The Zeeman Spectrum of the NO Molecule

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The Zeeman spectrum of the NO molecule in the $X\ ^2\Pi_{1/2}$, $J = \frac{1}{2}$ and $J = \frac{3}{2}$ rotational states has been studied using a molecular beam electric resonance spectrometer. High-resolution data were obtained in magnetic fields ranging from 0.1 to 0.8 T. The present measurements are combined with relevant data from the literature in a least-squares fit to determine basic molecular g factors. Seven molecular g factors and the anisotropy in the magnetic susceptibility could be determined, and a value of the electronic quadrupole moment $Q_\parallel^e$ was derived. The most prominent results are $g_s = 2.002095(40)$ and $Q_\parallel^e = -1.201(11) \times 10^{-38}$ C m², to be compared with the respective ab initio values which are 2.002087 and -0.826×10^{-38} C m². Furthermore, separate contributions from $^2\Sigma^+$, $^2\Sigma^-$, and Δ^2 states to the electronic part of the rotational g factor were obtained, showing that the unique perturber approximation is invalid for the present example. Finally, the combination of Zeeman- and zero-field data enabled a separate determination of the spin–rotation constant and the centrifugal distortion in the spin–orbit coupling (A_D). The value of A_D derived from experiment is $-1.43(20)$ MHz, in good agreement with the theoretical prediction of $-1.92(8)$ MHz.

1. INTRODUCTION

The $^2\Pi$ ground state in NO is presently attracting much interest among spectroscopists. The richness and spacings of energy levels in this electronic state offer opportunities of investigation by a wide variety of high-resolution spectroscopic techniques. Vibrational transitions are studied by use of Fourier spectrometers, laser magnetic resonance techniques yield information regarding the spin–orbit splitting, microwave spectroscopy applies to rotational transitions, and Λ-doubling transitions are detected by molecular beam apparatus. In addition, there are electron paramagnetic resonance measurements on the $^2\Pi_{3/2}$ substate.

The present work yields new high-resolution molecular beam measurements of the Zeeman spectrum for the two lowest rotational levels of the $^2\Pi_{1/2}$ substate. As is well known, the Zeeman effect of the paramagnetic $^2\Pi_{3/2}$ substate is governed by the g factor combination $g_l + 1/2\ g_s \approx 2$. The $^2\Pi_{1/2}$ substate, on the other hand, shows much smaller Zeeman shifts since in this case the crucial

parameter is $g_l - 1/2\,g_s$. According to standard theory the difference $g_l - 1/2\,g_s$ is expected to yield the radiation correction to g_s. There are, however, significant contributions to this difference from various relativistic corrections to both g_l and g_s and from second-order corrections to g_l. The new molecular beam Zeeman data now enable a precise determination (better than 2 parts in 10^{-4}) of the small but interesting quantity $g_l - (1/2)g_s$. Combined with the EPR determinations of $g_l + 1/2\,g_s$ separate values of g_l and g_s are readily obtained with an accuracy of about 20 ppm. The relativistic corrections to g_s can be computed from ab initio calculations to an accuracy of about 5 ppm. Hence, we have the unique opportunity to compare an accurate experimental value for g_s with an even better theoretical prediction. This is a rather unusual situation in molecular spectroscopy. It should be noted that the correct value for g_s can only be abstracted from the experimental Zeeman data if the zero-field spectrum is treated properly.

A precise value of the nuclear g factor g_I has been determined from the present Zeeman data on the $^2\Pi_{1/2}$ substate. A comparison of fitted and theoretical (bare nucleus) values of g_I provided another opportunity to test the model used to describe these complex spectra. Finally, we were able to derive for the first time in a diatomic $^2\Pi$ molecule the anisotropy in the magnetic susceptibility which combined with the values of the g factors allows the determination of the electronic quadrupole moment.

In the analysis of the data the emphasis is put on obtaining the basic molecular g factors. This is achieved by a weighted nonlinear least-squares fit in which the present measurements as well as all other relevant available data were used simultaneously.

2. THEORY OF THE ZEEMAN EFFECT FOR $^2\Pi$ STATES

2.1. The Hamiltonian

The formal expression for the hamiltonian is

$$H = H_{ev} + H_{rot} + H_{hf} + H_z, \tag{1}$$

where H_{ev} denotes the electronic and vibrational contribution, H_{rot} is the rotational part, and H_{hf} refers to the hyperfine interaction. The present paper will not be concerned with this zero-field part of the hamiltonian. Explicit expressions and relevant matrix elements have been given in previous publications (1–3). The Zeeman hamiltonian of a diatomic molecule with a single nuclear spin has the general form,

$$H_z = \mu_B(g_l\mathbf{L} + g_s\mathbf{S} - g_I\mathbf{I} + g_R^N\mathbf{R})\cdot\mathbf{B}. \tag{2}$$

Here μ_B denotes the Bohr magneton and $\mathbf{B}$ the external magnetic field. The various g factors g_l, g_s, g_I, and g_R^N are in principle unknown adjustable parameters. There are, however, rather accurate theoretical estimates to all of them. In the standard theory of the Zeeman effect one has $g_l = 1$, representing the orbital g factor, and $g_s = 2.00232$ if the radiation correction is included in the electronic spin g factor. The nuclear spin g factor $g_I = 2.19792(3) \times 10^{-4}$ (4) for a bare ^{14}N nucleus, while the predicted nuclear rotational g factor in NO $g_R^N = -2.722 \times 10^{-4}$ (2).

The Zeeman hamiltonian of Eq. (2) is derived from a reduction of the Breit equation to a nonrelativistic form. Reduction to the first Pauli limit yields $g_l = 1$ and $g_s = 2$. A reduction to the second Pauli limit produces the following corrections to the standard Zeeman hamiltonian:

$$H' = -\mu_B \mathbf{B} \cdot \sum_i (\mathbf{l}_i + 2\mathbf{s}_i) T_i / mc^2 - \frac{\mu_B e^2}{mc^2} \sum_{i,N} Z_N \left[\nabla_i \left(\frac{1}{r_{iN}} \right) \times \mathbf{A}_i \right] \cdot \mathbf{s}_i$$

$$+ \frac{\mu_B e^2}{mc^2} \sum_{i,j(i\neq j)} \left[\nabla_i \left(\frac{1}{r_{ij}} \right) \times \mathbf{A}_i \right] \cdot (\mathbf{s}_i + 2\mathbf{s}_j)$$

$$- \frac{\mu_B e^2}{mc^2} \sum_{i,j(i\neq j)} \left[\frac{\mathbf{A}_i \cdot \mathbf{p}_j}{r_{ij}} + \frac{(\mathbf{r}_{ij} \cdot \mathbf{A}_i)(\mathbf{r}_{ij} \cdot \mathbf{p}_j)}{r_{ij}^3} \right] . \tag{3}$$

The indices i, j, and N label the electrons and nuclei, respectively. A is the magnetic vector potential due to the external field, and T_i denotes the kinetic energy of electron number i. The first summation in Eq. (3) represents a relativistic correction arising from the electronic mass dependence of the Bohr magneton. The next two summations of Eq. (3) are associated with the spin–orbit and spin–other-orbit interactions, respectively, whereas the last summation stems from the orbit–orbit interaction. Hence, we denote the four summations of Eq. (3) as relativistic, spin–orbit, spin–other-orbit, and orbit–orbit types of corrections, respectively. The terms proportional to s_i or s_j in Eq. (3) add directly to the electronic spin g factor g_s, whereas the term proportional to l_i and the orbit–orbit type of correction add to g_l. Ab initio values of these various corrections are given in Table III, and they will cause deviations from the simple values $g_l = 1$ and $g_s = 2$ which are substantial compared to the present experimental accuracy.

The motion of the nuclear center of mass yields another small correction to the orbital g factor g_l and is obtained from (2)

$$H_{CM} = -\mu_B \frac{m}{M_O + M_N} \mathbf{B} \cdot (\mathbf{L} + \sum_{i,j(i\neq j)} \mathbf{r}_i \times \mathbf{p}_j), \tag{4}$$

where M_O and M_N denote the nuclear masses.

2.2. Second-Order Corrections

A theoretical model of the Zeeman effect of a $^2\Pi$ state is not adequate unless second-order terms due to the interaction with $^2\Delta$, $^2\Sigma^+$, and $^2\Sigma^-$ states are included. These second-order effects give rise to both new adjustable Zeeman parameters and to corrections on g_l and g_R^N. This topic has been treated previously in detail (2, 3), and only the main features are reproduced here. The effective orbital g factor $g_{l,\text{eff}}$, including second-order terms, takes the form:

$$g_{l,\text{eff}} = g_l + (g_l - g_R^N) \left[\sum_{^2\Delta,v'} \frac{\langle^2\Delta v'|L_+|^2\Pi v\rangle\langle^2\Delta v'|BL_+|^2\Pi v\rangle}{E_{\Pi v} - E_{\Delta v'}} \right.$$

$$\left. - \sum_{^2\Sigma,v'} \frac{\langle^2\Pi v|L_+|^2\Sigma v'\rangle\langle^2\Pi v|BL_+|^2\Sigma v'\rangle}{E_{\Pi v} - E_{\Sigma v'}} \right] , \tag{5}$$

while the molecular rotational g factor becomes

$$g_R = g_R^N - g_R^e. \tag{6}$$

The electronic contribution g_R^e is defined by

$$g_R^e = (g_l - g_R^N)\left[\sum_{^2\Delta,v'} \frac{\langle^2\Delta v'|L_+|^2\Pi v\rangle\langle^2\Delta v'|BL_+|^2\Pi v\rangle}{E_{\Pi v} - E_{\Delta v'}}\right.$$
$$\left. + \sum_{^2\Sigma,v'} \frac{\langle^2\Pi v|L_+|^2\Sigma v'\rangle\langle^2\Pi v|BL_+|^2\Sigma v'\rangle}{E_{\Pi v} - E_{\Sigma v'}}\right]. \tag{7}$$

The three newly introduced g factors are the two "Λ-doubling" g factors g_B^* and g_A^*, and Δg_s given by

$$g_B^* = (g_l - g_R^N)\sum_{^2\Sigma,v'}(-1)^S \frac{\langle^2\Pi v|L_+|^2\Sigma v'\rangle\langle^2\Pi v|BL_+|^2\Sigma v'\rangle}{E_{\Pi v} - E_{\Sigma v'}}$$

$$g_A^* = (g_l - g_R^N)\sum_{^2\Sigma,v'}(-1)^S \frac{\langle^2\Pi v|L_+|^2\Sigma v'\rangle\langle^2\Pi v|(A + 2B)L_+|^2\Sigma v'\rangle}{E_{\Pi v} - E_{\Sigma v'}}, \tag{8}$$

$$\Delta g_s = \tfrac{1}{2}(g_l - g_R^N)\left[\sum_{^2\Delta,v'} \frac{\langle^2\Delta v'|L_+|^2\Pi v\rangle\langle^2\Delta v'|AL_+|^2\Pi v\rangle}{E_{\Pi v} - E_{\Delta v'}}\right.$$
$$\left. + \sum_{^2\Sigma,v'} \frac{\langle^2\Pi v|L_+|^2\Sigma v'\rangle\langle^2\Pi v|AL_+|^2\Sigma v'\rangle}{E_{\Pi v} - E_{\Sigma v'}}\right], \tag{9}$$

where the phase factor $(-1)^S$ equals $+1$ for $^2\Sigma^+$ states and -1 for $^2\Sigma^-$ states. The presently used second-order g factors are equivalent to those introduced by Brown *et al.* (*6*) from a different coupling scheme (case (a_β)).

The problem arising from the high correlation between the spin–rotation coupling constant γ and the centrifugal distortion A_D in the spin–orbit coupling constant, in spectroscopic data of a $^2\Pi$ state also affects the determination of the g factors. In a previous investigation (*3*) it was shown that this problem could be removed by a basis transformation merging the parameters A_D, γ, and Δg_s, yielding two new effective parameters,

$$A_D' = A_D - \frac{2\gamma B_v}{A_v - 2B_v} \tag{10}$$

and

$$g_T = [\tfrac{1}{2}\gamma(g_s - g_R^N) - \Delta g_s B_v]/(A_v - 2B_v). \tag{11}$$

Here B_v and A_v denote the rotational constant and spin–orbit coupling constant, respectively.

The spin–rotation coupling is included by the effective hamiltonian

$$H_{SR} = \gamma\mathbf{N}\cdot\mathbf{S}, \tag{12}$$

where the coupling constant γ has both first-order and second-order contributions.

It can easily be shown that

$$\gamma = \gamma^{(1)} - \sum_{^2\Sigma,v'} \frac{\langle ^2\Pi v | AL_+ | ^2\Sigma v' \rangle \langle ^2\Pi v | BL_+ | ^2\Sigma v' \rangle}{E_{\Pi v} - E_{\Sigma v'}}$$

$$- \sum_{^2\Delta,v'} \frac{\langle ^2\Delta v' | AL_+ | ^2\Pi v \rangle \langle ^2\Delta v' | BL_+ | ^2\Pi v \rangle}{E_{\Pi v} - E_{\Delta v'}} . \tag{13}$$

The first-order part $\gamma^{(1)}$ is normally expected to be dominated strongly by the second-order contribution, which also seems to be the case for NO. If $\gamma^{(1)}$ is neglected, γ is often estimated from the Λ-doubling parameter p. Obviously, this procedure is correct only for the rare cases in which the second-order terms arise solely from the interaction of the $^2\Pi$ state with either $^2\Sigma^+$ or $^2\Sigma^-$ states. However, as will be shown below, there is a dominant second-order contribution from $^2\Delta$ states in NO. Hence the Λ-doubling parameters should appear only in the parity-dependent terms in the secular matrix. The parity-independent second-order terms are completely absorbed by the effective rotational constant, the effective spin–orbit coupling constant, and the effective spin–rotation constant γ (1, 3). If we assume that the electronic and vibrational motions are completely separable and ignore the vibrational dependences in $(E_{\Pi v} - E_{\Delta v'})$ and $(E_{\Pi v} - E_{\Sigma v'})$, an estimate for γ can be obtained from the definitions of γ and Δg_s ($\gamma^{(1)}$ neglected):

$$\gamma \approx -2\Delta g_s B_v. \tag{14}$$

2.3. Diamagnetism and Magnetic Shielding

The observable diamagnetism arises from the joint contribution of a first-order term and a second-order (high-frequency) part. The origin of the first-order contribution is the diamagnetic hamiltonian,

$$H_D = \sum_n \frac{q_n^2}{2 m_n c^2} \mathbf{A}_n^2, \tag{15}$$

where the summation includes electrons as well as nuclei. The second-order contribution from the Zeeman hamiltonian of Eq. (2) accounts for the high-frequency part. The nuclear part of Eq. (15) yields an insignificant contribution for the present case and is neglected. The matrix elements in the presently used basis $|\Omega \Omega_I F M_F\rangle$ can be obtained from a rather straightforward calculation. The relevant matrix elements for a $^2\Pi$ state of the effective diamagnetic hamiltonian H_D' are given by

$$\langle ^2\Pi\Omega\Omega_I F M_F | H_D' | ^2\Pi\Omega\Omega_I F' M_F \rangle$$

$$= -(1/3)B^2(\chi_\parallel - \chi_\perp)(-1)^{\Omega+\Omega_I-M_F}[(2F+1)(2F'+1)]^{1/2}$$

$$\times \begin{pmatrix} F & 2 & F' \\ M_F & 0 & -M_F \end{pmatrix} \begin{pmatrix} F & 2 & F' \\ (\Omega + \Omega_I) & 0 & -(\Omega + \Omega_I) \end{pmatrix} . \tag{16}$$

The new adjustable parameter $\chi_\parallel - \chi_\perp$ (anisotropy in the magnetic susceptibility)

is defined by

$$\chi_\| - \chi_\perp = \frac{1}{2}\mu_B^2(g_l - g_R^N)^2\left[\sum_{^2\Delta,v'}\frac{|\langle^2\Delta v'|L_+|^2\Pi v\rangle|^2}{E_{\Pi v} - E_{\Delta v'}} + \sum_{^2\Sigma,v'}\frac{|\langle^2\Pi v|L_+|^2\Sigma v'\rangle|^2}{E_{\Pi v} - E_{\Sigma v'}}\right]$$
$$+ \frac{e^2}{8m}\langle^2\Pi|\sum_i(3z_i^2 - r_i^2)|^2\Pi\rangle, \quad (17)$$

where the summation index i now runs over electrons only. The high-frequency contribution to $\chi_\| - \chi_\perp$ may now be rewritten in terms of the electronic rotational g factor g_R^e (Eq. (7)), using approximations similar to those used to derive Eq. (14),

$$\chi_\| - \chi_\perp = (1/2)\mu_B^2 g_R^e(g_l - g_R^N)/B_v + (e^2/(8m))\langle^2\Pi|\sum_i(3z_i^2 - r_i^2)|^2\Pi\rangle. \quad (18)$$

The electric quadrupole moment,

$$Q_\|^e = -(e/2)\langle^2\Pi|\sum_i(3z_i^2 - r_i^2)|^2\Pi\rangle, \quad (19)$$

can be calculated from the fitted values for $(\chi_\| - \chi_\perp)$ and the g factors.

The phenomenon known as magnetic shielding is closely related to diamagnetism. In Eq. (15), A_i is replaced by

$$A_i = A_{i\,ext} - \mu_B g_l\frac{\mu_0 I \times r_i}{4\pi r_i^3}, \quad (20)$$

where $A_{i\,ext}$ represents the external magnetic field, while the last part of Eq. (20) stems from the nuclear magnetic moment. Substitution of Eq. (20) in Eq. (15) gives rise to cross-terms between the external and nuclear fields that modify the contribution of the nuclear g factor g_l (Eq. (2)). The effective (shielded) nuclear spin g factor is given by (7)

$$g_l(1 - \sigma_{av}) = g_l\left(1 - \frac{\mu_0 e^2}{12\pi m}\langle^2\Pi|\sum_i\frac{1}{r_{iN}}|^2\Pi\rangle\right). \quad (21)$$

Here σ_{av} represents the average nuclear shielding, and r_{iN} denotes the distance between electron number i and the nucleus with spin. Additional magnetic shielding contributions arising from cross-terms between the hyperfine and Zeeman hamiltonians of Eq. (1) can be described by a single new parameter $(\sigma_\| - \sigma_\perp)$. No further details are discussed here since the accuracy of the present experimental data is too low to obtain significant values for the shielding constants.

3. EXPERIMENTAL DETAILS

The present Zeeman spectra were obtained with the molecular beam electric resonance spectrometer which has previously been used to study the zero field hyperfine Λ-doubling constants in NO (8). The apparatus has been described in detail elsewhere (9).

The magnetic field was produced with a Bruker Physik electromagnet that is capable of producing a field up to 0.87 T. The field homogeneity along the 8-cm-long

TABLE I

Observed Transition Frequencies (in MHz) of the $^2\Pi_{1/2}$, $J = \frac{1}{2}$ state of
NO in Various Magnetic Fields

F_+	M_{F+}	F_-	M_{F-}	0.099957(20) T	0.199381(49) T	0.399954(80) T	0.80031(16) T
3/2	3/2	3/2	3/2	427.8297(10)	424.4858(10)	417.744(2)	404.313(2)
	1/2		1/2		429.3756(10)	428.459(2)	429.101(2)
	-1/2		-1/2		433.7900(10)	437.014(2)	444.680(2)
	-3/2		-3/2	434.5337(10)	437.9023(10)	444.644(2)	458.173(2)
	3/2		1/2		426.053(3)	421.654(3)	414.929(3)
	1/2		3/2		427.809(3)	424.548(3)	418.485(3)
	1/2		-1/2		430.537(3)	430.502(3)	431.754(3)
	-1/2		1/2		432.629(3)	434.971(3)	442.027(3)
	-1/2		-3/2		434.718(3)	438.402(3)	446.170(3)
	-3/2		-1/2		436.979(3)	443.276(3)	456.686(3)
1/2	1/2	1/2	1/2		207.723(2)	208.607(2)	207.939(2)
	-1/2		-1/2		203.406(2)	200.248(2)	192.753(2)
	1/2		-1/2		205.412(3)	204.248(3)	200.652(3)
	-1/2		1/2		205.717(3)	204.608(3)	200.039(3)
3/2	1/2	1/2	1/2		410.486(2)	409.148(2)	404.942(2)
	-1/2		-1/2		411.422(2)	411.304(2)	410.579(2)
	3/2		1/2		407.164(3)	402.346(3)	390.770(3)
	1/2		-1/2		408.170(3)	404.791(3)	397.655(3)
	-1/2		1/2		413.739(3)	415.662(3)	417.867(3)
	-3/2		-1/2		414.610(3)	417.563(3)	422.586(3)
1/2	1/2	3/2	1/2		226.610(2)	227.916(2)	232.097(2)
	-1/2		-1/2		225.773(2)	225.963(2)	226.851(2)
	1/2		3/2		225.045(3)	224.007(3)	221.480(3)
	1/2		-1/2		227.773(3)	229.961(3)	234.751(3)
	-1/2		1/2		224.614(3)	223.917(3)	224.199(3)
	-1/2		-3/2		226.698(3)	227.349(3)	228.343(3)

transition region was 2 parts in 10^5. The magnetic fields have been measured with a Bruker B-NM 12 NMR probe outside the vacuum tank of the beam apparatus. The fluctuations in the field during the time of the measurements were smaller than 1 part in 10^5. The values of the magnetic field strength for relative purposes could be determined to 3 parts in 10^5. However, because it was not possible to measure the field at the position of the molecular beam, it is felt that the *absolute* magnetic field was known only to 2 parts in 10^4.

The observed Zeeman spectra involve the $\Delta J = 0$ electric dipole allowed transitions in the $J = \frac{1}{2}$ and $\frac{3}{2}$ rotational states of the $^2\Pi_{1/2}$ level. The magnetic field strengths range from 0.1 to 0.8 T. The results are presented in Tables I and II. The errors indicated on the values for the field strength represent the absolute uncertainties, while the errors in the frequencies are determined by the line-widths of the spectral lines and stability of the magnetic field.

4. RESULTS

4.1. The Least-Squares Fit

The present Zeeman data on the $^2\Pi_{1/2}$, $J = \frac{1}{2}$, and $J = \frac{3}{2}$ levels were combined with all available high-precision data for the lowest vibrational level in a weighted nonlinear least-squares fit. In this way a total of 23 parameters were determined

TABLE II

Observed Transition Frequencies (in MHz) of the $^2\Pi_{1/2}$, $J = \frac{3}{2}$ state of NO

F_+	M_{F+}	F_-	M_{F-}	0.50019(10) T	0.80020(16) T
5/2	5/2	5/2	5/2	781.210(1)	769.221(2)
	3/2		5/2	931.283(5)	1012.889(8)
	5/2		3/2	736.869(2)	
	3/2		3/2	886.938(3)	963.020(8)
	1/2		3/2	1039.994(3)	1216.939(5)
	-1/2		-1/2	1030.246(8)	
	-3/2		-1/2	1054.378(10)	1251.590(15)
	-3/2		-3/2	931.283(5)	1039.378(10)
	-5/2		-3/2	952.667(8)	1060.715(10)
	-5/2		-5/2	821.186(1)	833.182(2)
3/2	3/2	5/2	3/2	707.500(1)	689.895(2)
	1/2		3/2	872.820(5)	949.401(10)
	1/2		1/2	818.564(8)	890.859(8)
	-1/2		1/2	989.096(10)	1162.299(10)
	1/2		-1/2	707.500(1)	
	-1/2		-1/2	877.966(8)	
	-3/2		-1/2		972.365(10)
	-3/2		-3/2	759.632(1)	760.152(1)
	-3/2		-5/2	628.153(10)	532.616(8)
5/2	3/2	3/2	3/2	718.476(15)	720.059(10)
	-1/2		1/2	1018.778(15)	1229.798(20)
	-1/2		-1/2	858.253(8)	975.597(15)
	-3/2		-1/2		999.075(10)
	-1/2		-3/2	695.640(8)	
	-3/2		-3/2	719.941(2)	735.557(8)
1/2	1/2	3/2	1/2	503.002(5)	409.844(10)
	-1/2		-1/2	523.643(8)	
3/2	-1/2	1/2	-1/2	479.855(10)	386.110(15)
1/2	1/2	5/2	1/2	625.626(1)	602.749(1)
	-1/2		-1/2	695.639(1)	684.190(1)

simultaneously, comprising 2 rotational, 2 fine structure, 4 Λ-doubling, 7 hyperfine, and 8 Zeeman parameters. The experimental data used in addition to the present ones are as follows: new accurate microwave rotational transitions below 500 GHz (10),[1] radiofrequency Λ-doubling transitions (8), combination differences from high-resolution Fourier spectra (11), laser magnetic resonance frequencies (12), low-field Zeeman data for the $^2\Pi_{1/2}$, $J = \frac{1}{2}-\frac{3}{2}$ transition (13), electron paramagnetic resonance data for the $^2\Pi_{3/2}$, $J = \frac{3}{2}$, $\frac{5}{2}$ sublevels (14), and some new mm wave rotational lines ($J = 15/2 \rightarrow 17/2$, $J = 17/2 \rightarrow 19/2$, $J = 19/2 \rightarrow 21/2$) (15). The weighted rms error of the fit was 1.61, which indicates that the differences between observed and computed frequencies on an average are 1.61 times the estimated measurement errors. This figure seems satisfactory in view of the various different types of data fitted simultaneously.

Except for A_D and γ the present investigation yields no essential new informa-

[1] Frequencies for the following rotational transitions were used: $J = \frac{3}{2}-\frac{5}{2}$, $\frac{5}{2}-\frac{7}{2}$, and $\frac{7}{2}-\frac{9}{2}$ for both substates, and $\frac{1}{2}-\frac{3}{2}$ for the $^2\Pi_{1/2}$ substate. The measurement errors range from 0.02 to 0.05 MHz.

tion on the zero-field parameters; hence, their fitted values will not be reproduced here.

4.2. g Factors

Fitted values of the g factors $g_{l,\text{eff}}$, g_s, and $g_I(1 - \sigma_{\text{av}})$ are given in Table III. The combination of the present $^2\Pi_{1/2}$ Zeeman data with those available for the $^2\Pi_{3/2}$ substate (14) enables an accurate simultaneous determination of the orbital as well as the electronic spin g factors. The $^2\Pi_{1/2}$, $J = \frac{1}{2}$ singular level in particular yields new and interesting information, since its Zeeman effect is in this case governed by the small quantity $g_{l,\text{eff}} - 1/2\, g_s$, the nuclear spin g factor and the second-order g factor g_A^*.

The theoretical (ab initio) value of g_s has been computed previously (16, 17), and the agreement with the experimental one is excellent. This good agreement can be fortuitous, but it might also indicate that the absolute uncertainty in the magnetic field measurements of Brown and Radford (14) on the $^2\Pi_{3/2}$ EPR spectrum is lower than that estimated by the investigators.

The theoretical (ab initio) value of g_l represents the deviation from unity due to the relativistic correction $-\langle T \rangle/mc^2$, the orbit–orbit part of Eq. (3), and the center-of-mass correction, Eq. (4). The computed values of these corrections are in the order mentioned above: -1.37×10^{-4}, -2.1×10^{-5}, and -1.3×10^{-6}. The latter two corrections have been calculated in the one-center approximation. The difference between the fitted value of $g_{l,\text{eff}}$ and the theoretical value of g_l, which is $6.5(2.0) \times 10^{-5}$, is now attributed to the second-order contribution to $g_{l,\text{eff}}$ in Eq. (5).

Table III also reveals an excellent agreement between the fitted value of $g_I(1 - \sigma_{\text{av}})$ and the unshielded (bare N-nucleus) value. Hence, the present Zeeman data do not yield a significant magnetic shielding contribution. This result agrees very well with the ab initio value for $g_I\sigma_{\text{av}} = 8.6 \times 10^{-8}$ (18), whereas the standard deviation of $g_I(1 - \sigma_{\text{av}})$ from the fit is 10^{-7}.

Table III shows the fitted values of the total rotational g factor g_R and of the "Λ-doubling" g factors g_B^* and g_A^*. The calculated nuclear contribution g_R^N to g_R is also listed, together with the electronic part g_R^e which is derived from Eq. (6).

From the fitted value of g_B^*, the value of g_R^e and the difference $g_{l,\text{eff}} - g_l$ (theor.), we can separate the contributions from the $^2\Sigma^+$, $^2\Sigma^-$, and $^2\Delta$ states to $g_{l,\text{eff}}$, g_R^e, and g_B^*. The results for g_R^e are shown in Table III. The dominant contribution stems rather unexpectedly from the $^2\Delta$ states, whereas the interaction with $^2\Sigma^-$ states only slightly outweighs that with $^2\Sigma^+$ states. Table III also gives ab initio values for the contribution to $g_R^e(^2\Sigma^+)$ from the $A\ ^2\Sigma^+$ state, and to $g_R^e(^2\Sigma^-)$ from the $G\ ^2\Sigma^-$ state (19). The disagreement with the present derived results indicates that g_R^e contains contributions from several $^2\Sigma^+$ and $^2\Sigma^-$ states. Hence, there is no unique perturbing state for the $^2\Pi$ ground state, and the pure precession model is obviously invalid. Accordingly, the explanation for the Λ-doubling of the $^2\Pi$ ground state is more complex than previously believed (20), since there are considerable contributions from $^2\Sigma^+$ states.

4.3. Separate Values of A_D and γ

Fitted values of the two remaining Zeeman parameters g_T and $(\chi_\parallel - \chi_\perp)$ are given in Table III. This table also lists the fitted value of A'_D. With the help of Eq. (14) separate values for Δg_s, γ, and the true centrifugal distortion constant

TABLE III

Molecular Parameters for the $^2\Pi$ Ground State ($v = 0$) in NO as Determined from the Present Fit, Derived Quantities, and Theoretical Calculations

Quantity	Experimental value[a]	Theoretical value
$g_{\ell,\text{eff}}$	0.999906(20)	0.999841[b]
g_s	2.002095(40)	2.002087[b]
$g_I(1-\sigma_{av})\times10^4$	2.1984(10)	2.19792(3)[c]
$g_R\times10^4$	1.459(30)	
$g_B^*\times10^4$	0.303(12)	
$g_A^*\times10^4$	35.8512(70)	
$g_T\times10^4$	-1.020(30)	
$(\chi_\parallel - \chi_\perp)$ $(10^{-31}$ J/T$^2)$	-54(47)	
A'_D (MHz)	5.4973(17)	
$g_R^N\times10^4$		-2.722
$g_R^e\times10^4$	-4.181(30)	
$g_R^e(^2\Sigma^+)\times10^4$	-1.059(50)	
$g_R^e(^2\Sigma^-)\times10^4$	-1.362(50)	
$g_R^e(^2\Delta)\times10^4$	-1.76(10)	
$g_R^e(^2\Sigma^+)\times10^4$		-0.14[d]
$g_R^e(^2\Sigma^-)\times10^4$		-0.52[d]
$\Delta g_s\times10^4$	24.01(70)	
γ(MHz)	-244.1(7.0)	
A_D(MHz)	-1.43(20)	-1.92(8)

[a] Numbers in parenthesis represent one standard deviation. The standard deviations in $g_{\ell,\text{eff}}$, g_s, g_R, g_A^*, and g_T resulting from the fit are as low as $4\cdot10^{-6}$, $7\cdot10^{-6}$, $1\cdot10^{-6}$, $2\cdot10^{-7}$, and $1\cdot10^{-6}$, respectively. Those given in the table have been enhanced to take account of the absolute uncertainties in the magnetic field measurements in the EPR spectrum (15), and in the present work.

[b] Theoretical (ab initio) values of g_ℓ and g_s. The two-electron, two-center integrals previously neglected in the computation of g_s (16, 17) have now been included. Their effect is to lower the g_s-value by $1.9\cdot10^{-5}$.

[c] Unshielded value of g_I.

[d] These values represent the ab initio contributions to $g_R^e(^2\Sigma^+)$ from the $A^2\Sigma^+$ state, and to $g_R^e(^2\Sigma^-)$ from the $C^2\Sigma^-$ state (19).

A_D in the spin–orbit coupling can be computed. The results are given in Table III. Although the correlation between g_T and Δg_s is not 100%, an attempt to obtain separate fitted values of A_D, γ, and Δg_s failed. A possible confusion between Δg_s and the susceptibility parameter $(\chi_\| - \chi_\perp)$ (3) is ruled out by the data on the $^2\Pi_{1/2}$ singular level.

The value obtained for A_D may now be compared with theoretical predictions. The dependence of the spin–orbit coupling constant A on the internuclear distance R is approximated by

$$A(R) = A_e + A_1(R - R_e)/R_e + A_2(R - R_e)^2/R_e^2, \tag{22}$$

where A_1 and A_2 are independent of R. Similarly, the spin–orbit coupling constant in the vibrational stave v is given by

$$A_v = A_e - \alpha_A(v + \tfrac{1}{2}) + \beta_A(v + \tfrac{1}{2})^2, \tag{23}$$

where α_A and β_A denote another set of constants. If A is assumed to depend linearly on R $(A_2 = 0)$ one has (21, 22)

$$A_D = \frac{2(A_{v+1} - A_v)D_{v=0}}{B_v - B_{v+1} + 6B_e^2/\omega_e} . \tag{24}$$

For NO in its $X\ ^2\Pi$ state, Eq. (24) yields $A_D = -3.00$ MHz. This value does not agree too well with the experimental value. Zaidi and Verma (23) have derived a better approximation for A_D that allows a nonlinear dependence of A on R, i.e., both the linear and quadratic terms in Eq. (22) are retained. A_D is then determined by A_1 and A_2, which can be expressed in the constants α_A and β_A. The full expression for A_D is rather complex and will not be reproduced here. Accurate values of α_A and β_A have recently been obtained from high-resolution Fourier spectroscopy (11): $\alpha_A = 0.23404(47)$ cm^{-1}, and $\beta_A = -5.11(21) \times 10^{-3}$ cm^{-1}. The theoretical prediction for A_D becomes A_D (theor.) $= -1.92(8)$ MHz, where the indicated uncertainty stems from the errors in α_A and β_A. So the theoretical value of A_D derived from the more sophisticated approximation is in good agreement with the experimental one (Table III). The difference is small enough to be accounted for by the approximate relation (Eq. (14)) used to derive the "experimental" value of A_D. The present results also show that the assumption of a linear dependence of A on R is not justified for the ground state of NO.

4.4. The Electronic Quadrupole Moment

The fitted value of the susceptibility parameter $(\chi_\| - \chi_\perp)$ given in Table III may at a first glance seem rather insignificant. However, $(\chi_\| - \chi_\perp)$ contains two different significant contributions of opposite sign, both of which have estimated numerical values which are considerably larger than $(\chi_\| - \chi_\perp)$ itself. From the experimental value of $(\chi_\| - \chi_\perp)$ and with the help of Eqs. (18) and (19) we can determine the electronic quadrupole moment $Q_\|^e = -26.8(3)$ (atomic units) $= -1.201(11) \times 10^{-38}$ C m^2. An ab initio value for $Q_\|^e$ based on an accurate CI calculation (18) gives $Q_\|^e$ (ab initio) $= -18.4$ (atomic units). The error limit given for the experimental electronic quadrupole moment might be too optimistic

in view of the approximations made to derive Eq. (18). However, in our opinion the agreement between the observed and theoretical values is encouraging.

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Note added in proof. A recent *ab initio* calculation of the first order spin-rotation coupling constant $\gamma^{(1)}$ of Eq. (13) by Dr. B. Grimeland justifies our neglect of this parameter. The *ab initio* value is $\gamma^{(1)} = 2.9$ MHz for the $^2\Pi$ ground state in NO.

REFERENCES

1. L. VESETH, *J. Mol. Spectrosc.* **59**, 51–62 (1976).
2. L. VESETH, *J. Mol. Spectrosc.* **63**, 180–192 (1976).
3. L. VESETH, *J. Mol. Spectrosc.* **77**, 195–201 (1979).
4. M. R. BAKER, C. H. ANDERSON, AND N. F. RAMSEY, *Phys. Rev.* **133**, A1533–A1536 (1964).
5. A. ABRAGAM AND J. H. VAN VLECK, *Phys. Rev.* **92**, 1448–1455 (1953).
6. J. M. BROWN, M. KAISE, C. M. L. KERR, AND D. J. MILTON, *Mol. Phys.* **36**, 553–582 (1978).
7. N. F. RAMSEY, "Molecular Beams," Oxford Univ. Press, Oxford, 1956.
8. W. L. MEERTS AND A. DYMANUS, *J. Mol. Spectrosc.* **44**, 320–346 (1972).
9. F. H. DE LEEUW AND A. DYMANUS, *J. Mol. Spectrosc.* **48**, 427–445 (1973).
10. H. M. PICKETT, E. A. COHEN, J. W. WATERS, AND T. G. PHILLIPS, Thirty-Fourth Symposium on Molecular Spectroscopy, Columbus, Ohio, 1979; and private communication.
11. C. AMIOT, R. BACIS, AND G. GUELACHVILI, *Canad. J. Phys.* **56**, 251–265 (1978).
12. M. MIZUSHIMA, K. M. EVENSON, AND J. S. WELLS, *Phys. Rev. A* **5**, 2276–2287 (1972).
13. M. MIZUSHIMA, J. T. COX, AND W. GORDY, *Phys. Rev.* **98**, 1034–1038 (1955).
14. R. L. BROWN AND H. E. RADFORD, *Phys. Rev.* **147**, 6–12 (1966).
15. E. VAN DEN HEUVEL, W. L. MEERTS, AND A. DYMANUS, *J. Mol. Spectrosc.*, in press.
16. L. VESETH, *J. Mol. Spectrosc.* **66**, 259–271 (1977).
17. H. CHRISTENSEN AND L. VESETH, *J. Mol. Spectrosc.* **72**, 438–444 (1978).
18. S. GREEN, *Chem. Phys. Lett.* **23**, 115–119 (1973).
19. R. K. HINKLEY, J. A. HALL, T. E. H. WALKER, AND W. G. RICHARDS, *J. Phys. B* **5**, 204–212 (1972).
20. A. LOFTHUS AND E. MIESCHER, *Canad. J. Phys.* **42**, 848–859 (1964).
21. T. C. JAMES, *J. Chem. Phys.* **41**, 631–641 (1964).
22. L. VESETH, *J. Phys. B* **3**, 1677–1691 (1970).
23. H. R. ZAIDI AND R. D. VERMA, *Canad. J. Phys.* **53**, 420–423 (1975).