The Hyperfine Λ-Doubling Spectrum of $^{14}N^{16}O$ and $^{15}N^{16}O$

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The molecular beam electric resonance method was used for the investigation of the hyperfine Λ-doubling transitions $\Delta J = 0$, $\Delta F = 0$, ± 1 for a number of J values of both the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ states of the molecules $^{14}N^{16}O$ and $^{15}N^{16}O$. The observed spectrum is explained using the degenerate perturbation theory introduced by Freed (1). This theory is adapted for a $^2\Pi$ molecule and includes contributions up to third order in fine and hyperfine structure. The agreement between observed and calculated values is satisfactory.

I. INTRODUCTION

The microwave spectrum of NO was measured previously by Gallagher and Johnson (2), Favero *et al.* (3), and by Brown and Radford (4). The Λ-splitting constants and the hyperfine structure constants were determined from these measurements. Recently Neumann (5) measured the hyperfine Λ-doubling spectrum of $^{14}N^{16}O$ with the molecular beam electric resonance method and obtained accurate frequencies of the $\Delta J = 0$ transitions and values of the molecular coupling constants. For theoretical interpretation of the spectrum Neumann used the degenerate perturbation theory (DPT) discussed by Freed (1) with fine-structure contributions up to fourth order and hyperfine structure contributions up to second order. The agreement between experimental and theoretical results looked very satisfactory.

The present investigation on NO was intended both as a first step and as a test case in a program on hyperfine structure of open-shell molecules using the molecular beam electric resonance method. In addition to reproducing the measurements of Neumann (5) we were able to measure a large number of transitions in higher J states of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of both ^{14}NO and ^{15}NO. These transitions extend over a region from about 0.7 MHz to about 1.5 GHz. Especially the high-frequency transitions might be of interest to radioastronomers. When fitting the present measurements in ^{14}NO it was discovered that the frequencies predicted by Neumann (5) for the $^2\Pi_{1/2}$ state deviated from our experimental values by even as much as 250 kHz. It was not possible to explain these deviations within the scope of the theory used by Neumann. Consequently we decided to extend the theory by including hyperfine-structure contributions

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up to third order. This yields new contributions to the energy, which have a J dependence which differs from that present in the theory used by previous investigations (2–5). The new contributions result in a much better agreement between theoretical and experimental frequencies for both molecules.

II. THEORY

II. 1. *Hamiltonian*

The complete Hamiltonian for a diatomic molecule can be written formally as

$$\mathbf{H} = \mathbf{H}_0 + \lambda\mathbf{V} + \lambda^2\mathbf{V}', \tag{1}$$

where $\mathbf{H}_0$ is the nonrelativistic Hamiltonian for electronic energies in the Born–Oppenheimer approximation, $\mathbf{V}$ contains the spin–orbit and gyroscopic terms which give rise to the Λ splitting, and $\mathbf{V}'$ describes the hyperfine contributions. For $\mathbf{V}$ we used

$$\mathbf{V} = B(\mathbf{J}^2 - \mathbf{L}_z^2 + \mathbf{S}^2) + A\mathbf{L}_z\mathbf{S}_z - 2B\mathbf{J}\cdot\mathbf{S}$$
$$+ (B + \tfrac{1}{2}A)(\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+) - B(\mathbf{J}_+\mathbf{L}_- + \mathbf{J}_-\mathbf{L}_+). \tag{2}$$

The Hamiltonian $\mathbf{V}$ of Eq. (2) is in accordance with that of Van Vleck (6), but differs slightly from the one used by Freed (1). For the hyperfine Hamiltonian $\mathbf{V}'$ we used the expression given by Freed (1). This rather complex expression will not be reproduced here.

With the Hamiltonian (1) the spectrum of a $^2\Pi$ state is calculated using the degenerate perturbation theory (DPT) described by Freed (1). The contributions of the fine and hyperfine interactions to the energy are taken into account up to third order. In the final expressions for state energies we separate terms with different dependence on the rotational quantum number J, as only these terms can be determined from the experimental data. The results show that the fine-structure effects up to third order describe, within experimental accuracy, the J dependence of the contributions to the Λ splitting. The hyperfine contributions up to third order have to be considered in order to obtain an acceptable agreement with experimental results, but the fourth-order contributions are below the experimental accuracy and are neglected (see also Section V). In the calculations the interactions of excited $^2\Sigma$, $^2\Pi$, and $^2\Delta$ states with the ground $X^2\Pi$ state are considered.

II. 2. *Wavefunctions, Symmetry and Energy Matrix*

The ground electronic state of NO is a $^2\Pi$ state. Application of DPT with the Hamiltonian (1) makes it necessary to solve a 4×4 secular equation (1). However, the Hamiltonian (1) is invariant under reflections of the coordinates and spins of all particles in a plane containing the nuclei. Consequently, if wavefunctions are used with the proper symmetry (called Kronig symmetry) with

respect to these reflections (see also Appendix A), the secular determinant factors in two 2×2 determinants.

The coupling scheme of the angular momenta in the NO molecule is nearly a Hund case (a) ($7, 8$). Wavefunctions, including the rotation of the nuclear frame, are formally written as $|\,^2\Gamma^{\pm}_{|\Omega|} J\,\rangle$, where $\Gamma \equiv \Sigma^s,\, \Pi,\, \Delta,\, \cdots$, and Ω is the projection of the total angular momentum J on the molecular axis. These wavefunctions are defined by

$$|\,^2\Gamma^{\pm}_{|\Omega|} J\,\rangle = (1/\sqrt{2})\,[|\,J\Lambda\Sigma\Omega\rangle \pm (-1)^s\,|\,J-\Lambda-\Sigma-\Omega\,\rangle] \qquad (3)$$

with $\Omega = \Lambda + \Sigma$. The functions on the right-hand side of Eq. (3) are given by Freed (1). Their Kronig symmetry is $\pm\,(-1)^{J-1/2}$ (see also Appendix A). The phase factor $(-1)^s$ has significance only if $\Gamma \equiv \Sigma^s$, $s = \pm$, in which case $(-1)^s = 1$ for $s = +$, and $(-1)^s = -1$ for $s = -$.

The matrix elements of the fine- and hyperfine-structure Hamiltonian for a $^2\Pi$ state on the basis defined in Eq. (3) are calculated using the results of Freed (1). The nuclear spin $\mathbf{I}$ of the nitrogen atom is coupled with the rotational angular momentum $\mathbf{J}$ to $\mathbf{F}$ in the conventional way: $\mathbf{J} + \mathbf{I} = \mathbf{F}$. The results are given in Tables I and II.[1] Only matrix elements, which are important for further calculations are tabulated. The matrix is Hermitian.

In $\mathbf{V}$ should also be included the term $\gamma\,\mathbf{N}\cdot\mathbf{S}$. This term is discussed extensively by Freed (1). Its contributions to the energy are of the order of 100 MHz. However, in first order (see Section II. 3) this term does not contribute to the Λ splitting. The matrix elements of $\gamma\,\mathbf{N}\cdot\mathbf{S}$ can easily be calculated using the formulas of Ref. (1). They have exactly the same J dependence as $\mathbf{V}$ of Table I, and give only a correction to ζ_i and θ_i, which are an order of magnitude smaller than those from $\mathbf{V}$. It is clear that these terms can be absorbed in $\mathbf{V}$ for further calculations, if we are only interested in terms with a different J dependence. This has been done without changing the definitions of these constants used in Table I.

In Tables I and II (and in the following) the symbols $^2\Sigma^{s\pm}$ (i), $^2\Pi^{\pm}$ (l), and $^2\Delta^{\pm}$ (k) indicate a $^2\Sigma$, $^2\Pi$, and $^2\Delta$ excited electronic state, respectively; the index in the brackets numbers the state. Table III defines the quantities used in Tables I and II, where G, D, K, and Q are the molecular constants defined by Freed (1). The indices correspond to the Λ values of the initial and final states, respectively.

II. 3. Fine Structure

Because we measured Λ-doubling transitions from a Kronig $+$ to a Kronig $-$ state within one J state, only contributions to the Λ splitting are of interest, i.e., contributions different for states with an opposite symmetry. From Table I it is seen that only the $^2\Sigma^s$ states give a contribution to the Λ splitting.

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[1] A factor $\sqrt{[I(2I+1)(I+1)]}$ is missing in the 4th equation of Table V of Ref. (1).

Table I   Matrix elements of V.

The upper and the lower sign in the matrix refer to the (+) and (−) sign of the wavefunctions, respectively. Only matrix elements which are important for further calculations are given.

	$X^2\Pi_{\frac{1}{2}}^{\pm}$	$X^2\Pi_{3/2}^{\pm}$	$^2\Sigma_{\frac{1}{2}}^{s\pm}(i)$
$X^2\Pi_{\frac{1}{2}}^{\pm}$	$-\frac{1}{2}A_\Pi + B_\Pi{}^a(J+\frac{1}{2})^2$		
$X^2\Pi_{3/2}^{\pm}$	$B_\Pi z$	$\frac{1}{2}A_\Pi + B_\Pi(x - ^7/4)$	
$^2\Sigma_{\frac{1}{2}}^{s\pm}(i)$	$\Theta_i \pm (-1)^s \zeta_i(J+\frac{1}{2})$	$\zeta_i z$	$B_\Sigma'(J+\frac{1}{2})^2 \pm (-1)^s B_\Sigma(J+\frac{1}{2})$
$^2\Pi_{\frac{1}{2}}^{\pm}(1)$	$-\frac{1}{2}\bar{A}_\Pi(1) + \bar{B}_\Pi(1)(J+\frac{1}{2})^2$	$\bar{B}_\Pi(1)z$	
$^2\Pi_{3/2}^{\pm}(1)$	$\bar{B}_\Pi(1)z$	$\frac{1}{2}\bar{A}_\Pi(1) + \bar{B}_\Pi(1)(x - ^7/4)$	
$^2\Delta_{3/2}^{\pm}(k)$	$n_1(k)z$	$n_2(k)$	
$^2\Delta_{5/2}^{\pm}(k)$	0	$n_1(k)w$	

a. For B_Π we substituted $B_\Pi - J(J+1)D_\Pi$, where D_Π is the centrifugal distortion constant.

Table II Matrix elements of the hyperfine structure hamiltonian (V').

	$X^2\Pi_{\frac{1}{2}}^{\pm}$	$X^2\Pi_{3/2}^{\pm}$
$X^2\Pi_{\frac{1}{2}}^{\pm}$	$y\{\frac{1}{2}(G_{11}-\frac{1}{6}\sqrt{6}K_{11}-\frac{1}{3}\sqrt{6}D_{11})+C_{RS}x \pm D_{1-1}(J+\frac{1}{2})\}$ $+4Q_{11}(\frac{3}{4}-x)u$	
$X^2\Pi_{3/2}^{\pm}$	$\frac{1}{6}\sqrt{6}(D_{11}-K_{11})zy \pm Q_{1-1}\sqrt{6}(2J+1)zu$	$y\{\frac{3}{2}(G_{11}+\frac{1}{6}\sqrt{6}K_{11}+\frac{1}{3}\sqrt{6}D_{11})+C_{RS}x\}+4Q_{11}(\frac{27}{4}-x)u$
$^2\Sigma_{\frac{1}{2}}^{s\pm}(i)$	$y\{D_i \pm(-1)^S(G_i+D_i)(J+\frac{1}{2})\}$	$-(G_i+D_i)zy + Q_i zu$
$^2\Pi_{\frac{1}{2}}^{\pm}(1)$	$y\{\gamma_1(1)\pm(J+\frac{1}{2})\gamma_2(1)\}+\gamma_3(1)u(\frac{3}{4}-x)$	$Y_4(1)zy \pm Y_5(1)zu(J+\frac{1}{2})$
$^2\Pi_{3/2}^{\pm}(1)$	$Y_4(1)zy \pm Y_5(1)zu(J+\frac{1}{2})$	$Y_6(1)y + Y_3(1)u(\frac{27}{4} - x)$
$^2\Delta_{3/2}^{\pm}(k)$	$yz(G_\Delta(k)-D_\Delta(k)) + uzQ_\Delta(k)$	$- 3D_\Delta(k)y$
$^2\Delta_{5/2}^{\pm}(k)$	0	$yw(G_\Delta(k)+D_\Delta(k)) + 2uwQ_\Delta(k)$

Table III Definition of the quantities used in Table I
and II.

$x \quad = \quad J(J+1)$

$y \quad = \quad \dfrac{F(F+1) - J(J+1) - I(I+1)}{2J(J+1)}$

$z \quad = \quad \sqrt{(J-\frac{1}{2})(J+3/2)}$

$u \quad = \quad \dfrac{\frac{3}{4}C(C-1) - J(J+1)\,I(I+1)}{2I(2I-1)\,J(J+1)(2J-1)(2J+3)}$

$C \quad = \quad I(I+1) + J(J+1) - F(F+1)$

$w \quad = \quad \sqrt{(J-3/2)(J+5/2)}$

A_{Π} spin-orbit coupling constant of the $X^2\Pi$ state

B_{Π} rotational constant of the $X^2\Pi$ state

B_{Σ} rotational constant of the $^2\Sigma$ state

C_{RS} Describes the nuclear spin-rotation interaction

$\Theta_i \quad = \quad \langle {}^2\Sigma(i) || (B+\frac{1}{2}A)L_- || X^2\Pi \rangle$

$\zeta_i \quad = \quad \langle {}^2\Sigma(i) || BL_- || X^2\Pi \rangle$

$\bar{A}_{\Pi}(1) \quad = \quad \langle {}^2\Pi(1) || A || X^2\Pi \rangle$

$\bar{B}_{\Pi}(1) \quad = \quad \langle {}^2\Pi(1) || B || X^2\Pi \rangle$

$\eta_1(k) \quad = \quad \langle X^2\Pi || BL_- || {}^2\Delta(k) \rangle$

$\eta_2(k) \quad = \quad \langle X^2\Pi || (B+\frac{1}{2}A)L_- || {}^2\Delta(k) \rangle - A_{21}^{\frac{1}{2}\frac{1}{2}} /\sqrt{3}$

$G_i \quad = \quad G_{10(i)}/\sqrt{2}$

$D_i \quad = \quad \frac{1}{2}\,D_{10(i)}$

$Q_i \quad = \quad 4\sqrt{6}\,Q_{10(1)}$

$\gamma_1(1) \quad = \quad \frac{1}{2}(G_{11(1)} - \frac{1}{6}\sqrt{6}\,K_{11(1)} - \frac{1}{3}\sqrt{6}\,D_{11(1)})$

Table III   (continued)

$$\gamma_2{}^{(1)} = D_{1-1(1)}$$

$$\gamma_3{}^{(1)} = 4Q_{11(1)}$$

$$\gamma_4{}^{(1)} = (D_{11(1)} - K_{11(1)})/\sqrt{6}$$

$$\gamma_5{}^{(1)} = 2\sqrt{6}\, Q_{1-1(1)}$$

$$\gamma_6{}^{(1)} = 3/2(G_{11(1)} + \frac{1}{\sqrt{6}} K_{11(1)} + \frac{1}{3} \sqrt{6}\, D_{11(1)})$$

$$G_\Delta(k) = G_{12(k)}/\sqrt{2}$$

$$D_\Delta(k) = \tfrac{1}{2} D_{12(k)}$$

$$Q_\Delta(k) = 4\sqrt{6}\, Q_{12(k)}$$

The n-th $(n = 1, 2, 3)$-order perturbation Hamiltonian $\mathbf{V}^{(n)}$ is defined by Freed (1, Eq. (3.2))

$$\mathbf{V}^{(1)} = \mathbf{V}, \tag{4}$$

$$\mathbf{V}^{(2)} = \sum_i \frac{\mathbf{V} \mid {}^2\Sigma_{1/2}^{s\pm}(i)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(i) \mid \mathbf{V}}{(\Pi\Sigma_i{}^s)}, \tag{5}$$

$$\mathbf{V}^{(3)} = \mathbf{V}_1^{(3)} + \mathbf{V}_2^{(3)}, \tag{6}$$

$$\mathbf{V}_1^{(3)} = \sum_{i,j} \frac{\mathbf{V} \mid {}^2\Sigma_{1/2}^{s\pm}(i)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(i) \mid \mathbf{V} \mid {}^2\Sigma_{1/2}^{s\pm}(j)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(j) \mid \mathbf{V}}{(\Pi\Sigma_j{}^s)(\Pi\Sigma_i{}^s)}, \tag{7}$$

$$\mathbf{V}_2^{(3)} = -\sum_{i,\alpha} \frac{\mathbf{V} \mid {}^2\Sigma_{1/2}^{s\pm}(i)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(i) \mid \mathbf{V} \mid \psi_\alpha{}^\pm\rangle\langle\psi_\alpha{}^\pm \mid \mathbf{V}}{(\Pi\Sigma_i{}^s)^2}. \tag{8}$$

Herein $\mid \psi_\alpha{}^\pm \rangle$ is one of the $X^2\Pi^\pm$ states, and $(\Pi \Sigma_i{}^s) = E_{X^2\Pi} - E_{{}^2\Sigma^s(i)}$, the energy difference between the $X^2\Pi$ and the i-th excited ${}^2\Sigma^s$ state.

Now we make the following approximation:

$$\langle{}^2\Sigma_{1/2}^{s\pm}(i) \mid \mathbf{V} \mid {}^2\Sigma_{1/2}^{s\pm}(j)\rangle = B_\Sigma(J + \tfrac{1}{2})^2 \pm (-1)^s B_\Sigma(J + \tfrac{1}{2}),$$

where B_Σ is an effective rotational constant of the Σ states. With this approximation $\mathbf{V}_1^{(3)}$ becomes

$$\mathbf{V}_1^{(3)} = \sum_i \frac{\mathbf{V} \mid {}^2\Sigma_{1/2}^{s\pm}(i)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(i) \mid \mathbf{V}}{(\Pi\Sigma_i{}^s)^2} [B_\Sigma(J + \tfrac{1}{2})^2 \pm (-1)^s B_\Sigma(J + \tfrac{1}{2})]. \tag{9}$$

In the Tables IV, V, and VI, are tabulated the first-, the second-, and the third-

Table IV First order energy contributions due to fine structure.

$$\langle {}^2\Pi_{\frac{1}{2}}^{\pm} | \underline{V}^{(1)} | {}^2\Pi_{\frac{1}{2}}^{\pm} \rangle = -\tfrac{1}{2} A_\Pi + B_\Pi (J+\tfrac{1}{2})^2$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \underline{V}^{(1)} | {}^2\Pi_{3/2}^{\pm} \rangle = \tfrac{1}{2} A_\Pi + B_\Pi (J(J+1) - {}^7/4)$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \underline{V}^{(1)} | {}^2\Pi_{\frac{1}{2}}^{\pm} \rangle = B_\Pi \ z$$

Table V Second order energy conditions due to fine structure.

$$\langle {}^2\Pi_{\frac{1}{2}}^{\pm} | \underline{V}^{(2)} | {}^2\Pi_{\frac{1}{2}}^{\pm} \rangle = A_2^{(2)} (J+\tfrac{1}{2})^2 \pm (2J+1)\bar{A}_1^{(2)} + A_3^{(2)}$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \underline{V}^{(2)} | {}^2\Pi_{3/2}^{\pm} \rangle = A_2^{(2)} (J-\tfrac{1}{2})(J+\tfrac{3}{2})$$

$$\langle {}^2\Pi_{3/2}^{\pm} | \underline{V}^{(2)} | {}^2\Pi_{\frac{1}{2}}^{\pm} \rangle = z\, A_1^{(2)} \pm \bar{A}_2^{(2)} z\, (J+\tfrac{1}{2})$$

order contributions to the energy due to the fine structure, respectively, while in Table VII are defined the quantities used in Tables IV–VI. The $(+)$ and $(-)$ signs in Table VII indicate that the sums extend only over Σ^s states with $s = +$ and $s = -$, respectively. The fine-structure contributions from Tables IV–VI are collected in Table VIII according to their J dependence.

II. 4. *Hyperfine Contributions*

The hyperfine structure gives contributions to the energy in second and third order. The second-order hyperfine Hamiltonian is V', the third order consists of three parts. These parts describe the interaction with the excited Σ, Π, and Δ states. The interaction Hamiltonian can be written formally as

$$V_{hf}^{(3)} = V_{hf}^{(3)}(\Sigma) + V_{hf}^{(3)}(\Pi) + V_{hf}^{(3)}(\Delta), \tag{10}$$

Table VI Third order energy contribution due to fine structure.

$$\langle {}^2\Pi_{\frac{1}{2}}^{\pm} | V_-^{(3)} | {}^2\Pi_{\frac{1}{2}}^{\pm} \rangle = \frac{1}{2}\bar{A}_2^{(3)} A_\Pi (J+\tfrac{1}{2})^2 + A_2^{(3)}(B_\Sigma - B_\Pi)(J+\tfrac{1}{2})^4 \pm \bar{A}_2^{(3)} B_\Sigma (J+\tfrac{1}{2})^3 \pm A_\Pi \bar{A}_1^{(3)}(J+\tfrac{1}{2})^2$$

$$\pm 2\bar{A}_1^{(3)}(B_\Sigma - B_\Pi)(J+\tfrac{1}{2})^3 + 2A_1^{(3)}B_\Sigma(J+\tfrac{1}{2})^2 + \tfrac{1}{2}A_3^{(3)}A_\Pi + A_3^{(3)}(B_\Sigma - B_\Pi)(J+\tfrac{1}{2})^2$$

$$\pm \bar{A}_3^{(3)}B_\Sigma(J+\tfrac{1}{2}) - A_1^{(3)}B_\Pi z^2 \mp \bar{A}_2^{(3)}B_\Pi z^2(J+\tfrac{1}{2})$$

$$\langle {}^2\Pi_{3/2}^{\pm} | V_-^{(3)} | {}^2\Pi_{3/2}^{\pm} \rangle = -\tfrac{1}{2}(A_\Pi - 4B_\Pi)A_2^{(3)}z^2 + A_2^{(3)}(B_\Sigma - B_\Pi)(J+\tfrac{1}{2})^2 z^2 \pm \bar{A}_2^{(3)}(B_\Sigma - B_\Pi)(J+\tfrac{1}{2})z^2$$

$$- A_1^{(3)}B_\Pi z^2$$

$$\langle {}^2\Pi_{\frac{1}{2}}^{\pm} | V_-^{(3)} | {}^2\Pi_{3/2}^{\pm} \rangle = -\tfrac{1}{2}z\{A_2^{(3)}B_\Pi(J+\tfrac{1}{2})^2 \pm B_\Pi \bar{A}_1^{(3)}(2J+1) + A_3^{(3)}B_\Pi + A_2^{(3)}B_\Pi z^2$$

$$+ 2(-B_\Pi + B_\Pi(J+\tfrac{1}{2})^2)(A_1^{(3)} \pm \bar{A}_2^{(3)}(J+\tfrac{1}{2}))\}$$

$$+ B_\Sigma(J+\tfrac{1}{2})^2 z\{A_1^{(3)} \pm \bar{A}_2^{(3)}(J+\tfrac{1}{2})\} \pm B_\Sigma \bar{A}_1^{(3)}(J+\tfrac{1}{2})z$$

$$+ B_\Sigma A_2^{(3)}(J+\tfrac{1}{2})^2 z.$$

Table VII Definitions of the molecular constants used in

Table V and VI.

$$A_k^{(n)} = A_k^{(n)+} + A_k^{(n)-}$$

$$\bar{A}_k^{(n)} = A^{(n)+} - A_k^{(n)-} \qquad n = 2, 3$$

$$A_1^{(n)\pm} = \sum_{\Sigma^\pm} \frac{\zeta_i \Theta_i}{(\Pi\Sigma_i^\pm)^{n-1}} \quad {}^a \qquad k = 1, 2, 3$$

$$A_2^{(n)\pm} = \sum_{\Sigma^\pm} \frac{\zeta_i \zeta_i}{(\Pi\Sigma_i^\pm)^{n-1}}$$

$$A_3^{(n)\pm} = \sum_{\Sigma^\pm} \frac{\Theta_i \Theta_i}{(\Pi\Sigma_i^\pm)^{n-1}}$$

a The sums extend for the (+)sign only over Σ^+ states, for

the (-)sign only over the Σ^- states.

with

$$\mathbf{V}_{hf}^{(3)}(\Sigma) = \sum_i \left\{ \frac{\mathbf{V}\mid {}^2\Sigma_{1/2}^{s\pm}(i)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(i)\mid\mathbf{V}'}{(\Pi\Sigma_i{}^s)} + \frac{\mathbf{V}'\mid {}^2\Sigma_{1/2}^{s\pm}(i)\rangle\langle{}^2\Sigma_{1/2}^{s\pm}(i)\mid\mathbf{V}}{(\Pi\Sigma_i{}^s)} \right\}, \quad (11)$$

$$\mathbf{V}_{hf}^{(3)}(\Pi) = \sum_l \left\{ \frac{\mathbf{V}\mid {}^2\Pi_{1/2}^{\pm}(l)\rangle\langle{}^2\Pi_{1/2}^{\pm}(l)\mid\mathbf{V}'}{(\Pi\Pi_l)} + \frac{\mathbf{V}'\mid {}^2\Pi_{1/2}^{\pm}(l)\rangle\langle{}^2\Pi_{1/2}^{\pm}(l)\mid\mathbf{V}}{(\Pi\Pi_l)} \right. $$
$$\left. + \frac{\mathbf{V}\mid {}^2\Pi_{3/2}^{\pm}(l)\rangle\langle{}^2\Pi_{3/2}^{\pm}(l)\mid\mathbf{V}'}{(\Pi\Pi_l)} + \frac{\mathbf{V}'\mid {}^2\Pi_{3/2}^{\pm}(l)\rangle\langle{}^2\Pi_{3/2}^{+}(l)\mid\mathbf{V}}{(\Pi\Pi_l)} \right\}, \quad (12)$$

and

$$\mathbf{V}_{hf}^{(3)}(\Delta) = \sum_k \left\{ \frac{\mathbf{V}\mid {}^2\Delta_{3/2}^{\pm}(k)\rangle\langle{}^2\Delta_{3/2}^{\pm}(k)\mid\mathbf{V}'}{(\Pi\Delta_k)} + \frac{\mathbf{V}'\mid {}^2\Delta_{3/2}^{\pm}(k)\rangle\langle{}^2\Delta_{3/2}^{\pm}(k)\mid\mathbf{V}}{(\Pi\Delta_k)} \right. $$
$$\left. + \frac{\mathbf{V}\mid {}^2\Delta_{5/2}^{\pm}(k)\rangle\langle{}^2\Delta_{5/2}^{\pm}(k)\mid\mathbf{V}'}{(\Pi\Delta_k)} + \frac{\mathbf{V}'\mid {}^2\Delta_{5/2}^{\pm}(k)\rangle\langle{}^2\Delta_{5/2}^{\pm}(k)\mid\mathbf{V}}{(\Pi\Delta_k)} \right\}. \quad (13)$$

Table VIII   Collected contributions to the fine structure

up to third order $(\underline{V}^{(1)} + \underline{V}^{(2)} + \underline{V}^{(3)} = \underline{H}_F)$.

$$\langle {}^2\Pi^{\pm}_{\frac{1}{2}} | \underline{H}_F | {}^2\Pi^{\pm}_{\frac{1}{2}} \rangle \quad =$$

$$-\tfrac{1}{2}\alpha_1 + \alpha_2(J+\tfrac{1}{2})^2 + \alpha_{10}(J+\tfrac{1}{2})^4 \pm \alpha_3(2J+1) \pm \alpha_4(J+\tfrac{1}{2})^3 \pm \alpha_5(J+\tfrac{1}{2})z^2$$

$$\langle {}^2\Pi^{\pm}_{3/2} | \underline{H}_F | {}^2\Pi^{\pm}_{3/2} \rangle = \tfrac{1}{2}A_\Pi + B_\Pi(J(J+1) - \tfrac{7}{4}) + \alpha_9 z^2 + \alpha_{10}(J+\tfrac{1}{2})^2 z^2 \pm \alpha_8(J+\tfrac{1}{2})z^2$$

$$\langle {}^2\Pi^{\pm}_{\frac{1}{2}} | \underline{H}_F | {}^2\Pi^{\pm}_{3/2} \rangle = \alpha_6 z + \alpha_{11} z(J+\tfrac{1}{2})^2 \pm \alpha_7 z(J+\tfrac{1}{2}) \pm \alpha_8 z(J+\tfrac{1}{2})^3$$

With $\alpha_1 = A_\Pi - A_3^{(3)}A_\Pi - 2A_3^{(2)} + 2A_1^{(3)}B_\Pi$

$\alpha_2 = B_\Pi + A_2^{(2)} + \tfrac{1}{2}A_\Pi A_2^{(3)} + (A_1^{(3)} + A_3^{(3)})(B_\Sigma - B_\Pi) + A_1^{(3)}B_\Sigma$

$\alpha_3 = \bar{A}_1^{(2)} + \tfrac{1}{2}\bar{A}_1^{(3)}A_\Pi + \tfrac{1}{2}\bar{A}_3^{(3)}B_\Sigma$

$\alpha_4 = \bar{A}_2^{(3)}B_\Sigma + 2\bar{A}_1^{(3)}(B_\Sigma - B_\Pi)$

$\alpha_5 = -\bar{A}_2^{(3)}B_\Pi$

$\alpha_6 = B_\Pi + A_1^{(2)} + B_\Sigma(A_1^{(3)} + \tfrac{1}{2}A_2^{(3)} - \tfrac{1}{2}A_3^{(3)})$

$\alpha_7 = \bar{A}_2^{(2)} + \bar{A}_1^{(3)}(B_\Sigma - B_\Pi) + \bar{A}_2^{(3)}B_\Pi$

$\alpha_8 = \bar{A}_2^{(3)}(B_\Sigma - B_\Pi)$

$\alpha_9 = A_2^{(2)} - \tfrac{1}{2}A_2^{(3)}(A_\Pi - 4B_\Pi) - A_1^{(3)}B_\Pi$

$\alpha_{10} = A_2^{(3)}(B_\Sigma - B_\Pi)$

$\alpha_{11} = (A_1^{(3)} + A_2^{(3)})(B_\Sigma - B_\Pi)$

Table IX Energy contributions due to the hyperfine structure up to third order.

$$(V_{hf}^{(2)} + V_{hf}^{(3)}) = H_{hf}).$$

$$\langle {}^2\Pi_{\frac{1}{2}}^{\pm}|H_{hf}|{}^2\Pi_{\frac{1}{2}}^{\pm}\rangle = y\{\beta_1 + \beta_5(J+\tfrac{1}{2})^2 + \beta_9 z^2 + C_{RS}x \pm C_{RS}x \pm \beta_2(J+\tfrac{1}{2}) \pm \beta_{10}(J+\tfrac{1}{2})^3\} +$$

$$+ u\{\phi_1(\tfrac{3}{4}-x) + \phi_4(\tfrac{3}{4}-x)(J+\tfrac{1}{2})^2 \pm \phi_5 z^2(J+\tfrac{1}{2})\}$$

$$\langle {}^2\Pi_{3/2}^{\pm}|H_{hf}|{}^2\Pi_{3/2}^{\pm}\rangle = y\{\beta_3 + \beta_6 z^2 + \beta_7(J+\tfrac{1}{2})^2 + \beta_8 w^2 + C_{RS}x\} +$$

$$+ u\{\phi_2(\tfrac{27}{4} - x) + \phi_4(\tfrac{27}{4} - x)(J+\tfrac{1}{2})^2 + \phi_6 z^2 \pm \phi_5 z^2(J+\tfrac{1}{2})\}$$

$$\langle {}^2\Pi_{3/2}^{\pm}|H_{hf}|{}^2\Pi_{\frac{1}{2}}^{\pm}\rangle = zy\{\beta_4 + \beta_{11} z^2 \pm \beta_{12}(J+\tfrac{1}{2})\} +$$

$$+ zu\{\pm \phi_3(J+\tfrac{1}{2}) + \phi_7 - \phi_4 w^2 \pm \phi_5 z^2(J+\tfrac{1}{2})\}$$

Table X   Definition of the molecular constants from Table IX.

$$\beta_1 = \tfrac{1}{2}(G_{11} - \tfrac{1}{6}\sqrt{6}K_{11} - \tfrac{1}{3}\sqrt{6}D_{11}) + 2\sum_i \frac{D_i\theta_i}{(\Pi\Sigma_i^s)} - \sum_l \frac{\gamma_1(1)\bar{A}_\Pi(1)}{(\Pi\ \Pi_1)}$$

$$\beta_2 = D_{1-1} + 2\sum_i (-1)^s \frac{D_i\zeta_i + \theta_i(G_i + D_i)}{(\Pi\ \Sigma_i^s)} - \sum_l \frac{\gamma_2(1)\bar{A}_\Pi(1)}{(\Pi\ \Pi_1)}$$

$$\beta_3 = \tfrac{3}{2}(G_{11} + \tfrac{1}{6}\sqrt{6}K_{11} + \tfrac{1}{3}\sqrt{6}D_{11}) - 6\sum_k \frac{\eta_2(k)D_\Delta(k)}{(\Pi\ \Delta_k)} +$$

$$+ 2\sum_l \frac{(\tfrac{1}{2}\bar{A}_\Pi(1) - 2\bar{B}_\Pi(1))\gamma_6(1)}{(\Pi\ \Pi_1)}$$

$$\beta_4 = \tfrac{1}{6}\sqrt{6}(D_{11} - K_{11}) + \sum_i \frac{D_i\zeta_i - \theta_i(G_i + D_i)}{(\Pi\ \Sigma_i^s)} - 3\sum_k \frac{D_\Delta(k)\eta_1(k)}{(\Pi\ \Delta_k)} +$$

$$+ \sum_k \frac{\eta_2(k)\{G_\Delta(k) - D_\Delta(k)\}}{(\Pi\ \Delta_k)} + \sum_l \frac{\bar{B}_\Pi(1)\{\gamma_1(1) + \gamma_6(1)\}}{(\Pi\ \Pi_1)}$$

$$\beta_5 = 2\sum_i \frac{\zeta_i(G_i + D_i)}{(\Pi\ \Sigma_i^s)} + \sum_l \frac{\gamma_1(1)\bar{B}_\Pi(1)}{(\Pi\ \Pi_1)}$$

$$\beta_6 = -2\sum_i \frac{(G_i + D_i)\zeta_i}{(\Pi\ \Sigma_i^s)} + 2\sum_l \frac{\gamma_4(1)\bar{B}_\Pi(1)}{(\Pi\ \Pi_1)}$$

$$\beta_7 = 2\sum_l \frac{\bar{B}_\Pi(1)\gamma_6(1)}{(\Pi\ \Pi_1)}$$

$$\beta_8 = 2\sum_k \frac{\eta_1(k)\{G_\Delta(k) + D_\Delta(k)\}}{(\Pi\ \Delta_k)}$$

Table X (continued)

$$\beta_9 = 2\sum_k \frac{\eta_1(k)\left[G_\Delta(k)-D_\Delta(k)\right]}{(\Pi\ \Delta_k)} + 2\sum_l \frac{\gamma_4(l)\bar{B}_\Pi(l)}{(\Pi\ \Pi_l)}$$

$$\beta_{10} = 2\sum_l \frac{\gamma_2(l)\bar{B}_\Pi(l)}{(\Pi\ \Pi_l)}$$

$$\beta_{11} = 2\sum_l \frac{\gamma_4(l)\bar{B}_\Pi(l)}{(\Pi\ \Pi_l)}$$

$$\beta_{12} = \sum_i (-1)^s \frac{\zeta_i(D_i+G_i)}{(\Pi\ \Sigma_i^s)} + \sum_l \frac{\bar{B}_\Pi(l)\gamma_2(l)}{(\Pi\ \Pi_l)}$$

$$\phi_1 = 4Q_{11} - \sum_l \frac{\gamma_3(l)\bar{A}_\Pi(l)}{(\Pi\ \Pi_l)} - 2\sum_k \frac{\eta_1(k)Q_\Delta(k)}{(\Pi\ \Delta_k)}$$

$$\phi_2 = 4Q_{11} + 2\sum_l \frac{(\tfrac{1}{2}\bar{A}_\Pi(l)-2\bar{B}_\Pi(l))\gamma_3(l)}{(\Pi\ \Pi_l)} - \sum_k \frac{\eta_1(k)Q_\Delta(k)}{(\Pi\ \Delta_k)}$$

$$\phi_3 = 2\sqrt{6}\ Q_{1-1} + \sum_i (-1)^s \frac{Q_i\zeta_i}{(\Pi\ \Sigma_i^s)}$$

$$\phi_4 = 2\sum_l \frac{\gamma_3(l)\bar{B}_\Pi(l)}{(\Pi\ \Pi_l)}$$

$$\phi_5 = 2\sum_l \frac{\gamma_5(l)\bar{B}_\Pi(l)}{(\Pi\ \Pi_l)}$$

Table X (continued)

$$\phi_6 = 2\sum_i \frac{Q_i \zeta_i}{(\Pi \ \Sigma_i^s)} + \sum_k \frac{\eta_1(k)Q_\Delta(k)}{(\Pi \ \Delta_k)}$$

$$\phi_7 = \sum_i \frac{Q_i \Theta_i}{(\Pi \ \Sigma_i^s)} + \sum_k \frac{\eta_2(k)Q_\Delta(k)}{(\Pi \ \Delta_k)}$$

The second- and third-order hyperfine contributions due to the fine structure are easily calculated using Eqs. (11)–(13), and Tables I and II. The result is given in Table IX, while in Table X are defined the relations between the molecular constants of Tables IX and III.

Experimentally we can separate only terms with a different J dependence. This reduces the equations of Table IX to those of Table XI. The equations given in Tables VIII and XI are the final results. The molecular constants defined in these equations should describe the hyperfine Λ-doubling spectrum up to third order in energy. The theory outlined above is used to analyze the experimental spectrum. The constants are adjusted by a least-squares method to fit the experimental data.

III. EXPERIMENTAL RESULTS

The experiments were performed using the molecular beam electric resonance method. The experimental setup has been described in detail elsewhere (9). For the measurements on $^{15}N^{16}O$ we used an enriched (95 %) sample. The gas was recovered after every run of about 4 hr. The loss was approximately 1.5 % per run. The measured frequencies involved the electric dipole transitions from a +Kronig symmetry level to a −Kronig symmetry level, within one J state.

The NO molecule in its $^2\Pi$ state has a very strong Zeeman effect, and the transitions of the $^2\Pi_{3/2}$ state are strongly split by the earth's magnetic field. These splittings decrease with increasing J value. The $\Delta F = 0$ transitions are seen as triplets. The frequencies of the central lines of these triplets are, within experimental accuracy, those of the zero field transitions. The $\Delta F = \pm 1$ transitions appear as broad doublets (^{14}NO) or triplets (^{15}NO) symmetrically located about the zero field frequencies. We were able to minimize the magnetic field to ~ 5 mG, The full line widths were 10–20 kHz for $J = \tfrac{3}{2}$ and $\tfrac{5}{2}$ of $^2\Pi_{3/2}$, and less than 10 kHz for the other transitions.

Table XI   Hyperfine structure contributions up to third order

after collecting terms with the same J dependence.

$$\langle ^2\Pi_{\frac{1}{2}}^{\pm} | H_{hf} | ^2\Pi_{\frac{1}{2}}^{\pm} \rangle = y\{(\chi_1 + z^2\chi_5) \pm (J+\tfrac{1}{2})(\chi_2 + z^2\chi_6)\} +$$

$$+ u\{(\tfrac{3}{4}-x)(\zeta_1 + \zeta_4 J(J+1)) \pm \zeta_5 z^2 (J+\tfrac{1}{2})\}$$

$$\langle ^2\Pi_{3/2}^{\pm} | H_{hf} | ^2\Pi_{3/2}^{\pm} \rangle = y\{\chi_3 + z^2\chi_7\} +$$

$$+ u\{(\tfrac{27}{4}-x)(\zeta_2 + \zeta_4 J(J+1)) + (\zeta_7 \pm \zeta_5(J+\tfrac{1}{2}))z^2\}$$

$$\langle ^2\Pi_{\frac{1}{2}}^{\pm} | H_{hf} | ^2\Pi_{3/2}^{\pm} \rangle = zy\{(\chi_4 + z^2\chi_8) \pm \chi_9(J+\tfrac{1}{2})\} +$$

$$+ zu\{\pm(\zeta_3 + \zeta_5 J(J+1))(J+\tfrac{1}{2}) + (\zeta_6 - \zeta_4 J(J+1))\}$$

with

$$\chi_1 = \beta_1 + \beta_5 + \tfrac{3}{4}C_{RS} \qquad \zeta_1 = \phi_1 + \tfrac{1}{4}\phi_4$$

$$\chi_2 = \beta_2 + \beta_{10} \qquad \zeta_2 = \phi_2 + \tfrac{1}{4}\phi_4$$

$$\chi_3 = \beta_3 + \beta_7 - 3\beta_8 + \tfrac{3}{4}C_{RS} \qquad \zeta_3 = \phi_3 - \tfrac{3}{4}\phi_5$$

$$\chi_4 = \beta_4 \qquad \zeta_4 = \phi_4$$

$$\chi_5 = \beta_5 + \beta_9 + C_{RS} \qquad \zeta_5 = \phi_5$$

$$\chi_6 = \beta_{10} \qquad \zeta_6 = \phi_7 + \tfrac{15}{4}\phi_4$$

$$\chi_7 = \beta_6 + \beta_7 + \beta_8 + C_{RS} \qquad \zeta_7 = \phi_6$$

$$\chi_8 = \beta_{11}$$

$$\chi_9 = \beta_{12}$$

The observed transition frequencies at zero electric and magnetic fields and their uncertainties are given in Table XII for $^{14}N^{16}O$, and in Table XIII for $^{15}N^{16}O$.

As can be seen from Table XII the experimental results of Neumann (5) on

Table XII Observed and predicted hyperfine Λ-doubling transitions for $^{14}N^{16}O$.

J	Ω	F_+	$F_-{}^a$	This work	previous measurements (5)	Calculated frequencies
				Observed frequencies (MHz)		
0.5	0.5	0.5	0.5	205.9510(2)	205.951(1)	205.9582
		1.5	1.5	431.1905(2)	431.191(1)	431.1587
		1.5	0.5	411.2056(2)	411.206(1)	411.1886
		0.5	1.5	225.9357(2)	225.936(1)	225.9282
1.5	0.5	0.5	0.5	560.8538(2)		560.8529
		1.5	1.5	651.5425(2)	651.543(1)	651.5275
		2.5	2.5	801.1963(2)		801.2179
		1.5	2.5	758.9106(2)		758.9379
		2.5	1.5	693.8282(2)		693.8076
		0.5	1.5	624.6494(2)		624.6259
		1.5	0.5	587.7467(2)		587.7545
2.5	0.5	1.5	1.5	929.259 (4)		929.2441
		3.5	3.5	1160.7768(3)		1160.8073
		3.5	2.5	1114.677(15)		1114.7102
		2.5	3.5	1072.596(12)		1072.6308
		2.5	1.5	991.7338(2)		991.7351
		1.5	2.5	964.023 (2)		964.0428
3.5	0.5	4.5	4.5	1514.768 (1)		1514.7580
		4.5	3.5	1434.588 (1)		1434.6099
		3.5	4.5	1467.511 (1)		1467.4984
		3.5	2.5	1325.299 (1)		1325.2872
		2.5	3.5	1348.459 (4)		1348.4151
1.5	1.5	1.5	1.5	0.612 (1)	0.612(1)	0.6118
		2.5	2.5	1.029 (1)	1.029(1)	1.0288
		1.5	2.5	74.931 (3)	74.930(1)	74.9212
		2.5	1.5	73.286 (3)	73.289(1)	73.2806
		0.5	1.5	46.464 (3)	46.470(5)	46.4567

Table XII (continued)

				Observed frequencies (MHz)		
J	Ω	F_+	F_- [a]	This work	previous measurement (5)	Calculated frequencies
2.5	1.5	2.5	1.5	3.121 (1)	3.121(1)	3.1203
		3.5	3.5	3.923 (1)	3.923(1)	3.9226
		3.5	2.5	47.211 (1)	47.212(1)	47.2122
		2.5	3.5	40.172 (6)		40.1693
		2.5	1.5	34.390(30)		34.3715
3.5	1.5	3.5	4.5	39.221 (2)		39.2310
		2.5	3.5	31.550 (4)		31.5415
4.5	1.5	5.5	4.5	40.512 (1)		40.5129
		4.5	3.5	35.045 (2)		35.0452
5.5	1.5	4.5	4.5	31.124 (1)	31.124(1)	31.1251
		5.5	5.5	30.265 (1)	30.265(1)	30.2649
		6.5	6.5	32.425 (1)	32.425(1)	32.4242
		5.5	6.5	48.786 (1)		48.7861
		6.5	5.5	13.905 (1)		13.9029
6.5	1.5	5.5	5.5	49.405 (1)	49.405(1)	49.4056
		6.5	6.5	48.578 (1)	48.577(1)	48.5772
		7.5	7.5	51.260 (1)	51.260(1)	51.2598
		7.5	6.5	63.640 (1)		63.6409
		6.5	7.5	36.196 (1)		36.1960
		6.5	5.5	59.742 (1)		59.7421
		5.5	6.5	38.243 (1)		38.2406
7.5	1.5	6.5	6.5	73.540 (1)	73.540(1)	73.5397
		7.5	7.5	72.786 (1)	72.786(1)	72.7853
		8.5	8.5	76.025 (1)	76.025(1)	76.0240
		7.5	8.5	85.255 (1)		85.2563
		8.5	7.5	63.552 (1)		63.5530
		6.5	7.5	81.547 (1)		81.5468
		7.5	6.5	64.778 (1)		64.7783

Table XII　(continued)

J	Ω	F_+	F_-[a]	Observed frequencies (MHz)		Calculated frequencies
				This work	previous measurements	
8.5	1.5	7.5	7.5	104.216 (2)		104.2147
		8.5	8.5	103.575 (2)		103.5746
		9.5	9.5	107.400 (1)		107.3400
		9.5	8.5	114.024 (1)		114.0220
		8.5	9.5	96.951 (1)		96.9526
		8.5	7.5	110.306 (1)		110.3057
		7.5	8.5	97.483 (1)		97.4836

[a] $F_\pm$ F-state with Kronig symmetry ±.

$^{14}N^{16}O$ agree very well with ours. However, his predicted frequencies (5), especially for the $^2\Pi_{1/2}$ state, show a great discrepancy with our experimental results.

IV. ANALYSIS OF THE SPECTRUM

From Table VIII it follows that the Λ splitting is determined by the constants α_3, α_4, α_5, α_7, and α_8. We make the following approximations for the other molecular constants from Table VIII:

$$\alpha_1 = A_\Pi; \quad \alpha_2 = B_\Pi + \alpha_7; \quad \alpha_6 = B_\Pi + \alpha_3; \quad \alpha_9 = \alpha_7; \quad \alpha_{10} = \alpha_{11} = 0.$$

This is a permitted approximation, because terms which do not contribute directly to the Λ splitting must be at least of the order of 10 MHz to give higher-order effects on the energy within the present experimental accuracy (about 1 kHz). From Table VIII it follows that $\alpha_8 = \alpha_5(B_\Pi - B_\Sigma)/B_\Pi$. As A_Π and B_Π are known from other experiments the Λ splitting is described up to third order by four constants α_3, α_4, α_5, and α_7.

IV. 1. $^{15}N^{16}O$.

The absence of the contributions from electric quadrupole interaction in $^{15}N^{16}O$ ($I = \frac{1}{2}$) simplifies the spectrum considerably. Nine hyperfine structure constants, all χ, have to be determined for this molecule.

We calculated the coefficient matrix, which describes the dependence of the calculated frequencies on the various constants. The rank of this matrix was

Table XIII Observed and calculated hyperfine Λ-doubling
transitions for $^{15}N^{16}O$.

J	Ω	F_+	F_-	Observed frequencies (MHz)	Calculated frequencies (MHz)
0.5	0.5	0	0		501.1979
		0	1	482.6212(2)	482.6189
		1	0	309.2256(2)	309.2217
		1	1	290.6565(2)	290.6426
1.5	0.5	1	1	790.9748(3)	790.9651
		2	1	742.8364(3)	742.8346
		1	2	670.7076(3)	670.7201
		2	2	622.5690(3)	622.5896
2.5	0.5	2	2	1121.1513(3)	1121.1691
		2	3		1064.6944
		3	2	1015.4147(5)	1015.3914
		3	3	958.9183(3)	958.9167
3.5	0.5	3	3	1454.9160(5)	1454.9013
		4	3		1394.6320
		3	4		1355.0719
		4	4		1294.8026
1.5	1.5	2	1	84.589 (2)	84.5877
		1	2		82.9340
		1	1		0.8732
		2	2	0.780 (5)	0.7804
2.5	1.5	2	3	55.738 (3)	55.7429
		3	2		49.1965
		2	2	3.393 (3)	3.3923
		3	3	3.154 (1)	3.1542
3.5	1.5	4	3		45.5804
		3	4		29.3107
		3	3		8.3544
		4	4		7.9152
4.5	1.5	4	5		44.5249
		4	4		16.5308
		5	5		15.8352
		5	4		12.1591
5.5	1.5	6	5	50.2509(5)	50.2511
		5	5	28.6642(5)	28.6634
		6	6	27.6570(5)	27.6578
		5	6	6.0702(5)	6.0701
6.5	1.5	6	7	62.2184(5)	62.2183
		6	6	45.4609(5)	45.4604
		7	7	44.0920(5)	44.0927
		7	6	27.3347(5)	27.3349
7.5	1.5	8	7	80.4891(5)	80.4891
		7	7	67.5905(5)	67.5905
		8	8	65.8107(5)	65.8110
		7	8	52.9121(5)	52.9124

Table XIII (continued)

8.5	1.5	8	9	105.3590(5)	105.3590	
		8	8	95.6788(5)	95.6795	'
		9	9	93.4413(5)	93.4403	
		9	8	83.7610(5)	83.7608	

a $F_\pm$ F-state with Kronig symmetry ±.

smaller than the number of constants. Consequently not all constants can be determined independently from the experimental data. It turned out that there is a relation between χ_4, χ_5, and χ_7. From the coefficient matrix it follows, that the effect of χ_4 on the energy can be absorbed in an effective χ_5', and χ_7':

$$\chi_5' = \chi_5 - \alpha\chi_4, \tag{14}$$

$$\chi_7' = \chi_7 + \alpha\chi_4. \tag{15}$$

The constants χ_5 and χ_7 in Table XI are replaced by χ_5' and χ_7', respectively, whereas the effect of χ_4 in the matrix element $\langle {}^2\Pi_{1/2}^\pm \,|\, \mathbf{H}_{hf} \,|\, {}^2\Pi_{3/2}^\pm \rangle$ of Table XI can be taken as zero in the fitting procedure. The value of α is calculated from the coefficient matrix. The resulting α (Table XIV) is varying very slowly with increasing J. The error in the value of α is set equal to the maximum variation in α with increasing J.

The molecular constants α_3, α_4, α_5, α_7, χ_1, χ_2, χ_3, χ_5', χ_6, χ_7', χ_8, and χ_9 are varied in a least-squares fit of the experimental spectrum. The constant χ_8 was found to be very small, and was subsequently set at zero.

Using Eqs. (14) and (15) we calculated χ_4 and $(\chi_5 + \chi_7)$ from χ_5' and χ_7'. Table XIV lists the values of the molecular constants of the best least-squares fit. The calculated frequencies are given in Table XIII.

IV. 2. $^{14}N^{16}O$

The hyperfine-structure constants χ_1 through χ_9 are determined in the same way as for $^{15}N^{16}O$. The nuclear spin $I = 1$ of ^{14}N introduces a contribution to the hyperfine energy due to the electric quadrupole interaction. This makes it necessary to determine seven additional molecular constants ζ_1 through ζ_7. The electric quadrupole constants adjusted in the least-squares fit of the spectrum of $^{14}N^{16}O$ are ζ_1, ζ_2, ζ_3, and ζ_5. The remaining three constants ζ_4, ζ_6, and ζ_7 were found to be less than 1 kHz without giving any improvement of the fit and are as taken zero. The results are listed in Table XIV. The calculated frequencies are tabulated in Table XII. Table XV lists the molecular constants taken from other sources and used as known in the fit.

Table XIV Molecular constants of $^{14}\mathrm{N}^{16}\mathrm{O}$ and $^{15}\mathrm{N}^{16}\mathrm{O}$ obtained in this work (all values are in MHz, except α, which is dimensionless).

constant name	value for $^{14}\mathrm{N}^{16}\mathrm{O}$	value for $^{15}\mathrm{N}^{16}\mathrm{O}$
α_3	89.0235(2)	85.8210(2)
α_7	1.4132(4)	1.3149(4)
α_4	$(-1.06(5))\times10^{-3}$	$(-1.36(5))\times10^{-3}$
α_5	$(-0.10(1))\times10^{-3}$	$(-0.10(1))\times10^{-3}$
χ_1	46.3151(7)	$-65.0240(7)$
χ_2	56.3001(5)	$-78.9582(4)$
χ_3	113.639 (2)	-159.468 (3)
χ_5'	0.6015(7)	$-0.8444(7)$
χ_6	$(0.56(6))\times10^{-3}$	$(-3.77(6))\times10^{-3}$
χ_7'	$-0.5837(3)$	0.7888(1)
χ_9	$(-5.2\ (5))\times10^{-3}$	$(8.2\ (5))\times10^{-3}$
ζ_1	-1.841 (1)	
ζ_2	-1.862 (1)	
ζ_3	12.115 (40)	
ζ_5	$(-15.4\ (7))\times10^{-3}$	
α	0.02836(2)	0.027334(8)
χ_4	-20.896 (25)	29.875 (25)
$\chi_5 + \chi_7$	$(17.8\ (8))\times10^{-3}$	$(-55.6\ (8))\times10^{-3}$

Table XV Molecular constants of $^{14}N^{16}O$ and $^{15}N^{16}O$ taken from

other sources and used in the present fit.

	value for $^{14}N^{16}O$	value for $^{15}N^{16}O$	Ref.
A_Π	123.160 cm^{-1}	123.160 ^{a} cm^{-1}	(15)
B_Π	50 838.56 MHz	49 041.34 MHz	(2)
D_Π	0.177 MHz	0.139 MHz	(2)
B_Σ	59 568.76 MHz	57 206 MHz	(7)

^{a} We used for $^{15}N^{16}O$ the value of $^{14}N^{16}O$.

V. DISCUSSION

The differences between the experimental frequencies and the frequencies calculated as outlined above (Tables XII and XIII) are approximately an order of magnitude smaller than between the experimental and the predicted frequencies of Neumann (5). The third-order hyperfine-structure contributions give rise to a number of terms with a different J dependence. These contributions are responsible for the better agreement between experiment and theory; they were not included in previous calculations of the spectrum. The additional coupling constants are χ_5 through χ_9, and ζ_5.

However, the fit for the frequencies of the $^2\Pi_{1/2}$ state is not as good as we expected. An obvious thought is that neglect of higher-order contributions from fine and hyperfine structure might be responsible for the remaining discrepancy.

The fourth-order fine structure can be separated into two parts. One part containing terms with a similar J dependence as those of Table VIII and may be absorbed in α_1 through α_{11} without changing anything in the mathematics of the least-squares fit. The other part contains terms with a different J dependence. However, calculations of these contributions and rough estimates similar to those of Ref. (1) showed that they were smaller than the experimental accuracy. So fourth-order fine structure cannot explain the discrepancy.

The fourth-order hyperfine contributions were calculated by Freed (1) for a $^3\Pi$ state. They were calculated by us for a $^2\Pi$ state and included in the least-

Table XVI   Relations between hyperfine constants of Table XI

            and conventional constants (neglecting third

            order effects).

conventional constants	present constants	Ref.
a	$\frac{1}{3}(3x_1 + x_3)$	(10)
b	$-2x_4$	(10)
c	$2(-x_1+x_4) + \frac{2}{3}x_3$	(10)
d	$2x_2$	(10)
eQq_1	$\frac{1}{2}(\zeta_1 + \zeta_2)$	(16)
eQq_2	$2\zeta_3$	(16)

squares fit of the spectrum. It was not necessary to introduce new coupling constants. Unfortunately no improvement of the fit was obtained. For this reason we did not discuss here the explicit expressions for the fourth-order contribution of the hyperfine structure. We did not find any other contribution which could explain the discrepancy between the experimental and theoretical frequencies.

No attempt was made to perform the very tedious fifth-order calculations.

Comparison with previous experiments (2–5) is not simple, because the third-order hyperfine effects were always neglected. Especially the molecular fine-structure constants α_3 and α_7 include third-order as well as second-order effects. However, if the third-order effects in the hyperfine-structure constants are neglected, one can easily deduce relations between the hyperfine constants defined by Frosh and Foley (8), and by Dousmanis et al. (10), and the constants used in this work. This is done in Table XVI.

Neglecting third-order effects in the hyperfine structure, we calculated from Tables XVI and XIV the hyperfine coupling constants of Table XVII. In this table are also listed the results of previous investigations. It should be noted

Table XVII Values of the conventional constants obtained in the present work and by other investigations.

In these constants third order effects are neglected. (All values in MHz).

Constant	Present value	Neumann (5)	Radford and Brown (4)	Favero et al (3)	Gallagher and Johnson (2)
a ($^{14}N^{16}O$)	84.195(2)	84.208 (2)	84.28(52)	83.82	83.40
b ($^{14}N^{16}O$)	41.79 (5)	41.508(75)	41.8 (6.3)	68.49	68.91
c ($^{14}N^{16}O$)	-58.66 (5)	-58.37 (7)	-58.8 (7.4)	-86.34	-87.60
d ($^{14}N^{16}O$)	112.600(1)	112.6196(3)	116 (30)	...	112.60
eQq_1($^{14}N^{16}O$)	-1.852(2)	-1.876 (8)	-1.81(30)	-2	-1.75
eQq_2($^{14}N^{16}O$)	24.23 (8)	23.04 (5)	23.1 (4)	33	27.9
a ($^{15}N^{16}O$)	-118.189(3)		-118.21(50)		-116.94
b ($^{15}N^{16}O$)	-59.78 (5)		-59.8 (5.8)		-96.63
c ($^{15}N^{16}O$)	83.51 (5)		83.4 (6.8)		122.82
d ($^{15}N^{16}O$)	-157.929(1)		-159 (33)		-157.88

that the accuracy of the molecular constants, especially a and d, claimed by Neumann (5) is too high, because he neglects the third-order hyperfine effects. Our calculated hyperfine-structure constants agree quite well with those of Neumann (5) and Brown and Radford (4).

APPENDIX

The molecular Hamiltonian **H** of a diatomic molecule is invariant under reflections σ_{xz} in a plane containing the molecular axis, so that

$$\sigma_{xz}^{-1} \mathbf{H} \, \sigma_{xz} = \mathbf{H} \tag{A1}$$

and the wavefunctions, which are used as basis for the calculation of the matrix elements of **H**, must have the proper symmetry with respect to these reflections.

The zero-th-order molecular wavefunctions in a Hund case (a) can formally be written as $|\, J\Lambda\Sigma\Omega\rangle$. They can be split into a rotational and a rotationless part:

$$|\, J\Lambda\Sigma\Omega\rangle = |J\Omega\rangle \,|\, \Lambda \rangle \,|\, S\Sigma\rangle, \tag{A2}$$

where $|\, J\Omega\rangle$ is the rotational part. Under the reflections σ_{xz} the functions $|J\Lambda\Sigma\Omega\rangle$ behave as (6, 11–14)

$$\sigma_{xz} |\, J\Lambda\Sigma\Omega\rangle = (-1)^s (-1)^{J-\Omega+s-\Sigma+\Lambda} |\, J-\Lambda-\Sigma-\Omega\rangle. \tag{A3}$$

Herein s is even or odd for Σ^+ or Σ^- states, respectively, and zero otherwise.

So functions with a proper symmetry can be defined as

$$|\, ^{2S+1}\Gamma^{\pm}_{|\Omega|}J\rangle = (1/\sqrt{2})[|\, J\Lambda\Sigma\Omega\rangle \pm (-1)^s |\, J-\Lambda-\Sigma-\Omega\rangle], \tag{A4}$$

where Γ stands for Σ^s, Π, Δ, $\cdots$.

The symmetry of these functions under the reflections σ_{xz} is $\pm(-1)^{J-S}$:

$$\sigma_{xz} |\, ^{2S+1}\Gamma^{\pm}_{|\Omega|} \, J\rangle = \pm (-1)^{J-S} \,|\, ^{2S+1}\Gamma^{\pm}_{|\Omega|} \, J\rangle. \tag{A5}$$

This is called the Kronig symmetry of the functions. These definitions of symmetry are in agreement with Herzberg (7), but differ slightly from those of Freed (1).

The symmetry considerations halve the number of matrix elements which must be calculated. From Eqs. (A1) and (A3) it follows.

$$\begin{aligned}
\langle J\Lambda\Sigma\Omega \,|\, \mathbf{H} \,|\, J'\Lambda'\Sigma'\Omega'\rangle &= \langle J\Lambda\Sigma\Omega \,|\, \sigma_{xz}^{-1} \mathbf{H}\sigma_{xz} \,|\, J'\Lambda'\Sigma'\Omega'\rangle \\
&= f \,\langle J-\Lambda-\Sigma-\Omega \,|\, \mathbf{H} \,|\, J'-\Lambda'-\Sigma'-\Omega'\rangle,
\end{aligned} \tag{A6}$$

where

$$f = (-1)^{(s+s')+J+J'+s+s'+\Omega+\Omega'-(\Sigma+\Sigma')+(\Lambda+\Lambda')}. \tag{A7}$$

With

$$J = J', \ S = S', \ (-1)^{\Lambda+\Lambda'} = (-1)^{-(\Lambda+\Lambda')},$$

Eq.(A7) becomes

$$f = (-1)^{s+s'}. \tag{A8}$$

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