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L-Uncoupling Effects on the Electron-Paramagnetic-Resonance Spectra of $N^{14}O^{16}$ and $N^{15}O^{16}$

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High-resolution paramagnetic-resonance spectra have been obtained for the molecules $N^{14}O^{16}$ and $N^{15}O^{16}$ in the $J=\frac{3}{2}$ and $J=\frac{5}{2}$ rotational levels of the $^2\Pi_{3/2}$ ground state at X-band and S-band microwave frequencies. The results are: $g_J(N^{14}O^{16};\ J=\frac{3}{2})=0.777246\pm0.000018$, $g_J(N^{15}O^{16};\ J=\frac{3}{2})=0.778072\pm0.000020$; $g_J(N^{14}O^{16};\ J=\frac{5}{2})=0.316648\pm0.000045$; and $g_J(N^{15}O^{16};\ J=\frac{5}{2})=0.317617\pm0.000040$ for the molecular g factors. The measured g factors were compared with those calculated from the theory of magnetic effects on Λ-type doubling previously developed by Radford. Somewhat improved values for the Λ-type doubling frequencies and nuclear hyperfine-structure coupling constants were also obtained.

INTRODUCTION

THE magnetic moment of the nitric-oxide molecule arises primarily from the magnetism associated with its electronic-orbital-angular momentum and the spin of its unpaired electron. From an analysis of the microwave paramagnetic-resonance spectrum it is possible to determine experimentally the total magnetic moment to an accuracy of 1 part in 10^5 or better. A theoretical calculation of the moment to this accuracy requires a detailed knowledge of the molecular wave functions, particularly with regard to the effect of molecular rotation. In NO, the coupling scheme of the electronic-angular momenta in the $^2\Pi$ ground state very closely approximates that of Hund's case (a), in which both orbital and spin-angular momenta are strongly coupled to the internuclear axis. The most important effect of molecular rotation is to decouple the spin from the internuclear axis. From a knowledge of the rotational and spin-orbit coupling constants it is possible to calculate the effect of the spin uncoupling on the magnetic moment. To predict its magnitude, however, to an accuracy of 1 part in 10^5, it is necessary to have values of the rotational and spin-orbit coupling constants accurate to within 4 parts in 10^4. Although the rotational constant has been known to this accuracy for some time, lack of a sufficiently accurate value for the spin-orbit constant has hampered the theoretical interpretation of the magnetic-resonance spectrum.

Beringer, Henry, and Rawson[1] measured the $N^{14}O^{16}$ resonance spectrum in the $^2\Pi_{3/2}$, $J=\frac{3}{2}$ rotational level at X-band microwave frequencies. Mizushima, Cox, and Gordy[2] have measured the Zeeman effect on the rotational spectrum of the $^2\Pi_{1/2}$ state of $N^{14}O^{16}$ involving the levels with $J=\frac{1}{2}$ and $\frac{3}{2}$. Lin and Mizushima[3] gave a theoretical treatment of the magnetic resonance spectrum of the $^2\Pi_{3/2}$ state which neglected Λ-doubling effects. They were able to fit the experimental data within 5 MHz. In this work they used a value of 124.2 cm^{-1} for the spin-orbit coupling constant. Lin[4] recalculated the magnetic-resonance frequencies using a newer value of 122.094 cm^{-1} for the coupling constant, as determined from the microwave rotational spectrum and obtained agreement with experiment within 1 MHz. Recently James and Thibault[5] have made a direct determination of this constant by observing a very weak infrared absorption arising from a transition between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ multiplet components. They obtained a value of 123.160 ± 0.020 cm^{-1} which lies between the two older values. Their value is undoubtedly the most reliable one available because of the high-resolution infrared techniques they employed, the refined theoretical treatment of $^2\Pi$ states, developed by James[6] and used in their analysis, and the fact that the frequencies measured corresponded to direct transitions between the two $^2\Pi$ spin components. Since the stated uncertainty in their value is within our required limits of 4 parts in 10^4, it should be possible to calculate the magnetic moment with an accuracy equal to that obtainable in its experimental determination. A comparison of the observed and calculated moments should provide a direct experimental determination of the sum of several smaller contributions arising from relativistic effects and molecular rotation.

Radford[7] has examined theoretically the magnetic effects arising from the Λ doubling. (The papers containing this work will hereafter be referred to as R1 and R2.) The main purpose of the present work is to apply this theory to new measurements of the NO spectrum. To test the theory adequately, it is desirable to have experimental values of the magnetic moment for several rotational levels. We have measured the spectrum of both $N^{14}O^{16}$ and $N^{15}O^{16}$ in the $^2\Pi_{3/2}$, $J=\frac{3}{2}$ and $\frac{5}{2}$ levels at S band and that of $N^{15}O^{16}$ in $J=\frac{3}{2}$ also at X band. Work at S band was required because, with the magnetic-field strengths available to us, the $J=\frac{5}{2}$ spectra could not be observed at X band. Since our relative

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[1] R. Beringer, E. B. Rawson, and A. F. Henry, Phys. Rev. **94**, 343 (1954).

[2] M. Mizushima, J. T. Cox, and W. Gordy, Phys. Rev. **98**, 1034 (1955).

[3] C. C. Lin and M. Mizushima, Phys. Rev. **100**, 1726 (1955).

[4] C. C. Lin, Phys. Rev. **119**, 1027 (1960).

[5] T. C. James and R. J. Thibault, J. Chem. Phys. **41**, 2806 (1964).

[6] T. C. James, J. Chem. Phys. **41**, 631 (1964).

[7] H. E. Radford, Phys. Rev. **122**, 114 (1961); **126**, 1035 (1962).

linewidths were about one half those achieved by Beringer *et al.*, it has been possible to obtain somewhat improved values for the Λ-doubling frequencies and nuclear hyperfine structure (hfs) coupling constants.

EXPERIMENT

Paramagnetic resonance spectra at X band were obtained with a crystal-video EPR spectrometer. Nitric oxide at a pressure of 35μ Hg was contained in a cylindrical silver-plated brass cavity having a volume of about 100 cm^3. It was operated in the TE_{011} mode at 9680 MHz and had a Q of approximately 10^4. Its orientation put the cylinder axis parallel to the field provided by a 12-in. Varian electromagnet. Low-amplitude modulation of the field at 200 Hz was provided by a pair of coils attached to the magnet pole faces. With a band pass of 1 Hz, a signal-to-noise ratio of about 20 was obtained for the weakest lines. Only the $N^{15}O^{16}$ spectrum was recorded at X band.

At S band, spectra were obtained with a superheterodyne spectrometer. An oil-cooled 724C klystron was employed as the master oscillator. Another of these tubes, operated at 30 MHz above the master oscillator frequency, served as the local oscillator. A ferrite circulator was used to isolate microwave power incident on the cavity from that reflected out of the cavity. The reflected power and local oscillator power were combined in a balanced crystal mixer with associated intermediate-frequency (IF) preamplifier. After further amplification, the IF signal was demodulated and fed to a standard lock-in detector and strip chart recorder. The master oscillator was locked in frequency to the cavity by a 10-kHz FM stabilizer. A silver-plated brass coaxial cavity (volume, 250 cm^3) operated in $\lambda/2$ TEM mode at 2786 MHz was used with the axis of the center conductor parallel to the dc magnetic field. The cavity Q was about 2500. Coaxial transmission line was used throughout the spectrometer. At 40μ Hg pressure and a 1-Hz band pass, the signal-to-noise ratio on the weakest lines in the $N^{15}O^{16}$ $J=\frac{3}{2}$ spectrum was about 80. The minimum NO concentration detectable with this S-band superheterodyne instrument was 1.6×10^{13} molecules cm^{-3} (for unity signal-to-noise ratio and a 1-Hz band pass). For the crystal-video X-band spectrometer the minimum detectable concentration was 6.4×10^{13} molecules cm^{-3}.

At a NO pressure of 40μ Hg, linewidths determined from the separation between derivative maxima were as follows: for $J=\frac{3}{2}$, X band, 500 kHz (0.36 G); for $J=\frac{3}{2}$, S band, 400 kHz (0.29 G); and for $J=\frac{5}{2}$, S band, 760 kHz (0.54 G). The amplitudes of the field modulation and the microwave power fed to the cavity were kept below levels which would have contributed significantly to line broadening. Measurement of the magnetic-field distribution revealed inhomogeneities large enough to account for 20 to 30% of the observed linewidth. The remaining width appeared to arise primarily from collision broadening.

Line positions were determined by making repeated measurements of the magnetic field strength and microwave frequency at the line center. Microwave frequencies were measured to a precision of 1 part in 10^6 with a transfer oscillator and frequency counter. Magnetic fields were measured in terms of the nuclear magnetic resonance frequency of protons contained in a 0.1 molar aqueous solution of $MnCl_2$. The oscillator used was of the type described by Robinson.[8] Its frequency was measured with the same frequency counter that was used for the microwave measurements. In the X-band experiment the field was measured at a point just outside the cavity. The small field differential existing between this point and the center of the cavity was determined after each measurement of a particular Λ-type doublet pair of lines. Relative linewidths at X band were 4 parts in 10^5 and the signal-to-noise ratio was such that the line center could be determined to approximately $\frac{1}{10}$ of a linewidth. Thus the precision obtainable for the relative line positions was about ±1 part in 10^5 or better. Because of the uncertainty in applying corrections for the field differential between the proton resonance probe and the parts of the cavity containing the largest microwave electric field, the precision on absolute line positions was limited to about ±3 parts in 10^5.

For the work at S band, the proton sample was placed at the middle of the cavity inside its hollow-center conductor. After each experiment the field distribution existing in the region normally occupied by the cavity was measured. Relative line widths for the $J=\frac{3}{2}$ spectra were 15 parts in 10^5, while the signal-to-noise ratio was such as to allow the line center to be determined to within 1/30 of a linewidth. The precision on the relative line positions was comparable to that obtained at X band. Precision on absolute positions was somewhat greater at S band (about ±2 parts in 10^5) owing to a smaller correction for the field differential between the cavity center and the transition region. Uncertainties in relative and absolute line determinations for the $J=\frac{5}{2}$ spectra were approximately twice those obtainable for $J=\frac{3}{2}$ (at S band).

THEORY

The theory of the Zeeman effect in $^2\Pi$ electronic states of diatomic molecules may be found in R1 and R2. One point not covered in these papers is the effect of an electric-quadrupole interaction of one nucleus with the rest of the molecule. Since the N^{14} nucleus possesses a quadrupole moment which exhibits a measurable interaction, this effect must be included in the analysis. This problem has been treated theoretically by Lin and Mizushima.[3]

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[8] F. N. H. Robinson, J. Sci. Instr. 36, 481 (1959).

Table I. Experimental resonance field values for $N^{14}O^{16}$ and $N^{15}O^{16}$ at X- and S-band microwave frequencies. The transitions are $(m_J, m_I, \pm) \leftrightarrow (m_J-1, m_I, \mp)$; $\Delta J=0$.

m_J, m_I	Resonance field $\mathcal{H}(G)$[a] $(m_J, m_I, +)$[b]	Resonance field $\mathcal{H}(G)$ $(m_J, m_I, -)$[b]
$N^{14}O^{16}$ at 2879.930 MHz; $J=\frac{3}{2}$		
$\frac{3}{2}, 1$	2609.279[c]	2610.930[c]
$\frac{3}{2}, 0$	2636.375	2637.963
$\frac{3}{2}, -1$	2664.786	2666.301
$\frac{1}{2}, 1$	2619.289	2620.852
$\frac{1}{2}, 0$	2646.444	2648.351
$\frac{1}{2}, -1$	2674.165	2675.708
$-\frac{1}{2}, 1$	2629.159	2630.850
$-\frac{1}{2}, 0$	2656.668	2658.430
$-\frac{1}{2}, -1$	2683.410	2685.223
$N^{14}O^{16}$ at 2879.899 MHz; $J=\frac{5}{2}$		
$\frac{5}{2}, 1$	6643.521[e]	6660.022[e]
$\frac{5}{2}, 0$	6672.897	6687.927
$\frac{5}{2}, -1$	6700.826	6716.138
$\frac{3}{2}, 1$	6543.728	6559.601
$\frac{3}{2}, 0$	6571.755	6588.124
$\frac{3}{2}, -1$	6600.493	6615.693
$\frac{1}{2}, 1$	6456.674	6472.373
$\frac{1}{2}, 0$	6483.946	6501.077
$\frac{1}{2}, -1$	6512.917	6528.474
$-\frac{1}{2}, 1$	6378.387	6395.776
$-\frac{1}{2}, 0$	6406.918	6424.161
$-\frac{1}{2}, -1$	6435.475	6451.890
$-\frac{3}{2}, 1$	6311.208	6327.917
$-\frac{3}{2}, 0$	6338.817	6355.415
$-\frac{3}{2}, -1$	6366.297	6384.091

m_J, m_I	Resonance field $\mathcal{H}(G)$[a] $(m_J, m_I, +)$[b]	Resonancs field $(\mathcal{H}G)$ $(m_J, m_I, -)$[b]
$N^{15}O^{16}$ at 9486.322 MHz; $J=\frac{3}{2}$		
$\frac{3}{2}, -\frac{1}{2}$	8587.341[d]	8588.452[d]
$\frac{3}{2}, \frac{1}{2}$	8625.726	8626.802
$\frac{1}{2}, -\frac{1}{2}$	8698.286	8699.698
$\frac{1}{2}, \frac{1}{2}$	8736.862	8738.257
$-\frac{1}{2}, -\frac{1}{2}$	8807.497	8809.099
$-\frac{1}{2}, \frac{1}{2}$	8846.109	8847.837
$N^{15}O^{16}$ at 2879.926 MHz; $J=\frac{3}{2}$		
$\frac{3}{2}, -\frac{1}{2}$	2614.728[c]	2616.189[c]
$\frac{3}{2}, \frac{1}{2}$	2652.695	2654.067
$\frac{1}{2}, -\frac{1}{2}$	2624.641	2626.137
$\frac{1}{2}, \frac{1}{2}$	2663.115	2664.599
$-\frac{1}{2}, -\frac{1}{2}$	2634.493	2636.027
$-\frac{1}{2}, \frac{1}{2}$	2673.477	2675.097
$N^{15}O^{16}$ at 2879.903 MHz; $J=\frac{5}{2}$		
$\frac{5}{2}, -\frac{1}{2}$	6639.699[e]	6653.994[e]
$\frac{5}{2}, \frac{1}{2}$	6678.975	6692.521
$\frac{3}{2}, -\frac{1}{2}$	6535.663	6550.013
$\frac{3}{2}, \frac{1}{2}$	6575.004	6588.857
$\frac{1}{2}, -\frac{1}{2}$	6445.492	6459.970
$\frac{1}{2}, \frac{1}{2}$	6484.904	6499.233
$-\frac{1}{2}, -\frac{1}{2}$	6366.356	6381.000
$-\frac{1}{2}, \frac{1}{2}$	6405.777	6420.675
$-\frac{3}{2}, -\frac{1}{2}$	6296.180	6311.083
$-\frac{3}{2}, \frac{1}{2}$	6335.622	6351.201

[a] Resonance field values $\mathcal{H}$ were obtained from the proton-nuclear magnetic-resonance frequencies ν_I using a value of 4.25759×10^3 $\sec^{-1}G^{-1}$ for the gyromagnetic ratio of the proton, uncorrected for the diamagnetism of water.

[b] This designation refers to the upper state involved in the transition.

[c] Absolute uncertainty in $\mathcal{H}$ is ±0.07 G; it arises from the uncertainty in the field differential existing between the position of the NMR probe and those regions of the cavity where the transitions occur. Relative uncertainty is ±0.014 G.

[d] Absolute uncertainty, ±0.21 G; relative uncertainty, ±0.029 G.

[e] Absolute uncertainty, ±0.14 G; relative uncertainty, ±0.021 G.

Since the coupling scheme in NO is so close to Hund's case (a), one may expand the quantity $X=[4(J+\frac{1}{2})^2+\lambda(\lambda-4)]^{1/2}$, wherever it appears in the equations of R1 and R2, in terms of powers of $Y(2-\lambda)^{-1}$, where $Y=[(J-\frac{1}{2})(J+\frac{3}{2})]^{1/2}$ and $\lambda=A/B_p$ is the spin-uncoupling parameter. This technique is better suited for the calculation of quantities which involve the difference between X and $|2-\lambda|$, since for NO these numbers are almost equal at small J values.

Zeeman Effect

Mulliken and Christy[9] on the basis of molecular-orbital considerations have shown that the Λ doubling in the $^2\Pi$ NO ground state is caused principally by an interaction with an excited $^2\Sigma^-$ state. Since this case is slightly different from the one involving an interaction with a $^2\Sigma^+$ state treated in R1, several of the formulas in that paper must be generalized somewhat to include this type of interaction. The wave functions given in Eq. (2) of R1 are generalized by inserting the quantity $(-1)^s$ (defined by Van Vleck to have s an even integer for Σ^+ states and an odd integer for Σ^- states), before the case (a) function $\Sigma_{-1/2}$ wherever it appears. The formula for $(\delta g_J)_L^{\pm}$ given by Eq. (8) of R1 is generalized by inserting $(-1)^s$ before $(J+\frac{1}{2})$ and δ wherever they appear. The effect of an interaction with more than one Σ state can be accounted for simply by summing the quantities $(\delta g_J)_L^{\pm}$ over all Σ states.

Because of the relatively small separation of the NO rotational levels compared to the splitting caused by the magnetic field, higher-order Zeeman effects are important. These were calculated (through the fifth order) using the formulas of Condon and Shortley[10] and the matrix elements of Lin and Mizushima,[3] and applied to the measured line positions as corrections.

Hyperfine Structure

Magnetic interaction. The first-order magnetic hfs energies in a strong field are given by Eqs. (12a) and

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[9] R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).

[10] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 34.

(12b) of R1. In the present experiment it is necessary to consider small effects arising from states off-diagonal in J which are mixed in by the Zeeman operator. This merely adds a small correction to the hfs energies proportional to $\mathcal{H}$, the magnitude of the magnetic field.

An expression for the second-order hfs energies is given in R2 for the case where the nuclear-spin quantum number is $I=\frac{1}{2}$. A more general formula which is applicable for all values of I is

$$\Delta W^{\pm}=(A_1\pm A_2)^2[m_Jm_I(m_J-m_I)-J(J+1)m_I +I(I+1)m_J]\times[2(g^{\pm}{}_J-g_I)\mu_0\mathcal{H}h^{-1}]^{-1}.$$

Electric quadrupole interactions. An expression for the strong-field quadrupole energy may be obtained from Ref. 3. Calculations of the Zeeman and second-order contributions to the quadrupole energy show that they are too small to be measurable in the present experiment.

ANALYSIS AND RESULTS

The spectra of $N^{14}O^{16}$ and $N^{15}O^{16}$ taken at S-band frequencies are shown in Fig. 1, (a) and (b). The transitions have $\Delta J=0$, $\Delta m_J=1$, $\Delta m_I=0$, and $\pm\rightarrow\mp$. Assignments and experimental line positions are given in Table I. Field values were obtained from the proton nuclear-magnetic-resonance frequencies ν_I using a value of 4.25759×10^3 sec^{-1}G^{-1} for the gyromagnetic ratio of the proton (uncorrected for the diamagnetism of water). For the calculations in the present work, the value of the spin-orbit coupling constant A, given in Ref. 5 was used for $N^{14}O^{15}$ and $N^{14}O^{16}$. Values for rotational constants were obtained from Ref. 1 and from the microwave-absorption experiments of Favero, Mirri, and Gordy,[11] and Gallagher and Johnson.[12] Table II lists the experimental g factors and the constant K_2 involved in the second-order Zeeman effect. The observed Λ-type doubling frequencies ν_Λ are given in Table III. Formulas for these frequencies have been given by Dousmanis, Sanders, and Townes.[13] For the $^2\Pi_{3/2}$ levels, Eq. (22) of their paper represents the energy spacing satisfactorily. This expression contains two parameters α_p and β_p. In the present experiment, more accurate values were obtained for the doublet separations in the $^2\Pi_{3/2}$ levels than were obtained in the microwave-absorption experiments. This resulted in improved values for β_p derived from the present data and the values of α_p obtained from the microwave-absorption experiments of Gallagher and Johnson. The resulting changes in the values of β_p have a negligible effect on the calculated doublet frequencies of the $^2\Pi_{1/2}$ levels. Thus the new values are consistent with the available data on the Λ-type doublet frequencies. Experimental nuclear-hyperfine coupling constants are given in Table IV.

TABLE II. Experimental results. Mean molecular g factors and second-order Zeeman effect.

$^2\Pi_{3/2}$ level	$\bar{g}_J=\frac{1}{2}(g_J{}^++g_J{}^-)$	K_2 (sec^{-1})
$N^{14}O^{16}$ $J=\frac{3}{2}$	0.777246 ± 0.000018	$(38.988\pm0.035)\times10^{-8}$
$J=\frac{5}{2}$	0.316648 ± 0.000045	$(-22.092\pm0.080)\times10^{-8}$
$N^{15}O^{16}$ $J=\frac{3}{2}$	0.778072 ± 0.000020	$(40.463\pm0.030)\times10^{-8}$
$J=\frac{5}{2}$	0.317617 ± 0.000040	$(-22.940\pm0.060)\times10^{-8}$

TABLE III. Observed Λ-type doubling frequencies and those calculated from Eq. (22) of Ref. 13 using values $\alpha_p=-178.94$ MHz, $\beta_p=-1.396$ MHz for $N^{14}O^{16}$ and $\alpha_p=-173.05$ MHz, $\beta_p=-1.298$ MHz for $N^{15}O^{16}$.

$^2\Pi_{3/2}$ level	ν_Λ(MHz)$_{\text{obs}}$[a]	ν_Λ(MHz)$_{\text{calc}}$
$N^{14}O^{16}$ $J=\frac{3}{2}$	0.906 ± 0.010	0.905
$J=\frac{5}{2}$	3.601 ± 0.025	3.606
$N^{15}O^{16}$ $J=\frac{3}{2}$	0.814 ± 0.010	0.811
$J=\frac{5}{2}$	3.224 ± 0.025	3.237

[a] The present data for the $^2\Pi_{3/2}$ levels have been used only to determine β_p. Values of α_p used to calculate ν_Λ were obtained from Gallagher and Johnson, Ref. 12.

Within our experimental errors, the values for these parameters for $N^{15}O^{16}$ obtained from the X-band measurements were the same as at S band. Our results were also in agreement with the X-band measurements on $N^{14}O^{16}$ of Beringer, Rawson, and Henry,[1] when allowance was made for the uncertainty in the two sets of data.

TABLE IV. Experimental nuclear-hyperfine coupling constants.

$^2\Pi_{3/2}$ level	A_1 (MHz)[a]	A_2 (MHz)[a]	R (MHz)[b]	R_Λ (MHz)[b]
$N^{14}O^{16}$ $J=\frac{3}{2}$	29.836 ± 0.025	0.019 ± 0.005	-0.064 ± 0.005	-0.042 ± 0.005
$J=\frac{5}{2}$	12.440 ± 0.040	0.031 ± 0.010	0.0060 ± 0.0008	-0.029 ± 0.008
$N^{15}O^{16}$ $J=\frac{3}{2}$	-41.886 ± 0.020	-0.024 ± 0.005		
$J=\frac{5}{2}$	-17.480 ± 0.035	-0.040 ± 0.009		

[a] The definitions for the magnetic-hyperfine coupling constants may be found in Ref. 7.
[b] The definitions for the nuclear-quadrupole coupling constants may be found in Ref. 11.

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[11] P. O. Favero, A. M. Mirri, and W. Gordy, Phys. Rev. **114**, 1534 (1959).

[12] J. J. Gallagher and C. N. Johnson, Phys. Rev. **103**, 1727 (1956).

[13] G. C. Dousmanis, T. M. Sanders, Jr., and C. H. Townes, Phys. Rev. **100**, 1735 (1955).

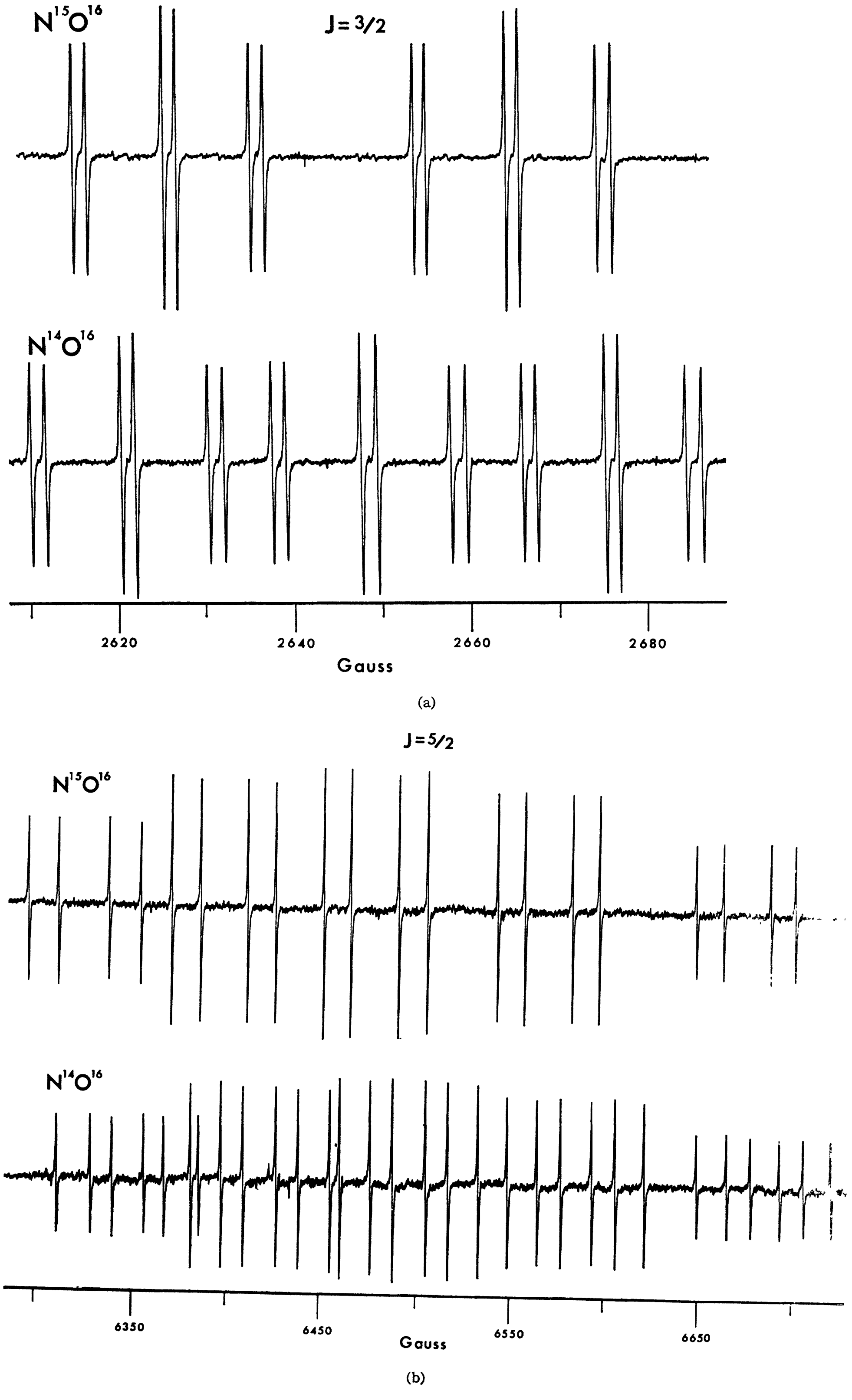

FIG. 1. (a) Paramagnetic resonance spectra of $N^{14}O^{16}$ and $N^{15}O^{16}$ in the $J=\frac{3}{2}$ rotational level of the $^2\Pi_{3/2}$ state at S-band microwave frequency. The transitions have $\Delta J=0$, $\Delta M_J=1$, $\Delta M_I=0$, and $\pm\rightarrow\mp$. Assignment and experimental line positions are given in Table I. The microwave frequency at which the transitions occurred was 2879.9 MHz. (b) Spectra of the molecules in the $J=\frac{5}{2}$ level.

EXPERIMENT VERSUS THEORY

Zeeman Effect

When the fomulas for the molecular g factors given by Eq. (8) of R1 are generalized to include effects of more than one $^2\Sigma$ state, the molecular matrix elements appearing as parameters in the equation become sums of matrix elements over Σ states. The Λ-type doubling parameters α_p and β_p yield values for the quantities $\theta E^{-1/2}$, $\zeta E^{-1/2}$, and $\eta E^{-1/2}$ which appear in Eq. (8). The quantity $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$ must be determined from the experimental g-factor differences. Table V lists the experimental differences and the values of $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$ determined from them through the theoretical expression for $g_J^- - g_J^+$.

TABLE V. Values of $\Sigma_s (\Pi|L_y|\Sigma)E^{-1/2}$ calculated from the observed g-factor differences.

$^2\Pi_{3/2}$ level	$(g_J^- - g_J^+)_{\text{obs}}$	$\Sigma_s (\Pi\|L_y\|\Sigma)E^{-1/2}$ ($\text{MHz}^{-1/2}$)
$N^{14}O^{16}$ $J=\frac{3}{2}$	$(1.10\pm0.10)\times10^{-5}$	$(0.161\pm0.016)\times10^{-4}$
$J=\frac{5}{2}$	$(1.86\pm0.18)\times10^{-5}$	$(0.159\pm0.018)\times10^{-4}$
$N^{15}O^{16}$ $J=\frac{3}{2}$	$(1.02\pm0.10)\times10^{-5}$	$(0.160\pm0.015)\times10^{-4}$
$J=\frac{5}{2}$	$(1.73\pm0.15)\times10^{-5}$	$(0.158\pm0.016)\times10^{-4}$

The g-factor differences for the $^2\Pi_{1/2}$ levels are also given by Eq. (8) of R1 if one uses the upper signs. From the observed value of $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$ given in Table V, a value of 0.0026±0.0005 was calculated for $g_J^- - g_J^+$ in the $J=\frac{3}{2}$ level of the $^2\Pi_{1/2}$ state. This compares favorably with the experimental value of 0.0020 measured by Mizushima, Cox, and Gordy.[2] The much larger g factor differences in the $^2\Pi_{1/2}$ state are correlated with the large Λ-type doublings. A pure case-(a) $^2\Pi_{3/2}$ state would not exhibit such splittings. For such a state $g_J^- - g_J^+$ would also be zero as may be seen from Eq. (8) by examining the limit as $\lambda \to \infty$.

In addition to the terms appearing in Eq. (8), the molecular g factors contain a contribution from relativistic effects. The major part of this correction takes the form $-g_J^0\langle T\rangle/mc^2$ where $\langle T\rangle$ is the average kinetic energy of a single π electron.[7] A value for $\langle T\rangle$ can be estimated roughly by taking a weighted average of $\langle T\rangle_{2p}$ for $2p$ electrons of atomic nitrogen and atomic oxygen, the weighting factors being respectively 0.65 and 0.35 as determined from the hyperfine structure of NO.[14] Using accurate analytic wave functions,[15] we find for this weighted average the value $\langle T\rangle/mc^2 = 1.1\times10^{-4}$. Since the corresponding corrections are not much larger than the experimental uncertainty in the g factors, this rough estimate of the relativistic correction, which is probably accurate to within 20%, should be adequate for the present analysis.

TABLE VI. Contributions to the theoretical g factors. See R1.

$^2\Pi_{3/2}$ level	g_J^0 (10^{-6})	$(\delta g_J)_s$ (10^{-6})	$(\delta g_J)_N$ (10^{-6})	$\frac{1}{2}[(\delta g_J)_{L^+} + (\delta g_J)_{L^-}]$ (10^{-6})	$-g_J^0\langle T\rangle/mc^2$ (10^{-6})
$N^{14}O^{16}$ $J=\frac{3}{2}$	776889±4	437	−113	121±15	−86±17
$J=\frac{5}{2}$	316497±12	168	−206	137±10	−36±7
$N^{15}O^{16}$ $J=\frac{3}{2}$	777739±4	438	−113	117±15	−86±17
$J=\frac{5}{2}$	317464±12	169	−206	133±10	−35±7

The calculated values[16] of the terms in Eq. (8) of R1 are given in Table VI; also included are calculated values of $-g_J^0\langle T\rangle/mc^2$. Since the experimental g-factor differences have been used to determine $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$, only the mean **L** uncoupling corrections $\frac{1}{2}[(\delta g_J)_{L^+} + (\delta g_J)_{L^-}]$ are given. The calculated mean g factors $(\bar{g}_J)_{\text{calc}}$ and their comparison with experiment appear in Table VII. For the $J=\frac{3}{2}$ levels, the agreement with experiment is well within the uncertainties expected. The fact that the differences $(\bar{g}_J)_{\text{calc}} - (\bar{g}_J)_{\text{exp}}$ in the $J=\frac{5}{2}$ level fall very slightly outside the error limits may indicate that $\frac{1}{2}[(\delta g_J)_{L^+} + (\delta g_J)_{L^-}]$, as given by the theory, does not quite account for all of the **L** coupling. This could arise from the failure to include in the theory the contributions of $^2\Delta$ states to the **L** uncoupling. (See R2 for a discussion of this problem.) These considerations, together with an examination of the calculated values of $(\delta g_J)_N$ and $\frac{1}{2}[(\delta g_J)_{L^+} + (\delta g_J)_{L^-}]$ given in Table VI suggest that the g factor associated with the perpendicular component of **L** largely cancels that arising from the rotation of the bare nuclei.

TABLE VII. Theoretical g factors and their comparison with experiment

$^2\Pi_{3/2}$ level	$(g_J)_{\text{calc}}$ (10^{-6})	$(\bar{g}_J)_{\text{calc}} - (\bar{g}_J)_{\text{exp}}$
$N^{14}O^{16}$ $J=\frac{3}{2}$	777248±36	2±54
$J=\frac{5}{2}$	316561±29	−87±74
$N^{15}O^{16}$ $J=\frac{3}{2}$	778095±36	23±56
$J=\frac{5}{2}$	317525±29	−92±69

Hyperfine Structure

Magnetic interaction. From the experimental values of A_1 given in Table IV one may calculate from Eq. (12b) of R1, the coupling constants $a+(b+c)/2$ and b, although the uncertainty in the latter will be rather large. Using values of $a-(b+c)/2$ obtained from the microwave absorption experiments on the $^2\Pi_{1/2}$ levels one obtains values listed in Table VIII for the parameters a, b, and c.

Since A_2 has such small values in the $^2\Pi_{3/2}$ levels, our measurements do not provide any improvement in the values of d determined from the microwave experi-

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[14] G. C. Dousmanis, Phys. Rev. **97**, 967 (1955).

[15] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

[16] The effects of centrifugal distortion on the spin-orbit coupling parameter λ were estimated from Eqs. (30) and (44) of Ref. 13 and found to alter the calculated values of g_J^0 less than 1 part in 10^5.

TABLE VIII. Magnetic-hyperfine-structure coupling constants.

Coupling constant	$N^{14}O^{16}$ (MHz)	$N^{15}O^{16}$ (MHz)
$a+(b+c)/2$	75.81± 0.24	−106.39± 0.21
$a-(b+c)/2$[a]	92.74± 0.80	−130.03± 0.80
a	84.28± 0.52	−118.21± 0.50
b	41.8 ± 6.3	−59.8 ± 5.8
c	−58.8 ± 7.4	83.4 ± 6.8
d	116 ±30	−159 ±33

[a] Values of $a-(b+c)/2$ have been taken from Ref. 12. The uncertainties indicated here were estimated from the quoted uncertainty in the microwave line positions, since no error limits were given for the constant itself.

ments. They are, however, consistent with these values. The values obtained for b and c are different from the microwave absorption values. The theoretical relationship $c=3(a-d)$, used in the analysis of the microwave absorption experiments fails to predict c accurately, giving values 1.4 times those observed. The assumption involved in this relationship, that the same electrons carry both the orbital and spin angular momentum, does not appear to be valid for NO. A detailed discussion of this problem has been given by Mizushima.[17]

Nuclear quadrupole interaction. The analysis of the nuclear quadrupole parameters, R and R_Λ (whose experimental values are given in Table IV) yield the following values for the coupling constants; $eQq_1=1.81\pm0.30$ MHz, and $eQq_2=15.4\pm3.0$ MHz. This may be compared with the values obtained by Favero, Mirri, and Gordy,[11] $eQq_1=2$ MHz, and $eQq_2=22\pm9$ MHz (see Ref. 4 for source of this error limit), and those obtained by Gallagher and Johnson,[12] $eQq_1=1.75$ MHz and $eQq_2=28.9$ MHz (no error limit given).

CONCLUSIONS

The main result of the molecular Zeeman theory given in R1 and R2 was the prediction of a difference in the g factors for the two components of a particular Λ-type doublet. This difference can be calculated from a knowledge of the Λ-type doubling parameters α_p and β_p, the location of the perturbing $^2\Sigma$ state (or states), and the matrix $(\Pi|L_y|\Sigma)$ whose values are known if the "pure precession" condition is satisfied. In NO, the exact locations of the perturbing states are not known; neither does one expect the pure precession hypothesis to be a good approximation. In this case, an experimental value for the quantity $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$ may be determined from the observed g factor difference for one rotational level of one of the isotopic molecules. (The small difference in $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$ for $N^{14}O^{16}$ and $N^{15}O^{16}$ would not be detectable in the present experiment.) The g-factor differences for all rotational levels in either molecule may then be predicted from the empirical value of this parameter. Alternatively, one would expect to obtain the same value for $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$ from all of the observed g-factor differences. The results in Table VII show this to be the case. Within the experimental error, the four levels studied yielded the same value for $\sum_s (\Pi|L_y|\Sigma)E^{-1/2}$.

The existence of an accurate value for the spin-orbit coupling parameter A has made it possible to accurately calculate the following contributions to the molecular g factor: g_J^0, the g factor that would be calculated from the approximate Zeeman operator $\mu_0(\mathbf{L}+2\mathbf{S})\cdot\mathcal{H}$ and wave functions that account for $\mathbf{S}$ uncoupling but not the smaller effects of $\mathbf{L}$ uncoupling; (δg_J) the correction arising from the anomalous spin magnetic moment of the electron; $(\delta g_J)_N$, the correction which accounts for rotation of the bare nuclei. The relativistic term $g_J^0\langle T\rangle/mc^2$ can probably be estimated with an accuracy sufficient for our present purpose. The differences between the observed g factors and the sum of the above four calculated quantities should be equal to the $\mathbf{L}$ uncoupling contributions arising from the interaction of the $^2\Pi$ ground state with excited $^2\Sigma$ and $^2\Delta$ states. The fact that the differences were found to be approximately equal to the values calculated for $(\delta g_J)_N$ indicates that the part of the g factor associated with the perpendicular component of $\mathbf{L}$ largely cancels that arising from the end-over-end rotation of the bare nuclei. Furthermore, since the observed $\mathbf{L}$ uncoupling contributions agree well with those calculated on the basis of interactions with $^2\Sigma$ states only, the effects of $^2\Delta$ states on the $\mathbf{L}$ uncoupling are evidently not very important.

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[17] M. Mizushima, Phys. Rev. **105**, 1262 (1957).