Molecular g-Values, Magnetic Susceptibility Anisotropies, Molecular Quadrupole Moments and Second Moments of the Electron Charge Distribution in Ethyleneoxide and Pyridine Isotopes

An Attempt to Determine the Sign of the Electric Dipole Moment

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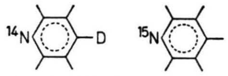
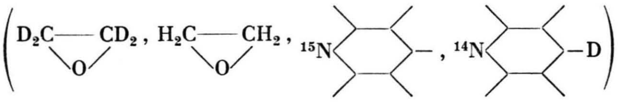
The high-field first and second order Zeeman effect has been observed in Ethyleneoxide

and Pyridine



in order to determine the sign of the electric dipole moments from the g-values of different isotopes. The experimental data indicate that in Ethyleneoxide the negative end is at the Oxygen while in Pyridine the result is not conclusive. The effect of vibrations is discussed in some detail and it is concluded that the vibrational dependance of the g-values should be accounted for if the sign of the dipole moment is determined from Zeeman data (at least if H ⟷ D substitutions are involved).

The rotational Zeeman effect of the most abundant species of Ethyleneoxide [1] and Pyridine [2] has been investigated previously. In the following we report the results of rotational Zeeman effect studies on several isotopic species.



They were carried out in an attempt to determine experimentally the sign of the electric dipole moment in both molecules.

The microwave spectrometer and the electromagnet used for these investigations has been described in a previous publication [3]. The samples were studied at pressures close to 10 mTorr and at temperatures about $-65\,^{\circ}\mathrm{C}$. Typical experimental linewidths were on the order of 150 to 300 kHz full width at half height. As an example Fig. 1 shows a broad band scan of the $5_{33} \to 5_{32}$ transition of ^{15}N-Piridine at a magnetic field strength of 24170 Gauß.

The Zeeman splittings of the rotational transitions were analyzed using the effective rotational Hamiltonian given in Equation (1). This Hamiltonian results from a second order perturbation treatment within the electronic states and under the assumption of a rigid nuclear frame [4].

$$\begin{aligned}
\mathcal{H}_{\text{eff}} = {} & h\,[A\,\mathbf{J}_a^2 + B\,\mathbf{J}_b^2 + C\,\mathbf{J}_c^2] && \text{(a)}\\
& - \mu_{\mathrm{N}}\, H_Z\,[\mathbf{\cos\,a\,Z}\, g_{aa}\,\mathbf{J}_a + \mathbf{\cos\,b\,Z}\, g_{bb}\,\mathbf{J}_b \\
& + \mathbf{\cos\,c\,Z}\, g_{cc}\,\mathbf{J}_c] && \text{(b)}\\
& - \tfrac{1}{2} H_Z^2\,[\mathbf{\cos^2 a\,Z}\,\chi_{aa} + \mathbf{\cos^2 b\,Z}\,\chi_{bb} \\
& + \mathbf{\cos^2 c\,Z}\,\chi_{cc}] && \text{(c)}\\
& - \mu_{\mathrm{N}} \sum_{i}^{\substack{\text{quadrupole}\\ \text{nuclei}}} g_i\,\boldsymbol{H}\cdot\boldsymbol{I}_i && \text{(d)}\\
& - \tfrac{1}{6} \sum_{i}^{\substack{\text{quadrupole}\\ \text{nuclei}}} \mathbf{Q}_i : \nabla\,\boldsymbol{E}_i && \text{(e)}\\
& - \boldsymbol{\mu}_{\mathrm{el}} \cdot (\boldsymbol{V}_0 \times \boldsymbol{H})/c && \text{(f)}
\end{aligned}$$

with $\mu_{\mathrm{N}} = |e|\,\hbar/2\,M_{\mathrm{p}}\,c$ the nuclear magneton.
Phaenomenologically spoken part (a) corresponds to the rotational kinetic energy with A, B and C the rotational constants and J_a, J_b and J_c the components of the rotational angular momentum in units of $\hbar$. Part (b) corresponds to the potential energy of the rotational magnetic moment in the exterior

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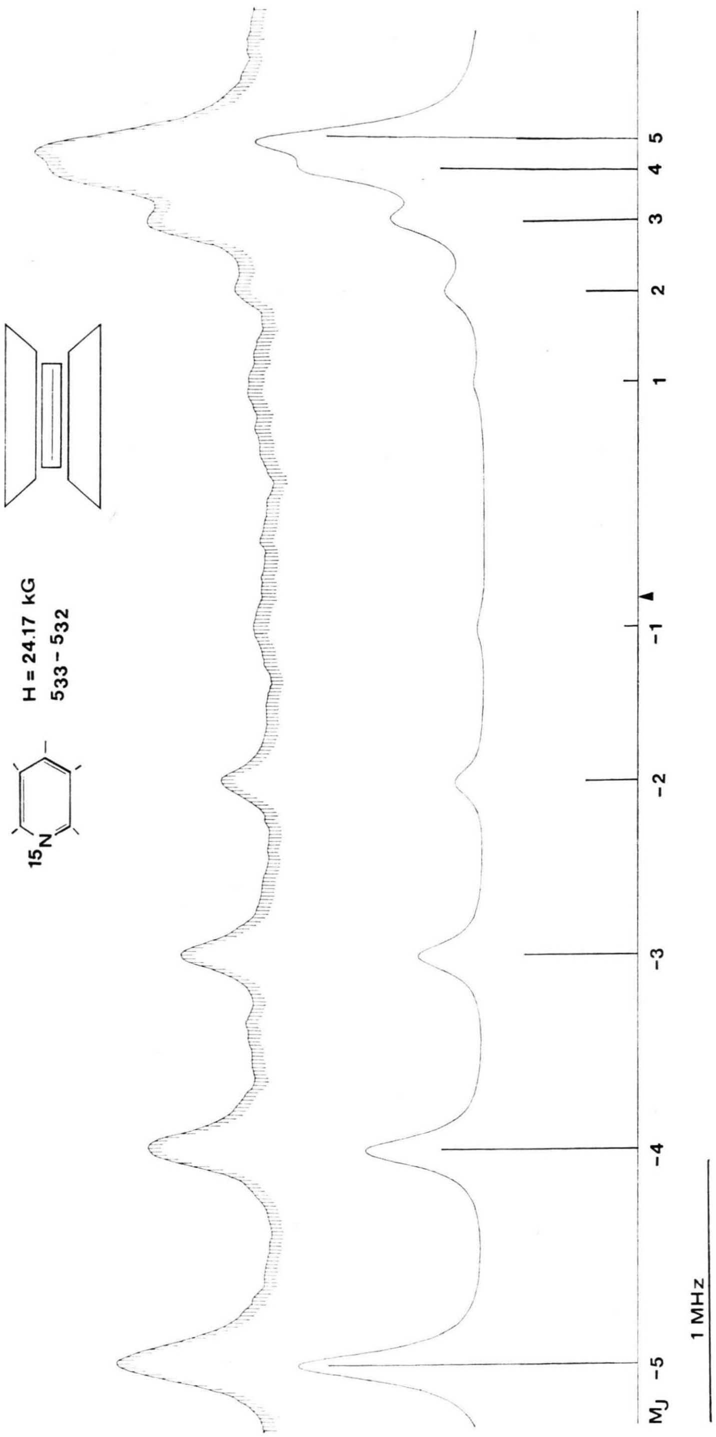


Fig. 1. Broad band scan of the $5_{33} \rightarrow 5_{32}$ rotational transition of ^{15}N-Pyridine observed at 24170 Gauss under $\Delta M = 0$ selection rule. The frequency markers are at every 14 kHz. The center trace shows a computer calculated spectrum. It was calculated under the assumption of Lorentzian line shapes with half widths of 140 kHz full width at half height and using the g-values, susceptibility anisotropies, and rotational constants given in Table 1. The bar spectrum at the bottom shows the exact frequencies of the calculated Zeeman satellites each labelled with the appropriate M-value. The zero field frequency is indicated by a dagger (13.876838 GHz). The lower height and broadening of the satellites with higher M-values is due to power saturation.

magnetic field $\boldsymbol{H}$ which is assumed to point in the space fixed Z-direction. g_{aa}, g_{bb} and g_{cc} are the diagonal elements of the molecular g-tensor. Part (c) corresponds to the potential energy of the field induced molecular magnetic moment. χ_{aa}, χ_{bb} and χ_{cc} are the diagonal elements of the molecular susceptibility tensor. (In molecules with C_{2v} symmetry such as Ethyleneoxide and Pyridine the molecular

g-tensor, the magnetic susceptibility tensor and the moment of inertia tensor are simultaneously diagonal with identical principal axes systems. (For the theoretical expressions of the g- and χ-tensor elements the reader is referred to the derivation presented in Ref. [4] and references cited therein.) Parts (d) and (e) are important in the presence of quadrupole nuclei such as ^{14}N in Pyridine. Part (d) corresponds to the nuclear Zeeman effect (shielding neglected) with g_i the nuclear g-value of the i-th quadrupole nucleus and $\boldsymbol{I}_i$ its spin vector. Part (e) corresponds to the potential energy of the nuclear electric quadrupole moments within the intramolecular electric field gradient at the positions of the quadrupole nuclei. Finally part (f) corresponds to the translational Zeeman effect [5] which must be accounted for in transitions showing first order Stark effects but which proofed to be negligible in the present investigation.

For all molecules except for ^{14}N-Pyridine parts (d) and (e) were neglected and the matrix of $\mathcal{H}_{\text{eff}}$ was set up within the basis of the appropriate asymmetric top eigenfunction $|J, \tau, M_J\rangle$ [6]. (The Deuterium quadrupole coupling in Ethyleneoxide-D$_4$ is sufficiently small to justify this approximation.) The Zeeman splittings were then analyzed by the standard first order treatment [7]. In the case of ^{14}N-Pyridine the matrix was set up in the uncoupled basis $|J, \tau, M_J, I, M_I\rangle$ with I and M_I referring to the spin and spin-projection quantum numbers of the ^{14}N nucleus. (Again the weak Deuterium quadrupole coupling was neglected.) From the nonvanishing off-diagonal elements [8] only the quadrupole coupling matrix elements diagonal in I and in the rotational quantum numbers J and τ but off-diagonal in M_I and M_J were accounted for and treated by second order perturbation theory. At fields close to 25 kG as were used throughout the present work this approximation is sufficient, since the magnetic field quite effectively uncouples nuclear spin and overall rotation. This was also checked by complete numerical diagonalization (compare Figure 2).

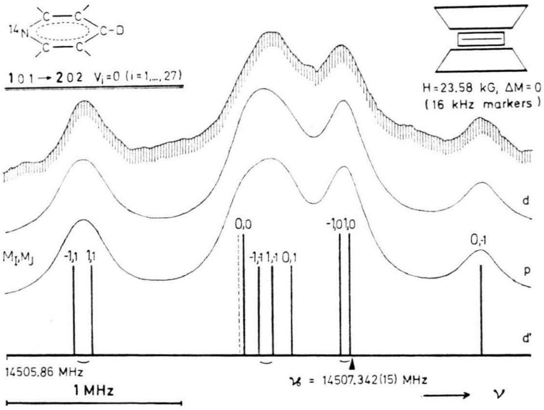


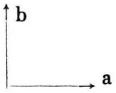
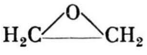
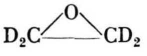
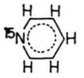
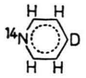
Fig. 2. $\Delta M=0$ Zeeman multiplet of the $1_{01} \rightarrow 2_{02}$ rotational transition of Pyridine-4D recorded at a magnetic field strength $H=23.58$ kG. Curves (d) and (p) show computer plots calculated from the molecular parameters listed in Table 1 under the assumption of Lorentzian lineshapes with 140 kHz full width at half height. Profile (d) is calculated by numerical diagonalization of the M_I, M_J submatrices of the two rotational states. Profile (p) is calculated by second order perturbation theory. Except for the $M_I=0$, $M_J=0$ satellite both calculated spectra coincide within the drawing width of the bar spectrum (d′) which shows the satellite frequencies and intensities obtained by numerical diagonalization. (The less accurate second order frequency of the 0, 0-satellite is indicated by the dotted line.) The dagger indicates the center frequency of the zero field hyperfine multiplet [18].

During the analysis of the experimental splittings the slight inhomogeneity of the magnetic field was accounted for [9]. For the complete listings of the measured splittings the reader is referred to Ref. [10] which may be obtained by the authors. The final results of the least squares fits are given in Table 1. Also listed in this Table are the nuclear quadrupole coupling constants for ^{14}N in Pyridine-4-D since they enter into the analysis of the Zeeman data via Equation (1, e). They were determined seperately from the zero field hyperfine splittings of the rotational transitions [11] and are in close agreement with the values determined previously by Sørensen et al.[12].

Table 2 shows lists of molecular quantities which may be derived from the molecular g-values, magnetic susceptibility anisotropies and rotational constants together with the bulk susceptibility and the molecular structure [13]. Since the evaluation is based on the rigid rotor theoretical expressions of the g-values etc. the listed values should be used with appropriate caution. In general they will come close to ground state vibrational expectation values. For a discussion of this problem the reader is referred to Reference [14].

With the shift of the molecular center of mass upon isotopic substitution the partial compensation of positive and negative electric currents due to the rotation of the molecular charge distribution is also changed. This makes it possible, at least in principle, to determine the sign of the molecular electric dipole moment from the molecular g-values and rotational

Table 1. g-values and magnetic susceptibility anisotropies of Ethyleneoxide and Pyridine. Also given are the ^{14}N-nuclear quadrupole coupling constants for 4D-Pyridine and the rigid rotor rotational constants fitted to the same low J rotational transitions that were used for the Zeeman analyses. Quoted uncertainties are standard deviations from the least squares fit. (With the present experimental setup only the relative signs of the g-values can be determined. The choice in bracketts would lead to unreasonable values for the electric quadrupole moment and in the case of Pyridine to a negative value of the electronic ground state expectation value for the sum of the squares of the c-coordinates of the electrons, $\langle 0 \,|\, \sum_{\varepsilon}^{\text{electrons}} C_\varepsilon^2 \,|\, 0 \rangle$ and may thus be discarded.)

					
Molecular g-values	g_{aa}	$-0.09692(4)$ $(+)$	$-0.07794(9)$ $(+)$	$-0.08086(19)$ $(+)$	$-0.07935(7)$ $(+)$
	g_{bb}	$+0.01848(5)$ $(-)$	$+0.01436(17)$ $(-)$	$-0.09974(16)$ $(+)$	$-0.09438(6)$ $(+)$
	g_{cc}	$+0.03361(7)$ $(-)$	$+0.02683(11)$ $(-)$	$+0.04101(17)$ $(-)$	$+0.04063(6)$ $(-)$
Magnetic susceptibility anisotropies	$N_L(2\chi_{aa}-\chi_{bb}-\chi_{cc})$ $[10^{-6}\,\text{erg}/(\text{G}^2\,\text{mole})]$	18.46 (7)	18.45 (16)	54.12 (40)	53.3 (10)
	$N_L(2\chi_{bb}-\chi_{cc}-\chi_{aa})$ $[10^{-6}\,\text{erg}/(\text{G}^2\,\text{mole})]$	$-0.05(10)$	0.24 (22)	62.02 (40)	60.1 (16)
Rotational constants	A [MHz]	25483.66 (16) [a]	20398.32 (7) [a]	6039.41 (1) [b]	6038.98 (1) [b]
	B [MHz]	22121.13 (18) [a]	15456.13 (9) [a]	5680.37 (1) [b]	5420.06 (1) [b]
	C [MHz]	14097.95 (16) [a]	11542.71 (7) [a]	2926.54 (1) [b]	2855.82 (1) [b]
^{14}N-quadrupole coupling constants	χ_{aa}^{N} [MHz]	—	—	—	$-4.894(20)$ [b]
	χ_{bb}^{N} [MHz]	—	—	—	$+1.400(40)$ [b]
	χ_{cc}^{N} [MHz]	—	—	—	$+3.50(6)$ [b]

[a] Compare too C. Hirose, Bull. Chem. Soc. Japan **47**, 1311 [1974].

[b] Compare too G. O. Sørensen, L. Mahler, and J. Rastrup-Andersen, J. Mol. Structure **20**, 119 [1974].

constants of two isotopic species. If the principal axes system is parallel shifted (not rotated) upon isotopic substitution, the theoretical expressions for the g-values etc. lead to the following relation [15]

$$-\frac{|e|\,h}{16\,\pi^2 M_p}\left(\frac{g'_{aa}}{A'}-\frac{g_{aa}}{A}\right)=\Delta b\,\mu_b+\Delta_c\,\mu_c \qquad (2)$$

and cyclic permutations. On the right hand side of Eqs. (2) Δa, Δb and Δc are the coordinates of the center of mass of the primed isotropic species if referred to the principal axes system of the unprimed species, and μ_a, μ_b, and μ_c are the components of the electric dipole moment defined as $\boldsymbol{\mu}=|e|\cdot\{\sum_n^{\text{nuclei}} Z_n \boldsymbol{r}_n - \langle 0 \,|\, \sum_\varepsilon^{\text{electrons}} \boldsymbol{r}_\varepsilon \,|\, 0\rangle\}$. M_p is the Proton mass. Again Eqs. (2) are only valid within the rigid nuclear frame approximation. In molecules with C_{2v} symmetry such as Ethyleneoxide and Pyridine the symmetry of the frame should lead to zero right hand sides in one of the three Equations (2). In the following this Equation will be called "controle Equation". As will be discussed shortly it may be used as a check on the approximations used in the derivation of Equations (2).

If one uses the g-values and rotational constants given in Table 1 together with the structures shown in Fig. 3, the numerical results listed in Table 3 are

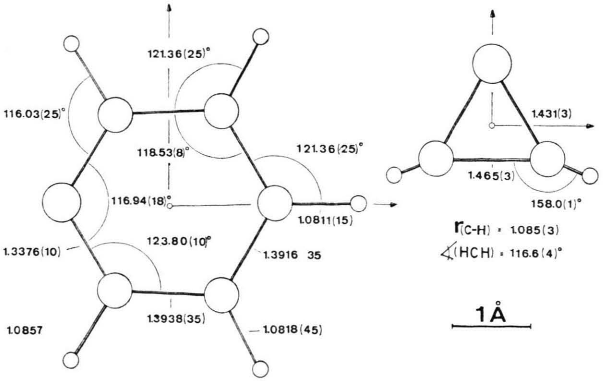
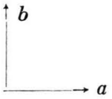
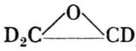
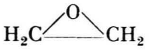
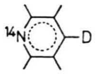
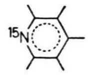


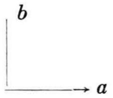
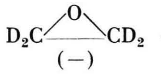
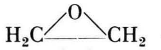
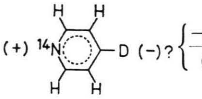
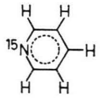
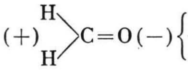
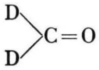
Fig. 3. To scale drawings of the structures of Pyridine and Ethyleneoxide taken from Refs. [11] and [12]. Uncertainties (in bracketts) are given in units of the last significant figure. They are believed to embrace the equilibrium values [for a discussion of the uncertainties (r_s-structures, vibrational corrections, etc. see [11] and [12])].

Table 2. Molecular quantities derived from the experimental data given in Table 1, the geometries of the nuclear frames (see Fig. 3) and the bulk magnetic susceptibilities [13]. Quoted uncertainties follow from standard error propagation and do not account for possible deficiencies of the rigid rotor model.

	 				
Molecular quadrupole moments in units of 10^{-26} esu cm^2 $Q_{aa} = \frac{\lvert e\rvert}{2}\{\sum_n^{\text{nuclei}}(2a_n^2-b_n^2-c_n^2)$ $-\langle 0 \vert \sum_\varepsilon^{\text{electrons}} 2a_\varepsilon^2-b_\varepsilon^2-c_\varepsilon^2 \vert 0\rangle\}$ $= -\frac{h\lvert e\rvert}{16\pi^2 M_\text{p}}\left\{\frac{2g_{aa}}{A}-\frac{g_{bb}}{B}-\frac{g_{cc}}{C}\right\}$ $-\frac{2mc^2}{\lvert e\rvert}\{2\chi_{aa}-\chi_{bb}-\chi_{cc}\}$	Q_{aa}	+2.7 ±0.13	2.6 ±0.05	−2.3 ±1.2	−2.6 ±0.4
	Q_{bb}	−4.2 ±0.17	3.7 ±0.07	+9.3 ±1.5	8.0 ±0.4
	Q_{cc}	+1.5 ±0.26	1.1 ±0.11	−6.9 ±2.2	−5.4 ±0.6
Second moments of the nuclear charge distribution calculated from the structures shown in Figure 3. The units are Å^2.	$\sum Z_n a_n^2$	12.88±0.10	12.81±0.10	49.52±0.05	49.61±0.05
	$\sum Z_n b_n^2$	8.92±0.05	8.99±0.05	50.46±0.05	50.46±0.05
	$\sum Z_n c_n^2$	3.41±0.02	3.41±0.02	0.0	0.0
Paramagnetic susceptibilities in units of 10^{-6} erg/(G^2 mole). $\chi^{(\text{p})}_{\text{aa,mole}} = -\frac{e^2}{2m^2c^2}N_L\cdot\left(\frac{L_a L_a}{\Delta}\right)$ $= -\frac{e^2}{4mc^2}$ $\cdot\left\{\frac{h}{8\pi^2 M_\text{p}}\frac{g_{aa}}{A} - \sum_n^{\text{nuclei}} Z_n(b_n^2-c_n^2)\right\}N_L$	$\chi^{(\text{p})}_{aa,\text{mole}}$	60.59±0.31	60.79±0.3	242.1 ±0.4	242.7 ±0.2
	$\chi^{(\text{p})}_{bb,\text{mole}}$	67.07±0.53	67.25±0.50	247.3 ±0.4	247.9 ±0.2
	$\chi^{(\text{p})}_{cc,\text{mole}}$	87.79±0.53	87.88±0.5	394.0 ±0.5	394.0 ±0.3
Bulk magnetic susceptibilities in units of 10^{-6} erg/(G^2 mole) $\chi_\text{bulk} = N_L\cdot(\chi_{aa}+\chi_{bb}+\chi_{cc})/3$	χ_bulk	30.7 ±1.0	30.7 ±1.0	− 49.21±0.9	− 49.21±0.9
Diamagnetic susceptibilities in units of 10^{-6} erg/(G^2 mole). $\chi^{(\text{d})}_{\text{aa,mole}} = -N_L\frac{e^2}{4mc^2}$ $\cdot\langle 0 \vert \sum_\varepsilon^{\text{electrons}} b_\varepsilon^2+c_\varepsilon^2 \vert 0\rangle$ $=\chi_{aa}\,\text{mole} - \chi^{(\text{p})}_{\text{aa,mole}}$ etc.	$\chi^{(\text{d})}_{aa,\text{mole}}$	− 84.1 ±1.4	− 85.3 ±1.3	−273.6 ±1.2	−273.8 ±0.7
	$\chi^{(\text{d})}_{bb,\text{mole}}$	− 97.7 ±1.6	− 98.0 ±1.5	−276.4 ±1.3	−276.4 ±0.7
	$\chi^{(\text{d})}_{cc,\text{mole}}$	−124.7 ±1.7	−124.7 ±1.6	−481.0 ±1.8	−482.8 ±0.9
Second moments of the electronic charge distribution in Å^2. $\langle 0 \vert \sum_\varepsilon^{\text{electrons}} a_\varepsilon^2 \vert 0\rangle$ $= -\frac{2mc^2}{e^2}(\chi_{bb}+\chi_{cc}-\chi_{aa})$ $-\frac{h}{16\pi^2 M_\text{p}}\left(\frac{g_{bb}}{B}+\frac{g_{cc}}{C}-\frac{g_{aa}}{A}\right)$ $+\sum_n^{\text{nuclei}} Z_n a_n^2$	$\langle 0 \vert \sum a_\varepsilon^2 \vert 0\rangle$	16.17±0.56	16.18±0.54	57.0	57.2
	$\langle 0 \vert \sum b_\varepsilon^2 \vert 0\rangle$	13.21±0.56	13.21±0.56	56.3 ±0.7	56.6 ±0.3
	$\langle 0 \vert \sum c_\varepsilon^2 \vert 0\rangle$	6.85±0.56	6.90±0.54	8.1	8.0

obtained. They indicate that in Ethyleneoxide the negative end of the molecule is at the Oxigen side just as expected, while unexpectedly in the case of pyridine the positive end of the molecule turns out to be at the Nitrogen side. The large experimental uncertainties however indicate that the latter result is not conclusive. As is seen from the numbers given in Table 3 these large uncertainties stem from the

Table 3. Electric dipole moment of Ethylenoxide and Pyridine from the rotational Zeeman effect. Typically the two leading figures drop out of the differences in column one thus sharply reducing the accuracy of determined dipole moments. Quoted uncertainties follow from the standard deviations of the g-values. The results listed in column two indicate that in Ethyleneoxide Oxygen is at the negative end. (C. E. stands for the controle Equation which from symmetry should give zero within the rigid rotor approximation.) For Pyridine the result is not conclusive because of the large uncertainties. It would indicate Nitrogen to be at the positive end. In column three accurate absolute dipole moments obtained from Stark effect determinations as well as values calculated by the semiempirical INDO-method are listed for comparison. Also for comparison Zeeman results obtained for Formaldehyde by Flygare and coworkers [17] are listed at the bottom of the Table. The discrepancies between Stark-effect and Zeeman values indicate that the neglect of vibrations in the analysis of the data is at least problematic.

Primed species unprimed species Δa, Δb, Δc in Å$=10^{-8}$ cm 	$(g_{aa}'/A'-g_{aa}/A)$ $(g_{bb}'/B'-g_{bb}/B)$ $(g_{cc}'/C'-g_{cc}/C)$ [sec]	Electric dipole moment according to Eq. (2) in Debye [10^{-18} esu·cm]	Calculated dipole moment μ^{INDO} absolute value $\lvert\mu\rvert$ from Stark-effect
 (−)	$\left\{\frac{-0.07794(9)}{2.039832\cdot 10^{10}} - \frac{0.09692(4)}{2.548366\cdot 10^{10}}\right\} = -1.77(60)\cdot 10^{-14}$	$\mu_{b,\text{Zeeman}} = -0.39(13)$	$\mu_b^{\text{INDO}} = -2.1$
 (+)	$\left\{\frac{0.01436(17)}{1.545613\cdot 10^{10}} - \frac{0.01848(5)}{2.212113\cdot 10^{10}}\right\} = -9.37(132)\cdot 10^{-14}$	C. E.	$\lvert\mu_{b,\text{Stark}}\rvert = 1.88$
0.0, −0.0538, 0.0	$\left\{\frac{0.02683(11)}{1.154271\cdot 10^{10}} - \frac{0.03361(7)}{1.409795\cdot 10^{10}}\right\} = -5.96(144)\cdot 10^{-14}$	$\mu_{b,\text{Zeeman}} = -1.34(32)$	
	$\left\{\frac{-0.07935(70)}{6.03898\cdot 10^{9}} - \frac{-0.08086(19)}{6.03941\cdot 10^{9}}\right\} = +2.49(147)\cdot 10^{-13}$	C. E.	$\mu_a^{\text{INDO}} = 2.07$
	$\left\{\frac{-0.09438(60)}{5.420061\cdot 10^{9}} - \frac{-0.09974(16)}{5.68037\cdot 10^{9}}\right\} = 1.46(139)\cdot 10^{-13}$	$\mu_{a,\text{Zeeman}} = -3.61(344)$	$\lvert\mu_{a,\text{Stark}}\rvert = 2.24$
+0.0487, 0.0, 0.0	$\left\{\frac{0.04063(60)}{2.85582\cdot 10^{9}} - \frac{0.04101(17)}{2.92654\cdot 10^{9}}\right\} = 2.14(268)\cdot 10^{-13}$	$\mu_{a,\text{Zeeman}} = -5.29(663)$	
 $(+)\,\mathrm{H_2C{=}O}\,(-)$	$\left\{\frac{-2.9017(8)}{2.82106\cdot 10^{11}} - \frac{-1.445(2)}{1.41732\cdot 10^{11}}\right\} = -9.06(169)\cdot 10^{-14}$	C. E.	$\mu_a^{\text{INDO}} = -1.88$
 $\mathrm{D_2C{=}O}$	$\left\{\frac{-0.22430(1)}{3.883400\cdot 10^{10}} - \frac{-0.1917(5)}{3.23686\cdot 10^{10}}\right\} = +1.47(16)\cdot 10^{-13}$	$\mu_{a,\text{Zeeman}} = -2.40(26)$	$\lvert\mu_{a,\text{Stark}}\rvert = 2.34$
+0.0737, 0.0, 0.0	$\left\{\frac{-0.0994(1)}{3.40040\cdot 10^{10}} - \frac{-0.0788(4)}{2.62725\cdot 10^{10}}\right\} = +7.62(182)\cdot 10^{-14}$	$\mu_{a,\text{Zeeman}} = -1.25(30)$	

fact that the leading well determined digits drop out of the differences in Equations (2). However we believe that apart from the experimental uncertainties systematic errors may play some role too. The discrepancies of the two values for μ determined from the Zeeman data according to Eqs. (2), the differences between the absolute values for μ determined from the Zeeman effect and those determined with considerably higher accuracy from Stark effect investigations, and the failure of the "controle Equations" [Eqs. (2)] to give zero right hand sides within the experimental uncertainties all point in that direction. In Ethyleneoxide for instance the "controle Equation" (see Table 3) leads to a right hand side which is off zero by more than 7 standard deviations! Such deviations have been found also in other molecules. As an example the results for Formaldehyde which have been obtained by Flygare and coworkers are listed for comparison at the bottom of Table 3. In this case the "controle Equation" leads to a value which is 5.4 standard deviations off zero.

Apart from the experimental uncertainties these observed discrepancies are most likely due to the neglect of vibrations during the analysis of the data.

Thus for instance vibrations perpendicular to the plane of the heavy nuclei will generally lead to nonzero expectation values at the right hand sides of the "controle Equations". Furthermore individually averaged g-values and rotational constants are used at the left hand sides rather than vibrational averages of the type $\langle v=0 \mid g_{aa}/A \mid v=0 \rangle$ etc. Finally and probably most important, the vibrational functions for "Proton-" and "Deuterium-vibrations" which enter into the vibrational ground state averages differ considerably.

In order to account for these vibrational effects an experimental knowledge of the vibrational dependence of the g-values would be necessary. At the present stage only an estimate is possible which is based on the results obtained by Honerjäger and Tischer for some diatomics [16]. If one assumes that the order of magnitude of the v-dependence of the g-values in diatomics and polyatomics will be about the same, a rough estimate of possible "vibrational uncertainties" in Eqs. (2) leads to the conclusion that even the rather large off zero value in the controle Equation for Ethyleneoxide may still fall within the range of necessary vibrational corrections. We therefore conclude that sign of the dipole moment determinations from the rotational Zeeman effect of different isotopic species, especially if Hydrogen-Deuterium substitutions are used, should include the analysis of excited vibrational states so that equilibrium values can be used in Eqs. (2) (to further substantiate this result a systematic study of Formaldehyde is planed).

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