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Uncoupling Effects in the Microwave Spectrum of Nitric Oxide

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The results obtained from the microwave measurements of the rotational spectra of $N^{15}O^{16}$ and $N^{14}O^{16}$ in their $^2\Pi_{\frac{1}{2}}$ ground state are compared by isotopic substitutions and shown to be in excellent agreement. The NO molecule is considered as an intermediate case, slightly removed from Hund's case (a). The theory of spin uncoupling and l uncoupling, developed by Van Vleck and extended by Dousmanis, Sanders, and Townes, is applied to the two molecules, and the molecular parameters are calculated accordingly. The resulting rotational constants are $B_0=49\,041.34$ Mc/sec and $D_0=0.139$ Mc/sec for $N^{15}O^{16}$, and $B_0=50\,838.56$ Mc/sec and $D_0=0.177$ Mc/sec for $N^{14}O^{16}$. The Λ-doubling constants are found to have the following values: $p_\Lambda=170.45$ Mc/sec for $N^{15}O^{16}$ and 176.15 Mc/sec for $N^{14}O^{16}$; and $q_\Lambda=0.71$ Mc/sec for $N^{15}O^{16}$ and 1.15 Mc/sec for $N^{14}O^{16}$.

The magnetic hyperfine structure is treated by an extension of the theory of Frosch and Foley to the intermediate case, and an expression is given for the quadrupole energy in the intermediate case. However, a very slight disagreement still exists between the measured and the calculated hyperfine separations.

A complete list of the measured line frequencies is presented along with the calculated values. Also, a complete list of all of the molecular and nuclear parameters that have been determined is given.

1. INTRODUCTION

RECENTLY, preliminary results on the microwave spectrum of $N^{15}O^{16}$ were reported.[1] These measurements together with the results[2-4] given earlier on the $N^{14}O^{16}$ spectrum provide the necessary information for the analysis of the uncoupling and isotopic effects in the molecule and for a closer examination of the hyperfine structure of the spectra.

The nitric oxide molecule possesses an unpaired electron and has a normal $^2\Pi$ ground state with the $^2\Pi_{\frac{3}{2}}$ state lying approximately 123.8 cm^{-1} above the $^2\Pi_{\frac{1}{2}}$ state. In the original discussions[3] of the $N^{14}O^{16}$ spectrum, the ground state was described in terms of an ideal Hund's case (a) representation. In this paper, the molecule is treated as an intermediate case, slightly removed from case (a), and the $(B_0)_{\text{eff}}$ value is corrected for the various distortions resulting from the mixing of states. These distortions are the effects commonly known as spin uncoupling and l uncoupling. Both effects also contribute to the hyperfine structure, although the contribution from l uncoupling is extremely small in the case of NO. When all of these effects are taken into consideration, good agreement results between the spectrum of $N^{14}O^{16}$ and that of $N^{15}O^{16}$.

During the preparation of this paper, an article by Dousmanis, Sanders, and Townes[5] on the microwave spectrum of OH has appeared. Since many of the effects which have to be considered for the NO molecule are similar to those treated in the paper by DST, reference will be made to that work for details of the derivations.

2. MEASUREMENTS

The experimental procedures used for observing the rotational transitions of NO in the 1 to 2-mm region have been described in references 1, 3, and 4 and will not be repeated here. The measured frequencies of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ lines of $N^{14}O^{16}$ are available in journal articles,[2,3] but the measured frequencies of the $J=\frac{3}{2}\rightarrow 5/2$ lines[4] of $N^{14}O^{16}$ and of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ and $J=\frac{3}{2}\rightarrow 5/2$ lines[1] of $N^{15}O^{16}$ were presented on slides at meetings and are not available elsewhere in the literature. Table I gives a complete list of these measured frequencies along with the values calculated from expressions developed in subsequent sections.

3. THEORETICAL CONSIDERATIONS

The $^2\Pi$ ground state of nitric oxide is a close approximation to Hund's case (a) representation. However, small effects caused by the interaction of the electronic motion with the rotational motion make it necessary to consider the state as being intermediate between Hund's case (a) and Hund's case (b). Beginning with Hund's case (a), one can introduce the rotational interaction effects as perturbations. Such a representation has for its good quantum numbers J, M_J, Σ, Λ, and Ω, where Σ is the quantum number representing the component of the electronic spin, S, along the internuclear axis; Λ the quantum number representing the component of electronic orbital angular momentum, L, along the internuclear axis; Ω the sum of Λ and Σ; J the total angular momentum (electronic and rotational), and M_J the component of J along a space-fixed axis.

To obtain the appropriate energy expression for the above representation, one must consider the following Hamiltonian:

$$H=H^{\text{mol}}+H^{\text{hfs}}+H^{Q}, \tag{1}$$

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[1] Gallagher, King, and Johnson, Phys. Rev. **98**, 1551(A) (1955).

[2] C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1953).

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

[4] C. M. Johnson and J. J. Gallagher, post deadline paper, American Physical Society Meeting, New York, January, 1954 (unpublished).

[5] Dousmanis, Sanders, and Townes, Phys. Rev. **100**, 1735 (1955), henceforth referred to as DST.

TABLE I. Microwave spectrum of nitric oxide $^2\Pi_{\frac{1}{2}}$ ground state.[a]

Transition	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	$\Delta\nu$ (Mc/sec)	Intensity (cm^{-1})
	$N^{14}O^{16}$			$T=80°K$
	$J=1/2\rightarrow3/2$			
Π^+ band				*1.19×10^{-2}*
$F=3/2\rightarrow5/2$	150 176.30±0.25	150 176.27	−0.03	0.59×10^{-2}
$F=1/2\rightarrow3/2$	150 198.52	150 198.24	−0.28	0.22
$F=3/2\rightarrow3/2$	150 218.57	150 218.33	−0.24	0.18
$F=1/2\rightarrow1/2$	150 225.47	150 224.10	−1.37	0.18
$F=3/2\rightarrow1/2$	150 245.38	150 244.05	−1.33	0.02
Π^- band				*1.19×10^{-2}*
$F=3/2\rightarrow1/2$	150 375.02	150 374.82	−0.20	0.02×10^{-2}
$F=3/2\rightarrow3/2$	150 438.72	150 438.14	−0.58	0.18
$F=3/2\rightarrow5/2$	150 546.25	150 546.56	+0.31	0.59
$F=1/2\rightarrow1/2$	150 580.38	150 580.14	−0.24	0.18
$F=1/2\rightarrow3/2$	150 644.11	150 643.58	−0.53	0.22
	$J=3/2\rightarrow5/2$			
Π^+ band				*4.75×10^{-2}*
$F=5/2\rightarrow7/2$	250 435.60±0.50	250 435.54	−0.06	2.11×10^{-2}
$F=3/2\rightarrow5/2$	250 439.20	250 439.29	+0.09	1.33
$F=1/2\rightarrow3/2$	250 447.16	250 446.81	−0.35	0.79
$F=3/2\rightarrow3/2$	250 474.02	250 472.72	−1.30	0.25
$F=5/2\rightarrow5/2$	250 481.52	250 481.40	−0.12	0.25
$F=5/2\rightarrow3/2$	···	250 514.18	···	0.01
Π^- band				*4.75×10^{-2}*
$F=5/2\rightarrow3/2$	···	250 643.40	···	0.01×10^{-2}
$F=5/2\rightarrow5/2$	250 707.12	250 706.04	−1.08	0.25
$F=3/2\rightarrow3/2$	250 752.61	250 752.01	−0.60	0.25
$F=5/2\rightarrow7/2$	250 794.99	250 795.66	+0.67	2.11
$F=3/2\rightarrow5/2$	250 814.64	250 814.31	−0.33	1.33
$F=1/2\rightarrow3/2$	250 816.24	250 815.34	−0.90	0.79
	$N^{15}O^{16}$			
	$J=1/2\rightarrow3/2$			
Π^+ band				*4.5 ×10^{-3}*
$F=1\rightarrow1$	144 927.81±0.25	144 928.33	+0.52	0.6 ×10^{-3}
$F=0\rightarrow1$	144 946.34	144 946.86	+0.52	1.1
$F=1\rightarrow2$	144 976.00	144 975.68	−0.32	2.8
Π^- band				*4.5 ×10^{-3}*
$F=0\rightarrow1$	145 236.09	145 236.55	+0.46	1.1 ×10^{-3}
$F=1\rightarrow2$	145 307.81	145 307.51	−0.30	2.8
$F=1\rightarrow1$	145 428.07	145 428.46	+0.39	0.6
	$J=3/2\rightarrow5/2$			
Π^+ band				*1.90×10^{-2}*
$2\rightarrow2$	···	241 668.35	···	0.08×10^{-2}
$1\rightarrow2$	241 715.40±0.50	241 715.71	+0.31	0.71
$2\rightarrow3$	241 723.79	241 723.45	−0.34	1.11
Π^- band				*1.90×10^{-2}*
$1\rightarrow2$	242 046.03	242 046.21	+0.18	0.71×10^{-2}
$2\rightarrow3$	242 060.35	242 060.17	−0.18	1.11
$2\rightarrow2$	···	242 167.17	···	0.08

[a] The data for the $J=1/2\rightarrow3/2$ and the $J=3/2\rightarrow5/2$ transitions of $N^{14}O^{16}$ were reported in references 3 and 4, respectively, and the results for $N^{15}O^{16}$ were given in reference 1. The very weak lines, for which no values of measured frequency are given, were observed by a recording technique but were not measured accurately.

where H^{mol}, H^{hfs}, and H^{Q} are the contributions of molecular rotation, nuclear magnetic interaction, and nuclear quadrupole interaction, respectively.

3.1. Molecular Energy Effects

The part of the molecular Hamiltonian which is of interest here is given by the expression[6]

$$H^{\mathrm{mol}}=B_v[(J_{x'}-P_{x'})^2+(J_{y'}-P_{y'})^2]+A\mathbf{L}\cdot\mathbf{S}, \quad (2)$$

where **P** is the sum of the spin and orbital electronic angular momenta, **J** the total angular momentum of the molecule (except for nuclear spin), B_v the rotational constant related to the moment of inertia of the nuclei by $h/8\pi^2I_v$, and A the measure of the coupling between the spin, **S**, and the orbital angular momentum, **L**. The first term gives the rotational energy and also the interaction of the rotational motion with the electronic motion. The second term represents the spin-orbit interaction. The calculations are carried out in a rectangular coordinate system, $x'y'z'$, fixed in the molecule.[7,8]

When these calculations are performed for Hund's case (a), the off-diagonal terms of Eq. (2) result in a mixing of the states of the molecule and cause a distortion of the rotational levels. The first effect to be considered is the mixing of the two states of the spin doublet, resulting in spin uncoupling. Taking into account this spin uncoupling, Hill and Van Vleck[9] calculated the following expression for the rotational energy levels (the centrifugal distortion term as derived by Almy and Horsfall[10] is included to terms significant for our measurements):

$$E=B_v[(J+\tfrac{1}{2})^2-\Lambda^2]\pm\tfrac{1}{2}B_v[\lambda\Lambda^2(\lambda-4)+4(J+\tfrac{1}{2})^2]^{\frac{1}{2}} \\ -D_v[J^2(J+1)^2-J(J+1)+13/16], \quad (3)$$

where $\lambda=A/B_v$ and D_v is the rotational distortion constant. The upper sign of the ± applies to the $^2\Pi_{\frac{3}{2}}$ state and the lower sign to the $^2\Pi_{\frac{1}{2}}$ state in the case of a normal doublet. For small spin uncoupling, i.e., $\lambda\gg1$, the radical can be expanded to terms of the order of magnitude of the quoted accuracy. Thus, for our purpose, one obtains

$$E=(B_v')_{\mathrm{eff}}(J+\tfrac{1}{2})^2-(D_v)_{\mathrm{eff}}(J+\tfrac{1}{2})^4+\mathrm{const}, \quad (4)$$

where

$$(B_v')_{\mathrm{eff}}=B_v\left(1\pm\frac{B_v}{[A\Lambda^2(A-4B_v)]^{\frac{1}{2}}}\right)+D_v,$$

$$(D_v)_{\mathrm{eff}}=D_v\pm B_v^4/[A\Lambda^2(A-4B_v)]^{\frac{3}{2}},$$

and

$$\mathrm{const}=-B_v\Lambda^2\pm\tfrac{1}{2}[A\Lambda^2(A-4B_v)]^{\frac{1}{2}}-D_v+A\Lambda\Sigma \\ +B_v[L(L+1)-\Lambda^2]+B_v[S(S+1)-\Sigma^2].$$

To this expression, one must add the effects of l uncoupling, i.e., the mixing of $^2\Sigma$ states with the $^2\Pi$ ground state. This l uncoupling breaks down the degeneracy of the J levels and produces the Λ-doubling effect. Thus each component of the spin doublet is itself split into two sets of levels, Π^+ and Π^- (or Π_d and Π_c in Mulliken's notation[11]). In addition, the

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[6] J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

[7] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[8] R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952), henceforth referred to as FF.

[9] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

[10] G. M. Almy and R. B. Horsfall, Phys. Rev. **51**, 491 (1937).

[11] R. S. Mulliken, Revs. Modern Phys. **3**, 90 (1931).

l-uncoupling yields a term which adds to $(B_v')_{\mathrm{eff}}$ of Eq. (4) and terms which further shift the rotational levels.

These l-uncoupling effects have been calculated to first order by Van Vleck[7] and by Mulliken and Christy,[12] and some higher order terms have been added by DST.[5] The two sets of energy levels, with the inclusion of only the higher order terms which are significant for low J values, are given by

$$E_{c/d}{}^{\mathrm{mol}}=E_{\mathrm{rot}}[\pm]E_{\Lambda}, \tag{5}$$

where

$$\begin{aligned}E_{\mathrm{rot}}=\Bigg[&B_v\pm\frac{B_v{}^2}{[A\Lambda^2(A-4B_v)]^{\frac{1}{2}}}\\&+D_v-4\sum_{\substack{\text{all }\Sigma\\\text{states}}}\frac{|(\Pi|BL_{x'}|\Sigma)|^2}{\nu(\Pi\rightarrow\Sigma)}\Bigg](J+\tfrac{1}{2})^2\\&-\left[D_v\pm\frac{B_v{}^4}{[A\Lambda^2(A-4B_v)]^{\frac{3}{2}}}\right](J+\tfrac{1}{2})^4\mp 4X^{-1}\\&\times\sum_{\substack{\text{all }\Sigma\\\text{states}}}\left\{\frac{(\Pi|AL_{x'}+2BL_{x'}|\Sigma)(\Sigma|BL_{x'}|\Pi)}{\nu(\Pi\rightarrow\Sigma)}\right\}\\&\times(J-\tfrac{1}{2})(J+\tfrac{3}{2})\mp\tfrac{1}{2}(2X^{-1}-\lambda X^{-1})\\&\times\sum_{\substack{\text{all }\Sigma\\\text{states}}}\Bigg\{\frac{|(\Pi|AL_{x'}+2BL_{x'}|\Sigma)|^2}{\nu(\Pi\rightarrow\Sigma)}\\&\qquad\qquad\times\frac{+4|(\Pi|BL_{x'}|\Sigma)|^2}{\nu(\Pi\rightarrow\Sigma)}\Bigg\},\end{aligned}$$

and

$$\begin{aligned}E_{\Lambda}=\tfrac{1}{2}\Bigg\{&4\sum_{\Sigma}\frac{(-1)^{\Sigma}}{\nu(\Pi\rightarrow\Sigma)}(\Pi|AL_{x'}|\Sigma)(\Sigma|BL_{x'}|\Pi)\\&\times\Bigg[(J+\tfrac{1}{2})(1+2X^{-1}\mp\lambda X^{-1})\pm\frac{(J+\tfrac{1}{2})}{\nu(\Pi\rightarrow\Sigma)X}\\&\times\{\langle 2(J-\tfrac{1}{2})(J+\tfrac{3}{2})\pm X\rangle\langle(B_v{}^s-B_v)(J+\tfrac{1}{2})^2\\&+B_v[\tfrac{1}{2}(\lambda\mp X)+(J-\tfrac{1}{2})(J+\tfrac{3}{2})]\rangle\\&-2B_v{}^s\langle(J+\tfrac{1}{2})^2[J(J+1)-(7/4)+\tfrac{1}{2}\lambda]\\&-(J-\tfrac{1}{2})(J+\tfrac{3}{2})\rangle-B_v{}^s(\lambda-2\mp X)(1+\lambda/4)\}\Bigg]\\&+4\sum_{\Sigma}\frac{(-1)^{\Sigma}}{\nu(\Pi\rightarrow\Sigma)}|(\Pi|BL_{x'}|\Sigma)|^2\\&\times[2(J+\tfrac{1}{2})(1\pm 2X^{-1}\mp\lambda X^{-1})\\&\qquad\pm 4X^{-1}(J+\tfrac{1}{2})(J-\tfrac{1}{2})(J+\tfrac{3}{2})]\Bigg\}.\end{aligned}$$

In these expressions, $X=[\lambda(\lambda-4)+4(J+\frac{1}{2})^2]^{\frac{1}{2}}$, $\nu(\Pi\rightarrow\Sigma)=E_{\Sigma}-E_{\Pi}$, and $B_v{}^s$ is the B_v value for the perturbing Σ state. The total constant multiplying the term $(J+\frac{1}{2})^2$ in the expression for E_{rot} is the $(B_v)_{\mathrm{eff}}$ given in the tables. It is, of course, equal to $(B_v')_{\mathrm{eff}}$ plus an additional term due to the l uncoupling.

The sign convention followed in Eq. (5), and throughout the paper, is that for normal doublets the upper sign of ± (or ∓) applies to the $^2\Pi_{\frac{3}{2}}$ state and the lower to the $^2\Pi_{\frac{1}{2}}$ state, while the upper sign of [±] applies to the Π^- or c levels and the lower to the Π^+ or d levels.

3.2. Magnetic Hyperfine Effects

The second term of the Hamiltonian, H^{hfs}, must now be considered. This term arises from the interaction of the unpaired electron with the magnetic moment of the nitrogen nucleus, and the resulting magnetic hyperfine structure has been treated by Frosch and Foley.[8] A slight correction of FF's constants has been given by Dousmanis,[13] and reference is made to his paper for the correct form of H^{hfs} and for the definition of the constants to be used throughout this work on NO.

For NO the molecular representation most applicable for the inclusion of nuclear spin is the case a_{β} of FF,[8] i.e., Hund's case (a) with the nuclear spin, **I**, coupled to **J**. The good quantum numbers for such a representation are Λ, Σ, Ω, I, J, F, and M_F, where F is the vector sum of J and I, M_F is the component of F on a space-fixed axis, and the other quantities are as defined previously. Frosch and Foley used the symmetric and antisymmetric combinations of the basic wave functions to obtain the nuclear magnetic interaction energy. To FF's expression, the spin-uncoupling effects as calculated by DST [see their Eq. (10)] must be added. The resulting energy contribution of the magnetic interaction becomes

$$\begin{aligned}E_{c/d}{}^{\mathrm{hfs}}=&\frac{X\pm 2+\lambda}{2X}\left[\left\{a-\frac{(b+c)}{2}\right\}[\pm]d(J+\tfrac{1}{2})\right]\frac{\mathbf{I}\cdot\mathbf{J}}{2J(J+1)}\\&+2bX^{-1}(J-\tfrac{1}{2})(J+\tfrac{3}{2})\frac{\mathbf{I}\cdot\mathbf{J}}{2J(J+1)}\\&+\frac{X+2\pm\lambda}{2X}\left(\frac{3}{2}\right)\left(a+\frac{b+c}{2}\right)\frac{\mathbf{I}\cdot\mathbf{J}}{J(J+1)},\end{aligned}\tag{6}$$

where the first $\mathbf{I}\cdot\mathbf{J}$ term is the expression given by FF for the $^2\Pi_{\frac{1}{2}}$ state except for the normalizing factor $(X-2+\lambda)/2X$, and the last two terms are contributed by the spin uncoupling. The constants a, b, c, and d are the same as defined by FF (as corrected by reference 13); the expression for each is given in Table II in

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

[13] G. C. Dousmanis, Phys. Rev. **97**, 967 (1955). See Eq. (2) of this reference and also Eq. (31) of reference 5.

terms of r_1, the distance from the nucleus with spin, I, to the interacting electron; χ, the angle between r_1 and the internuclear axis; g_I, the nuclear g factor; μ_n, the nuclear magneton; μ_0, the Bohr magneton; and $|\psi(0)|^2$, the probability density of the electron spin at the nucleus of spin I. The averages indicated in the expressions for these constants are taken over the electrons which provide the spin and orbital electronic angular momenta. The product $\mathbf{I}\cdot\mathbf{J}$ in Eq. (6) and throughout the paper means $\frac{1}{2}[F(F+1)-I(I+1)-J(J+1)]$.

The effect of l uncoupling on E^{hfs} has also been considered, but it was found that the contribution from this perturbation is less than 0.25 Mc/sec for each energy level and is thus not significant in view of the accuracy of the measurements. The same is true for perturbations by states off-diagonal in J. Such an interaction is between states which are of opposite symmetry. The resultant effect amounts to less than 0.1 Mc/sec in the case of NO.

3.3. Nuclear Quadrupole Interaction

The total energy expression is further affected, in the case of $N^{14}O^{16}$, by H^Q, the nuclear quadrupole interaction. This interaction of the electric quadrupole moment of N^{14} with the electrons is given by the following expression,[14]

$$H^Q=\frac{e^2Q}{I(2I-1)}\Bigg\{\left(\frac{3\cos^2\chi-1}{2r_1^3}\right)\left(\frac{3I_{z'}^2-I^2}{2}\right)+\frac{3}{4}\left(\frac{\sin\chi\cos\chi}{r_1^3}\right)\times\{[I_{z'}(I_{x'}-iI_{y'})+(I_{x'}-iI_{y'})I_{z'}]e^{+i\phi}+[I_{z'}(I_{x'}+iI_{y'})+(I_{x'}+iI_{y'})I_{z'}]e^{-i\phi}\}+\frac{3}{8}\left(\frac{\sin^2\chi}{r_1^3}\right)[e^{2i\phi}(I_{x'}-iI_{y'})^2+e^{-2i\phi}(I_{x'}+iI_{y'})^2]\Bigg\}, \quad (7)$$

where ϕ is the angle of rotation about the symmetry axis, Q the electric quadrupole moment of the nucleus as defined by Bardeen and Townes,[15] and the other quantities are as defined above.

Considering Eq. (7) now, one sees that for wave functions in a pure Hund's case (a) representation the terms in $e^{\pm i\phi}$ and $e^{\pm 2i\phi}$ do not contribute to the energy, while for a Hund's case (b) representation the terms in $e^{\pm 2i\phi}$ yield results for $(\Lambda|H^Q|-\Lambda)$. For the more general case, it is appropriate to use the intermediate wave functions given by Eq. (10) of DST in order to obtain the effect of the mixing of states upon the quadrupole interaction. This calculation has been carried out and is given in the appendix. The resulting expression is

$$E_{c/d}^Q=\frac{3}{I(2I-1)16X}\left(\frac{\mathbf{I}\cdot\mathbf{J}}{J(J+1)}\right)^2\{eQq_1(5X\mp8\pm4\lambda)\mp[\pm]2eQq_2[X^2-(2-\lambda)^2]^{\frac{1}{2}}\times[(J(J+1)+\tfrac{1}{4})(J(J+1)-\tfrac{3}{4})]^{\frac{1}{2}}\}+3\left[\frac{(J+F-I)(F+I-J+1)(F+I+J+1)(I+J-F)}{I(2I-1)64XJ^2(4J^2-1)}\right]\times\left\{eQq_1(4J^2X-5X\pm8\mp4\lambda)\pm[\pm]\frac{eQq_2}{2}[X^2-(2-\lambda)^2]^{\frac{1}{2}}(2J+1)[(2J+3)(2J-1)]^{\frac{1}{2}}\right\}+3\left(\frac{(F+I-J)(F+J-I+1)(F+I+J+2)(J+I-F+1)}{I(2I-1)64X(J+1)^2(2J+1)(2J+3)}\right)\left\{[4(J^2+2J)X-X\pm8\mp4\lambda]eQq_1\pm[\pm]\frac{eQq_2}{2}[X^2-(2-\lambda)^2]^{\frac{1}{2}}(2J+1)[(2J-1)(2J+3)]^{\frac{1}{2}}\right\}-\left(\frac{I(I+1)}{4}\frac{eQq_1}{I(2I-1)}\right), \quad (8)$$

where

$$eQq_1=e^2Q\left(\frac{3\cos^2\chi-1}{r_1^3}\right)_{\mathrm{Av}},\quad eQq_2=e^2Q\left(\frac{\sin^2\chi}{r_1^3}\right)_{\mathrm{Av}}.$$

The averages in these constants are taken over all electrons in the molecule.

For a pure case (a) molecule, Eq. (8) will reduce to the expression for the symmetric top molecule. A more compact form of the quadrupole interaction has been obtained by Lin and Mizushima,[16] using Racah coefficients and a Hund's case (b) representation.[17]

It is also possible to calculate the quadrupole energy from Eq. (7) by using a case $(b_{\beta J})$ representation.[8] To obtain the intermediate case, one must consider the magnetic interaction rather than the rotational energy as the perturbation and form the appropriate wave

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[14] H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, Haarlem, 1936); see also Eq. (7.6) of reference 8.

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

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

[17] The results given by Lin and Mizushima agree with Eq. (8) except that they associated the Λ doublets with the [±] signs in the sense opposite to that given above.

TABLE II. Molecular parameters for nitric oxide.[a]

	$N^{14}O^{16}$	$N^{15}O^{16}$
$(B_0)_{\text{eff}}(^2\Pi_{\frac{1}{2}})$	50 121.15	48 375.04
$(D_0)_{\text{eff}}(^2\Pi_{\frac{1}{2}})$	0.034	0.017
$(B_0)_{\text{eff}}(^2\Pi_{\frac{3}{2}})$	51 553.91	49 689.35
$(D_0)_{\text{eff}}(^2\Pi_{\frac{3}{2}})$	0.319	0.261
B_0	50 838.56	49 041.34
D_0	0.177	0.139
I_0	$16.505_1\times 10^{-40}$ g cm^2	$17.101_0\times 10^{-40}$ g cm^2
r_0	1.153_9A	1.153_9A
B_e	51 109.51	49 298.14
α_e	0.0181 cm^{-1}	0.0171 cm^{-1}
I_e	$14.416_3\times 10^{-40}$ g cm^2	$17.019_5\times 10^{-40}$ g cm^2
r_e	1.150_8A	1.150_8A
	Λ-doubling constants:	
$4\sum_s \frac{(-1)^s}{\nu(\Pi\rightarrow\Sigma)}(\Pi\lvert AL_{x'}\rvert\Sigma)(\Sigma\lvert BL_{x'}\rvert\Pi)=p_\Lambda$	176.15	170.45
$4\sum_s \frac{(-1)^s}{\nu(\Pi\rightarrow\Sigma)}\lvert(\Pi\lvert BL_{x'}\rvert\Sigma)\rvert^2=q_\Lambda$	1.15	0.71
	l-uncoupling constants:	
$4\sum_{\substack{\text{all }\Sigma\\ \text{states}}} \frac{\lvert(\Pi\lvert BL_{x'}\rvert\Sigma)\rvert^2}{\nu(\Pi\rightarrow\Sigma)}$	+1.15	+0.71
$4\sum_{\substack{\text{all }\Sigma\\ \text{states}}} \frac{(\Pi\lvert AL_{x'}\rvert\Sigma)(\Sigma\lvert BL_{x'}\rvert\Pi)}{\nu(\Pi\rightarrow\Sigma)}$	+176.15	+170.45
$\sum_{\substack{\text{all }\Sigma\\ \text{states}}} \frac{\lvert(\Pi\lvert AL_{x'}\rvert\Sigma)\rvert^2}{\nu(\Pi\rightarrow\Sigma)}$	+3216.99	+3224.79
	Magnetic hfs constants:	
$[a-\frac{1}{2}(b+c)]$	92.74	−130.03
$d=g_I\mu_0\mu_n[3\sin^2\chi/r_1^3]_{\text{Av}}$	112.60	−157.88
$a=2g_I\mu_0\mu_n(1/r_1^3)_{\text{Av}}$	83.40	−116.94
$b=2g_I\mu_0\mu_n\left[\frac{8\pi\psi^2(0)}{3}-\left(\frac{3\cos^2\chi-1}{2r_1^3}\right)_{\text{Av}}\right]$	68.91	−96.63
$c=3g_I\mu_0\mu_n[(3\cos^2\chi-1)/r_1^3]_{\text{Av}}$	−87.60	+122.82
	Quadrupole constants:	
$e^2Q\left(\frac{3\cos^2\chi-1}{2r_1^3}\right)_{\text{Av}}$	−1.75	...
$e^2Q\left(\frac{\sin^2\chi}{r_1^3}\right)_{\text{Av}}$	9.3	...
	Constants taken from other sources:	
A[b]	123.8 cm^{-1}	
B_v^s[c]	1.9870 cm^{-1}	1.9082 cm^{-1}
$\nu(\Pi\rightarrow\Sigma)$[c]	43 966 cm^{-1}	
M^{14}/M^{15} (mass ratio)[d]	0.933532	
μ (magnetic moment of nitrogen)[e]	+0.40369±4 nm	−0.28299±3 nm
$[a+\frac{1}{2}(b+c)]$[f]	74.05	−113.84

[a] All parameters given here were determined in this paper unless otherwise referenced. Values are given in Mc/sec, except in cases where the appropriate units are specified. Those parameters which are listed and which were not determined here are the values which were used to obtain consistency in the results.
[b] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).
[c] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 558.
[d] Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).
[e] W. G. Proctor and F. C. Yu, Phys. Rev. **77**, 716 (1950); **81**, 20 (1951).
[f] Beringer, Rawson, and Henry, Phys. Rev. **94**, 343 (1954).

functions accordingly.[18] These calculations have been carried out and yield a very complicated energy expression which is not as convenient to use as Eq. (8). The sum of Eqs. (5), (6), and (8) gives the total energy expression for the rotational levels in the ground $^2\Pi$ state of NO.

4. INTERPRETATION OF EXPERIMENTAL DATA

4.1. Molecular Effects

An analysis of the experimental work on $N^{14}O^{16}$ and $N^{15}O^{16}$ will now be given based upon the equations of

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[18] See Eq. (43) of reference 5. In using this equation, one must make the following corrections, to which Dr. Dousmanis has agreed: The ± before the second bracket should be replaced by a + sign, a ± should be placed before the first bracket, and the relation of the signs to the $\Pi_{\frac{1}{2}}$ and $\Pi_{\frac{3}{2}}$ states as given in the paragraph following Eq. (43) should be reversed. This correction does not alter the calculations of DST.

Sec. 3, and the results for the two molecules will be compared by the proper isotopic substitutions. The calculated frequencies of all the observed lines, together with the experimental values, are given in Table I.

Since N^{15} has no quadrupole moment, $N^{15}O^{16}$ is the simpler form to treat. For this case the displacement of the hyperfine levels from their parent level is proportional to $F(J)\mathbf{I}\cdot\mathbf{J}$ and therefore the interval rule can be applied to the observed lines of frequency $\nu(F\rightarrow F')$ to obtain the hypothetical frequencies, ν_c and ν_d, of the unsplit lines of the Λ doublet. Then the frequency, $\nu_0(J-1\rightarrow J)$, of the rotational line, without either Λ doubling or hyperfine splitting, can be obtained from the following expressions:

$$\nu_c(J-1\rightarrow J)=\nu_0(J-1\rightarrow J)+\tfrac{1}{2}\Delta\nu_{cd}(J)-\tfrac{1}{2}\Delta\nu_{cd}(J-1),$$

and

$$\nu_d(J-1\rightarrow J)=\nu_0(J-1\rightarrow J) -\tfrac{1}{2}\Delta\nu_{cd}(J)+\tfrac{1}{2}\Delta\nu_{cd}(J-1), \quad (9)$$

where $\Delta\nu_{cd}$ gives the Λ splitting of the rotational level. Thus, $\nu_0(J-1\rightarrow J)=(\nu_c+\nu_d)/2$, and in addition $\Delta\nu_{cd}(J)-\Delta\nu_{cd}(J-1)=\nu_c-\nu_d$.

When the measured frequencies are treated by the above procedure, the following values are obtained:

$$\begin{aligned}\nu_0(1/2\rightarrow 3/2)&=145\ 133.74\ \text{Mc/sec},\\ \nu_0(3/2\rightarrow 5/2)&=241\ 888.84\ \text{Mc/sec},\\ \Delta\nu_{cd}(3/2)-\Delta\nu_{cd}(1/2)&=342.35\ \text{Mc/sec},\\ \Delta\nu_{cd}(5/2)-\Delta\nu_{cd}(3/2)&=341.11\ \text{Mc/sec}.\end{aligned} \quad (10)$$

These values are related to E_{rot} and E_Λ of Eq. (5) in the following manner:

$$\begin{aligned}\nu_0(J-1\rightarrow J)&=E_{\text{rot}}(J)-E_{\text{rot}}(J-1),\\ \Delta\nu_{cd}(J)-\Delta\nu_{cd}(J-1)&=2[E_\Lambda(J)-E_\Lambda(J-1)],\end{aligned} \quad (11)$$

thus providing the means of evaluating the rotational and the Λ-doubling constants. In order to make these determinations, however, the values of the quantities A, $\nu(\Pi\rightarrow\Sigma)$, and B_v[8] must be taken from other work. Fortunately, the accuracy required for these supplementary quantities is not very great since they are parts of small correction terms. The values used are given in Table II.

The fact that the last two quantities of Eq. (10) are not equal is a manifestation of intermediate coupling, and two constants, p_Λ and q_Λ (see Table II for definitions) are required to describe the Λ doubling. Both these constants can be evaluated since two transitions were observed. These constants can also be used as the l-uncoupling constants in E_{rot} if two assumptions are made. One is that the $^2\Pi$ ground state interacts principally with $^2\Sigma$ states of one symmetry type, positive[12] in the case of NO. The other is that the "hypothesis of pure precession" is applicable so that

$$\sum_{\Sigma}\frac{|(\Pi|AL_{x'}|\Sigma)|^2}{\nu(\Pi\rightarrow\Sigma)}=\lambda\sum_{\Sigma}\frac{(\Pi|AL_{x'}|\Sigma)(\Sigma|BL_{x'}|\Pi)}{\nu(\Pi\rightarrow\Sigma)}. \quad (12)$$

This hypothesis has also been used in evaluating one of the small terms of the second-order correction to the Λ doubling. The "hypothesis of pure precession" is a poor approximation for the NO molecule, but it has been applied here only to terms which contribute a very small effect. It should be pointed out however that the "hypothesis of pure precession" is considered a reasonable assumption when applied to the spin matrices,[7] and this application has been used throughout the paper.

For $N^{14}O^{16}$ the same procedure can be followed for obtaining the molecular constants except that a small correction to the hfs due to the quadrupole effect must be made before the interval rule can be applied. The evaluation of this quadrupole effect is contained in the next section. When this correction is made and the measured frequencies substituted into Eq. (9), the following results are obtained:

$$\begin{aligned}\nu_0(1/2\rightarrow 3/2)&=150\ 372.78\ \text{Mc/sec},\\ \nu_0(3/2\rightarrow 5/2)&=250\ 619.89\ \text{Mc/sec},\\ \Delta\nu(3/2)-\Delta\nu(1/2)&=355.27\ \text{Mc/sec},\\ \Delta\nu(5/2)-\Delta\nu(3/2)&=353.62\ \text{Mc/sec}.\end{aligned} \quad (13)$$

All of the molecular constants obtained for both $N^{15}O^{16}$ and $N^{14}O^{16}$ are given in Table II. In addition the sum of the l-uncoupling contributions to the unsplit rotational levels are evaluated in Table III and denoted as ΔE_{rot}. It is apparent that even the net contribution to the transition frequencies is quite appreciable.

Likewise in Table III, the contributions of the higher order terms of DST[5] to the Λ doubling are given. These terms are denoted by ΔE_Λ, and it can be seen that for $^2\Pi_{\frac{1}{2}}$ levels they are significant also. For $^2\Pi_{\frac{3}{2}}$ levels, however, ΔE_Λ is quite negligible.

4.2. Nuclear Hyperfine Effects

The hyperfine splittings of the energy levels are given by Eqs. (6) and (8). Comparing the hfs of $N^{14}O^{16}$ with that of $N^{15}O^{16}$, one sees that both spectra show an asymmetry in the Λ doublets because of the hyperfine doubling[19] term, $[\pm]d(J+\frac{1}{2})\mathbf{I}\cdot\mathbf{J}/2J(J+1)$. Since the magnetic moments of N^{15} and N^{14} are opposite in sign, the order of the hyperfine levels is reversed in the two molecules. The spectra thus confirm the negative value of the magnetic moment for N^{15} as found by Proctor and Yu.[20]

The hyperfine parameters for both $N^{15}O^{16}$ and $N^{14}O^{16}$ obtained from the measurements by means of Eqs. (6)

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[19] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

[20] W. G. Proctor and F. C. Yu, Phys. Rev. **77**, 716 (1950).

and (8) are listed in Table II. The values given for the magnetic constants a, b, c, and d of $N^{14}O^{16}$ are practically the same as the values originally[3,13] obtained without including the interaction with the ${}^2\Pi_{\frac{3}{2}}$ state.

For $N^{14}O^{16}$ the value of the quadrupole coupling, eQq_1, which gives the best fit of the measured lines is -1.75 Mc/sec. This result is consistent with the values obtained by others.[13,16,21] The other quadrupole constant $eQq_2 = e^2Q(\sin^2\chi/r_1^3)_{\text{Av}}$ has been estimated from the value $Q = 0.02\times 10^{-24}$ cm^2 given by Townes and Dailey,[22] and for $(\sin^2\chi/r_1^3)_{\text{Av}} = 13.4\times 10^{24}$ cm^{-3} as obtained from the magnetic hfs constants.[13] Unfortunately, since the effect of eQq_2 on the spectrum is so small, the quadrupole moment, Q, cannot be accurately determined from this expression.

Despite all of the foregoing considerations, it can be seen from Table I that the calculated spectrum does not fit the measured spectrum within the experimental error. The existing small discrepancies are apparently still in the magnetic hyperfine energy expression, since the calculations for $N^{15}O^{16}$ where no quadrupole effects exist also exhibit these deviations from the experimental values. The small contributions from mixing with the ${}^2\Sigma$ states and with states off-diagonal in J amount to 0.25 Mc/sec or less and are not large enough to alter the calculations significantly. A better fit of the $N^{14}O^{16}$ hyperfine structure has been obtained by Lin and Mizushima[16]; however, the term of their calculation arising from the matrix element $(\Pi_{\frac{1}{2}}|H^{\text{hfs}}|\Pi_{\frac{3}{2}})$ is one-half the value that DST[3] and the authors have obtained independently.[23] It is possible to obtain an exact fit of the spectrum, if one does not consider the value obtained from the magnetic resonance work[21] on the ${}^2\Pi_{\frac{3}{2}}$ state. The value for the parameter b so obtained differs greatly from that obtained by using the ${}^2\Pi_{\frac{3}{2}}$ state data and is no longer consistent with atomic orbital calculations.[13]

4.3. Comparison of Isotopic Effects

Spectroscopy in the millimeter region offers the possibility of comparing the isotopic species of relatively light molecules. In these cases, the large rotational velocities cause l-uncoupling effects to become more evident than in heavier molecules. For ${}^1\Sigma$ states, a Zeeman-effect measurement[19,24] is necessary in order to estimate the l-uncoupling effects; however, for ${}^2\Pi$ states, the molecule provides its own magnetic effects, and it is possible to obtain an excellent estimate of the l uncoupling from the Λ-doubling constants. This estimate, of course, is made under the assumption that the interaction with the ${}^2\Sigma$ states is mainly with states of one symmetry type, a situation which seems to exist for NO.

TABLE III. Effects of l uncoupling on rotation energy, ΔE^{rot}, and of higher order effects on Λ-doubling energy, ΔE_{Λ}.

	ΔE_{rot} (Mc/sec)		ΔE_{Λ} (Mc/sec)	
	${}^2\Pi_{\frac{1}{2}}$	${}^2\Pi_{\frac{3}{2}}$	${}^2\Pi_{\frac{1}{2}}$	${}^2\Pi_{\frac{3}{2}}$
$N^{14}O^{16}$				
$J=1/2$	-1697.749	$\cdots$	$[\pm]0.393$	$\cdots$
$J=3/2$	-1691.651	$+1682.434$	$[\pm]0.793$	$[\mp]0.0006$
$J=5/2$	-1681.565	$+1660.827$	$[\pm]1.205$	$[\mp]0.002$
$N^{15}O^{16}$				
$J=1/2$	-1699.185	$\cdots$	$[\pm]0.389$	$\cdots$
$J=3/2$	-1693.157	1687.477	$[\pm]0.784$	$[\mp]0.0005$
$J=5/2$	-1681.986	1669.206	$[\pm]1.192$	$[\mp]0.0015$

From the experimental data for NO, B_0 has been calculated for both $N^{14}O^{16}$ and $N^{15}O^{16}$. With the value of α_e for $N^{14}O^{16}$ taken from Gillette and Eyster,[25] one can calculate $B^{(1)}$ where the superscript (1) indicates the value for $N^{14}O^{16}$. From the constants obtained for $N^{14}O^{16}$, it is possible to calculate $B_0^{(2)}$, where (2) indicates the value for $N^{15}O^{16}$, as follows:

$$B_0^{(2)} = \rho^2 B_0^{(1)} + \tfrac{1}{2}\alpha_e^{(1)}(\rho^2 - \rho^3), \qquad (14)$$

where $\rho^2 = \mu^{(1)}/\mu^{(2)}$ is the ratio of the reduced masses of the two molecules.

The value thus obtained is $B_0^{(2)} = 49\,041.39$ Mc/sec, which is in excellent agreement with the value determined directly from the $N^{15}O^{16}$ data (see Table II). In Eq. (14), the effect of any inaccuracy in the constant $\alpha_e^{(1)}$ is lessened since the inaccuracy is multiplied by $(\rho^2 - \rho^3)$. Thus, while it appears that the experimental value[25] for α_e is only accurate to within about ± 0.0004 cm^{-1}, this deviation amounts to an error of less than 0.25 Mc/sec in the value of $B_0^{(2)}$ for $N^{15}O^{16}$. Alternatively, it is possible to determine the B_e's and α_e's from the following relations:

$$\begin{aligned} B_0^{(1)} &= B_e^{(1)} - \tfrac{1}{2}\alpha_e^{(1)}, \\ B_0^{(2)} &= \frac{\mu^{(1)}}{\mu^{(2)}} B_e^{(1)} - \tfrac{1}{2}\left(\frac{\mu^{(1)}}{\mu^{(2)}}\right)^{\frac{3}{2}} \alpha_e^{(1)}, \end{aligned} \qquad (15)$$

where $B_0^{(1)}$ and $B_0^{(2)}$ are determined experimentally. Solving for $B_e^{(1)}$, one obtains

$$B_e^{(1)} = \left[B_0^{(2)} - \left(\frac{\mu^{(1)}}{\mu^{(2)}}\right)^{\frac{3}{2}} B_0^{(1)}\right] \Big/ \left[\frac{\mu^{(1)}}{\mu^{(2)}} - \left(\frac{\mu^{(1)}}{\mu^{(2)}}\right)^{\frac{3}{2}}\right]. \qquad (16)$$

The values for $B_e^{(1)}$, $B_e^{(2)}$, $\alpha_e^{(1)}$, and $\alpha_e^{(2)}$ obtained in this manner are given in Table II. Since the previous α_e's obtained experimentally[25] are relatively inaccurate, the above method of calculation, based on the mass ratios, probably yields more accurate values of the

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

[22] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[23] M. Mizushima (private communication) has agreed that his value is wrong.

[24] B. Rosenblum and A. H. Nethercot, Jr., Phys. Rev. **97**, 84 (1955); Bull. Am. Phys. Soc. Ser. II, **1**, 13 (1956).

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

B_e's. The masses used throughout this paper are those obtained from nuclear reaction data.[26]

The reverse of the above procedure could be used to calculate the mass ratios, but the values obtained, because of the uncertainty in α_e and A, would not be of comparable accuracy to those given in reference 26.

The hyperfine structure separations were treated in two ways. In one case, the constants a, b, c, and d were calculated independently for both $N^{14}O^{16}$ and $N^{15}O^{16}$. These constants for the two molecules are related by $a^{(2)}=(g_I{}^{(2)}/g_I{}^{(1)})a^{(1)}$, etc., where g_I is the g factor of the nitrogen nucleus and (1) and (2) again refer to $N^{14}O^{16}$ and $N^{15}O^{16}$, respectively. The electronic averages contained in these constants are assumed to be independent of the isotopic substitutions, and the ratio $g_I{}^{(2)}/g_I{}^{(1)}$ is taken as -1.4021 from nuclear resonance data.[20] When substituted into these expressions, the corresponding constants for the two isotopic molecules show very good agreement. The negative sign in the ratio is, of course, the cause of the inversion of the order of the hyperfine levels of one isotopic species with respect to the other.

In the other manner of calculating the hyperfine structure effects, the $N^{15}O^{16}$ separations, which have no quadrupole contributions, were treated first, and then the isotopic substitutions were made to obtain the $N^{14}O^{16}$ magnetic hyperfine separations. The quadrupole interaction was then added. The calculated frequencies of Table I and the constants in Table II have been obtained in this manner.

While there is excellent agreement between the B_0 values for $N^{15}O^{16}$ and $N^{14}O^{16}$, it should be emphasized that some of the assumptions made in evaluating the small uncoupling effects may not be exact enough to warrant the agreement which has been obtained. For example, the constant A, used for both isotopic species, should not be appreciably affected by the isotopic change, but a more accurate determination of A (here, $A=123.8$ cm^{-1}, as given by Margenau and Henry,[27] was used) may necessitate slight changes in the results for B_0. Also, the use of the "hypothesis of pure precession" in evaluating one of the l-uncoupling constants may be the source of a slight inaccuracy in the determination of the B_0 values. Finally, there is a small term which originates from the spin-molecular rotation interaction,[5,7,19] $\gamma\mathbf{K}\cdot\mathbf{S}$, where $K=J\pm\frac{1}{2}$ and γ is a small constant indicating the strength of coupling between the magnetic field of the molecular rotation and the electron spin $\mathbf{S}$. Lack of an accurate value for the small constant γ has necessitated our neglecting the term. It is, of course, believed that inclusion of this term would cause only a very small change in B_0 and no relative shift of the B_0 values of the two isotopic molecules.

Besides the above effects whose contribution is somewhat uncertain, several other interactions which have exceedingly small effects on the energy levels have also been neglected in the calculations. These effects have been discussed by DST and are summarized as follows:

(1) The influence of $^2\Delta$ states on the Λ doubling. Recently, Miescher[28] has obtained results involving a $^2\Delta_i$ state in NO. The value for $\nu(\Pi\rightarrow\Delta)$ so obtained is 60 365 cm^{-1}. The effect of this state on the Λ doubling of the $^2\Pi_{\frac{1}{2}}$ state is $\cong[A/\nu(\Pi\rightarrow\Sigma)][B/\nu(\Pi\rightarrow\Delta)]\nu_\Lambda{}^{(1)}$ $\cong 50$ cps for the low J states involved.

(2) The influence of $\gamma\mathbf{S}\cdot\mathbf{K}$ interaction on Λ doubling. This effect would contribute about 5 kc/sec for the low J states of this experiment.

(3) The effect of vibration on the l-uncoupling and Λ-doubling constants. Since $D_0/B_0\cong 3\times10^{-6}$, this correction must only be made for the transitions involving higher J values.

(4) The effect of $^2\Sigma$ in third order on Λ doubling. For low J values, the contribution of this effect is about 5×10^{-3} Mc/sec.

(5) The effect of distortion correction to the order $(B/\omega_{\text{vib}})^4$. The rotational energy is affected by an amount $0.2J^3(J+1)^3$ cps while the effect on the Λ doubling is about $100J^2(J+1)$ cps.

(6) The contribution of very small nuclear terms of the type $f(J)(\mathbf{I}\cdot\mathbf{J})^2$ from second-order perturbation. This factor corresponds to a pseudo-quadrupole effect with a complicated factor, $f(J)$. The result, however, is small and is of the order of a few kc/sec.

(7) The contribution of the small interaction of the form $a'\mathbf{I}\cdot\mathbf{N}$ which accounts for the interaction of the nuclear magnetic moment with the magnetic field due to the rotation of the molecule. This term would yield small contributions of about 50 kc/sec to the other $\mathbf{I}\cdot\mathbf{J}$ terms.

4.4. $^2\Pi_{3/2}$ State of NO

In order to confirm the results obtained for the $^2\Pi_{\frac{1}{2}}$ state, it would be most advantageous to measure the $J=3/2\rightarrow5/2$ transition of the $^2\Pi_{\frac{3}{2}}$ state. This transition lies at a slightly higher frequency than the corresponding transition for the $^2\Pi_{\frac{1}{2}}$ state, and the rotational levels in $^2\Pi_{\frac{3}{2}}$ state are much less populated than the corresponding levels of the $^2\Pi_{\frac{1}{2}}$ state. Intensity calculations indicate that with the realizable spectrometer sensitivity in the 1-mm region these lines should be detectable. However, the search for them has thus far been unsuccessful. Because of spin uncoupling effects, the $J=3/2\rightarrow5/2$ rotational transition in the $^2\Pi_{\frac{3}{2}}$ state lies approximately 7 kMc/sec higher than the corresponding transition in the $^2\Pi_{\frac{1}{2}}$ state. The Λ doubling of the $^2\Pi_{\frac{3}{2}}$ levels is extremely small compared to that of

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[26] Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).

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

[28] E. Miescher, Can. J. Phys. **33**, 355 (1955).

TABLE IV. Values of $|\mu_{ij}|^2$.

Case (a)	Intermediate	Case (b)
$\Delta J=0, \quad \Delta\Omega=0:$		
$\dfrac{\mu^2\Omega^2(2J+1)}{J(J+1)}$	$\dfrac{(2J+1)\mu^2}{J(J+1)}[a^2\Omega_1{}^2+2ab\Omega_1\Omega_2+b^2\Omega_2{}^2]$	$\dfrac{2\mu^2\Lambda^2(2K-1)}{K(2K+1)}$
$J\rightarrow J+1, \quad \Omega=0:$		$K\rightarrow K+1, \quad K=J-S$
$\dfrac{\mu^2(J+\Omega+1)(J-\Omega+1)}{(J+1)}$	$\dfrac{\mu^2[a\{(J+1)^2-\Omega^2\}^{\frac{1}{2}}+b\{(J+1)^2-\Omega_2{}^2\}^{\frac{1}{2}}]^2}{(J+1)(2J+1)}$	$\dfrac{2\mu^2(K+\Lambda+1)(K-\Lambda+1)(K+2)}{(K+1)(2K+3)}$
		$K\rightarrow K+1, \quad K=J+S$
		$\dfrac{\mu^2[(K+1)^2-\Lambda^2]2K}{(2K+1)(K+1)}$

the $^2\Pi_{\frac{1}{2}}$ levels. Furthermore, the hfs is practically void of the hyperfine doubling effects and, as a result, is approximately equal in both symmetry levels. The lines should thus appear as close doublets, the small separations being due to the small Λ doubling and the mixing with the $^2\Pi_{\frac{1}{2}}$ state and the $^2\Sigma$ state.

4.5. Line Intensities

The peak absorption of a microwave line is given by

$$\gamma_{\max}=\frac{8\pi^2Nf|\mu_{ij}|^2\nu_0{}^2}{3ckT\Delta\nu}, \tag{17}$$

where N is the number of molecules per cm^3, f the fraction of molecules in the lower state, $|\mu_{ij}|^2$ the square of the dipole moment matrix element for the transition, ν_0 the frequency of the line, $\Delta\nu$ the line-breadth parameter, c the velocity of light, k Boltzmann's constant, and T the absolute temperature.

The fraction of molecules in the lower state is given by

$$f=\frac{\exp\{-BJ(J+1)h/kT\}\exp\{-(A+2B)h/kT\}}{(kT/hB)[1+\exp\{-(A+2B)h/kT\}]},$$

for the $^2\Pi_{\frac{3}{2}}$ state, and

$$f=\frac{\exp\{-BJ(J+1)h/kT\}}{(kT/hB)[1+\exp\{-(A+2B)h/kT\}]},$$

for the $^2\Pi_{\frac{1}{2}}$ state. The exponential in the denominator arises because the $^2\Pi_{\frac{3}{2}}$ state of NO is low enough in energy to be appreciably populated.

The fraction is usually multiplied by a factor $(2J+1)$ due to the degeneracy in the magnetic quantum number, M_j. Here, this factor is included in the calculation of the dipole moment matrix elements. These elements are calculated from the relation $\boldsymbol{\mu}=\mu\mathbf{k}'$, where $\mathbf{k}'$ is the unit vector along the molecular axis. The calculation can be carried out by using the direction cosines[29] or by using the sum rules of Condon and Shortley[30] since $\boldsymbol{\mu}$ is a **T** matrix. Here, the sum rules are used with the amplitude matrices, $(J\Omega\vdots\mathbf{k}'\vdots J',\Omega)$, given by FF.[8] It is necessary to use the wave function for the intermediate case, given by Eq. (10) of DST. When these calculations are carried out, the results shown in Table IV are obtained.

In the intermediate case matrix elements, $a=(\mp X-2+\lambda)/2X$ and $b=(\mp X+2-\lambda)/2X$. The lower sign applies to the state $J=K+\frac{1}{2}$ in case (b) or to the $\Pi_{\frac{1}{2}}$ state in a normal case (a), while the upper sign applies to the state $J=K-\frac{1}{2}$ in case (b) or to the $\Pi_{\frac{3}{2}}$ state in a normal case (a). It can be shown that with $\Omega=\frac{1}{2}$ and $\Omega=\frac{3}{2}$ it is possible to obtain either the case (a) or case (b) matrix elements from the intermediate case by proper choice of the ratio $\lambda=A/B$ and of the signs in a and b. It is easier, however, to obtain the case (b) elements by using the $b_{\beta J}$ representation[8] and the elements given by FF. The sums obtained in this calculation have been made symmetric in the upper and lower states, thus yielding the factor $(2J+1)$ usually included in the fraction f.

From the foregoing expressions and the following assumptions: $P\approx0.1$ mm, $T=80°$K, $(\Delta\nu)_1=\Delta\nu/P=5$ Mc/sec per mm, and $\mu=0.16$ Debye units[31] the intensities of the lower rotational transitions in the $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$ states of NO have been calculated. The concentration of N^{15} for the $N^{15}O^{16}$ measurements was 40%, and this factor has been included in the calculations. The results for the $^2\Pi_{\frac{1}{2}}$ state are listed in Table I. For the $^2\Pi_{\frac{3}{2}}$ state the results show that the strongest lines $(\Delta F=+1)$ of the $J=3/2\rightarrow5/2$ transition in $N^{14}O^{16}$

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[29] See reference 19, page 96, for the direction cosines with phases as chosen in this paper.

[30] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951).

[31] L. G. Wesson, *Tables of Electric Dipole Moments* (Technology Press, Cambridge, 1948).

TABLE V. Intensities of low-frequency $\Delta J=0$ transitions between Λ doublets of the $^2\Pi_{\frac{1}{2}}$ state of $N^{14}O^{16}$.

J	$\gamma_{\max}(T=300°\mathrm{K})$	$\gamma_{\max}(T=80°\mathrm{K})$
11/2	8.11×10^{-9}	5.22×10^{-8}
13/2	8.58×10^{-9}	4.16×10^{-8}
15/2	8.76×10^{-9}	3.06×10^{-8}
17/2	8.68×10^{-9}	2.09×10^{-8}
19/2	8.36×10^{-9}	1.33×10^{-8}
39/2	1.77×10^{-9}	3.94×10^{-12}

have intensities of the order of the $F=2\rightarrow2$ lines of the $J=3/2\rightarrow5/2$ transition in the $^2\Pi_{\frac{1}{2}}$ state for $N^{15}O^{16}$. The latter lines have been observed by recorder techniques; and it therefore seems possible to observe the strong lines of the $^2\Pi_{\frac{3}{2}}$ transition. The information obtained from transitions in the $^2\Pi_{\frac{3}{2}}$ state would be most useful in confirming the calculations made for the $^2\Pi_{\frac{1}{2}}$ state.

It should also be possible to observe transitions in the $^2\Pi_{\frac{1}{2}}$ state between the Λ doublets ($\Delta J=0$) of excited rotational states. Intensity calculations have been made for some of these transitions of $N^{14}O^{16}$ which occur in the 3 to 12 kMc/sec region, and the results are given in Table V. The $\Delta F=0$ lines, which are the strongest for $\Delta J=0$ transitions, would have intensities of about one-third the value given in the table. The lines are extremely weak, but sensitive cavity spectrometers[32] operating in this low frequency region are capable of detecting lines with absorption coefficients as small as 1×10^{-10} cm^{-1}. Thus, all the $\Delta F=0$ lines of the transitions given in Table V, except for the $J=39/2$ state at 80°K, should be detectable and should provide very interesting comparisons with the present work. The degree of intermediacy of the states becomes greater with J until the rotation eventually uncouples $\mathbf{S}$ from the molecular axis. The spin-uncoupling effects would, of course, be considerably magnified for such transitions.

5. ACKNOWLEDGMENTS

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APPENDIX I. MATRIX ELEMENTS FOR THE QUADRUPOLE ENERGY EXPRESSION

The nuclear perturbations have been calculated by means of the matrix methods of CS[30] and FF.[8] The phase relations used in the matrix elements are consistent with the work of CS. These phase relations are given by

$$\begin{aligned}(\Lambda|L_{x'}|\Lambda\pm1)&=\mp i(\Lambda|L_{y'}|\Lambda\pm1),\\(\Sigma|S_{x'}|\Sigma\pm1)&=\mp i(\Sigma|S_{y'}|\Sigma\pm1)\\&=\tfrac{1}{2}[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}},\qquad\text{(A1)}\\(\Omega|J_{x'}|\Omega\pm1)&=\pm i(\Omega|J_{y'}|\Omega\pm1)\\&=\tfrac{1}{2}[J(J+1)-\Omega(\Omega\pm1)]^{\frac{1}{2}}.\end{aligned}$$

Here, the x' components are real,[33] and thus $L_{x'}$ appears in our results in place of $L_{y'}$ which has appeared in other work using the phases of Cross, Hainer, and King.[34] The "amplitude matrices" of the moving coordinates, $(\Omega\vdots\mathbf{i}'\vdots\Omega\pm1)$, etc., have been calculated with the proper phases from the matrix elements of the direction cosines consistent with Eq. (A1). The results for $(J,\Omega\vdots\mathbf{k}'\vdots J',\Omega)$ are properly given in the appendix of FF. The results for $\mathbf{i}'$ are the following:

$$\begin{aligned}(J,\Omega\vdots\mathbf{i}'\vdots J+1,\Omega\pm1)&=\mp\frac{[(J\pm\Omega+1)(J\pm\Omega+2)]^{\frac{1}{2}}}{2(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}},\\(J,\Omega\vdots\mathbf{i}'\vdots J,\Omega\pm1)&=\frac{[(J\mp\Omega)(J\pm\Omega+1)]^{\frac{1}{2}}}{2J(J+1)},\qquad\text{(A2)}\\(J,\Omega\vdots\mathbf{i}'\vdots J-1,\Omega\pm1)&=\pm\frac{[(J\mp\Omega)(J\mp\Omega-1)]^{\frac{1}{2}}}{2J(4J^2-1)^{\frac{1}{2}}}.\end{aligned}$$

With Eqs. (A1) and (A2) and FF's results for $\mathbf{k}'$, the quadrupole interaction energy can be calculated from the following relation:

$$E_{c/d}{}^{Q}=(\psi_{\mathrm{int}}|H^{Q}|\psi_{\mathrm{int}}),\qquad\text{(A3)}$$

where

$$\begin{aligned}\psi_{\mathrm{int}}=&\left(\frac{X\mp2\pm\lambda}{2X}\right)^{\frac{1}{2}}\psi_{c/d}{}^{0}(\Pi_{\frac{3}{2}})\\&\mp\left(\frac{X\pm2\mp\lambda}{2X}\right)^{\frac{1}{2}}\psi_{c/d}{}^{0}(\Pi_{\frac{1}{2}}),\qquad\text{(A4)}\end{aligned}$$

and

$$\begin{aligned}\psi_{c/d}{}^{0}(\Pi_{\frac{1}{2}})&=[(\Pi_{\frac{1}{2}}|\pm(\Pi_{-\frac{1}{2}}|]/\sqrt{2},\\\psi_{c/d}{}^{0}(\Pi_{\frac{3}{2}})&=[(\Pi_{\frac{3}{2}}|\pm(\Pi_{-\frac{3}{2}}|]/\sqrt{2}.\end{aligned}$$

In Eq. (A4) for a normal doublet, the upper signs apply to the $^2\Pi_{\frac{3}{2}}$ state and the lower signs to the $^2\Pi_{\frac{1}{2}}$ state in the limit of Hund's case (a). Equation (A4) is Eq. (10) of DST with a change in the sign preceding the second function to agree with the phases chosen here.

When H^Q is given by Eq. (7), it is seen that the terms $(\Pi_{\frac{1}{2}}|H^Q|\Pi_{\frac{1}{2}})$, $(\Pi_{\frac{3}{2}}|H^Q|\Pi_{\frac{3}{2}})$ and $(\Pi_{-\frac{1}{2}}|H^Q|\Pi_{\frac{3}{2}})=(\Pi_{\frac{1}{2}}|H^Q|\Pi_{-\frac{3}{2}})$ contribute to the energy, $E_{c/d}{}^{Q}$. These

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[32] R. J. Collier, Rev. Sci. Instr. **25**, 1205 (1954).

[33] See footnote 16 of reference 6.

[34] Cross, Hainer, and King, J. Chem. Phys. **12**, 210 (1944).

elements are given by

$$
\begin{aligned}
(\Pi_{\frac{1}{2}}|H^Q|\Pi_{\frac{1}{2}}) &= \frac{e^2Q}{I(2I-1)}\left(\frac{3\cos^2\chi-1}{2r_1^3}\right)_{\mathrm{Av}}\left(\Pi_{\frac{1}{2}}\left|\frac{3I_{z'}{}^2-I^2}{2}\right|\Pi_{\frac{1}{2}}\right) \\
&= \frac{e^2Q}{I(2I-1)}\left(\frac{3\cos^2\chi-1}{2r_1^3}\right)_{\mathrm{Av}}\left\{\frac{3}{2}\sum_{J'}|(\Pi_{\frac{1}{2}},J|\mathbf{I}\cdot\mathbf{k}'|\Pi_{\frac{1}{2}},J')|^2-\frac{I(I+1)}{2}\right\} \\
&= \frac{e^2Q}{I(2I-1)}\left(\frac{3\cos^2\chi-1}{2r_1^3}\right)_{\mathrm{Av}}\left\{\frac{3}{2}\frac{\Omega^2}{J^2(J+1)^2}(\mathbf{I}\cdot\mathbf{J})^2\right. \\
&\quad +\frac{3}{8}\frac{(J+\Omega+1)(J-\Omega+1)}{(J+1)^2(2J+1)(2J+3)}[(I+F-J)(F+J-I+1)(F+I+J+2)(I+J+1-F)] \\
&\qquad \left. +\frac{3}{2}\frac{(J^2-\Omega^2)}{J^2(4J^2-1)}[(J+F-I)(F+I-1)(F+I+J+1)(J+I-F)]-\tfrac{1}{2}I(I+1)\right\}_{\Omega=\frac{1}{2}}. \quad \text{(A5)}
\end{aligned}
$$

$$
\begin{aligned}
(\Pi_{-\frac{1}{2}}|H^Q|\Pi_{\frac{3}{2}}) &= \frac{3}{8}\frac{e^2Q}{I(2I-1)}\left(\frac{\sin^2\chi}{r_1^3}\right)_{\mathrm{Av}}(\Pi_{-\frac{1}{2}}|e^{-2i\phi}(I_{x'}+iI_{y'})^2|\Pi_{\frac{3}{2}}) \\
&= \frac{3}{2}\frac{e^2Q}{I(2I-1)}\left(\frac{\sin^2\chi}{r_1^3}\right)_{\mathrm{Av}}\sum_{J'}(\Pi_{-\frac{1}{2}}J|\mathbf{I}\cdot\mathbf{i}'|\Sigma_{\frac{1}{2}},J')(\Sigma_{\frac{1}{2}},J'|\mathbf{I}\cdot\mathbf{i}'|\Pi_{\frac{3}{2}}J) \\
&= \frac{3}{8}\frac{e^2Q}{I(2I-1)}\left(\frac{\sin^2\chi}{r_1^3}\right)_{\mathrm{Av}}\left\{\frac{([J(J+1)+\frac{1}{4}][J(J+1)-\frac{3}{4}])^{\frac{1}{2}}}{J^2(J+1)^2}(\mathbf{I}\cdot\mathbf{J})^2\right. \\
&\quad -\frac{1}{16}\frac{(2J-1)^{\frac{1}{2}}}{(J+1)^2(2J+3)^{\frac{1}{2}}}[(F+J+1-I)(F+I-J)(F+I+J+2)(I+J+1-F)] \\
&\qquad \left. -\frac{1}{16J^2}\frac{(2J+3)^{\frac{1}{2}}}{(2J-1)^{\frac{1}{2}}}[(F+J-I)(F+I-J+1)(F+I+J+1)(I+J-F)]\right\}. \quad \text{(A6)}
\end{aligned}
$$

An expression similar to Eq. (A5) results for $(\Pi_{\frac{3}{2}}|H^Q|\Pi_{\frac{3}{2}})$, with $\Omega=\frac{1}{2}$ replaced by $\Omega=\frac{3}{2}$. The elements $(\Pi_{\frac{1}{2}}|H^Q|\Pi_{\frac{1}{2}})$ and $(\Pi_{\frac{3}{2}}|H^Q|\Pi_{\frac{3}{2}})$ are the correct terms for pure $\Pi_{\frac{1}{2}}$ and $\Pi_{\frac{3}{2}}$ states, respectively, in a Hund's case (a) representation. Also, it can be shown that Eq. (A5) is the symmetric-top quadrupole energy expression.

If Eq. (A3) is expanded in terms of Eq. (A4) and the matrix elements as calculated above are substituted, then Eq. (8) of the text results for $E_{c/d}{}^Q$.