result in the same direction, an error of 13 percent would be present. As this is rather unlikely, we feel that our determination is reliable to within about 10 percent.

A number of absolute measurements were made under widely differing circumstances regarding the magnitudes of the relevant parameters. These data were taken with filters 3486 and 2412. The average of these values states that

$$P_{\text{exp}}/P_{\text{theor}}=1.01\ (\pm 0.02)\ (\pm 0.10).$$

Here the two figures in parenthesis are taken to describe the reproducibility of the result and to give an estimate of its reliability, respectively.

When the nine filters, with cutoff wavelengths ranging from 4250 to about 9000 A, were placed successively in the beam, the relative ratios of $P_{\text{exp}}/P_{\text{theor}}$ varied as shown in Table III. Filter 3389 has an absorption near the intensity peak, which causes the transmitted energy to be more sensitive to temperature than in the other filters. There is nothing in these data to suggest that the theoretical cross section is in error between 4000 and 9000 A.

VII. CONCLUSIONS

The theoretical value of the cross section for photodetachment of electrons from H^- has been confirmed experimentally, although this cross section could be modified by perhaps 10 percent without being adjudged in conflict with experiment. The method can be applied to other negative ions for the determination of electron affinities and photodetachment cross sections for those ions whose affinities lie in the range from 0.6 to 2.5 ev.

VIII. ACKNOWLEDGMENTS

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Zeeman Effect in the Rotational Spectrum of NO*

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The Zeeman splitting of the 2-mm wave, $J=1/2\rightarrow 3/2$ rotational transition of $N^{14}O^{16}$ in the $^2\Pi_{1/2}$ electronic state has been measured with fields of the order of 100 gauss. The observations were made with a wave-guide cell coiled between the poles of a Varian magnet. Magnetic field measurements were made with the electronic resonance of DPPH at frequencies of the order of 300 Mc/sec. A general theory of the Zeeman effect with hfs has been developed and applied specifically to $N^{14}O^{16}$. The g factors for the four states under investigation were found theoretically to be expressed as: $J=1/2$, $g_c=0.0007-\alpha$, $g_d=0.0007+\alpha$; $J=3/2$, $g_c=\bar{g}-\frac{2}{5}\alpha$, $g_d=\bar{g}+\frac{2}{5}\alpha$, where c and d are the lower and upper components of the Λ-type doublet, respectively. This relation was found to hold experimentally well with the values, $\bar{g}=-0.0230$ and $\alpha=+0.0025$. Theoretically, $\bar{g}$ comes from the mixing of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states and α comes from that of $^2\Pi_{1/2}$ and $^2\Sigma$ states. It was found by the theory, in which the centrifugal force and the spin orbit coupling were taken into account, that the electronic wave function of the two rotational states should be: $J=1/2$, $(^2\Pi_{1/2}|-0.0021(^2\Sigma|$; $J=3/2$, $(^2\Pi_{1/2}|-0.0247(^2\Pi_{3/2}|-0.0021(^2\Sigma|$. These wave functions give $\bar{g}(\text{theor.})=-0.0229$ and and $\alpha(\text{theor.})=+0.0020$, which agree very well with the observed values. The observed g factor in $J=3/2$ state, $\bar{g}=0.0230$ Bohr magnetons, shows that in the supposedly "nonmagnetic" $^2\Pi_{1/2}$ state the NO molecule has a sizeable magnetic moment.

INTRODUCTION

Nitric oxide is special among all stable molecules, since it has an odd number of electrons whereas all the others have an even number of electrons. This odd electron has an orbital rotational angular momentum $\hbar$ around the molecular axis in the ground state. The spin angular momentum of this electron is also strongly coupled to the molecular axis, resulting in $\Pi_{1/2}$ and $\Pi_{3/2}$ states, where $\Omega=1/2$ and $3/2$, respectively.[1] In the ground state $\Pi_{1/2}$ the magnetic moments due to the orbital motion and spin cancel, while in the $\Pi_{3/2}$ state, which is 121 cm^{-1} above the ground state, they give the resulting magnetic moment of 2 Bohr magnetons. The susceptibility data were explained well by these assumptions. The hfs data in the microwave spectra of this molecule observed by Gordy and Burrus[2] and Gallagher *et al.*[3] showed, how-

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* This research was supported by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

[1] For a review see, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibility* (Oxford University Press, London, 1932), p. 269.

[2] C. A. Burrus and W. Gordy, Phys. Rev. **93**, 419 (1954).

[3] Gallagher, Bedard, and Johnson, Phys. Rev. **93**, 729 (1954).

ever, that because of the end-over-end rotation the $\Pi_{1/2}$ and $\Pi_{3/2}$ electronic wave functions mix to a significant extent,[4] so that the ground state may have some amount of magnetic moment. The present study shows that the Zeeman effect of this molecule in the ground state is much larger than that expected by the assumption of pure $^2\Pi_{1/2}$ state. Although to our knowledge no previous investigation of the Zeeman effect of the $^2\Pi_{1/2}$ state has been made, the magnetic $^2\Pi_{3/2}$ state has been investigated through paramagnetic resonance absorption by Beringer and Castle[5] and its magnetic properties have been explained theoretically by Margenau and Henry.[6]

EXPERIMENTAL METHOD

The first rotational transition of NO (the $J=1/2\rightarrow 3/2$) falls at the rather short wavelength of 2 mm. Because of the small dipole moment of the molecule, ~0.07 Debye, and because of the splitting of the transition into several components by internal interaction, the individual lines are extremely weak at normal temperatures. Detection of the individual Zeeman components requires a sensitive 2-mm wave spectrometer having an absorption cell which can be placed in a cooling bath as well as in the magnetic field. Fortunately, NO has a sufficient vapor pressure at 90°K so that the measurements could be made with the cell immersed in liquid air. A considerable increase of the line strength as well as some decrease in cell wall attenuation was thereby achieved.

The absorption cells were made of two-meter length coin silver *I*-band guide (inside cross section 0.180 in. by 0.086 in.), coiled so that it could be placed between the pole pieces (12-in. diameter) of a Varian magnet. The cooling jacket was made of polyfoam lined with copper. Although oversized wave guide was employed, it was found possible to avoid undesirable modes by careful and smooth coiling of the cell. The cell was coiled in the E plane so that only the $\Delta M=\pm 1$ components were observed.

The millimeter wave generator and detector employed were those described by King and Gordy.[7] Video-type detection was used with a p amplifier and cathode ray display of the lines. The magnetic fields employed were of the order of a hundred gauss. Magnetic field measurements were made with an electronic resonance probe employing the organic radical diphenyl-picryl hydrazyl, which has a very sharp resonance with an accurately known g factor[8] of 2.0036 ±0.0002. Frequency measurements for the probe oscillator were made with a Gertsch Meter, Model FM3. Frequency measurements of the Zeeman components were made with the usual secondary frequency standard monitored by station WWV. The Varian magnet was operated from storage batteries.

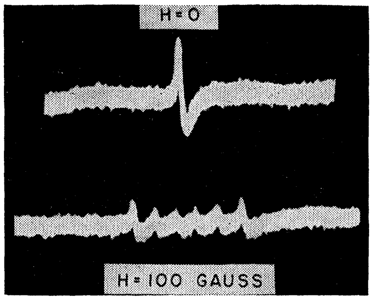

FIG. 1. Zeeman splitting of the $J=1/2\rightarrow 3/2$, $F=3/2\rightarrow 5/2$ transition of $N^{14}O^{16}$ at 1.99-mm wavelength.

EXPERIMENTAL RESULTS

Figure 1 shows a cathode-ray display of one of the hyperfine lines, the $F=3/2\rightarrow 5/2$ transition of the upper frequency component of the Λ doublet, with no externally applied field and with a magnetic field of 100 gauss applied perpendicular to the E lines of the microwave radiation. There are actually eight components theoretically predicted for this transition but two pairs are too close to be resolved, so that only six components are apparent. In this type of transition $F\rightarrow F+1$, the intensities of the outer components are the greatest. The component intensities vary according to the formulas:

$$\left.\begin{array}{l}\mathrm{Int}(M\rightarrow M+1)=A(F+M+1)(F+M+2)\\ \mathrm{Int}(M\rightarrow M-1)=A(F-M+1)(F-M+2)\end{array}\right\}F\rightarrow F+1.$$

For an $F\rightarrow F$ line, the outer components are weakest and the relative intensities have the M dependence given by the formulas:

$$\left.\begin{array}{l}\mathrm{Int}(M\rightarrow M+1)=B(F-M)(F+M+1)\\ \mathrm{Int}(M\rightarrow M-1)=B(F+M)(F-M+1)\end{array}\right\}F\rightarrow F,$$

where A and B are constant for a given J.

Table I lists the observed frequencies and calculated relative intensities of the Zeeman components of the different $J=1/2\rightarrow 3/2$ lines for the $^2\Pi_{1/2}$ state with an applied field of 97 gauss. These are analyzed below.

ZEEMAN EFFECT OF ROTATING MOLECULES WITH HFS

The theoretical formula for the case of a weak field Zeeman effect with hfs has been discussed by some authors.[9,10] Although our present experiment is done

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[4] M. Mizushima, Phys. Rev. **94**, 569 (1954). There were some mistakes in this paper. The errata will be published in this journal.

[5] R. Beringer and J. G. Castle, Phys. Rev. **78**, 581 (1950). Beringer, Rawson, and Henry, Phys. Rev. **94**, 343 (1954).

[6] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).

[7] W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953); **93**, 407 (1954).

[8] Holden, Kittel, Merritt, and Yager, Phys. Rev. **75**, 1614 (1949); **77**, 147 (1950).

[9] C. K. Jen, Phys. Rev. **74**, 1396 (1948).

[10] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).

TABLE I. Zeeman spectrum of NO, $^2\Pi_{1/2}$ state, $J=1/2\rightarrow 3/2$ transition.

$F\rightarrow F'$	$M_F\rightarrow M_{F'}$	Obs ν in Mc/sec with $H=97.45$ gauss	Calc. rel. int.
	Lower component of Λ doublet		
$3/2\rightarrow 5/2$	$3/2\rightarrow 5/2$	150 171.67	25
	$1/2\rightarrow 3/2$	150 173.52	15
	$3/2\rightarrow 1/2$		2.5
	$-1/2\rightarrow 1/2$	150 175.40	7.5
	$1/2\rightarrow -1/2$	150 177.32	7.5
	$-3/2\rightarrow -1/2$		2.5
	$-1/2\rightarrow -3/2$	150 179.40	15
	$-3/2\rightarrow -5/2$	150 181.29	25
$1/2\rightarrow 3/2$	$1/2\rightarrow 3/2$	150 195.15	14
	$-1/2\rightarrow 1/2$	150 197.49	4.6
	$1/2\rightarrow -1/2$	150 199.81	4.6
	$-1/2\rightarrow -3/2$	150 202.48	14
$3/2\rightarrow 3/2$	$1/2\rightarrow 3/2$	150 215.29	4.4
	$-1/2\rightarrow 1/2$	150 217.45	4.4
	$3/2\rightarrow 1/2$		5.9
	$-3/2\rightarrow -1/2$	150 219.82	5.9
	$1/2\rightarrow -1/2$		4.4
	$-1/2\rightarrow -3/2$	150 228.57	4.4
$1/2\rightarrow 1/2$	$-1/2\rightarrow 1/2$	150 223.28	15
	$1/2\rightarrow -1/2$	150 228.57	15
	Upper component of Λ doublet		
$3/2\rightarrow 3/2$	$1/2\rightarrow 3/2$	150 435.83	4.4
	$-1/2\rightarrow 1/2$	150 438.06	4.4
	$3/2\rightarrow 1/2$		5.9
	$-3/2\rightarrow -1/2$	150 440.39	5.9
	$1/2\rightarrow -1/2$		4.4
	$-1/2\rightarrow -3/2$	150 442.52	4.4
$3/2\rightarrow 5/2$	$3/2\rightarrow 5/2$	150 541.82	25
	$1/2\rightarrow 3/2$	150 543.81	15
	$3/2\rightarrow 1/2$		2.5
	$-1/2\rightarrow 1/2$	150 545.75	7.5
	$1/2\rightarrow -1/2$	150 547.49	7.5
	$-3/2\rightarrow -1/2$		2.5
	$-1/2\rightarrow -3/2$	150 549.35	15
	$-3/2\rightarrow -5/2$	150 551.27	25
$1/2\rightarrow 1/2$	$-1/2\rightarrow 1/2$	150 577.99	15
	$1/2\rightarrow -1/2$	150 583.13	15
$1/2\rightarrow 3/2$	$1/2\rightarrow 3/2$	150 641.19	14
	$-1/2\rightarrow 1/2$		4.6
	$1/2\rightarrow -1/2$		4.6
	$-1/2\rightarrow -3/2$	150 647.68	14

under a rather weak field, it was found that the weak field approximation was not exact enough and the effect of nondiagonal matrix elements was not entirely negligible.

The Hamiltonian of our problem is

$$H=\mathfrak{H}\cdot(-\beta\mathbf{L}-2.002\beta\mathbf{S}+g_n\beta_n\mathbf{N})\equiv\mathfrak{H}\cdot\mathbf{M}\beta\hbar, \quad (1)$$

where $\mathfrak{H}$ is the external magnetic field, β is the Bohr magneton, β_n is the nuclear magneton, **L**, **S**, and **N** are the angular momenta of electronic orbital motion, spin, and the end-over-end rotation, respectively, g_n is the g factor of the nuclear rotation, which is about 1/2, and **M** is a quantity defined by the above formula. The contribution from the nuclear spin magnetic moment[11] was neglected. The matrix element of M (component of **M** along $\mathfrak{H}$) can be obtained by the usual procedure; the result is shown below:

$$(JIFM_F|M|JIFM_F)=gM_F\{J(J+1)+F(F+1)-I(I+1)\}/\{2F(F+1)\}, \quad (2)$$

$$(JIFM_F|M|JI\,F-1\,M_F)=g(F^2-M_F^2)^{\frac{1}{2}}\times\{(I+F+J+1)(I+J-F+1)(I+F-J)(J+F-I)\}^{\frac{1}{2}}/\{4F^2(2F+1)(2F-1)\}^{\frac{1}{2}}, \quad (3)$$

where

$$g=(JJ|M|JJ)/J. \quad (4)$$

It can be shown that in the case of very strong field where hfs is negligible, the eigenvalue of the above matrix gives the strong field solution gM_J. The hfs of the NO molecule has been discussed by one of the present authors.[4] Combining that result with the above formula, we can obtain the solution for any value of field strength. The result for the $J=1/2$ state is shown in Fig. 2 as an example.

CALCULATION OF g FACTOR

The wave function of a rotating NO molecule is, according to the former consideration by one of the present authors,[4]

$$c\text{ state: }\psi_c=(1/\sqrt{2})\{\mu(\Pi_{1/2}J_+M_J|+\mu(\Pi_{1/2}J_-M_J|+\nu(\Pi_{3/2}J_+M_J|+\nu(\Pi_{3/2}J_-M_J|\}, \quad (5)$$

$$d\text{ state: }\psi_d=\sqrt{2}\{\mu(\Pi_{1/2}J_+M_J|-\mu(\Pi_{1/2}J_-M_J|+\nu(\Pi_{3/2}J_+M_J|-\nu(\Pi_{3/2}J_-M_J|\}, \quad (6)$$

where J_+ and J_- mean the same states except that the component of J along the molecular axis has an opposite sign. The quantities μ, ν, are constants which depend on J; $\mu=1$, $\nu=0$ for the $J=1/2$ states, $\mu=0.9998$, $\nu=-0.0247$ for $J=3/2$ states. The symbols c and d designate components of the Ω-type doublet, c being

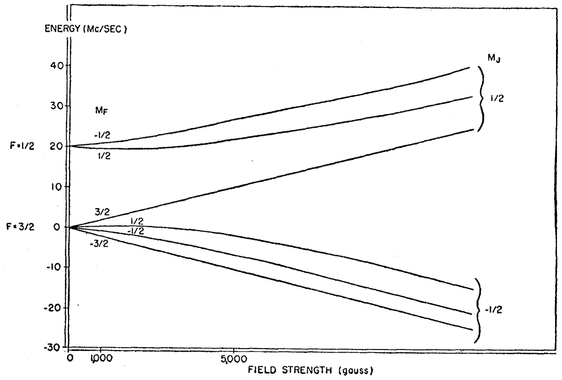

FIG. 2. Energy-field strength diagram for the NO molecule in $^2\Pi_{\frac{1}{2}}$, $J=1/2$, c state.

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[11] The fact that the term $0.001\mu^2/(J^2+J)$, which comes from the anomalous magnetic moment of the electronic spin, is small but not entirely negligible was suggested by G. C. Dousmanis (private communication).

TABLE II. Comparison between observed and calculated Zeeman shift.

$F\rightarrow F'$	$M_F\rightarrow M_{F'}$	First order theor	Complete theor		Observed
	Lower component of Λ doublet (Mc/sec)				
3/2 → 3/2	+1/2 → +3/2	−3.53	−3.49		−3.52
	+3/2 → +1/2	−1.00	−1.24	−1.33[a]	−1.36
	−1/2 → +1/2	−1.26	−1.39		
	+1/2 → −1/2	1.26	1.11	1.04[a]	1.01
	−3/2 → −1/2	1.0	0.96		
	−1/2 → −3/2	3.53	3.61		3.65
3/2 → 5/2	+3/2 → +5/2	−4.70	−4.79		−4.81
	+1/2 → +3/2	−2.87	−2.97		−2.96
	+3/2 → +1/2	−0.79	−0.96		...
	−1/2 → +1/2	−1.04	−1.11		−1.08
	+1/2 → −1/2	1.04	0.93		0.84
	−3/2 → −1/2	0.79	0.78		...
	−1/2 → −3/2	2.87	2.85		2.92
	−3/2 → −5/2	4.70	4.79		4.81
1/2 → 1/2	−1/2 → +1/2	−2.66	−2.44		−2.41
	+1/2 → −1/2	2.66	2.94		2.88
1/2 → 3/2	+1/2 → +3/2	−3.66	−3.57		−3.61
	−1/2 → +1/2	−1.13	−1.31		−1.27
	+1/2 → −1/2	1.13	1.03		1.05
	−1/2 → −3/2	3.66	3.69		3.72
	Upper component of Λ doublet (Mc/sec)				
3/2 → 3/2	+1/2 → +3/2	−3.37	−3.38		−3.36
	+3/2 → +1/2	−1.30	−1.25	−1.09[a]	−1.13
	−1/2 → +1/2	−1.03	−0.98		
	+1/2 → −1/2	1.03	1.08	1.19[a]	1.20
	−3/2 → −1/2	1.30	1.35		
	−1/2 → −3/2	3.37	3.35		3.35
3/2 → 5/2	+3/2 → +5/2	−4.70	−4.70		−4.73
	+1/2 → +3/2	−2.77	−2.75		−2.74
	+3/2 → +1/2	−1.10	−1.07		...
	−1/2 → +1/2	−0.84	−0.80		−0.80
	+1/2 → −1/2	0.84	0.86		0.94
	−3/2 → −1/2	1.10	1.13		...
	−1/2 → −3/2	2.77	2.78		2.80
	−3/2 → −5/2	4.70	4.70		4.72
1/2 → 1/2	−1/2 → +1/2	−2.57	−2.64		−2.65
	+1/2 → −1/2	2.57	2.49		2.49
1/2 → 3/2	+1/2 → +3/2	−3.24	−3.25		−3.26
	−1/2 → +1/2	−1.17	−1.12		...
	+1/2 → −1/2	1.17	1.22		...
	−1/2 → −3/2	3.24	3.22		3.23

[a] Averaged value of two components taking the intensity as the weight.

the lower component, and $(J_+|L_x+S_x|J_-)$ is defined as positive.

The g factor defined in Eq. (4) is

$$c \text{ state:}\quad g_c=(A+B)/J, \tag{7}$$

$$d \text{ state:}\quad g_d=(A-B)/J, \tag{8}$$

where

$$\begin{aligned}A=\mu^2\{&(\Pi_{1/2}J_+J|M|\Pi_{1/2}J_+J)+(\Pi_{1/2}J_-J|M|\Pi_{1/2}J_-J)\}\\&+2\mu\nu\{(\Pi_{1/2}J_+J|M|\Pi_{3/2}J_+J)\\&+(\Pi_{1/2}J_-J|M|\Pi_{3/2}J_-J)\}\\&+\nu^2\{(\Pi_{3/2}J_+J|M|\Pi_{3/2}J_+J)\\&+(\Pi_{3/2}J_-J|M|\Pi_{3/2}J_-J)\},\end{aligned} \tag{9}$$

$$\begin{aligned}B=\mu^2\{&(\Pi_{1/2}J_+J|M|\Pi_{1/2}J_-J)+(\Pi_{1/2}J_-J|M|\Pi_{1/2}J_+J)\}\\&+2\mu\nu\{(\Pi_{1/2}J_+J|M|\Pi_{3/2}J_-J)\\&+(\Pi_{1/2}J_-J|M|\Pi_{3/2}J_+J)\}\\&+\nu^2\{(\Pi_{3/2}J_+J|M|\Pi_{3/2}J_-J)\\&+(\Pi_{3/2}J_-J|M|\Pi_{3/2}J_+J)\}.\end{aligned} \tag{10}$$

Since M is a linear sum of L, S, and N, we can consider these terms separately.

The matrix elements of L are

$$\begin{aligned}(\Pi_{1/2}J_+J|L|\Pi_{1/2}J_+J)&=\hbar/(J+1)\\&=(\Pi_{1/2}J_-J|L|\Pi_{1/2}J_-J)=(\Pi_{3/2}J_+J|L|\Pi_{3/2}J_+J)\\&=(\Pi_{3/2}J_-J|L|\Pi_{3/2}J_-J),\end{aligned} \tag{11}$$

all the other elements being zero.

The matrix elements of S are

$$\begin{aligned}(\Pi_{1/2}J_+J|S|\Pi_{1/2}J_+J)&=-\hbar/(2J+2)\\&=-(\Pi_{3/2}J_-J|S|\Pi_{3/2}J_-J)=(\Pi_{1/2}J_-J|S|\Pi_{1/2}J_-J)\\&=-(\Pi_{3/2}J_+J|S|\Pi_{3/2}J_+J),\end{aligned} \tag{12}$$

$$\begin{aligned}(\Pi_{1/2}J_+J|S|\Pi_{3/2}J_+J)&=-\hbar\{(J+3/2)(J-1/2)\}^{\frac{1}{2}}/\\&(2J+2)=(\Pi_{1/2}J_-J|S|\Pi_{3/2}J_-J),\end{aligned} \tag{13}$$

all the other elements being zero. The sign in Eq. (13) is decided by the definition of the wave function.

The matrix elements of N are always zero, since it does not contain the electronic coordinates.

Since no term which contributes to B of Eq. (10) appears so far, all the above matrix elements give the same contribution to the g factors of the c and d states, that is,

$$\begin{aligned}g_1=\{\mu\nu[(2J+3)(2J-1)]^{\frac{1}{2}}\\+0.001\mu^2-3\nu^2\}/(J^2+J).\end{aligned} \tag{14}$$

There exist, however, some small terms which contribute to B. The largest term among them may be the nondiagonal matrix elements caused by the combined effect of $\mathfrak{H}\cdot\beta\mathbf{L}$ and $D\mathbf{L}\cdot\mathbf{S}$, the spin-orbit interaction. Because of the spin-orbit interaction term a small amount of $^2\Sigma_{1/2}$ state, in which the odd π electron is excited to the σ state, is mixed with the ground $\Pi_{1/2}$ state. Thus, in Eqs. (5) and (6), the wave function $(\Pi_{1/2}J_\pm|$ should be replaced by

$$(\Pi_{1/2}'J_\pm|=(\Pi_{1/2}J_\pm|-[D/\sqrt{2}E(^2\Sigma)](^2\Sigma J_\pm| \tag{15}$$

(the three upper or the three lower signs must be taken together), where the coefficient $[D/(2)^{\frac{1}{2}}E(^2\Sigma)]$ is calculated by the perturbation method, $E(^2\Sigma)$ is the energy difference between the $^2\Sigma$ state and the ground state. In obtaining this formula the assumption was made that the orbit of the odd electron is a p orbital. Through the $^2\Sigma$ states, we obtain a finite contribution from the $\mathfrak{H}\cdot\beta\mathbf{L}$ term which is effectively

$$\begin{aligned}(\Pi_{1/2}'J_+J|\mathfrak{H}\cdot\beta\mathbf{L}|\Pi_{1/2}'J_-J)\\=[H\beta D/E(^2\Sigma)]\{(2J+1)/(4J+4)\},\end{aligned} \tag{16}$$

where $(\Pi_{1/2}'|$ means the wave function expressed in Eq. (15). It must be noted that the same effect gives

TABLE III. Zero-field frequency obtained by adjusting the Zeeman components and its comparison with the former values (Mc/sec).

	Lower component		Upper component	
$F \rightarrow F'$	This work	Burrus and Gordy[a]	This work	Burrus and Gordy[a]
$3/2 \rightarrow 3/2$	150 218.88	150 218.89	150 439.19	150 439.22
$3/2 \rightarrow 5/2$	150 176.48	150 176.54	150 546.55	150 546.50
$1/2 \rightarrow 1/2$	150 225.67	150 225.75	150 580.64	150 580.70
$1/2 \rightarrow 3/2$	150 198.76	150 198.85	150 644.44	150 644.37

[a] See reference 2.

a contribution to some other terms, but in the ground state where $|\nu| \ll |\mu|$ they can be neglected.

Summing up all these results, we obtain

$$g_c = (A+B)/J, \quad g_d = (A-B)/J, \tag{17}$$

where

$$\begin{aligned} A &= \{\nu[(2J+3)(2J-1)]^{\frac{1}{2}} + 0.001 - 3\nu^2\}/(J+1), \\ B &= -[D/E(^2\Sigma)](2J+1)/(4J+4), \end{aligned} \tag{18}$$

where we assumed $\mu = 1$, $|\nu| \ll 1$. In $J=1/2$ and $J=3/2$ states, they are

$$J=\tfrac{1}{2}\begin{cases} g_c = 0.0007 - [D/E(^2\Sigma)]\frac{2}{3} \equiv 0.0007 - \alpha, & (19) \\ g_d = 0.0007 + \alpha, & (20) \end{cases}$$

$$J=\tfrac{3}{2}\begin{cases} g_c = \bar{g} + \frac{2}{5}\alpha, & (21) \\ g_d = \bar{g} - \frac{2}{5}\alpha, & (22) \end{cases}$$

where

$$\bar{g} = 8\sqrt{3}\nu/15 + 0.0004 - 0.8\nu^2. \tag{23}$$

ANALYSIS OF THE EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY

Using Eqs. (19), (20), (21), (22), (2), and (3), we can obtain a theoretical formula for each Zeeman shift $\Delta\nu$. In Table II, the theoretical values of $\Delta\nu$ are shown for

$$\bar{g}(\text{obs}) = -0.0230, \tag{24a}$$

$$\alpha(\text{obs}) = +0.0025. \tag{24b}$$

In our experiment, zero-field frequencies were not observed. They were observed by Burrus and Gordy,[2] but here we estimated them by fitting the observed shift $\Delta\nu$ with the theoretical one. The values of zero-field frequencies thus obtained are shown in Table III. They agree with the previous value within the experimental error.

The nondiagonal matrix element (3) contributes only 0.002 Mc/sec in the case of the c component of $J=1/2$, and much less for the d component, and is thus negligible for $J=1/2$ states; but it has a rather large effect for $J=3/2$ states. This effect explains the asymmetry of the Zeeman components. The secular equations were solved numerically for $J=3/2$ states. In Table II, the values calculated with all nondiagonal matrix elements neglected are also shown. The difference between these values and those of the complete theory gives the effect of the nondiagonal matrix elements. The effect is small in the upper component since the hfs splitting in this case is large, but in the lower component it is larger than the experimental error.

In our theory $\bar{g}$ is related to ν, the coefficient which gives the extent of the mixing of the $\Pi_{3/2}$ state into the $\Pi_{1/2}$ state, through Eq. (23). The ν was calculated by one of the present authors[4] to be -0.0247, which gives

$$\bar{g}(\text{theor}) = -0.0229 \text{ Bohr magneton}. \tag{25a}$$

This value agrees almost completely with the observed value shown in Eq. (24a). The same value of ν was used successfully in calculating the hfs (ΔW) of this molecule,[4] but the agreement there was not so complete as in the present case. In the hfs case, however, the theoretical results contained not only ν but the p-electron assumption (the assumption that the orbital of the odd electron is a p-atomic orbital), whereas in our case the $\bar{g}$ value comes only from the electronic spin, and no assumption about the orbit is made. Thus the slight deviation in the hfs may be attributed to the incorrectness of the p-electron approximation, as was done before.[4]

The quantity α can be calculated from formula (19). The spin-orbit coupling can be expressed as $D(S_xL_x + S_yL_y) + D'S_z\Lambda$, in which D may be different from D'. If, however, we assume the orbit is nearly atomic, $D \approx D' = 124$ cm^{-1}. The term $E(^2\Sigma)$ is observed spectroscopically[12] to be 44 000 cm^{-1}. Thus the theoretical value of α is

$$\alpha(\text{theor}) = +0.0020 \text{ Bohr magneton}. \tag{25b}$$

The agreement in this case with the observed value $+0.0029$ is good, although not so complete as in the case of $\bar{g}$. Either $D > D'$ or the contribution from the other excited electronic state may not be negligible and could explain the deviation of $+0.0005$.

The quantity α is closely related to what is called the rotational magnetic moment. If we interpret g_n in the formula (1) phenomenologically, forgetting about the electronic structure of the ground state, we shall obtain a term which behaves exactly like the α term. In this case the phenomenological g_n (which is different from the original g_n) is equal to $(3/2)\alpha$. It may be interesting to note that the observed magnetic moment α of 0.0025 Bohr magneton corresponds to the phenomenological g_n of seven nuclear magnetons, which is fairly large as a rotational magnetic moment.

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[12] H. Sponer, *Molekuelspektren I* (Verlag Julius Springer, Berlin, 1935).

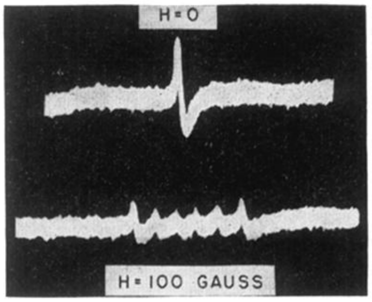

FIG. 1. Zeeman splitting of the $J=1/2 \rightarrow 3/2$, $F=3/2 \rightarrow 5/2$ transition of $N^{14}O^{16}$ at 1.99-mm wavelength.