

Microwave Resonance in Nitric Oxide: Lambda Doubling and Hyperfine Structure*

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The microwave spectrum arising from transitions between Zeeman levels in the ${}^2\Pi_{3/2}$, $J=3/2$ state of nitric oxide is reinvestigated with particular regard to the lambda doubling which is observable for electric-dipole transitions. This doubling is compared with the theory of Karnaugh. The experiments also give a new and improved determination of the nuclear hyperfine coupling constants and of the molecular splittings. The theory of the hyperfine effect is reexamined in detail.

INTRODUCTION

MICROWAVE studies¹ and the theory^{2,3} of the high-field Zeeman levels of the $J=3/2$, ${}^2\Pi_{3/2}$ state in $N^{14}O^{16}$ have appeared in this journal. After publication, J. H. Van Vleck pointed out to us that each Zeeman level is a lambda doublet, that electric-dipole transitions between the lambda-doublet components of adjacent Zeeman levels would occur, and that the lambda doubling would be observable with sufficient resolution. This paper reports an experimental investigation of these suggestions, a recalculation of the hyperfine structure constants from the improved data, and a further check of the molecular Zeeman theory. A forthcoming paper of Karnaugh⁴ discusses the theory of the lambda doubling in the nitric-oxide Zeeman levels.

The microwave spectrum of $N^{14}O^{16}$ in high magnetic fields was originally interpreted¹ as being due to magnetic-dipole transitions (M_J , $M_I \rightarrow M_J \pm 1$, M_I) between the twelve Zeeman levels arising from the lowest ($J=3/2$) rotational level of the ${}^2\Pi_{3/2}$ component. This interpretation is still correct for absorption and induced emission produced by microwave magnetic fields normal to the dc magnetic field. Also, no appreciable lambda doubling is present in this spectrum, since magnetic-dipole transitions are of the type $+\rightarrow+$ and $-\rightarrow-$ and the alternation of $+$ and $-$ levels serves almost to cancel the lambda-doublet intervals in the transition energies. For electric-dipole transitions, where the microwave electric field has a component normal to the dc magnetic field, each (M_J , $M_I \rightarrow M_J \pm 1$, M_I) transition is a doublet since $+\rightarrow-$ and $-\rightarrow+$, and the doublet spacing is the sum of the lambda-doubling intervals in the initial and final states. It is noted that the

electric-dipole and magnetic-dipole spectra arise from the same levels and are of the same frequency. They differ only in regard to the lambda doubling, intensity, and polarization.

The most effective way to separate the two spectra is by the polarization of the microwave fields; the greater intensity of the electric-dipole spectrum is also of use. In addition, the observation of lambda doubling identifies the electric-dipole spectrum.

POLARIZATION AND SATURATION EXPERIMENTS

The original experiments¹ used a circular TM_{011} mode cavity with the cavity axis parallel to the dc magnetic field. In this field configuration the microwave H , being purely azimuthal, is entirely perpendicular to the dc H , but only the radial component of the microwave E is perpendicular to the dc H . The electric-dipole spectral intensity is proportional to the square of this radial E integrated over the cavity volume, and the magnetic-dipole intensity is proportional to the integral of the square of the azimuthal H integrated over the cavity volume. This integration for the cavity used gives an electric-dipole spectrum 34 percent as intense as the magnetic-dipole spectrum for the same intrinsic intensity. The ratio of the intrinsic electric to magnetic intensity⁵ is μ_e^2/μ_0^2 , where⁶ μ_e is the permanent electric-dipole moment and μ_0 is the Bohr magneton. Assuming that $\mu_e=0.1 \times 10^{-18}$ esu, the intrinsic intensity ratio is about 120, and in the reported experiments¹ the electric spectrum would have been 40 times as intense as the magnetic spectrum. It appears, therefore, that the agreement cited in reference 1 between the measured intensity and that calculated for magnetic-dipole transitions was quite erroneous. Part of this discrepancy is attributable to power saturation of the electric-dipole spectrum which, for the conditions prevailing in reference 1, would have reduced the electric-dipole spectral intensity by a factor 2. This leaves a factor 20 for the

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¹ R. Beringer and J. G. Castle, Jr., *Phys. Rev.* **78**, 581 (1950).

² H. Margenau and A. Henry, *Phys. Rev.* **78**, 587 (1950).

³ A. Henry, *Phys. Rev.* **80**, 549 (1950).

⁴ M. Karnaugh, Ph.D. dissertation, Yale University, 1952 (unpublished).

⁵ Equation (15) of reference 2 gives the magnetic-dipole matrix element. The electric-dipole matrix element has the same dependence on J and M and the same factor 0.386.

⁶ Watson, Rao, and Ramaswamy, *Proc. Roy. Soc. (London)* **143**, 558 (1934), give $\mu_e=0.16 \times 10^{-18}$ esu. C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.* **1**, 60 (1933), give $\mu_e < 0.1 \times 10^{-18}$ esu.

discrepancy in the ratio of the calculated to observed intensities in reference 1.

The first experiment of the present work used a rectangular TE_{01} mode cavity one-half wavelength long. It was constructed of a copper wave guide of internal dimensions 0.900 in. \times 0.400 in. and coupled at either end to a similar wave guide by means of inductive irises. The microwave apparatus and experimental method were similar to those described.¹ Microwave radiation at the cavity-resonance frequency was coupled through the cavity to a dc biased bolometer. The cavity was in the gap of a magnet, and the magnetic field was varied to produce resonance between the cavity frequency and the spectral transitions. This resonance diminished the power coupled to the bolometer and was detected by modulating the magnetic field across the spectral line at a low audio-frequency and noting the modulation in the voltage across the bolometer. After amplification and demodulation in a lock-in mixer operating at the modulation frequency, the absorption signals were presented on a galvanometer.

The electromagnet, of recent construction, was operated from a motor-generator controlled by a simple, degenerative voltage stabilizer operating on the shunt field of the generator. A proton-resonance field regulator feeding back to a high impedance winding on one magnet pole was used for accurate field regulation. The 30-cy/sec field modulation was produced by a winding on the other pole.

In the rectangular TE_{011} mode the microwave magnetic field is confined to planes parallel to the broad sides of the wave guide, and the electric field is perpendicular to these planes. If the wave guide axis is perpendicular to the dc magnetic field, rotation of the wave guide about its axis can bring either the microwave electric or magnetic field entirely into planes perpendicular to

the dc field. When the magnetic dipole spectrum is being observed polarization entirely forbids the electric dipole transitions, but when the electric spectrum is observed some magnetic spectrum is mixed in. Experiments were tried in which the cavity was rotated as described. The electric dipole spectrum was easily observed but the magnetic dipole spectrum was too weak for detection. The indicated ratio μ_e^2/μ_0^2 from these observations was greater than 20, setting a very loose lower limit of 4×10^{-20} for μ_e .

Using the same cavity a measurement of μ_e^2 was made from power saturation of the electric spectrum. The energy density in the cavity was fixed and the gas pressure successively reduced to produce increasing saturation. Analysis of the results with the usual theory gave $\mu_e = 0.3 \times 10^{-18}$ esu. This is in disagreement with the static value⁶ and if used in calculating absolute intensity would give an even larger discrepancy in the measurements of reference 1 than that cited above. The situation regarding the spectral intensities in the various measurements is quite confused. It is further complicated by the recent work here of R. Collier, who has attempted without success to detect the direct Λ -doubling transitions. From his apparatus sensitivity he concludes that the μ_e is less than 0.06×10^{-18} esu.

In the saturation experiments the lambda doubling was not resolved at the lowest usable pressures, but there was some suggestion of doublet structure from the relatively greater breadth of the line at low pressure. This is shown in Fig. 1 where the line widths are plotted. In these measurements the modulation amplitude was scaled linearly with the pressure so as to minimize modulation broadening. Extrapolation to zero pressure yields about 2 gauss for the peak separation, which is consistent with a line having two components spaced by about the same amount. This extrapolated component spacing is somewhat high because of the broadening due to saturation.

Analysis of this and similar data also gives the width of the NO lines in the absence of lambda doubling and power saturation. This was found to be $\Delta H = 3.0$ gauss/mm Hg using the methods and notation of Fig. 4 in reference 1. This line width corresponds to 3.3 (Mc/sec) per mm Hg,⁷ whereas the earlier¹ value was $\Delta H = 3.5$ gauss/mm Hg at 9360 Mc/sec or 3.8 (Mc/sec) per mm Hg. The lower line width in the present experiments is due to improved field regulation.

In order to observe the unsaturated lines at pressures low enough to resolve the lambda doubling, it was necessary to modify the apparatus. A lower power level would have sufficed, but with our apparatus the signal-to-noise ratio of the bolometer system suffers severely at low microwave power. In the absence of

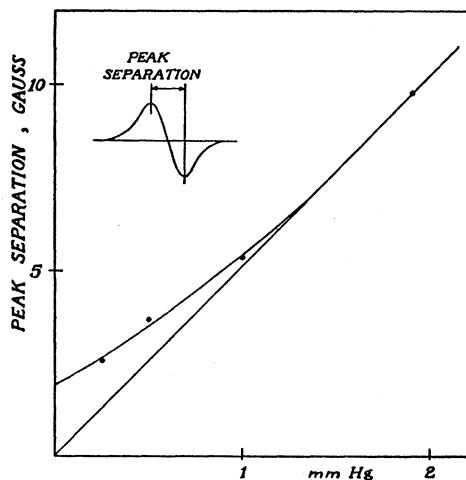


FIG. 1. Variation of width of electric-dipole line H_1 with pressure showing systematic broadening at low pressures. This was evidence for unresolved Λ components spaced by approximately 2 gauss.

⁷ It is not quite true that line widths in frequency units are $\Delta\nu = \nu(\Delta H/H)$ because of the nonlinear (Paschen-Back) type of variation of level energy with H . In the present experiment this correction to $\Delta\nu$ is small compared with the experimental error in ΔH .

TABLE I. Experimental lambda-doubling and resonance field values for N¹⁴O spectrum.

Line	$M_J, M_I \rightarrow M_J - 1, M_I$	Corrected A component separation (gauss)	Arithmetic average resonance field of A components (gauss)	Microwave frequency (Mc/sec)
H_1	$\frac{3}{2}, 1 \rightarrow \frac{1}{2}, 1$	1.48	8398.61	9269.94
H_2	$\frac{3}{2}, 0 \rightarrow \frac{1}{2}, 0$	1.34	8425.71	9270.65
H_3	$\frac{3}{2}, -1 \rightarrow \frac{1}{2}, -1$	1.32	8453.44	9270.65
H_4	$\frac{1}{2}, 1 \rightarrow -\frac{1}{2}, 1$	1.54	8501.49	9270.65
H_5	$\frac{1}{2}, 0 \rightarrow -\frac{1}{2}, 0$	1.86	8528.28	9270.65
H_6	$\frac{1}{2}, -1 \rightarrow -\frac{3}{2}, -1$	1.49	8555.84	9270.65
H_7	$-\frac{1}{2}, 1 \rightarrow -\frac{3}{2}, 1$	1.82	8600.97	9269.81 ₆
H_8	$-\frac{1}{2}, 0 \rightarrow -\frac{3}{2}, 0$	1.97	8629.71	9270.65
H_9	$-\frac{1}{2}, -1 \rightarrow -\frac{3}{2}, -1$	2.01	8656.46	9270.65

sensitive, low-power bolometers, saturation was alleviated by using a large cavity which lowered the microwave field intensity for a given power transmitted to the bolometer. A cylindrical TE_{011} mode cavity of 1.99-in. i.d. was used. The cavity axis was along the dc magnetic field. Another design feature was to make the input coupling much smaller than the output coupling to the bolometer. This serves to keep the loaded Q high, and hence the spectrometer sensitivity large for a given transmitted power. The cavity used had a power transmission of 31 percent, loaded Q of 2850 and unloaded Q of 21 000. At a bolometer power level of 10^{-3} w, a pressure of 0.1 mm Hg in this cavity produced the same degree of saturation as did 0.7 mm Hg in the rectangular TE_{011} cavity. With pressures of 0.1 mm Hg the lambda doubling could be resolved.

The Lambda Doubling

A number of runs were taken with the circular TE_{011} cavity to determine the lambda doubling in the nine absorption lines. The microwave frequency was fixed at the center of the cavity resonance in each run. The dc magnetic field was varied with a proton field control which employed a proton oscillator⁸ locked to a variable and accurately known frequency of about 36 Mc/sec provided by mixing harmonics of a BC 221 frequency meter with a 30-Mc/sec crystal-controlled signal. As in earlier work¹ the data were taken point-by-point, varying the dc magnetic field and noting the output of a lock-in mixer with a galvanometer.

The microwave cavity frequency was measured by mixing the microwave oscillator signal with a crystal-controlled 9270-Mc/sec signal and measuring the difference frequency with a calibrated communications receiver. The cavity frequency was fixed throughout a run to about ± 2 kc/sec.

Figure 2 is a typical example of these measurements. The two lambda-doublet components are seen to be

⁸ In these experiments a regenerative, proton oscillator-detector similar to that of N. J. Hopkins, Rev. Sci. Instr. 20, 401 (1949), was used with a water-filled coil.

resolved well enough to determine their separation. The two outer "crossovers" (points of zero lock-in mixer output) are slightly closer together than the centers of the two line components because of the slope of the overlapping line tails. This "squeezing" correction was evaluated by graphical analysis of the partially resolved patterns. In this analysis it was assumed that the two line components were identical but not necessarily symmetrical. Line contours were added until the experimental line shape was reproduced. Such fitting is very sensitive to the separation of the two line components when they are resolved as well as those of Fig. 2.

Table I gives the results of measurements on the nine lines. The line component separations have been corrected for "squeezing." The fields in the third column are the arithmetic mean fields of the two lambda components and are corrected for field difference between the proton probe and the center of the cavity.

The lambda-doubling theory of Karnaugh⁴ expresses the separation of + and - levels in a given (M_I, M_J) state of N¹⁴O¹⁶ in terms of four parameters which must be evaluated by experiment. Two of these arise from the nonhyperfine part of the doubling and the other two from hyperfine contributions. The nine ($M_I, M_J \rightarrow M_I, M_J - 1$) transitions between the twelve levels serve to evaluate these four parameters. Karnaugh does this in two stages: the average doubling in each group of three lines with the same $M_J, M_J - 1$ is used to evaluate the nonhyperfine contributions. These three averages are satisfied by the theory with two parameters to within 0.14 percent. The two hyperfine parameters are then evaluated by taking differences in the doubling in several states differing in M_I . Table II gives the result of these calculations. The deviations between the experimental and semitheoretical values of the lambda doubling are well within the experimental error which

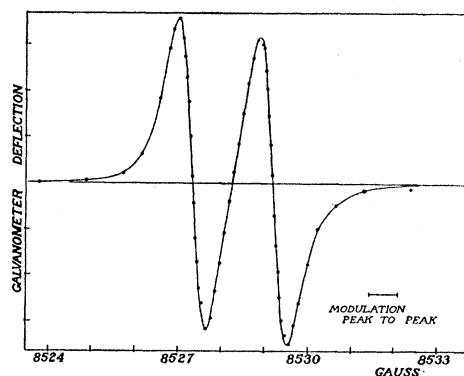


FIG. 2. Signal from line H_5 . The gas pressure was 0.096 mm Hg, 30 cy/sec, modulation was 0.68 gauss peak-to-peak, and the microwave frequency 9270.650 Mc/sec. The outer crossovers are separated by 1.84 gauss which is corrected by 0.02 gauss for "squeezing" to give 1.86 gauss for the separation of the A doublet components.

TABLE II. Comparison of theory and experiment in Λ doubling of the $N^{14}O$ spectrum.

Line	Experimental separation of Λ components (gauss)	Calculated separation of Λ components (gauss)	Deviation (percent)
H_1	1.48	1.482	+0.13
H_2	1.34	1.352	+0.89
H_3	1.32	1.311	-0.69
H_4	1.54	1.533	-0.46
H_5	1.86	1.858	-0.11
H_6	1.49	1.492	+0.13
H_7	1.82	1.829	+0.49
H_8	1.97	1.967	-0.15
H_9	2.01	2.009	-0.05

is estimated as 2 percent of the lambda-component separations. Certainly, the main features of the variation of the doubling with M_J and M_I are as predicted by Karnaugh's theory.

The Molecular Zeeman Effect

In the earlier work^{1,2} the molecular Zeeman splittings were a principal point of comparison of theory and experiment. The agreement at that time was quite satisfactory. It has not been improved by using the present data.

In the earlier work the molecular splittings were expressed as the resonance field values H_I , H_{II} , H_{III} of a hypothetical nitric oxide with spinless nitrogen. To obtain these field values directly from experimental data one must express the hyperfine couplings in field units. This method is only approximate and is not used here. Rather, the values of H_2 , H_5 , H_8 are compared with a new calculation of the molecular energies $E_{ab}(M_J) + \Delta E_{ab}(M_J)$ which proceeds directly from Eq. (1) using the calculation method of reference 2. As before, the value 123.8 cm^{-1} was taken for the $\mathbf{S} \cdot \mathbf{A}$ coupling constant.

The results of this calculation are given in Table III.

As a check on the method of energy calculation of reference 2, a second calculation of $E_{ab}(M_J) + \Delta E_{ab}(M_J)$ was made from the seventh-order determinant which arises when all seven eigenfunctions of reference 2 are combined at once. For a field of 8425.71 gauss and $M_J = \frac{3}{2}$ the energies calculated by the two methods differed by only 0.012 percent. Apparently then, the approximations in the calculation method are not responsible for the deviation between theory and experiment.

TABLE III. Molecular Zeeman splitting in the $N^{14}O$ spectrum at 9270.65 Mc/sec .

	H_5	$(H_8 - H_5)$	$(H_5 - H_2)$
Theory	8537.50 gauss	103.07 gauss	104.54 gauss
Experiment	8528.28 ± 0.1	101.43 ± 0.05	102.57 ± 0.05
Percent diff.	0.11 percent	1.6 percent	1.9 percent

The molecular coupling constant of $\mathbf{S} \cdot \mathbf{A}$, which is given from the band spectrum analysis of the doublet splitting, is not known very accurately. We have used 123.8 cm^{-1} for this constant. A value of 124.2 cm^{-1} has been used⁹ most recently in analysis of the rotation-vibration spectrum. The constant may be in error by as much as 0.5 cm^{-1} , and it is important to know how this affects the theoretical value for H_5 . This has not been determined using the complete theory of reference 2 but only with the stage 1 approximation using Hill's formula.¹⁰ This formula predicts H_5 quite well, although it does not give good values for the $H_8 - H_5$ and $H_5 - H_2$ differences. With Hill's formula an increase of 4.0 cm^{-1} in the coupling constant is required to decrease the theoretical 8537.5 gauss for H_5 resonance by the required 9.2 gauss . Such an increase in the coupling constant is out of the question, and it is concluded that this cannot account for the discrepancy.

A final point should be mentioned in connection with the H_5 discrepancy. In reference 2, the orbital Bohr magneton was used for both orbital and spin contributions to the magnetic energies. A better procedure would include the spin moment anomaly. For pure case (a) the g factor of a $J = \frac{3}{2}$, $^2\Pi_{3/2}$ level is $(4/5)(1 + 2\delta/3)$ rather than the usual $4/5$; here δ is the spin moment anomaly 0.0011454 . Since we are rather near to case (a), it is expected that the theoretical resonance fields of Table III will be multiplied by a factor $(1 + 2\delta/3)^{-1} = 0.999237$. This reduces the theoretical H_5 to 8531.0 gauss . Thus, the spin-moment correction together with an increase of about 1 cm^{-1} in the $\mathbf{S} \cdot \mathbf{A}$ coupling constant would remove the H_5 discrepancy in Table III. It is known, however, that other points in the theory of reference 2 should be reexamined if theoretical precision of 0.1 percent is desired.

Theory of the Hyperfine Structure

The hyperfine structure of the $^2\Pi_{3/2}$ state of $N^{14}O^{16}$ in high magnetic fields has been developed in two previous papers.^{2,3} The present calculation was performed in an attempt to provide a more stringent test of the theory of reference 3 by using the data which resulted from the lambda-doubling measurements. The lambda doubling itself does not appear in these calculations; it is assumed that it splits each hyperfine level symmetrically and that the hyperfine constants can be evaluated from the nine-line spectrum consisting of the arithmetic mean positions of the nine lambda doublets.

It is convenient to represent the energy of one of these nine components as $W(M_J, M_I)$ such that

$$W(M_J, M_I) = E_{ab}(M_J) + \Delta E_{ab}(M_J) + E_I(M_J, M_I) + \Delta E_I(M_J, M_I) + E_q(M_J, M_I). \quad (1)$$

Here $E_{ab}(M_J)$ and $\Delta E_{ab}(M_J)$ are the first- and second-order molecular Zeeman energies; they are

⁹ R. H. Gillette and E. H. Eyster, Phys. Rev. **56**, 1113 (1939).

¹⁰ E. L. Hill, Phys. Rev. **34**, 1507 (1929).

functions of the magnetic field strength and of M_J , the quantum number representing the component of the total angular momentum of the molecule (exclusive of nuclear spin) in the direction of the magnetic field. Expressions for $E_{ab}(M_J)$ and $\Delta E_{ab}(M_J)$ as power series in M_J and the magnetic field strength are given in Sec. 3 of reference 2.

The term $E_q(M_J, M_I)$ represents the energy due to the quadrupole moment of the N^{14} nucleus, M_I being the quantum number associated with the component of nuclear spin of N^{14} in the direction of the magnetic field. In the approximation employed here, $E_q(M_J, M_I)$ is independent of the magnetic field strength. It is given by Eq. 14 of reference 2 which, for the $J = \frac{3}{2}$, $^2\Pi_{\frac{3}{2}}$ level, is

$$E_q(M_J, M_I) = \frac{|e|Qq}{60} \left(\frac{15}{4} - 3M_J^2 \right) (2 - 3M_I^2), \quad (2)$$

where $|e|Qq$ is the nuclear quadrupole coupling constant defined in the manner of Bardeen and Townes.¹¹

The quantities $E_I(M_J, M_I)$ and $\Delta E_I(M_J, M_I)$ are the first- and second-order interactions between the magnetic moment of the N^{14} nucleus and the magnetic fields due to the spin and the orbital motion of the $^2\pi$ electron. Application of standard perturbation theory yields the usual expressions

$$E_I(M_J, M_I) = \langle \Psi(M_J, M_I) | \mathcal{H}_I | \Psi(M_J, M_I) \rangle \quad (3)$$

$$\begin{aligned} \Delta E_I(M_J, M_I) &= \frac{\langle \Psi(M_J, M_I) | \mathcal{H}_I | \Psi(M_J + 1, M_I - 1) \rangle^2}{W(M_J, M_I) - W(M_J + 1, M_I - 1)} \\ &+ \frac{\langle \Psi(M_J, M_I) | \mathcal{H}_I | \Psi(M_J - 1, M_I + 1) \rangle^2}{W(M_J, M_I) - W(M_J - 1, M_I + 1)}, \quad (4) \end{aligned}$$

in which $\Psi(M_J, M_I)$ is the state function of $^2\Pi_{\frac{3}{2}}$ level in the absence of any nuclear interaction, and \mathcal{H}_I is the operator representing the interaction.

The state function, $\Psi(M_J, M_I)$, can be expressed as a product of an electronic, a vibrational, a rotational, and a nuclear part. We shall write the product of the first three of these as $\Psi(M_J)$ and the nuclear part as $|I, M_I\rangle$, I being the quantum number associated with the nuclear spin. Moreover, since we are here concerned with only one electronic and vibrational level, we may write $\Psi(M_J)$ as a linear combination of a basic set of eigenfunctions each having the same electronic and vibrational parts but different rotational parts. So that use could be made of matrix elements already computed by Hill,¹⁰ the rotational parts were taken in reference 2 to be functions representing Hund's case (b), in which the rotational quantum number K , the total electron spin S , the total angular momentum quantum number J , and its component M_J , in the

direction of the magnetic field are sharp. These eigenfunctions are written $|K, J, M_J\rangle$; it was found that a combination of four of them yield a sufficiently accurate expression for $\Psi(M_J)$. This combination is (see reference 3, Eq. 5)

$$\begin{aligned} \Psi(M_J) &= a |1, \frac{3}{2}, M_J\rangle + b |2, \frac{3}{2}, M_J\rangle \\ &+ c |2, 5/2, M_J\rangle + d |3, 5/2, M_J\rangle, \quad (5) \end{aligned}$$

where the coefficients are functions of M_J and of the magnetic field strength; their values are such that $\Psi(M_J)$, although compounded of "case b" eigenfunctions, is fairly close to an eigenfunction representing Hund's case (a). Thus the state functions to be used in (3) and (4) have the form

$$\begin{aligned} \Psi(M_J, M_I) &= a |1, \frac{3}{2}, I, M_J, M_I\rangle \\ &+ b |2, \frac{3}{2}, I, M_J, M_I\rangle + c |2, 5/2, I, M_J, M_I\rangle \\ &+ d |3, 5/2, I, M_J, M_I\rangle, \quad (6) \end{aligned}$$

in which the product $|K, J, M_J\rangle |I, M_I\rangle$ is written $|K, J, I, M_J, M_I\rangle$, explicit dependence on electron spin, vibrational, and electronic quantum numbers being suppressed.

The interaction operator, averaged over electronic and vibrational coordinates is given by [reference 3, Eq. (9) with an obvious change in notation]

$$\begin{aligned} \mathcal{H}_I &= A \mathbf{I} \cdot \mathbf{A} + B [S_z I_z (3 \cos^2 \theta - 1) \\ &+ \frac{3}{2} I_z \sin \theta \cos \theta (iS^+ e^{-i\psi} - iS^- e^{i\psi}) \\ &+ \frac{3}{2} S_z \sin \theta \cos \theta (iI^+ e^{-i\psi} - iI^- e^{i\psi}) \\ &- \frac{3}{4} \sin^2 \theta (S^+ I^+ e^{-2i\psi} + S^- I^- e^{2i\psi}) \\ &- \frac{1}{4} (3 \cos^2 \theta - 1) (S^+ I^- + S^- I^+)], \quad (7) \end{aligned}$$

where \mathbf{I} is the nuclear spin operator, \mathbf{A} the operator representing the component of orbital angular momentum along the internuclear axis of the molecule, \mathbf{S} the electronic spin operator; the Euler angles θ and ψ specify the orientation of the molecule with respect to the direction of the magnetic field, and the constants A and B are averages over electronic and vibrational coordinates. Specifically,

$$\begin{aligned} A &\equiv \langle 4\mu_0 \mu_I / r^3 \rangle_{\text{elec, vib}}; \\ B &\equiv \langle 2\mu_0 \mu_I (3 \cos^2 \chi - 1) / r^3 \rangle_{\text{elec, vib}}, \quad (8) \end{aligned}$$

where μ_0 is the Bohr magneton; μ_I is one-half the magnitude of the nuclear magnetic moment of N^{14} , r is the distance between the $^2\pi$ electron and the N^{14} nucleus, and χ is the third Euler angle of the set θ, ψ, χ .

In a recent paper¹² Frosch and Foley obtained a relativistic expression for the hyperfine interaction operator; this expression reduces to (7) in the non-relativistic approximation. In the absence of any information about the electronic part of the state function for the $^2\Pi_{\frac{3}{2}}$ state of NO, it is difficult to determine whether or not a relativistic expression is needed. In this particular case, provided only effects diagonal in Λ are considered, the sole difference between the

¹¹ J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

¹² R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

relativistic and nonrelativistic expressions lies in the interpretation of the constants A and B . Application of Eqs. (1) of reference 3 allows (7) to be written in a form appropriate for case (a) eigenfunctions:

$$\mathfrak{H}_I = A\mathbf{I}\cdot\mathbf{A} + B(-\mathbf{I}\cdot\mathbf{S} + 3I_{Z'}S_{Z'}) \\ = (A\Lambda + 2B\Sigma)\mathbf{I}\cdot\mathbf{k}' - B(I_{X'}S_{X'} + I_{Y'}S_{Y'}), \quad (7')$$

where the components of \mathbf{I} and \mathbf{S} are now expressed in a coordinate system $X'Y'Z'$ fixed in the molecule, Z' being the direction of the intermolecular axis and \mathbf{k}' being a unit vector in this direction. The expression (7') is identical in form with Frosch and Foley's Eq. (10.4), the two differing only in the definition of the coefficients of the operators. The relativistic theory shows that $(A\Lambda + 2B\Sigma)$ should be replaced by

$$[a\Lambda + (b+c)\Sigma],$$

and B by $-b$, where

$$a \equiv A; \quad b \equiv -B + \left\langle \frac{8\mu_0\mu_I\delta(r)}{3r^3} \right\rangle_{\text{elec, vib}}; \quad c \equiv 3B.$$

Since only the two coefficients can be obtained from analysis of the data, a test of whether or not there is any spherically symmetric component to the electronic part of the state function ($3b+c \neq 0$) appears impossible from the first-order hyperfine interaction.

Matrix elements of the first term of (7) between eigenfunctions $|K_1, J_1, M_J\rangle$ and $|K_2, J_2, M_J\rangle$ are given by Hill;¹⁰ those of the remaining terms (except the one between $|K, J, M_J\rangle$ and $|K+2, J+1, M_J\rangle$ appear in reference 3). However, it was discovered during the analysis of the present data that the phases of the eigenfunctions employed in calculating the latter elements are inconsistent with those used (implicitly) by Hill. As a result, the second and third of Eqs. (11), reference 3, should be multiplied by (-1) if they are to be used in conjunction with the matrix elements given by Hill.

An exact calculation of (3) and (4) requires use of the following additional matrix elements:

$$\langle K, J, \frac{1}{2}, I, M_J, M_I | \mathfrak{H}_I | K+2, J+1, \frac{1}{2}, I, M_J, M_I \rangle \\ = \frac{3M_I}{2(K+1)(K+2)(2K+3)} \{ [(K+1)^2 - \Lambda^2][(K+2)^2 - \Lambda^2][(J+1)^2 - M_J^2] \}^{\frac{1}{2}}, \quad (9)$$

$$\langle K, J, \frac{1}{2}, I, M_J, M_I | \mathfrak{H}_I | K, J, \frac{1}{2}, I, M_J \pm 1, M_I \mp 1 \rangle = [(1 \pm M_I)(2 \mp M_I)(J \mp M_J)(J \pm M_J + 1)]^{\frac{1}{2}} \\ \times \left\{ \frac{A\Lambda^2}{(2K+1)(J+\frac{1}{2})} + \frac{B}{(4K^2-1)(2K+3)} \left[\frac{3\Lambda^2}{K(K+1)} - 1 \right] \left[-\frac{3}{2}(2K+1) + (J-K)(4K^2+K+3) \right] \right\}, \quad (10)$$

$$\langle K, J, \frac{1}{2}, I, M_J, M_I | \mathfrak{H}_I | K+1, J, \frac{1}{2}, I, M_J \pm 1, M_I \mp 1 \rangle \\ = \frac{A+3B\Lambda}{(K+1)(2K+1)(2K+3)} \{ (1 \pm M_I)(2 \mp M_I)(J \mp M_J)(J \pm M_J + 1)[(K+1)^2 - \Lambda^2] \}^{\frac{1}{2}}, \quad (11)$$

$$\langle K, J, \frac{1}{2}, I, M_J, M_I | \mathfrak{H}_I | K, J+1, \frac{1}{2}, I, M_J \pm 1, M_I \mp 1 \rangle \\ = \pm \frac{2A - (K^2 + K - 3)B}{4K(K+1)(2K+1)} \{ (1 \pm M_I)(2 \mp M_I)(J \pm M_J + 1)(J \pm M_J + 2) \}^{\frac{1}{2}}, \quad (12)$$

$$\langle K, J, \frac{1}{2}, I, M_J, M_I | \mathfrak{H}_I | K+1, J+1, \frac{1}{2}, I, M_J \pm 1, M_I \mp 1 \rangle \\ = \pm \{ (1 \pm M_I)(2 \mp M_I)(J \pm M_J + 1)(J \pm M_J + 2)[(K+1)^2 - \Lambda^2] \}^{\frac{1}{2}} \\ \times \left\{ -\frac{A}{4(J+1)(K+1)} + \frac{\Lambda B}{K(K+1)(K+2)(2K+1)(2K+3)} \left[-3(J-K)(K^2+2K+\frac{3}{2}) + \frac{9}{4}(K+1) \right] \right\}, \quad (13)$$

$$\langle K, J, \frac{1}{2}, I, M_J, M_I | \mathfrak{H}_I | K+2, J+1, \frac{1}{2}, I, M_J \pm 1, M_I \mp 1 \rangle \\ = \mp \frac{3B}{4(K+1)(K+2)(2K+3)} \{ [(K+1)^2 - \Lambda^2][(K+2)^2 - \Lambda^2](J \pm M_J + 1)(J \pm M_J + 2) \}^{\frac{1}{2}}. \quad (14)$$

The foregoing have been computed by applying the angular momentum addition laws given by Condon and Shortley¹³ to the matrix elements calculated by Rademacher and Reiche.¹⁴ Phases have been chosen so as to be consistent with the elements computed by Hill.

The Hyperfine Constants

If the theory being applied is correct, it should be possible to find a pair of constants A and B [Eqs. (7) and (8)] such that the three following difference equations are satisfied for $W(M_J, M_I)$:

$$\begin{aligned} & [W(\frac{3}{2}, 1) - W(\frac{1}{2}, 1)]_{H_1} \\ & \quad - [W(\frac{3}{2}, -1) - W(\frac{1}{2}, -1)]_{H_3} = \nu_1 - \nu_3, \\ & [W(\frac{1}{2}, 1) - W(-\frac{1}{2}, 1)]_{H_4} \\ & \quad - [W(\frac{1}{2}, -1) - W(-\frac{1}{2}, -1)]_{H_6} = \nu_4 - \nu_6, \quad (15) \\ & [W(-\frac{1}{2}, 1) - W(-\frac{3}{2}, 1)]_{H_7} \\ & \quad - [W(-\frac{1}{2}, -1) - W(-\frac{3}{2}, -1)]_{H_9} = \nu_7 - \nu_9. \end{aligned}$$

The $W(M_J, M_I)$ are given by (1), the subscripts H_i refer to the nine line positions of Table I, and the ν_i are the microwave frequencies at which each of the measurements were made.

Unfortunately, the best set of values of A and B obtained from (15) are inconsistent with the definitions (8) which require $A > 0$; $-(1/2)A < B \leq A$. This difficulty may arise from the fact that the value of B is very sensitive to experimental errors in magnetic field strength differences $H_1 - H_3$, $H_4 - H_6$ and $H_7 - H_9$ (a variation of 1 percent in these differences can change the value of B by a factor of several hundred), or it may be due to some small perturbation which we have failed to include. The fact that seemingly reasonable values of A and B were obtained from the earlier analysis³ is apparently an accident, due to the inconsistency in phases mentioned above.

¹³ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1951), second edition.

¹⁴ H. Rademacher and F. Reiche, *Z. Physik* **41**, 453 (1927).

If, as is suggested by (7'), we recast (15) in the form of three equations in $(A+B)$ and B , we find that the value of $(A+B)$ is relatively insensitive to the field strength errors and small perturbations which may have been neglected. In fact, $(A+B)$ changes by less than 3.7 percent, as B varies over the whole range of values consistent with the definitions (8).

In view of these considerations, we calculate only the sum $A+B$ which is fairly insensitive to limitations in theory and experiment. In the calculation B is assumed negligible as compared with $A+B$. Frosch and Foley suggested this assumption from examination of (7'). Use of (15) yields three independent values of $A+B$. None differ from $A+B = 0.00247 \text{ cm}^{-1} = 74.1 \text{ Mc/sec}$ by more than 0.9 percent. Frosch and Foley obtained $[a + \frac{1}{2}(b+c)] = 0.002607 \text{ cm}^{-1}$ using the former data¹ and a basic set of eigenfunctions corresponding to case (a).

Two values of the quadrupole interaction constant were determined from the equations

$$\begin{aligned} & [W(\frac{3}{2}, 1) - W(\frac{1}{2}, 1)]_{H_1} \\ & \quad + [W(\frac{3}{2}, -1) - W(\frac{1}{2}, -1)]_{H_3} \\ & \quad - 2[W(\frac{3}{2}, 0) - W(\frac{1}{2}, 0)]_{H_2} = \nu_1 + \nu_3 - 2\nu_2, \quad (16) \\ & [W(-\frac{1}{2}, 1) - W(-\frac{3}{2}, 1)]_{H_7} \\ & \quad + [W(-\frac{1}{2}, -1) - W(-\frac{3}{2}, -1)]_{H_9} \\ & \quad - 2[W(-\frac{1}{2}, 0) - W(-\frac{3}{2}, 0)]_{H_8} = \nu_7 + \nu_9 - 2\nu_8. \end{aligned}$$

The values are $|e|Qq = -0.000076 \text{ cm}^{-1} = -2.28 \text{ Mc/sec}$ and $|e|Qq = -0.000073 \text{ cm}^{-1} = -2.19 \text{ Mc/sec}$. The mean value $|e|Qq = -0.000075 \text{ cm}^{-1} = -2.23 \text{ Mc/sec}$ agrees with both determinations to within the limits of error of the experiment which is estimated as $\pm 0.06 \text{ Mc/sec}$ in the value of $|e|Qq$. These results are relatively insensitive to the values of A and B . Hence, provided the assumption that the lambda doubling splits each hyperfine line symmetrically is not grossly in error, the sign of the quadrupole coupling constant $|e|Qq$ is definitely negative.