

HYPERFINE STRUCTURE, ELECTRIC AND MAGNETIC PROPERTIES OF $^{14}\text{N}_2\ ^{16}\text{O}$ IN THE GROUND AND FIRST EXCITED BENDING VIBRATIONAL STATE

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The molecular beam electric resonance method has been used to obtain the components of the electric quadrupole coupling tensor (eQq_{zz}), of the electric dipole moment along the molecular axis (μ_{el}), the spin-rotation constant (c_{\perp}) and the molecular g -factor perpendicular to the molecular axis (g_{\perp}), and the anisotropy in the magnetic susceptibility ($\chi_{\parallel} - \chi_{\perp}$) for the ground vibrational state of nitrous oxide ($^{14}\text{N}\ ^{14}\text{N}\ ^{16}\text{O}$). The same quantities, except $\chi_{\parallel} - \chi_{\perp}$, have also been determined for the (01^10) excited vibrational state. For this state the l -doubling constants q_{v_2} and μ_{v_2} , perpendicular anisotropy ($eQq_{xx} - eQq_{yy}$) in nuclear quadrupole tensor, the anisotropy ($c_{\parallel} - c_{\perp}$) in the spin-rotation constant, and the molecular g -factor (g_{\parallel}) parallel to the molecular axis have been obtained.

1. Introduction

In the early days of the molecular-beam electric-resonance (MBER) method many high temperature diatomic molecules have been investigated [1,2]. Most of these molecules contained an alkali atom which made them accessible for the detection with a hot wire detector. A logical step in the continuation of these experiments is the study of linear triatomic molecules also containing an alkali atom. The only molecule of this type investigated using the MBER method is the LiOH molecule [3]. Two other obvious candidates are KOH and KCN. Several attempts, both in our laboratory [4] as by other investigators [2] have been made in the past to study the KCN molecule with the MBER technique. Although MBER transitions in KCN were finally observed, the spectra consisted of many overlapping lines which could not be resolved. This is explained by the fact that at the temperatures necessary to produce a beam of KCN molecules (about 1000 K) many vibrational and rotational states were populated, all of them contributing to the MBER spectrum. Similar problems are expected for KOH.

The present investigation was undertaken to obtain more insight in the spectra and properties of linear triatomic molecules using the high resolution MBER tech-

nique. The study is confined to stable triatomic gases at room temperature as the first step in the development of the MBER techniques for hot alkali hydroxides and cyanides. Nitrous oxide (N_2O) was chosen to start with because of its fairly complicated spectrum due to two quadrupole nuclei.

The hyperfine structure of the ground vibrational state of nitrous oxide has been determined by Casleton and Kukolich [5] using beam maser techniques, while the electric dipole moment in this state has been measured by Sharpen et al. [6]. Magnetic properties of $^{15}\text{N}_2\ ^{16}\text{O}$ also in the ground vibrational state have been reported by Flygare et al. [7] and by Bhattacharyya and Dailey [8]. The l -doubling constant q_{v_2} has been measured by Burrus and Gordy [9] but until now no accurate values for vibration-rotation constants μ_{v_2} and ΔH (see next section) and no values at all for hyperfine constants in the first excited bending vibration state of N_2O have been reported. This paper reports an MBER investigation which yielded accurate values of these constants and of the electric and magnetic properties of N_2O in the $v_2 = 0$ and $v_2 = 1$ state. In a forthcoming paper results will be reported for cyanogen chloride (CICN).

The spectra obtained presently for $^{14}\text{N}_2\text{O}$ in the ground vibrational state could be explained by the well

known theories for linear molecules in a $^1\Sigma$ state to within an experimental accuracy of 50–150 Hz. Extension of this theory was necessary for the interpretation of the observed spectra of excited bending vibrational states. The relevant matrix elements for the rotational energy, l -doubling and hyperfine structure contributions are presented. A discussion is given of the molecular properties derived, the molecular quadrupole moment, the sign of the electric dipole moment and anisotropy effects in the hyperfine structure. From the present results on the $^{14}\text{N}_2^{16}\text{O}$ isotope and the nuclear magnetic shielding of the nitrogen nuclei in $^{15}\text{N}_2^{16}\text{O}$ obtained by Bhattacharyya and Dailey [8], a prediction has been made for the diamagnetic contributions which can serve as a test of theoretical calculations.

2. Theory

Formally the hamiltonian used for the interpretation of MBER spectra of linear triatomic molecules may be written as

$$H = H_0 + H_{\text{VR}} + H_{\text{HF}} + H_E + H_B, \quad (1)$$

where H_0 represents the non-relativistic hamiltonian for the electronic energies in the Born–Oppenheimer approximation including the pure vibrational energy contributions. The term H_{VR} stands for the contributions due to rotation and vibration–rotation interaction. The remaining terms in eq. (1) represent the nuclear hyperfine energy (H_{HF}) and the interaction energy of the molecule in an external electric (H_E) and magnetic (H_B) field, respectively.

The electronic–vibrational hamiltonian H_0 is not relevant for the present investigation. The structure of the vibration–rotation hamiltonian H_{VR} and of its effect on the molecular energy levels is discussed by Nielsen and in various textbooks (see e.g. refs. [10, 11, 12]). In its simplest form H_{VR} contains terms due to rotation of the nuclear frame, and the interaction between rotation and the degenerate bending vibration. This interaction is responsible for the well known l -doubling of rotational energy levels in excited states of the bending vibration ($v_2 \neq 0$). The two levels of an l -doubling possess opposite (\pm) symmetry under reflection in a plane containing the molecular axis. The symmetrized wavefunctions of the l -doublet levels can

be written as a linear combination

$$|v_2^l J M_J \pm\rangle = 2^{-1/2} \{ |v_2 l\rangle |J l M_J\rangle \pm (-)^J |v_2 - l\rangle |J - l M_J\rangle \}, \quad (2)$$

where $|J \pm l M_J\rangle$ and $|v_2 \pm l\rangle \equiv |v_1 v_2^l v_3\rangle$ is the rotational and vibrational wavefunction, respectively. The quantum numbers v_1 , v_2 and v_3 indicate the three normal vibrational modes of a linear triatomic molecule. The constraints on l are: $l = v_2, v_2 - 2, v_2 - 4, \dots, 0$ or 1 and $l < J$. In eq. (2) and elsewhere in this paper l stands for $|l|$. The short-hand notation for the vibrational wavefunction $|v_2 l\rangle$ is appropriate to the (present) case when only the bending vibration is excited. The rotational wavefunction is related to the symmetric top functions [13] by

$$|J \pm l M_J\rangle = [(2J+1)/8\pi^2]^{1/2} \mathcal{D}_{\pm l M_J}^{(J)}(\alpha\beta\gamma), \quad (3)$$

where J , M_J and l is the quantum number of the total angular momentum and of its component on the space-fixed z axis and on the molecular axis, respectively.

If we neglect centrifugal distortion effects on the l -doubling then the contribution of H_{VR} to the energy of a $|v_2^l J M_J\rangle$ state is:

$$\begin{aligned} \langle v_2^l J M_J \pm | H_{\text{VR}} | v_2^l J M_J \pm \rangle \\ = A [J(J+1) - l^2] + D [J(J+1) - l^2]^2 \\ \pm \frac{1}{4} \delta_{l1} (v_2 + 1) q_{v_2 J} J(J+1), \end{aligned} \quad (4)$$

where A is the rotational constant, D the centrifugal distortion constant and $q_{v_2 J}$ the l -doubling constant [12]. The distortional effects in $q_{v_2 J}$ are, as usual, taken into account in a phenomenological way [14]

$$q_{v_2 J} = q_{v_2} - \mu_{v_2} J(J+1) + \Delta H J^2 (J+1)^2, \quad (5)$$

where q_{v_2} is the l -doubling constant in the vibrational state v_1, v_2, v_3 .

The contributions to the hyperfine structure for a molecule in a singlet electronic state can be written in tensor operator form as

$$\begin{aligned} H_{\text{HF}} = \sum_K \mathbf{O}_K \cdot \mathbf{V}_K + \sum_K \mathbf{I}_K \cdot \mathbf{M}_K \cdot \mathbf{J} \\ + \sum_{L>K} \mathbf{I}_K \cdot \mathbf{D}_{KL} \cdot \mathbf{I}_L. \end{aligned} \quad (6)$$

The first term represents the interaction of the nuclear

quadrupole moment with the gradient of the electric field at the position of the K th nucleus; the second term is the spin-rotation interaction and the third the interaction between nuclear spins; \mathbf{M}_K and \mathbf{D}_{KL} are the nuclear spin-rotation and spin-spin interaction tensor, respectively; the summation runs over all nuclei with $I \geq 1$ in the first term and with $I \geq 1/2$ in the remaining two terms.

Energy contributions from external fields are deduced from

$$\begin{aligned} H_E + H_B \\ = -\mu_{\text{el}} \cdot E - \frac{1}{2} E \cdot \alpha \cdot E - B \cdot G \cdot J - \frac{1}{2} B \cdot \chi \cdot B \\ - \sum_K (\mu_K / I_K) I_K \cdot (1 - \sigma_K) \cdot B - \mu_{\text{el}} \cdot \mathbf{v} \times B. \quad (7) \end{aligned}$$

The terms of hamiltonian (7) describe in this order Stark effect, electric polarizability molecular Zeeman effect, magnetic susceptibility, nuclear Zeeman effect and translational Stark effect. In eq. (7) the usual symbols are used for the electric dipole moment (μ_{el}), the electric polarizability tensor (α), the magnetic rotational tensor (\mathbf{G}), the magnetic susceptibility tensor (χ), the magnetic shielding tensor (σ_K), the velocity (\mathbf{v}) of the molecules, the electric (magnetic) field $E(B)$ and μ_K the magnetic moment of the K th nucleus with spin I_K .

Spherical tensor operator techniques [13] have been applied to calculate the matrix elements of the hamiltonian of eq. (6) and (7) using basis wavefunctions appropriate for the coupling scheme:

$$I_1 + J = F_1, \quad F_1 + I_2 = F,$$

where I_K is the spin operator of the K th nitrogen nucleus. For the vibration-rotation part of the basis functions the wavefunctions (2) have been used. The matrix elements containing contributions characteristic of the $v_2 = 1$ state are given in the appendix. The results for the $v_2 = 0$ state can readily be obtained by substituting $l = 0$ in the expressions for the matrix elements for the $v_2 = 1$ state. The missing matrix elements of Stark effect (H_E) are standard. A complete set of matrix elements is given in ref. [4]. In most cases it was sufficient to consider only matrix elements diagonal in J . However, off-diagonal elements in J yield non-negligible contributions to the energies of the electric quadrupole interaction and the Stark effect for $v_2 = 0$. In the last case there is no first order effect.

For the definitions of the cartesian tensor components we refer to de Leeuw and Dymanus [15].

3. Measurements and results

The molecular beam spectrometer used in this work has been described previously [15]. A supersonic nozzle beam source was used, the beam intensity was monitored at the parent ion peak $m/e = 44$.

The spectra of N_2O in the ground vibrational state were observed both in electric and in combined electric and magnetic fields. The spectra in the first excited state of the bending vibration were studied without the application of external fields as well as in electric and magnetic fields. The full linewidth at half maximum was 2.5 kHz for all observed transitions.

Theoretical expressions for the energies and for the transition frequencies in terms of the coupling constants have been obtained by diagonalization of the energy matrix. A least-squares minimizing procedure was performed to determine the coupling constants. Accuracies of all results reported in this paper are given with at least 95% confidence according to the confidence level tables of Fisher and Yates [16]. The physical constants as given by Cohen et al. [17] have been used in the evaluation of the results.

3.1. Nitrous oxide in the ground vibrational state

The $\Delta J = 0$, $\Delta M_J = 0, \pm 1$ transitions were observed in an electric field of 2357.19(10) V/cm. Two highly stable voltage power supplies (Fluke 332A and Fluke 335A) were connected in series in order to obtain the high field strength. The electric field strength was calibrated by observing the $\Delta J = 0$, $\Delta M_J = \pm 1$ Stark transition in $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ using the value for the electric dipole moment of OCS of 0.71519(3) D [18,19] and the anisotropy in the electric polarizability $\alpha_{\parallel} - \alpha_{\perp} = 4.67(16) \text{ \AA}^3$ [6].

The hyperfine energy level diagram with the observed transitions is shown in fig. 1. In total twenty transitions were used to determine the molecular constants (μ_{el} , $eQ_1q_{zz}^{(1)}$, $eQ_2q_{zz}^{(2)}$, $c_1^{(1)}$, $c_1^{(2)}$) given in table 1. In the least-squares fit the spin-spin coupling constant d_T was fixed at the value of 0.436 kHz calculated from the geometry of the molecule.

The Stark-Zeeman spectra were observed in an

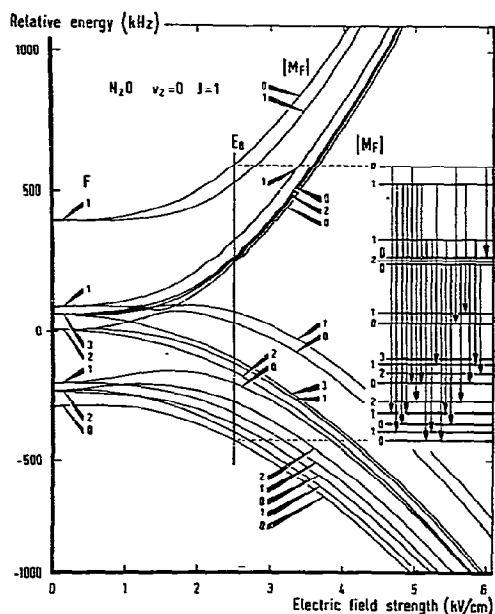


Fig. 1. Energy level diagram of N_2O ($v_2 = 0, J = 1$) in electric fields and observed transitions at 2357 V/cm.

electric field of 2357.19 V/cm parallel to a magnetic field of about 8.7 kG. The magnetic field was calibrated using the Zeeman splitting in the $\Delta J = 0, \Delta M_J = \pm 1$

transition of $J = 1$ in OCS [18]. The magnetic coupling constants ($g_{\parallel}, \chi_{\parallel} - \chi_{\perp}, \sigma_{\parallel}^{(1)} - \sigma_{\perp}^{(1)}, \sigma_{\parallel}^{(2)} - \sigma_{\perp}^{(2)}$) obtained for N_2O from seven observed Stark-Zeeman transitions are given in table 1. For the evaluation of the magnetic constants the hyperfine constants and electric dipole moment of table 1 have been accepted and were not further adjusted in the fit. The errors in the magnetic constants are determined both by the uncertainties in the magnetic field and the measured frequencies. In the evaluation of the present value of μ_{el} a value of $3.222(46) \text{ \AA}^3$ [6] for $\alpha_{\parallel} - \alpha_{\perp}$ of N_2O has been used.

3.2. Nitrous oxide in the first excited state of the bending vibration

Measurements have been performed on the $\Delta J = 0, \Delta F = 0, \pm 1$ l-doubling transitions of the three lowest rotational states. About hundred different transitions have been observed (table 2). Unless stated otherwise experimental errors in the transition frequencies are 150 Hz. The large vibrational effects on the electric quadrupole coupling constants made the initial interpretation of the spectrum very difficult. Information about the focusing properties provided by Stark energy plots (fig. 2 for $J = 1$) was of crucial importance in assigning the spectrum. Assuming a certain ordering of hyperfine levels it can readily be decided from the figure

Table 1

Hyperfine constants ^{a)}, electric dipole moment and magnetic constants of $^{14}\text{N}_2^{16}\text{O}$ in the (000) vibrational state

	This work	Other observations
$\mu_{\text{el}}(\text{D})$	0.160880(23)	0.160844(16) ^{b)}
$eQ_1q_{zz}^{(1)}$ (kHz)	-773.76(27)	-776.7(10) ^{c)}
$eQ_2q_{zz}^{(2)}$ (kHz)	-267.58(38)	-269.4(18) ^{c)}
$c_{\perp}^{(1)}$ (kHz)	1.829(65)	2.35(20) ^{c)}
$c_{\perp}^{(2)}$ (kHz)	3.06(12)	2.90(26) ^{c)}
ε_{\perp}	-0.07887(8)	-0.07606(10) ^{d)}
$\chi_{\parallel} - \chi_{\perp}$ (10^{-6} erg/G ² mole)	-10.43(6)	-10.10(15) ^{d)}
$\sigma_{\parallel}^{(1)} - \sigma_{\perp}^{(1)}$ (ppm)	322(400)	376(12) ^{e)}
$\sigma_{\parallel}^{(2)} - \sigma_{\perp}^{(2)}$ (ppm)	458(300)	508(10) ^{e)}

^{a)} The subscript or superscript 1(2) on the constants refers to the outer (inner) N-nucleus.

^{b)} Electric dipole moment of Sharpen et al. [6] has been corrected for the presently used value of Planck's constant [17].

^{c)} Results of Casleton and Kukulich [5].

^{d)} Results of Flygare et al. [7] on $^{15}\text{N}_2^{16}\text{O}$.

^{e)} Bhattacharyya and Dailey [8] from measurements on $^{15}\text{N}_2^{16}\text{O}$.

Table 2

Observed and calculated transition frequencies (in kHz) of $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ in the (01^10) state for $J = 1, 2$ and 3 in zero external fields

J	$F \rightarrow F'$	Observed	Obs.-calc.	J	F	F'	Observed	Obs.-calc.
1	1 2	47279.65	0.07	2	2 2		142536.45	-0.03
	1 1	47293.75	0.01		1 1		142540.66	-0.02
	3 2	47314.72	-0.07		3 3		142553.97	-0.31
	2 2	47341.12	-0.02		2 1		142563.09	0.07
	2 1	47355.27	-0.04		0 1		142572.37	-0.03
	1 0	47385.77(20)	-0.04		2 3		142586.22(100)	-0.02
	1 2	47402.01	0.09		4 3		142588.88(100)	-0.26
	2 2	47413.56	0.12		2 3		142620.02(100)	-0.75
	1 1	47416.16	0.08		1 1		142660.96	0.05
	2 1	47427.62	0.02		2 3		142683.33(100)	0.07
	1 2	47448.13	-0.04		1 2		142693.48	-0.09
	0 1	47453.26	0.09		2 2		142715.74	-0.17
	3 2	47483.37	-0.01	3	3 3		284562.04	0.07
	1 1	47488.11	0.03		2 1		284597.61	0.09
	3 3	47500.29	0.01		4 3		284612.89	0.02
	2 2	47509.70	-0.03		3 2		284626.78	-0.02
	2 3	47526.36	-0.27		2 3		284650.71	-0.05
	2 1	47549.65	0.01		4 5		284654.58(150)	-0.02
	1 2	47570.56	0.05		3 4		284679.94	-0.01
	2 2	47582.11	0.08		4 4		284730.92	0.08
	2 3	47599.05	0.12		3 4		284789.02(150)	-0.10
	1 1	47610.53	0.11		2 2		284835.82	0.05
	0 1	47647.65	0.14		4 4		284840.15(100)	0.14
	1 1	47739.57	0.06		3 3		284854.77	0.05
2 1	47801.26	0.19	4 5		284881.20(100)	-0.53		
1 1	47862.04	0.19	2 3		284902.67(50)	-0.10		
2 1	47873.46	0.09	4 3		284905.44(50)	-0.17		
0 1	47899.03	0.09	2 1		284915.02	0.05		
2	2 2	142215.11(100)	0.12	2 3		284927.57	0.09	
	3 2	142238.18	0.06	3 3		284935.91	-0.11	
	1 2	142267.50	-0.02	5 5		284941.92	-0.06	
	3 4	142275.59	0.01	4 4		284957.89(150)	-0.08	
	2 3	142299.38	0.10	1 1		284972.17	0.10	
	3 3	142322.44	0.02	3 3		284979.35	0.04	
	2 3	142361.86(100)	0.09	2 2		284992.30	0.00	
	1 1	142382.08	0.00	3 4		285013.16	-0.10	
	3 3	142384.95	0.04	5 4		285018.12(150)	-0.10	
	2 2	142394.43	0.01	3 2		285044.26	0.13	
	3 2	142417.50	-0.05	3 4		285121.05(100)	-1.38	
	3 2	142439.86(100)	0.14	5 4		285127.30	-0.09	
	3 4	142444.91	-0.04	4 3		285132.76	0.02	
	2 2	142471.63	-0.04	2 2		285153.22	-0.01	
	4 4	142479.72	-0.09	3 3		285188.04	0.01	
	3 3	142491.72	-0.07	3 4		285206.48(150)	0.02	
	1 2	142514.10	-0.04	1 2		285210.37	0.04	
	2 3	142523.71	-0.04	2 3		285220.28	0.06	
	4 3	142526.67(100)	0.03	3 3		285271.77	-0.29	

which states can be focused and which not. The repulsion of states within the same M_F influenced effectivity of the state selection by the electric quadrupole

field (A- and B-fields). Knowing which of the allowed electric dipole transitions obey the selection rules for the MBER machine (only transitions from a focused

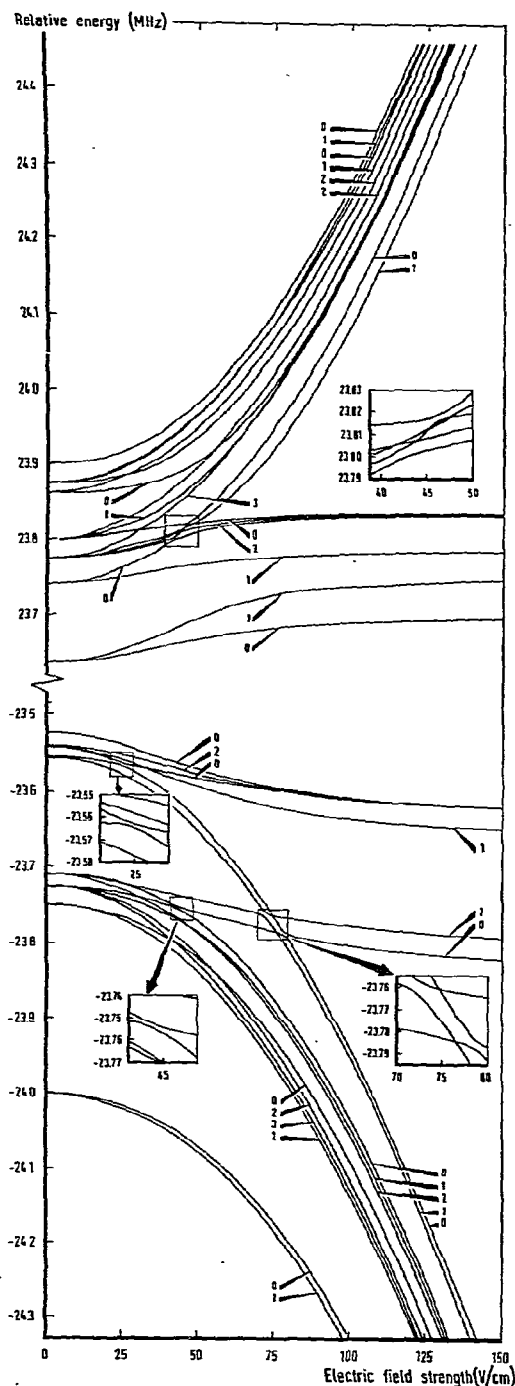


Fig. 2. Energy level diagram of the $\nu_2 = 1, J = 1$ l -doublet of N_2O . The energy levels are labeled with their M_F -values.

Table 3

Molecular constants ^{a)} of $^{14}\text{N}_2^{16}\text{O}$ in the (01^10) state. All values are in kHz except μ_{el} (in D) and the g -factors

Constant	This work
$q\nu_2$	23743.75(1) ^{b)}
$\mu\nu_2$	0.032(1)
$eQ_1q_{zz}^{(1)}$	-886.53(12)
$eQ_1(q_{xx}^{(1)} - q_{yy}^{(1)})$	318.78(14)
$eQ_2q_{zz}^{(2)}$	-258.14(18)
$eQ_2(q_{xx}^{(2)} - q_{yy}^{(2)})$	-60.84(18)
$c_{\perp}^{(1)}$	1.904(15)
$c_{\parallel}^{(1)} - c_{\perp}^{(1)}$	-1.78(7)
$c_{\perp}^{(2)}$	2.60(2)
$c_{\parallel}^{(2)} - c_{\perp}^{(2)}$	1.2(1)
μ_{el}	0.173484(9)
$g_{\perp} + g_{\parallel}$	-0.031(8)
g_{\parallel}	0.048(8) ^{c)}

a) The sub- and superscript 1 (2) on the constants refers to the outer (inner) N-nucleus.

b) Burrus and Gordy [9] measured a value of 23.736 MHz for

c) Assuming g_{\perp} of the (01^10) state equal to g_{\perp} of the (000) state within the experimental error.

to a defocused state are observable) was essential for the interpretation of the spectrum. Table 3 presents the hyperfine and l -doubling constants adjusted in the least-squares fit of the transitions from table 2. The spin-spin constant d_T has again been fixed at the calculated value of 0.436 kHz. The adjustment of $d_{xx} - d_{yy}$ and/or $c_{xx}^{(K)} - c_{yy}^{(K)}$ for $K = 1$ and 2 gave no significant improvement of the fits and these constants were set equal to zero.

The electric dipole moment was deduced from a measurement of nine $\Delta M_F = 0$ transitions in the $J = 1$ state at an electric field of 300 V/cm. The corresponding Stark shifts were about 7 MHz. The value of the electric dipole moment obtained from these lines is given in table 3.

At high magnetic fields (about 8 kG) the Zeeman spectra of N_2O in the (01^10) state were so complicated and rich in mostly overlapping lines that no unique identification could be made. In order to obtain the g -factors we decided to observe the Zeeman spectrum at a low magnetic field, at which the overlap was less severe. The Zeeman shifts of the $J = 1, F = 2 \rightarrow 1$ tran-

sition, in zero fields occurring at 47801.26 kHz, were observed in a field of 93.7 G. The magnetic field was calibrated using the $J=0, M_J=1 \rightarrow 0$ transition of the 1_{11} state of SO_2 [20]. The effective molecular g -factor for the $J=1, F=2 \rightarrow 1$ transition in N_2O was $\frac{1}{2}(g_{\perp} + g_{\parallel})$ and was found to be $-0.0155(42)$. Within the experimental error it is reasonable to assume g_{\perp} to be the same in the (000) and (01¹0) states. This assumption is supported by the results obtained previously for the OCS molecule [18,21]. The values for $(g_{\perp} + g_{\parallel})$ and g_{\parallel} are also given in table 3. The effects of the anisotropy in the g -factors ($g_{xx} - g_{yy}$) were too small to be observed at the low magnetic field.

4. Discussion

As can be seen from table 1 there is for the (000) state in general a reasonably good agreement between the molecular constants obtained in the present investigation with those of previous work whenever available. It should be noted that Casleton and Kukulich [5] determined the two quadrupole ($eQ_K q_{2z}^{(K)}$) and the two spin-rotation ($c_1^{(K)}$) constants from seven observed $J=1 \rightarrow 0$ transitions yielding in the table 1 reported 40% confidence intervals. In order to obtain 95% confidence intervals for the constants of reference [5] the errors have to be multiplied by a factor 4.5. The results of Casleton and Kukulich agree then very well with our more accurate values.

Various molecular properties can be deduced from the magnetic constants [1]. Of greatest interest here is the molecular quadrupole moment θ_{\parallel} which is obtained from g_{\perp} and $\chi_{\parallel} - \chi_{\perp}$ in a linear molecule using the relation

$$\theta_{\parallel} = -\frac{4m}{e}(\chi_{\parallel} - \chi_{\perp}) + \frac{h\mu_{\text{N}} g_{\perp}}{2\pi A} + me \sum_K \frac{Z_K r_K^2}{m_K}. \quad (8)$$

Herein m and e is the electron mass and proton charge, respectively, m_K is the mass and $Z_K e$ the charge of the K th nucleus in the molecule, r_K is the length of the position vector to the K th nucleus from the molecular center of mass, h is Planck's constant and μ_{N} the nuclear magneton. The last term of eq. (8), although small (0.026×10^{-26} esu cm^2) compared to the difference of the two other terms is not negligible in view of the high accuracy of the present measurements. Using the magnetic constants from table 1 and inter-

nuclear separations $r(\text{N}-\text{N}) = 1.126 \text{ \AA}$ and $r(\text{N}-\text{O}) = 1.191 \text{ \AA}$ [12] the value obtained for θ_{\parallel} is $\theta_{\parallel} = -3.296(15) \times 10^{-26}$ esu cm^2 . This value can be compared with the value of $-3.65(25) \times 10^{-26}$ esu cm^2 for θ_{\parallel} of $^{15}\text{N}_2^{16}\text{O}$ as determined by Flygare et al. [7] and the LCAO MO value of -3.69×10^{-26} esu cm^2 calculated by McLean and Yoshimine (eq. (24) of ref. [22]).

As shown by Townes et al. [23] the sign of the electric dipole moment can be obtained from the isotopic dependence of the molecular g -factor.

$$\frac{h\mu_{\text{N}}}{2\pi} \left[\frac{g_{\perp}^{(2)}}{A^{(2)}} - \frac{g_{\perp}^{(1)}}{A^{(1)}} \right] = -2\mu_{\text{el}} \cdot d. \quad (9)$$

Here $g_{\perp}^{(i)}$ and $A^{(i)}$ ($i=1, 2$) is the g_{\perp} -factor and rotational constant, respectively, of the isotopic species i ; d represents the displacement vector of the center of mass of isotope 2 referred to the center of mass of isotope 1. Eq. (9) is deduced assuming the Born-Oppenheimer approximation to be valid i.e. the internuclear distances and the electric structure are supposed to be the same for both isotopes. The presently obtained value for the g_{\perp} -factor for $^{14}\text{N}_2^{16}\text{O}$ (isotope 1) was combined with the value found by Flygare et al. [7] for $^{15}\text{N}_2^{16}\text{O}$ (isotope 2). The result $\mu_{\text{el}} = -0.52(45)$ D corresponds to a $^-\text{NNO}^+$ polarity of the electronic charge distribution. Although the value for μ_{el} obtained from Stark measurements $|\mu_{\text{el}}| = 0.16$ is not in disagreement with the above value the sign of the electric dipole moment is not yet well determined. This conclusion is based on the fact that (a) the sign determined above is opposite to the calculated sign [24,25], (b) the error in μ_{el} as determined with eq. (9) is about 90% and (c) the values for g_{\perp} originate from different experiments. A similar situation was recently discussed by Fabricant and Muentzer [26] for ClF.

The paramagnetic shielding anisotropy ($\sigma_{\parallel}^{(K)} - \sigma_{\perp}^{(K)}$)^p can be deduced from the electronic contribution to the spin-rotation constant ($c_1^{(K)}$)^e [1,15]:

$$(2\mu_{\text{N}} g_K A / \mu_B) (\sigma_{\parallel}^{(K)} - \sigma_{\perp}^{(K)})^{\text{p}} = (c_1^{(K)})^{\text{e}}. \quad (10)$$

The electronic contribution to the spin-rotation constant is calculated from the observed spin-rotation constant $c_1^{(K)}$ and the calculated value of the nuclear part $(c_1^{(K)})^{\text{n}} (c_1^{(K)}) = (c_1^{(K)})^{\text{e}} + (c_1^{(K)})^{\text{n}}$. In the rigid-rotor approximation holds:

$$(c_{\perp}^{(K)})^r = (-e\mu_0\mu_{\text{N}}g_K A/h) \times \sum_{L \neq K} \frac{Z_L}{r_{LK}^3} [r_{LK}^2 - \frac{1}{2}(x_{LK}^2 + y_{LK}^2)], \quad (11)$$

where $r_{LK} = |r_L - r_K|$, $x_{LK} = x_L - x_K$ and $y_{LK} = y_L - y_K$, while x_L (y_L) is the x -(y -) component of the position vector r_L of the L th nucleus. In a linear molecule x_{LK} and y_{LK} are zero. The nuclear contributions to the spin-rotation constants in N_2O is -0.752 kHz and -1.01 kHz for the outer and inner ^{14}N -nucleus, respectively. Herewith the calculated paramagnetic contributions to the anisotropies in the shieldings is (in ppm): outer N: $(\sigma_{\parallel} - \sigma_{\perp})^p = 561(36)$; inner N: $(\sigma_{\parallel} - \sigma_{\perp})^p = 707(47)$. The present value of $(\sigma_{\parallel} - \sigma_{\perp})^p$ for the outer N-nucleus is in disagreement with the value of $467(18)$ ppm reported by Casleton and Kukolich [5]. The difference is completely explained by the disagreements in the experimental value for the spin-rotation constant (table 1). The values for $(\sigma_{\parallel} - \sigma_{\perp})^p$ for the inner N-nucleus agree; Casleton and Kukolich found $737(22)$ ppm.

Using the accurate values of the total magnetic shielding constants σ_{\perp} and σ_{\parallel} as reported by Bhattacharyya and Dailey [8] for $^{15}\text{N}_2\text{O}$ and the present values for $(\sigma_{\parallel} - \sigma_{\perp})^p$ we find for the diamagnetic shielding anisotropy $(\sigma_{\parallel} - \sigma_{\perp})^d - 194(18)$ ppm and $-199(48)$ ppm for the outer and inner N-nucleus, respectively. At the moment there are no ab-initio calculations of diamagnetic contributions to the anisotropy in the nuclear shielding known to us. The present results may serve as a test for future calculations.

A discussion of the effects of the bending vibration on the electric dipole moments and nuclear electric quadrupole moments will be given in a separate paper comparing results from two other linear triatomic molecules, OCS and ClCN.

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Appendix: Non-vanishing matrix elements of hamiltonian of eqs. (7) and (8)

In order to reduce the number of matrix elements to be tabulated only those characteristic for the $v_2 = 1$ state and relevant for the present study are given. With

$$\langle \alpha | = \langle (I_1 J I) F_1 I_2 F M_F \pm |, \quad | \alpha' \rangle = | (I_1 J' I) F_1' I_2' F' M_F' \pm \rangle,$$

the matrix elements are

$$\begin{aligned} \langle \alpha | \sum_{K=1,2} \vec{Q}_K \cdot \vec{V}_K | \alpha' \rangle &= \delta(F_1', F_1) \delta(F', F) \delta(M_F', M_F) (-1)^{I_1+2J+F+1} \\ &\times \left[\frac{(2J+1)(2J'+1)(2I_1+3)(2I_1+2)(2I_1+1)}{2I_1(2I_1-1)} \right]^{1/2} \begin{Bmatrix} F_1 & J' & I_1 \\ 2 & I_1 & J \end{Bmatrix} \\ &\times \frac{1}{4} \left[\begin{pmatrix} J & 2 & J' \\ -1 & 0 & 1 \end{pmatrix} eQ_1 q_{zz}^{(1)} \pm 6^{-1/2} (-1)^J \begin{pmatrix} J & 2 & J' \\ -1 & 2 & -1 \end{pmatrix} eQ_1 (q_{xx}^{(1)} - q_{yy}^{(1)}) \right] \\ &+ \frac{1}{4} \delta(F', F) \delta(M_F', M_F) (-1)^{I_1+I_2+F_1+F_1'+F+J+J'+1} \\ &\times \left[\frac{(2J+1)(2J'+1)(2I_2+3)(2I_2+2)(2I_2+1)}{2I_2(2I_2-1)} \right]^{1/2} [(2F_1+1)(2F_1'+1)]^{1/2} \\ &\times \begin{Bmatrix} F_1' & I_2 & F \\ I_2 & F_1 & 2 \end{Bmatrix} \begin{Bmatrix} F_1 & 2 & F_1' \\ J' & I_1 & J \end{Bmatrix} \left[\begin{pmatrix} J & 2 & J' \\ -1 & 0 & 1 \end{pmatrix} eQ_2 q_{zz}^{(2)} \pm 6^{-1/2} (-1)^J \begin{pmatrix} J & 2 & J' \\ -1 & 2 & -1 \end{pmatrix} eQ_2 (q_{xx}^{(2)} - q_{yy}^{(2)}) \right], \end{aligned}$$

$$\begin{aligned}
 \langle \alpha | \sum_{K=1,2} I_K \cdot \mathbf{M}_K \cdot \mathbf{J} | \alpha' \rangle &= \frac{1}{2} \delta(F'_1, F_1) \delta(F', F) \delta(M'_F, M_F) [F_1(F_1 + 1) - I_1(I_1 + 1) - J(J + 1)] \\
 &\times \{c_{\perp}^{(1)} + [I^2/J(J + 1)](c_{\perp}^{(1)} - c_{\perp}^{(1)}) \pm \frac{1}{4}(-1)^J \delta_{I1}(c_{xx}^{(1)} - c_{yy}^{(1)})\} \\
 &+ \delta(F', F) \delta(M'_F, M_F) (-1)^{I_1+I_2+F_1+F_1'+F+J+1} \\
 &\times \begin{Bmatrix} F'_1 & I_2 & F \\ I_2 & F_1 & 1 \end{Bmatrix} \begin{Bmatrix} F_1 & 1 & F'_1 \\ J & I_1 & J \end{Bmatrix} [(2I_2 + 1)(I_2 + 1)I_2(2F_1 + 1)(2F'_1 + 1)(2J + 1)(J + 1)J]^{1/2} \\
 &\times \{c_{\perp}^{(2)} + [I^2/J(J + 1)](c_{\perp}^{(2)} - c_{\perp}^{(2)}) \pm \frac{1}{4}(-1)^J \delta_{I1}(c_{xx}^{(2)} - c_{yy}^{(2)})\},
 \end{aligned}$$

$$\begin{aligned}
 \langle \alpha | I_1 \cdot \mathbf{D}_{12} \cdot I_2 | \alpha' \rangle &= (30)^{1/2} \delta(F', F) \delta(M'_F, M_F) (-1)^{F_1+I_2+F+1} \\
 &\times [(2F_1 + 1)(2F'_1 + 1)I_1(I_1 + 1)(2I_1 + 1)I_2(I_2 + 1)(2I_2 + 1)]^{1/2} \left[\frac{J(J + 1)(2J + 1)}{(2J - 1)(2J + 3)} \right]^{1/2} \\
 &\times \begin{Bmatrix} F'_1 & I_2 & F \\ I_2 & F_1 & 1 \end{Bmatrix} \begin{Bmatrix} J & I_1 & F'_1 \\ J & I_1 & F'_1 \\ 2 & 1 & 1 \end{Bmatrix} \left[\frac{3I^2 - J(J + 1)}{J(J + 1)} d_T \pm \frac{1}{4}(-1)^J \delta_{I1}(d_{xx} - d_{yy}) \right],
 \end{aligned}$$

$$\begin{aligned}
 \langle \alpha | -\mathbf{B} \cdot \mathbf{G} \cdot \mathbf{J} | \alpha' \rangle &= \delta(M'_F, M_F) (-1)^{F-M_F} \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix} (-1)^{2F_1+I_1+I_2+F'+J+1} \\
 &\times [(2F + 1)(2F' + 1)(2F_1 + 1)(2F'_1 + 1)J(J + 1)(2J + 1)]^{1/2} \begin{Bmatrix} F & 1 & F' \\ F'_1 & I_2 & F_1 \end{Bmatrix} \begin{Bmatrix} F_1 & 1 & F'_1 \\ J & I_1 & J \end{Bmatrix} \\
 &\times \{g_{\perp} + [I^2/J(J + 1)](g_{\parallel} - g_{\perp}) \pm \frac{1}{4} \delta_{I1}(-1)^J(g_{xx} - g_{yy})\} B,
 \end{aligned}$$

$$\begin{aligned}
 \langle \alpha | -\frac{1}{2} \mathbf{B} \cdot \boldsymbol{\chi} \cdot \mathbf{B} | \alpha' \rangle &= \frac{1}{2} \chi_{av} B^2 + \delta(M'_F, M_F) (-1)^{F-M_F} \begin{pmatrix} F & 2 & F' \\ -M_F & 0 & M_F \end{pmatrix} (-1)^{2F_1+I_1+I_2+F'+J+1} \\
 &\times [(2F + 1)(2F' + 1)(2F_1 + 1)(2F'_1 + 1)]^{1/2} \left[\frac{J(J + 1)(2J + 1)}{(2J - 1)(2J + 3)} \right]^{1/2} \\
 &\times \begin{Bmatrix} F & 2 & F' \\ F'_1 & I_2 & F_1 \end{Bmatrix} \begin{Bmatrix} F_1 & 2 & F'_1 \\ J & I_1 & J \end{Bmatrix} \left[\frac{3I^2 - J(J + 1)}{3J(J + 1)} (\chi_{\parallel} - \chi_{\perp}) \pm \frac{1}{4} \delta_{I1}(-1)^J(\chi_{xx} - \chi_{yy}) \right] B^2,
 \end{aligned}$$

$$\begin{aligned}
 \langle \alpha | \sum_{K=1,2} (\mu_K / I_K) (1 - \sigma_K) \cdot \mathbf{B} | \alpha' \rangle &= \delta(M'_F, M_F) (-1)^{F-M_F} \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix} (-1)^{F_1+I_2+F'} \\
 &\times [(2F + 1)(2F' + 1)(2F_1 + 1)(2F'_1 + 1)]^{1/2} [(2I_1 + 1)(I_1 + 1)I_1]^{1/2} \\
 &\times \frac{\mu_1}{I_1} \begin{Bmatrix} F & 1 & F' \\ F'_1 & I_2 & F_1 \end{Bmatrix} \left[(-1)^{I_1+J+F_1+1} \begin{Bmatrix} I_1 & I_1 & 1 \\ F_1 & F'_1 & J \end{Bmatrix} (1 - \sigma_{av}^{(1)}) \right]
 \end{aligned}$$

$$\begin{aligned}
& + (30)^{1/2} \begin{pmatrix} I_1 & I_1 & 1 \\ J & J & 2 \\ F_1 & F_1' & 1 \end{pmatrix} \left[\frac{J(J+1)(2J+1)}{(2J-1)(2J+3)} \right]^{1/2} \left\{ \frac{3I^2 - J(J+1)}{3J(J+1)} (\sigma_{\parallel}^{(1)} - \sigma_{\perp}^{(1)}) \pm \frac{1}{4} \delta_{I1} (-1)^J (\sigma_{xx}^{(1)} - \sigma_{yy}^{(1)}) \right\} B \\
& + \delta(M_{F'}, M_F) (-1)^{F-M_F} \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix} (-1)^{F_1+I_1} \\
& \times [(2I_2+1)(I_2+1)I_2(2F+1)(2F'+1)(2F_1+1)(2F_1'+1)]^{1/2} \\
& \times \frac{\mu_2}{I_2} \left[(-1)^{I_1+I_2+2F_1+F} \frac{\delta(F_1', F_1)}{(2F_1+1)} \begin{pmatrix} F_1' & F & 1 \\ I_2 & I_2 & F_1 \end{pmatrix} (1 - \sigma_{av}^{(2)}) \right. \\
& + (30)^{1/2} \begin{pmatrix} F_1 & F_1' & 2 \\ I_2 & I_2 & 1 \\ F & F' & 1 \end{pmatrix} \begin{pmatrix} F_1 & 2 & F' \\ J & I_1 & J \end{pmatrix} \left[\frac{J(J+1)(2J+1)}{(2J-1)(2J+3)} \right]^{1/2} \\
& \left. \times \left\{ \frac{3I^2 - J(J+1)}{3J(J+1)} (\sigma_{\parallel}^{(2)} - \sigma_{\perp}^{(2)}) \pm \frac{1}{4} \delta_{I1} (-1)^J (\sigma_{xx}^{(2)} - \sigma_{yy}^{(2)}) \right\} \right] B.
\end{aligned}$$

Herein Q_K , the nuclear electric quadrupole moment is defined as

$$Q_K = (2\sqrt{6}/e) \langle I_K I_K | (Q_K)_0^{(2)} | I_K I_K \rangle,$$

with $K = 1$ and 2 for the outer and inner N-nucleus, respectively, in NNO;

$$q_{gg}^{(K)} = \partial^2 V_K / \partial g^2,$$

where $g = x, y, z$. The quantity $q^{(K)}$ represents the electric field gradient at the position of the K th nucleus. In all expressions the subscript \parallel and \perp refers to components parallel and perpendicular to the molecular axis, respectively.

The spin-rotation coupling constants are related to the components of the M tensor as:

$$c_{\parallel}^{(K)} = (M_K)_{zz}, \quad c_{\perp}^{(K)} = \frac{1}{2} [(M_K)_{xx} + (M_K)_{yy}].$$

The spin-spin coupling constant d_T is given by ($d_{gg} = (D_{12})_{gg}$):

$$d_T = \frac{1}{6} (d_{xx} + d_{yy} - 2d_{zz}) = -\frac{1}{2} d_{zz},$$

using $\sum_g (d_{gg}) = 0$.

For a diatomic molecule in its ground vibrational state $T_{xx} = T_{yy}$ for any tensor $T (= \alpha, D, M, \chi, G, \sigma)$ of rank two. This is no longer true for a linear triatomic molecule in an excited bending vibrational state, but in many cases $T_{xx} \approx T_{yy}$. Consequently $\frac{1}{2}(T_{xx} + T_{yy})$ can be interpreted as T_{\perp} .

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