The Rotational Zeeman Effect of Nitrosylfluoride

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The rotational Zeeman effect of low J transitions of Nitrosylfluoride in the centimetre and millimetre waveranges has been investigated with fields up to 24 kG.

g-Factors with signs could be determined using the effect of the nitrogen quadrupole coupling interactions. A value for the partial susceptibility contribution of the nitrogen $-N=$ has been estimated.

Introduction

Although the microwave spectra of the nitrosyl compounds $ON-X$ ($X = H, F, Cl, Br, CN$) are well known, no microwave Zeeman investigation of this series of molecules has, to our knowledge, so far been carried out.

In this paper we report the results of a microwave Zeeman investigation of the nitrosyl fluoride: ONF.

As the reactivity of this group of substances is high, it seems wortwhile to obtain information which could increase the knowledge of the electronic structure and thus help to explain the chemical behaviour.

Further, principally for ONF, where many a-priori calculations [1, 2] have been made to explain structural data [3, 4] and electric dipole moments [5], it is important to know other physical parameters to check the quality of these theoretical calculations.

Experimental

Nitrosyl fluoride, ONF, was prepared by condensing fluorine on to nitrogen oxide, NO, kept at liquid nitrogen temperature in a quartz trap. After the mixture was allowed to warm up to dry ice temperature, ONF was obtained with N_2O_2 as impurity. Because of the instability of nitrosyl fluoride in the waveguide cell a flow system was used.

ONF was slowly pumped through the wave guide cell keeping the temperature at -80 °C and the pressure at about 1.3 Pa (10 mTorr).

The low frequency spectra were recorded with a conventional 33 kHz Stark-effect spectrometer equipped with an electromagnet able to produce magnetic fields up to 24 kG through a gap of 50 mm [6].

For the high frequency spectrum the BWO-source has been replaced by an OKI 100 V 11 klystron stabilized by a phase stabilized X-band sweeper (Hewlett-Packard 8690 B). The high frequency detector was a run-in Gordy type detector made in our workshop. The frequency measurements, carried out by means of a synthesized signal generator Schomandl ND 800 continously monitored against the broadcasting station DCF 77 of the PTB (Physikalisch-Technische Bundesanstalt Braunschweig) with a relative accuracy of $5 \cdot 10^{-13}$, are believed to be as accurate as $1 \cdot 10^{-7}$.

Theory

The appropriate effective Hamilton operator for a rigid rotor molecule, containing a quadrupole nucleus and rotating in an external magnetic field is given by [7, 8]

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{Q}} + \mathcal{H}_{\text{mag}}\,, \qquad \mathcal{H}_{\text{mag}} = \mathcal{H}_{\text{g}}{}^{\text{mol}} + \mathcal{H}_{\text{g}}{}^{\text{nucl}} + \mathcal{H}_{\chi}\,, \tag{1}$$

where $\mathcal{H}_{\text{rot}}$ is the standard zero-field rigid rotor Hamilton operator and $\mathcal{H}_{\text{Q}}$ the nuclear quadrupole interaction Hamilton operator. $\mathcal{H}_{\text{g}}{}^{\text{mol}}$ and $\mathcal{H}_{\text{g}}{}^{\text{nucl}}$ describe the molecular and shielded nuclear Zeeman effect and $\mathcal{H}_{\chi}$ arises from the interaction between the field induced magnetic moment and the applied magnetic field. In the representation $|J, \tau, M_J, I, M_I\rangle$ which factorizes the Hamiltonian, the only non diagonal elements in the J, τ blocks result from $\mathcal{H}_{\text{Q}}$. Second order perturbation contributions are neglected because they are very small compared with the differences in the rotational levels.

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Due to the small quadrupole splitting, the case of strong field is promptly reached so that M_I and M_J are good quantum numbers to describe the energy levels.

Spectrum

Three transitions have been investigated:

$$0_{00} - 1_{01}\,,\quad 0_{00} - 1_{11}\,,\quad 1_{10} - 1_{01}$$

with a total of eleven HFS component lines at different field conditions.

Zero-field line measurements, together with the quadrupole coupling constants, obtained by evaluations of the HFS-splittings are listed in Table 1. Although these constants have been determined in two preceeding investigations [3, 9] we prefer in this paper the use of our presently measured constants in order to avoid possible sources of errors arising from the use of parameters which have been determined from different sets of lines.

The measured Zeeman lines are listed in Tables 2 and 3. The diagonal elements of the molecular g-tensor were obtained from a least squares fit of the observed splittings. Because of the quadrupole-Zeeman interaction the signs of the g-factors could be determined unambiguously [10].

The values for g_{aa}, g_{bb} and g_{cc} and the values for anisotropies of the diagonal elements of the magnetic susceptibility tensor are listed in Table 4.

Discussion

Using the five Zeeman parameters determined here and the known r_0-structure [3], the molecular electric quadrupole moment and the diagonal elements of the paramagnetic susceptibility tensor have been calculated. The knowledge of the bulk susceptibility of the molecule could allow the calculation of the diamagnetic and of the total susceptibility tensor. Due to the instability of the molecule and hence to the difficulty of performing a direct measurement, the bulk susceptibility has been estimated using the model of the local susceptibility increments. This method, first developed by Pascal [11], refined by Benson and Flygare [12] and in the last few years by Wiese and Sutter [13] uses susceptibility contributions which are typical

Table 1. Zero field line frequencies of Nitrosylfluoride. No centrifugal distortion correction has been made. ν_0-frequencies are corrected for the quadrupole coupling interactions. The errors of the quadrupole coupling constants are standard errors of the least squares fitting procedure.

$J_{K_-K_+} - J'_{K'_-K'_+}$	$F \to F'$	ν_{obs} (MHz)	ν_{cal} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (kHz)	ν_0 (MHz)
$0_{00} - 1_{01}$	1 – 2	22 352.309	22 352.306	3	
	1 – 1	22 352.823	22 352.828	– 5	22 352.393
	1 – 0	22 351.520	22 351.523	– 3	
$0_{00} - 1_{11}$	1 – 2	105 694.538	105 694.511	27	
	1 – 1	105 692.962	105 692.992	–30	105 694.258
	1 – 0	105 696.742	105 696.791	–49	
$1_{10} - 2_{11}$	2 – 3	46 039.862	46 039.863	– 1	
	1 – 2	46 040.494	46 040.482	12	
	0 – 1				46 040.059
	2 – 2	46 041.448	46 041.492	–44	
	1 – 1	46 037.959	46 037.962	– 3	

Nitrogen quadrupole coupling constants obtained from these data in comparison with the constants of References 3 and 9.

	χ_{aa}^{N}	χ_{bb}^{N}	χ_{cc}^{N}	
	1.73 (19)	– 5.02 (18)	3.29 (18)	this work
	1.69 (5)	– 4.83 (5)	3.14 (5)	Ref. (3)
	1.7 (1)	– 5.0 (1)	3.3 (1)	Ref. (9)

Table 2. Zeeman lines of Nitrosylfluoride, $\Delta M = 0$. ν_0 lines are obtained from the fitting of the susceptibility anisotropies. The given error results from the fitting procedure.

$J_{K_-K_+} - J'_{K'_-K'_+}$	Field (Gauß)	M_J	$\lvert M_I \rvert$	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (kHz)	ν_0 (MHz)
$0_{00} - 1_{01}$	0					22 352.385 (3)
	18 982	0	0	22 351.981	10	
			1	22 352.493	4	
	24 070	0	0	22 351.934	6	
			1	22 352.447	0	
	25 017	0	0	22 351.924	5	
			1	22 352.437	− 1	
	25 604	0	0	22 351.913	− 1	
			1	22 352.425	− 7	
$0_{00} - 1_{11}$	0					105 694.249 (4)
	18 984	0	0	105 695.225	− 2	
			1	105 693.726	0	
	24 068	0	0	105 695.219	3	
			1	105 693.711	− 2	
	25 001	0	0	105 695.217	3	
			1	105 693.709	− 2	
	25 580	0	0	105 695.220	8	
			1	105 693.708	− 1	
$1_{10} - 2_{11}$	0					46 040.047 (4)
	18 972	0		46 039.969	− 2	
		+1	0	46 035.155	−10	
			1	46 036.245	0	
		−1	0	46 043.664	4	
			1	46 044.652	8	
	22 598	0		46 039.934	− 6	
		+1	0	46 034.389	−11	
			1	46 035.474	2	
		−1	0	46 044.461	− 8	
			1	46 045.464	3	
	24 030	0		46 039.928	2	
		+1	0	46 034.085	−13	
			1	46 035.167	0	
		−1	0	46 044.792	2	
			1	46 045.789	4	

for a given atom with a characteristic bond configuration.

From the values estimated by Wiese [13] it is possible to calculate the contributions for Fluorine (F −) and for Oxygen (O =) as follows:

$$\text{F}-:\ 1/2\,(\chi^{s}_{aa} + \chi^{s}_{bb})_{\text{F}} = -7.60 \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole} = (\chi_{\parallel})_{\text{F}}$$

$$(\chi^{s}_{aa})_{\text{F}} = -5.56 \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole} = (\chi_{\perp})_{\text{F}}$$

$$(\chi_{\parallel} - \chi_{\perp})_{\text{F}} = -2.04 \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole}$$

$$O=:\ 1/2\,(\chi^{s}_{aa} + \chi^{s}_{bb})_{0} = 0.15 \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole} = (\chi_{\parallel})_{\text{O}}$$

$$(\chi_{cc})_{0} = -5.86 \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole} = (\chi_{\perp})_{\text{O}}$$

$$(\chi_{\parallel} - \chi_{\perp})_{0} = 6.01 \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole}.$$

The three single contributions for the double bonded nitrogen (−N=) are not known but it is possible to estimate $(\chi_{\parallel} - \chi_{\perp})$ from our measurements of $(\chi_{\parallel} - \chi_{\perp})_{\text{FNO}} = 7.5(9) \cdot 10^{-6}$ erg/Gauß² mole.

From the

$$(\chi_{\parallel} - \chi_{\perp})_{\text{FNO}} = (\chi_{\parallel} - \chi_{\perp})_{\text{F}} + (\chi_{\parallel} - \chi_{\perp})_{\text{O}} + (\chi_{\parallel} - \chi_{\perp})_{\text{N}}$$

it follows $(\chi_{\parallel} - \chi_{\perp})_{\text{N}} = 3.5(9) \cdot 10^{-6}$ erg/Gauß² mole.

Table 3. Zeeman lines of Nitrosylfluoride $\Delta M = 1$. ν_0 lines have the same meaning as in Table 2. Some $|M_I| = 0$-lines have been measured with less accuracy because perturbed by the stronger $|M_I| = 1$-lines.

$J_{K_-K_+} - J'_{K'_-K'_+}$	Field (Gauß)	$M_J - M_J$	$\|M_I\|$	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)	ν_0
$0_{00} - 1_{01}$	0					22 352.385 (3)
	13 880	0 −1	0	22 351.62	−0.02	
			1	22 351.377	0.004	
		0 1	0	22 353.49	−0.02	
			1	22 353.269	0.009	
	18 246	0 −1	0	22 351.34	−0.03	
			1	22 351.108	0.007	
		0 1	0	22 353.79	−0.02	
			1	22 353.563	0.004	
	21 359	0 −1	0	22 351.15	−0.02	
			1	22 350.921	0.013	
		0 1	0	22 354.01	−0.02	
			1	22 353.787	0.011	
$0_{00} - 1_{11}$	0					105 694.249 (4)
	13 880	0 −1	1	105 689.02	0.00	
		0 1	0	105 699.35	0.14	
			1	105 699.91	−0.09	
	18 246	0 −1	0	105 686.80	0.19	
			1	105 687.23	−0.12	
		0 1	0	105 701.03	0.13	
			1	105 701.64	−0.04	
	21 359	0 −1	1	105 686.07	−0.08	
		0 1	1	105 702.85	−0.03	
$1_{10} - 2_{11}$	0					46 040.047 (4)
	13 880	1 2	1	46 039.408	−0.001	
		−1 −2	0	46 040.862	−0.017	
			1	46 040.268	−0.065	
		0 1	1	46 042.409	−0.014	
		0 −1	0	46 037.791	−0.020	
			1	46 037.276	−0.012	
		−1 0	0	46 044.574	−0.104	
			1	46 046.178	0.074	
		1 0	0	46 033.284	−0.111	
			1	46 034.929	−0.015	
	18 246	1 2	1	46 039.273	0.017	
		−1 −2	1	46 040.514	0.006	
		0 1	1	46 043.223	0.029	
		0 −1	0	46 036.915	−0.042	
			1	46 036.335	−0.116	
	21 359	1 2	0	46 039.894	0.147	
			1	46 039.169	0.018	
		−1 −2	1	46 040.653	0.029	
		0 1	1	46 043.733	−0.006	
		0 −1	1	46 035.738	−0.110	

Wiese [14] estimated from measurements on oxazoles and thiazoles the value

$$(\chi_{\parallel})_{\text{N}} \cong 0 \text{ erg/Gauß}^2 \text{ mole},$$
$$(\chi_{\perp})_{\text{N}} \cong -4 \cdot 10^{-6} \text{ erg/Gauß}^2 \text{ mole},$$
$$(\chi_{\parallel} - \chi_{\perp})_{\text{N}} \cong 4 \cdot 10^{-6} \text{ erg/Gauß}^2 \text{ mole}$$

which are in good agreement with our data.

This allows the conclusion that the nitrogen atomic susceptibility in a nitrosyl and in an imine bond are equivalent. The molecular bulk susceptibility

$$\chi^{\text{s}}_{\text{bulk}}(\text{FNO}) = 1/3\,(\chi^{\text{s}}_{aa} + \chi^{\text{s}}_{bb} + \chi^{\text{s}}_{cc}),$$

estimated after Wiese [13, 14], has a value of

Table 4. Zeeman parameters of Nitrosylfluoride. The errors are given in units of the last figure and are three times the standard errors of the least squares fitting procedure.

Molecular g-values	g_{aa}		− 0.9542 (14)
	g_{bb}		− 0.1100 (13)
	g_{cc}		− 0.0640 (18)
Molar magnetic susceptibility anisotropies	$\frac{N_{\mathrm{L}}(2\chi_{aa}-\chi_{bb}-\chi_{cc})}{10^{-6}\,\mathrm{erg/(G^2\,mole)}}$		11.8 (9)
	$\frac{N_{\mathrm{L}}(2\chi_{bb}-\chi_{aa}-\chi_{cc})}{10^{-6}\,\mathrm{erg/(G^2\,mole)}}$		3.2 (9)
Molar magnetic bulk susceptibility	$\frac{\frac{1}{3}N_{\mathrm{L}}(\chi_{aa}+\chi_{bb}+\chi_{a})}{10^{-6}\,\mathrm{erg/(G^2\,mole)}}$		−10 (1)
Molecular quadrupole moment in units of 10^{-26} esu cm^2 $Q_{aa}=\frac{\lvert e\rvert}{2}\left\{\sum_{n}^{\text{nuclei}}(2a_n^2-b_n^2-c_n^2)-\langle 0\vert\sum_{\varepsilon}^{\text{electron}}(2a_\varepsilon^2-b_\varepsilon^2-c_\varepsilon^2)\vert 0\rangle\right\}=-\frac{h\lvert e\rvert}{16\pi^2 m_p}\left(\frac{2g_{aa}}{A}-\frac{g_{bb}}{B}-\frac{g_{cc}}{C}\right)-\frac{2mc^2}{\lvert e\rvert}(2\chi_{aa}-\chi_{bb}-\chi_{cc}).$		Q_{aa}	− 1.1 (9)
		Q_{bb}	1.2 (10)
		Q_{cc}	− 0.1 (16)
Second moments of the nuclear charge distribution calculated from the geometry of the nuclear frame given in Å^2		$\sum_n Z_n a_n^2$	20.74(41)
		$\sum_n Z_n b_n^2$	2.64 (7)
		$\sum_n Z_n c_n^2$	0.0
Paramagnetic susceptibilities in units of 10^{-6} erg/(G^2 mole) $\chi^{\mathrm{p}}_{aa,\mathrm{mole}}=-\frac{N_{\mathrm{L}}e^2}{2m^2c^2}\sum_{r}^{\text{excited states}}\frac{\lvert\langle 0\vert L_a\vert\nu\rangle\rvert^2}{E_0-E_\nu}=-\frac{e^2}{4mc^2}\left\{\frac{h}{8\pi^2 m_p}\frac{g_{aa}}{A}-\sum_{n}^{\text{nuclei}}Z_n(b_n^2+c_n^2)\right\}N_{\mathrm{L}}$		$\chi^{p}_{aa,\,\mathrm{mole}}$	32.6 (3)
		$\chi^{\mathrm{p}}_{bb,\,\mathrm{mole}}$	107.8 (17)
		$\chi^{p}_{cc,\,\mathrm{mole}}$	112.2 (18)
Diamagnetic susceptibilities in units of 10^{-6} erg/(G^2 mole) $\chi^{\mathrm{d}}_{aa,\mathrm{mole}}=-\frac{N_{\mathrm{L}}e^2}{4mc^2}\left\langle 0\vert\sum_{\varepsilon}^{\text{electrons}}b_\varepsilon^2+c_\varepsilon^2\vert 0\right\rangle=\chi_{aa,\,\mathrm{mole}}-\chi_{aa,\,\mathrm{mole}}$		$\chi^{\mathrm{d}}_{aa,\mathrm{mole}}$	− 38.7 (10)
		$\chi^{\mathrm{d}}_{pp,\,\mathrm{mole}}$	−116.7 (20)
		$\chi^{\mathrm{d}}_{cc,\,\mathrm{mole}}$	−127.2 (21)
Second moments of the electronic charge distribution in Å^2 $\left\langle 0\vert\sum_{\varepsilon}^{\text{electrons}}a_\varepsilon^2\vert 0\right\rangle=-\frac{2mc^2}{e^2}(\chi_{bb}+\chi_{cc}-\chi_{aa})-\frac{h}{16\pi^2 m_p}\left(\frac{g_{bb}}{B}+\frac{g_{cc}}{C}-\frac{g_{aa}}{A}\right)+\sum_{n}^{\text{nuclei}}Z_n a_n^2$		$\langle 0\vert\sum_\varepsilon a_\varepsilon^2\vert 0\rangle$	24.19 (30)
		$\langle 0\vert\sum_\varepsilon b_\varepsilon^2\vert 0\rangle$	5.79 (28)
		$\langle 0\vert\sum_\varepsilon c_\varepsilon^2\vert 0\rangle$	3.32 (33)
Electronic contribution to the inertial defect [15] in amu Å^2 $\Delta_{\mathrm{elec}}=-\frac{m}{m_p}(I_c g_{cc}-I_b g_{bb}-I_a g_{aa}).$		Δ_{elec}	− 0.00364 (8)

$-10.1 \cdot 10^{-6}$ erg/Gauß^2 mole and from our data, assuming $(\chi_{\|})_N = 0$, a value of $-9.9 \cdot 10^{-6}$ erg/Gauß^2 mole.

So we estimate the molecular bulk susceptibility to be:

$$\chi^{s}_{\text{bulk}}(\text{FNO}) = -(10 \pm 1) \cdot 10^{-6}\ \text{erg/Gauß}^2\ \text{mole}.$$

With this value of χ^{s}_{bulk}, the diagonal elements of the diamagnetic and total susceptibility tensors have been calculated together with the second moment of the electronic charge distribution. With the obtained values of g_{aa}, g_{bb} and g_{cc} the electronic contribution to the inertial defect [15] has also been calculated.

The results are given in Table 4.

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