1 MHz. From the standard perturbation theory,<sup>14</sup> the second-order energy is

$$W_2^{(2)} = \frac{1}{2} [m_I m_J (m_J - m_I) - m_I J (J+1) + m_J I (I+1)] (h a_J)^2 / (g_J \mu_0 H), \quad (9)$$

and the third-order energy is

$$W_2^{(3)} = -\frac{1}{2} m_I m_J [m_I m_J (m_I m_J - 1) - m_I^2 J (J+1) - m_J^2 I (I+1) + I (I+1) J (J+1)] (h a_J)^3 / (g_J \mu_0 H)^2. \quad (10)$$

Unlike the first-order energy (8), these terms are too small to require correction for the field-dependent mixing of the  $^2D_{3/2}$  and  $^2D_{5/2}$  levels.

In the central-field approximation, none of the levels of a  $p^3$  configuration can show electric-quadrupole hyperfine structure, and indeed there is none detectable in the  $^4S_{3/2}$  ground state of nitrogen. Because of polarization of the valence electrons, there can, however, be a nonvanishing quadrupole interaction in the  $^2D$  and  $^2P$  levels, and it is necessary to account for this possibility in the present analysis by including a first-order quadrupole energy term:

$$W_3 = b_J [3m_J^2 - J(J+1)] [3m_I^2 - I(I+1)] \times [4I(2I-1)J(2J-1)]^{-1}. \quad (11)$$

The Zeeman hyperfine-structure energy sublevels are represented by  $W = W_1 + W_2 + W_3$  [i.e., the sum of Eqs. (2), (7), (9), (10), and (11)], and a formula for the paramagnetic-resonance transition energies is obtained by taking the difference  $W(J, m_J, m_I) - W(J, m_J - 1, m_I)$ . We have fitted this formula to the  $^2D_{5/2}$  and  $^2D_{3/2}$  spectra by a single-step iterative method, in which the small correction terms are evaluated from rough values of the constants  $a_J$ ,  $a_{J-1}$ , and  $\delta$ , and then accurate values of these constants and the two  $g$  factors are found from simple averages and differences of the measured line positions. The constants  $a_{J, J-1}$  and  $b_J$  were evaluated in the same way but, because the corresponding energy terms are small, with much lower precision. The electric-quadrupole term in particular is so small that it was not feasible to determine the two constants  $b_{5/2}$  and  $b_{3/2}$  independently. Instead, we have imposed the theoretical<sup>15</sup> relation  $7b_{5/2} = 10b_{3/2}$  on the results given below. An attempt to fit the two spectra without invoking the quadrupole interaction was unsuccessful: The two spectra then yielded values of  $\delta$  which differed by 1%, five times the estimated uncertainty in the final value of  $\delta$ .

<sup>14</sup> Reference 8, p. 34.

<sup>15</sup> H. Koperfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958), p. 154.

The results of the analysis are

$$\begin{aligned} g_{5/2} &= 1.20036(1), \\ g_{3/2} &= 0.79949(2), \\ a_{5/2} &= 114.69(7) \text{ MHz}, \\ a_{3/2} &= 65.3(2) \text{ MHz}, \\ a_{5/2, 3/2} &= 38(2) \text{ MHz}, \\ b_{5/2} &= -0.4(2) \text{ MHz}, \\ b_{3/2} &= -0.3(2) \text{ MHz}, \\ \delta &= -8.69(2) \text{ cm}^{-1}, \end{aligned}$$

where the figures in parentheses are the uncertainties in the last digits, assigned in the manner to be described next. The quality of fit was determined by recalculating the position of each of the 24-paramagnetic-resonance lines, using the above constants, and comparing the calculated and measured positions. The rms deviations of the calculated and measured positions, including all measurements, were found to be 0.07 MHz, or 3% of the linewidth, for the  $^2D_{5/2}$  spectrum, and 0.23 MHz, or 7% of the linewidth, for the weaker  $^2D_{3/2}$  spectrum. The uncertainty assigned to each of the above constants is the minimum increment in that constant which shifts the calculated position of any line by an amount equal to the rms deviation of the spectrum which contains the line.

## DISCUSSION

Part of the difference of the measured  $g$  factors from the Lande values  $6/5$  and  $4/3$  comes from the electron-spin  $g$  factor, which instead of being exactly 2, is  $g_s = 2(1.0011596)$ .<sup>16</sup> With the approximate  $L$ - $S$  coupling correction given under Eq. (5) included, Eq. (4) then predicts the following values for the  $^2D$   $g$  factors:  $g_{5/2} = 1.20046$  and  $g_{3/2} = 0.79957$ . Attributing the difference between these and the experimental values to relativistic effects, one has  $\Delta g_{5/2}(\text{rel.}) = -1.0 \times 10^{-4}$  and  $\Delta g_{3/2}(\text{rel.}) = -0.8 \times 10^{-4}$ . These values are approximately equal to  $-\langle T \rangle_{2p} / mc^2$  for nitrogen,<sup>17</sup> where  $\langle T \rangle_{2p}$  is the kinetic energy of a  $2p$  electron; this is the correct sign and order of magnitude of the relativistic  $g$ -factor corrections.<sup>9</sup>

No single value of  $\langle r^{-3} \rangle$  will account for the observed magnetic-dipole hyperfine structure, and, as in the case of  $O^{17}$  and  $F^{19}$ , it is necessary to permit the spin and orbital contributions to be determined by different values of  $\langle r^{-3} \rangle$ . These two parameters, together with the value of  $\psi^2(0)$ , could be evaluated from the three measured coupling constants, but the precision would be limited by the relatively crude experimental value of  $a_{5/2, 3/2}$ . An alternative approach, which we take here, recognizes that the hyperfine-structure parameters should hold reasonably well for all terms of the  $p^3$

<sup>16</sup> D. T. Wilkinson and H. R. Crane, *Phys. Rev.* **130**, 852 (1963).

<sup>17</sup> Using the analytic wave functions of Ref. 19, we calculate  $\langle T \rangle_{2p} = 1.0 \times 10^{-4} mc^2$ .

TABLE I. Magnetic-dipole hyperfine-structure coupling constants of the  $p^3$  configuration of atomic nitrogen. The theoretical coupling constants are calculated from the following values of the hyperfine-structure parameters:  $8\pi\psi^2(0)/3 = 1.832 \times 10^{24} \text{ cm}^{-3}$ ;  $\langle r_l^{-3} \rangle = 20.21 \times 10^{24} \text{ cm}^{-3}$ ; and  $\langle r_s^{-3} \rangle = 22.22 \times 10^{24} \text{ cm}^{-3}$ .

Term	Coupling constant	Theoretical value (MHz)	Measured value (MHz) <sup>a</sup>
$^4S$	$a_{3/2}$	10.45 <sup>b</sup>	10.45(2) <sup>c</sup>
$^2D$	$a_{5/2}$	114.69 <sup>b</sup>	114.69(7)
	$a_{3/2}$	65.31 <sup>b</sup>	65.3(2)
$^2P$	$a_{5/2, 3/2}$	38.7	38(2)
	$a_{3/2}$	63.4	
	$a_{1/2}$	319.3	
	$a_{3/2, 1/2}$	17.6	

<sup>a</sup> Figures in parentheses are experimental uncertainties in the last digits.

<sup>b</sup> Fitted to experimental results.

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

configuration, and so the value of  $\psi^2(0)$  already known accurately from measurements on the  $^4S$  term<sup>2,18</sup> can be carried over to the  $^2D$  term. The value of  $a_{5/2, 3/2}$  then serves as a combined test of the validity of the three-parameter analysis and of the constancy of the parameters throughout the terms of the configuration. Table I shows the result of fitting Eqs. (8) to the measured coupling constants in the way just described. The predicted value of  $a_{5/2, 3/2}$ , which is the critical quantity, is seen to lie within 1 MHz of the measured value, well within the uncertainty of the latter. A further and definitive test of the hyperfine-structure theory would be provided by possible future measurements on the  $^2P$  term, and it is for this reason that the predicted coupling constants for the  $^2P_{1/2}$  and  $^2P_{3/2}$  levels are also included in Table I.

The values of  $\langle r^{-3} \rangle$  found from this analysis are  $\langle r_l^{-3} \rangle = 20.21(2) \times 10^{24} \text{ cm}^{-3}$  and  $\langle r_s^{-3} \rangle = 22.22(2) \times 10^{24} \text{ cm}^{-3}$ . These may be compared with the theoretical value  $\langle r^{-3} \rangle = 21.0 \times 10^{24} \text{ cm}^{-3}$ , which we calculate from the accurate analytic  $N(^2D)$  wave function of Clementi *et al.*<sup>19</sup> The differences among these three values are

<sup>18</sup> R. H. Lambert and F. M. Pipkin, Phys. Rev. **129**, 1233 (1963).

<sup>19</sup> E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

presumably due to the phenomenon of polarization of the valence electrons, which is not included in the theoretical wave function. Another indication of valence-electron polarization is the small but detectable electric-quadrupole hyperfine structure, which would be absent in an undistorted  $p^3$  electron configuration. The relation between the magnitude of the quadrupole hyperfine structure and the values of  $\langle r_l^{-3} \rangle$  and  $\langle r_s^{-3} \rangle$  could be explored profitably in a detailed calculation of polarization effects, like those already performed<sup>12</sup> for  $O^{17}$  and  $F^{19}$ .

Polarization effects also contribute to the fine-structure separation  $\delta$  of the  $^2D$  term, although the major part of  $\delta$  is due to the electron spin-spin interaction.<sup>10</sup> (The much stronger spin-orbit interaction does not affect the fine structure of a pure  $p^3$  configuration.) Earlier determinations of the  $^2D$  energies have been made by telescopic observation of the forbidden  $^2D$ - $^4S$  emissions of planetary nebulae, the most recent observations being those of Bowen with the 200-in. Hale reflector.<sup>20</sup> The value of  $\delta$  which results from these astronomical observations is  $-9.2 \text{ cm}^{-1}$ ; the observational uncertainty, although not stated explicitly, is implied to be in the neighborhood of  $\pm 0.5 \text{ cm}^{-1}$ . The discrepancy between this astronomical value and the present microwave value of  $-8.69 \pm 0.02 \text{ cm}^{-1}$  is considerable, but, in view of the observational uncertainty, is probably not significant. The new and more precise value of the  $^2D$  fine-structure interval, combined with a recent laboratory determination for the first time of the nitrogen  $^2P$  fine structure,<sup>21</sup> should permit more reliable calculations of two quantities of importance to astronomy, the transition probabilities of the nebular ( $^2D$ - $^4S$ ) and auroral ( $^2P$ - $^4S$ ) lines of atomic nitrogen.

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<sup>20</sup> I. S. Bowen, Astrophys. J. **121**, 306 (1955).

<sup>21</sup> J. W. McConkey and L. Herman, Phys. Letters **12**, 13 (1964).