# <sup>14</sup>N Quadrupole Coupling Constants and <sup>14</sup>N and <sup>19</sup>F Spin–Rotation Coupling Constants of Nitrosyl Fluoride, FNO, and Nitryl Fluoride, FNO<sub>2</sub>

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High-resolution pure rotational spectra of nitrosyl fluoride, FNO, and nitryl fluoride, FNO<sub>2</sub>, have been measured using a cavity pulsed microwave Fourier-transform spectrometer. The samples were prepared using a pulsed electric discharge through precursor substances, with the discharge apparatus mounted as part of the pulsed nozzle of the spectrometer. Nuclear quadrupole and magnetic hyperfine structures due to <sup>14</sup>N and <sup>19</sup>F have been resolved for both molecules, and precise values for the nuclear quadrupole and spin-rotation coupling constants have been obtained. The <sup>14</sup>N quadrupole coupling constants of FNO<sub>2</sub> have been rationalized in terms of a  $\sigma$ -withdrawal of electron density from NO<sub>2</sub> towards F. This view is corroborated by the magnetic shielding estimated from the F spin-rotation constants.

Both nitrosyl fluoride, FNO, and nitryl fluoride, FNO<sub>2</sub>, have been the subjects of several microwave spectroscopic investigations. Earlier studies of nitrosyl fluoride have produced precise values for its structural parameters<sup>1</sup> and centrifugal distortion constants.<sup>2</sup> The <sup>14</sup>N quadrupole coupling constants have also been determined, to moderate precision.<sup>1,3</sup> For nitryl fluoride, although the geometry has been evaluated,<sup>4</sup> the <sup>14</sup>N quadrupole hyperfine structure was evidently difficult to resolve with a Stark modulated spectrometer,<sup>4</sup> and only preliminary values for the coupling constants have been reported.<sup>5</sup>

The present work was undertaken to resolve and measure precisely the hyperfine structure in the rotational transitions of both molecules using a cavity microwave Fouriertransform (MWFT) spectrometer. This instrument is of the Balle-Flygare type<sup>6</sup> and has been described in detail recently.7 The inherent high resolution has been demonstrated in some recent studies,<sup>8-11</sup> and it seemed feasible to resolve both <sup>14</sup>N and <sup>19</sup>F nuclear hyperfine structure. The molecules themselves presented a problem, however, in that their conventional methods of preparation require special techniques, and are relatively inconvenient. However, the quantities of sample required for the measurements were very small, and it was hoped that the pulsed electric discharge apparatus we have recently described<sup>12</sup> could be used to prepare the molecules. The discharge would be applied to mixtures of appropriate reactant gases to produce the desired substances.

### Experimental

The cavity pulsed MWFT spectrometer described earlier<sup>7</sup> was used in this work, with the frequency range now extended up to 24 GHz. In the present experiments, samples were injected as supersonic jets entrained in an Ar carrier gas in a direction parallel to the direction of propagation of the microwaves. All lines were consequently doubled by the Doppler effect. However, in our instrument, both the sensitivity and resolution are greatly improved over those

obtained when samples are injected perpendicular to the direction of the microwave propagation. In this work, linewidths down to *ca.* 7 kHz full width at half maximum (FWHM) were obtained, to give measurement accuracies of  $\pm 1$  kHz. In order to minimize overlap effects found in power spectra, the final frequencies were obtained by fitting to the time domain signals.<sup>13</sup>

To synthesize the nitrosyl fluoride or nitryl fluoride molecules, a pulsed electric discharge was passed through gas mixtures containing SF<sub>6</sub> and NO or NO<sub>2</sub>, respectively. The best results were obtained using 1% NO<sub>x</sub> and 3% SF<sub>6</sub> in *ca.* 2 atm Ar. The design and operation of the discharge apparatus itself are described in detail in ref. 12. The small modification of melting the ends of both electrodes into small spheres prolonged their lifetimes considerably. This was important because with relatively weak signals we could greatly increase the number of time domain signals which could be accumulated. With an estimated rotational temperature of  $T_{\rm rot} \leq 3$  K, only the strongest lines, those involving J = 0, could be seen with a small number of experiment cycles (20–50). Weaker lines, particularly those involving J = 3, required the accumulation of several hundred cycles.

#### **Results and Analysis**

Three rotational transitions of nitrosyl fluoride, having a total of 15 hyperfine components, have been measured and analysed. The measured frequencies are given in Table 1. The observed hyperfine structure arises from interactions involving the <sup>14</sup>N and <sup>19</sup>F nuclei. The splittings due to <sup>19</sup>F are considerably smaller than those due to <sup>14</sup>N, so the assigned quantum numbers have been defined in terms of the 'serial' coupling scheme  $I_N + J = F_N$ ;  $I_F + F_N = F$ . The  $1_{0, 1} - 0_{0, 0}$  transition is depicted in Fig. 1.

A complete set of quadrupole and spin-rotation coupling constants has been determined for FNO by fitting the observed hyperfine splittings to the hypothetical centre frequencies,  $v_0$ , two <sup>14</sup>N quadrupole coupling constants,  $\chi_{aa}$  and  $\chi_{-}(=\chi_{bb} - \chi_{cc})$ , and three spin-rotation constants for each nucleus,  $M_{aa}$ ,  $M_{-}(=M_{bb} - M_{cc})$ , and  $M_{\perp}[=\frac{1}{2}(M_{bb} + M_{cc})]$ . The program used was written using a basis in the 'parallel' coupling scheme  $I_1 + I_2 = I$ ; I + J = F, but the fit was equivalent to what would be obtained with the 'serial' scheme, since off-diagonal terms in the quantum number I were included. Spin-spin coupling between <sup>14</sup>N and <sup>19</sup>F was accounted for using the g factors of the two nuclei<sup>14</sup> and the

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15030.6858 (3)

8013.3041 (2)

0.0

-0.3

0.3

0.4

0.0

0.0

-0.2

0.2

0.2

-0.2

-0.4

$J'_{K_a, K_c} - J''_{K_a, K_c}$	F'	<i>F</i> <sub>N</sub> '- <i>F</i> "	F <sub>N</sub> "	v <sub>obs</sub> /MHz	δv/kHz	v <sub>o</sub> /MHz
$1_{0,1} - 0_{0,0}$	2.5	2-1.5	1	22352.3263	-0.2	22352.3821 (3)
0,1 0,0	1.5	2 - 0.5	1	22352.2528	0.2	(-7
	1.5	1 - 1.5	1	22352.8291	0.5	
	0.5	1-0.5	1	22352.7873	-0.5	

22351.5091

15031.0743

15031.0455

15029.4585

15029.4365

8015.4143

8015.3697

8012.6283

8012.5788

8011.6495

8011.6071

1

4

4

3

3

3

3

4

4

2

2

**Table 1** Assignments, frequencies  $(v_{obs})$ , residuals  $(\delta v)$  and hypothetical centre frequencies  $(v_0)$  of the observed transitions of FNO

**Table 2** The assignments, frequencies  $(v_{obs})$ , residuals  $(\delta v)$ , and hypothetical centre frequencies  $(v_0)$  of the observed transitions of FNO<sub>2</sub>

$J'_{K_a, K_c} - J''_{K_a, K_c}$	F'	$F'_{\rm N}-F''$	$F_{N}''$	$v_{obs}/MHz$	δv/kHz	v <sub>0</sub> /MHz
$1_{0,1} - 0_{0,0}$	1.5	1-1.5	1	17 565.6858	0.1	17 565.2147 (1)
0,1 0,0	0.5	1-0.5	1	17 565.6531	-0.1	
	2.5	2 - 1.5	1	17 565,1486	-0.1	
	1.5	2 - 0.5	1	17 565.0865	0.1	
	0.5	0-1.5	1	17 564.2890	0.0	
$3_{2,1} - 3_{2,2}$	3.5	3-3.5	3	13 607.2834	-0.1	13 606.9996 (1)
	2.5	3-2.5	3	13 607.2543	0.1	
	4.5	4-4.5	4	13 606.9296	0.0	
	3.5	4-3.5	4	13 606.8875	0.0	
	2.5	2 - 2.5	2	13 606.7927	0.1	
	1.5	2-1.5	2	13 606.7596	-0.1	

geometry of ref. 1, following the procedure described earlier.<sup>15</sup>

0.5

3.5

2.5

2.5 1.5

3.5 2.5 4.5

3.5

2.5

1.5

0 - 1.5

3-4.5

3-3.5

2 - 3.5

2 - 2.5

3-3.5

3 - 2.5

4-4.5

4-3.5

2 - 2.5

2 - 1.5

Very few rotational transitions were available for nitryl fluoride, partly because of the low rotational temperature in the molecular expansion. Furthermore, all rotational energy levels with  $K_a$  = odd are missing because of the two equivalent oxygen nuclei with I = 0. Only two rotational transitions, with a total of eleven hyperfine components, were measured for this molecule. Their frequencies and their assignments, again using the 'serial' coupling scheme, are given in Table 2. The  $1_{0, 1}$ - $0_{0, 0}$  transition is depicted in Fig. 2.

The splittings provided enough information to determine a complete set of <sup>14</sup>N quadrupole coupling constants for FNO<sub>2</sub>. However, this was not the case for the spin-rotation constants. Because of a strong correlation between  $M_{aa}(N)$  and  $M_{-}(N)$ , the former was fixed at the same value as for



Fig. 1 Composite spectrum of the  $1_{0,1}-0_{0,0}$  rotational transition of FNO. Labels are  $F_N$  quantum numbers. The  $F_N = 0-1$  component was obtained by averaging over 200 cycles, the  $F_N = 2-1$  component over 50 cycles, and the  $F_N = 1-1$  component over 50 cycles. An 8 K data point Fourier transformation was used.

 $M_{bb}(N)$ . Small variations in  $M_{aa}(N)$  had little effect on the determined values of both  $M_{bb}(N)$  and  $M_{cc}(N)$ . The correlations were much smaller for the spin-rotation constants of <sup>19</sup>F, although  $M_{aa}$  was only barely determined. Spin-spin coupling was accounted for using the same method as with FNO.

The derived constants for both molecules are given in Table 3. The hypothetical unsplit line frequencies are given in Tables 1 and 2, as are the residuals from the least-squares



**Fig.2** Composite spectrum of the  $1_{0,1}-0_{0,0}$  rotational transition of FNO<sub>2</sub>. Labels are  $F_N$  quantum numbers. The  $F_N = 0-1$  component was obtained by averaging over 200 cycles, the  $F_N = 2-1$  component over 200 cycles, and the  $F_N = 1-1$  component over 483 cycles. A 4 K data point Fourier transformation was used.

 $2_{1,2} - 3_{0,3}$ 

 $3_{1,2} - 3_{1,3}$ 

Table 3 Quadrupole coupling constants (MHz) and spin-rotation coupling constants (kHz) of nitrosyl fluoride, FNO, and nitryl fluoride, FNO<sub>2</sub>

		FNO		DIO	
parameter	this work	ref. 3	ref. 1	this work	
χ <sub>aa</sub> (N)	1.7343 (9)	1.73 (19)	1.69 (5)	1.8430 (3)	
$\chi_{hh}(N)$	- 5.0407 (8)	-5.02(18)	-4.83(5)	-1.3560(6)	
$\chi_{cr}(N)$	3.3064 (8)	3.29 (18)	3.14 (5)	-0.4870 (6)	
$M_{aa}(N)$	38.5 (14)			1.5ª	
$M_{bb}(N)$	2.3 (2)			1.5 (1)	
$M_{cc}(N)$	2.4 (2)			1.9 (1)	
$M_{ar}(\mathbf{F})$	341.3 (26)			7.5 (27)	
$M_{bb}(\mathbf{F})$	70.6 (5)			62.9 (6)	
$M_{cc}(\mathbf{F})$	43.5 (5)			32.5 (6)	

<sup>a</sup> Constrained: this constant is highly correlated with  $(M_{bb} - M_{cc})$ .

fits; the latter are well within the estimated measurement uncertainties.

#### **Discussion and Conclusions**

The hyperfine constants are compared with earlier values in Table 3. All the <sup>14</sup>N quadrupole coupling constants are very well determined. For FNO, their precision is greatly increased over that of both ref. 1 and 3. For FNO<sub>2</sub>, these are the first precise values measured; the preliminary values given in ref. 5 are in complete disagreement with the present results, and must be considered incorrect.

Since this work presents the first measurements of the <sup>14</sup>N quadrupole coupling constants of FNO<sub>2</sub>, it is of interest to try to rationalize them. The molecule is structurally very interesting since the NO<sub>2</sub> molecule,<sup>16</sup> and the NF bond is unusually long.<sup>4</sup> There are several other molecules with these properties, all of which have F bonded to a stable open-shell molecule, including FNO and chloryl fluoride, FClO<sub>2</sub>.<sup>17</sup> For chloryl fluoride, an analysis of the Cl quadrupole coupling using the model of Townes and Dailey<sup>18</sup> showed that the FCl bond was formed simply by  $\sigma$ -withdrawal of electron density from the half-occupied orbital of ClO<sub>2</sub>, along the FCl bond.

A similar analysis has been done for  $FNO_2$ . The half-filled molecular orbital in  $NO_2$  is a totally symmetric  $a_1$  orbital, essentially localized on N.<sup>19</sup> According to the Townes–Dailey model, the differences between the nitryl fluoride and nitrogen dioxide coupling constants can be expressed as:

$$\Delta \chi_{aa} = [\Delta n_a - (\Delta n_b + \Delta n_c)/2] e Q q_{210}(N)$$
(1)

and cyclic permutations in *a*, *b* and *c*. Here,  $\Delta \chi_{aa}$  is the difference between  $\chi_{ad}(\text{FNO}_2)$  and  $\chi_{aa}(\text{NO}_2)$ ,<sup>20</sup> expressed in the FNO<sub>2</sub> principal inertial axis system. (Note that since the symmetry axes in FNO<sub>2</sub> and NO<sub>2</sub> are the *a* and *b* axes, respectively,  $\chi_{aa}$  for NO<sub>2</sub> in the FNO<sub>2</sub> axis system corresponds to the actual measured  $\chi_{bb}$  in NO<sub>2</sub>, and *vice versa*.)  $\Delta n_a$  are the changes in the 2p<sub>a</sub> orbital populations at N (similarly  $\Delta n_b$  etc.); and eQq<sub>210</sub>(N) is the coupling constant of a single <sup>14</sup>N 2p electron, taken as -10 MHz.<sup>14</sup>

Because the quadrupole tensor is traceless, a general solution of eqn. (1) cannot be obtained. However, a reasonable approximation can be made by assuming  $\Delta n_b = 0$ . This is justified on the grounds that this orbital is not involved in the NF  $\sigma$ -bond or the NO<sub>2</sub>  $\pi$ -system. It contributes only to NO<sub>2</sub>  $\sigma$ -bonding system, and is unlikely to contribute to an NF  $\pi$ -bond because this bond is so long. Substitution of this value into eqn. (1) gives  $\Delta n_a = -0.36$ ,  $\Delta n_c = 0.00$ . Thus the NF bond would seem to be formed entirely by  $\sigma$ -withdrawal towards F of 0.36 of an electron from the half-filled  $a_1$  orbital of NO<sub>2</sub>. There would appear to be a significant amount of ionic character to the bond. Because the N orbital is nonbonding in  $NO_2$ , the small change in the geometry of this moiety is reasonable.

The spin-rotation constants are the first reported for both FNO and FNO<sub>2</sub>. For FNO, perhaps the most notable feature is the value of  $M_{aa}(F)$ , which is very large, even larger than those of  $F_2^{21}$  and DF,<sup>22</sup> though exceeded by that of HF.<sup>22</sup> For both nuclei the  $M_{aa}$  values are much larger than the corresponding  $M_{bb}$  and  $M_{cc}$  values. However, these constants are proportional to  $g_N B_x$ , where  $g_N$  is the nuclear g factor and  $B_x$  the corresponding rotational constant.<sup>23</sup> For FNO, A is very large (ca. 95.2 GHz) and B and C rather smaller (ca. 11.8 GHz and ca. 10.5 GHz, respectively),<sup>1</sup> so the orders of magnitude for the <sup>19</sup>F constants are not unreasonable. In addition,  $g_N(F) \approx 5.257$  and  $g_N(N) \approx 0.4036$ .<sup>14</sup> It is thus also not unreasonable that the <sup>19</sup>F spin-rotation constants are an order of magnitude larger than the corresponding <sup>14</sup>N constants.

By the same token, it is not surprising that in FNO<sub>2</sub> the <sup>19</sup>F spin-rotation constants are also much bigger than those due to <sup>14</sup>N. There is an apparent anomaly in  $M_{aa}(F)$ , which, though barely determinate, is much smaller than  $M_{bb}(F)$  or  $M_{cc}(F)$ . This anomaly can, however, be rationalized. Flygare<sup>23</sup> has shown that spin-rotation constants can be accounted for with two terms. One, a nuclear term, depends only on the molecular geometry. The other, usually dominant, is an electronic term which can be approximated as being proportional to the following function of the p-density matrix elements,  $P_{aa}$  etc., of the atom in question:

$$M_{aa} \propto g_N A (P_{bb} + P_{cc} - P_{bb} P_{cc} + P_{bc} P_{cb})$$
(2)

The inertial axes, a, b and c, must be permuted cyclically to obtain  $M_{bb}$  and  $M_{cc}$ . For F in FNO<sub>2</sub>, both  $P_{bb}^{F}$  and  $P_{cc}^{F}$  are close to 2 (confirmed by an INDO calculation), and  $P_{bc}^{F} = P_{cb}^{F} = 0$  because of the planarity of the molecule, so the term in square brackets, and hence  $M_{aa}$ , should be small. It is interesting that corresponding calculations for N have  $M_{aa}(N) \approx M_{bb}(N)$ , in agreement with the assumption made in analysing the spectrum. For neither F nor N do the nuclear contributions to the spin-rotation constants affect these general conclusions. The results are summarized in Table 4, with the values of the right-hand side of eqn. (2) listed under 'proportionality'.

When eqn. (2) is applied to FNO, again with p-density matrix elements from an INDO calculation, the ratios of the calculated 'proportionalities' (Table 4) differ from the ratios of the experimental spin-rotation constants by factors of 2-3. Again the nuclear contributions do not affect the general conclusions. These results, which are only moderately satisfactory even with the approximations involved, are also summarized in Table 4.

The spin-rotation constants can, however, be discussed from a different perspective. For a given nucleus k, the spin-rotation constants are related to its magnetic shielding by the equations:<sup>23</sup>

$$\sigma_{\rm av}^{(k)} = \sigma_{\rm d}^{(k)} + \sigma_{\rm p}^{(k)} \tag{3}$$

$$\sigma_{\rm d}^{(k)} = \frac{e^2}{3mc^2} \left\langle \Psi_0 \left| \sum_i r_i^{-1} \right| \Psi_0 \right\rangle \tag{4}$$

$$\sigma_{p}^{(k)} = -\frac{e^{2}}{6mc^{2}} \left\{ \frac{\hbar c}{2e\mu_{N}g_{Nk}} \times \left( \frac{M_{aa}}{A} + \frac{M_{bb}}{B} + \frac{M_{cc}}{C} \right) + 2\sum_{l}' \frac{Z_{l}}{r_{kl}} \right\}$$
(5)

Here  $\sigma_{av}$  is the average shielding, obtainable from NMR data, with  $\sigma_d$  and  $\sigma_p$  the diamagnetic and paramagnetic contribu-

Table 4 Comparison of experimental spin-rotation constants of FNO and FNO, with proportionality constants from INDO calculations

parameter	$M_{gg}(\exp)/\mathrm{kHz}$	M <sub>gg</sub> (nuc)/kHz	$M_{gg}(elec)/kHz$	proportionality <sup>a</sup> /GHz
		FNO		
$M_{aa}(N)$	38.5 (14)	-3.0	41.5	39.4
$M_{bb}(N)$	2.3 (2)	-0.6	2.9	4.7
$M_{cc}(\mathbf{N})$	2.4 (2)	-0.8	3.2	4.4
$M_{aa}(\mathbf{F})$	341.3 (26)	- 8.8	350.1	67.9
$M_{bb}(\mathbf{F})$	70.6 (5)	- 7.0	77.6	33.5
$M_{\rm cc}({\rm F})$	43.5 (5)	-6.9	50.4	34.9
		FNO <sub>2</sub>		
$M_{aa}(N)$	1.5	-1.0	2.5	5.3
$M_{bb}(N)$	1.5 (1)	-0.6	2.1	4.6
$M_{cc}(\mathbf{N})$	1.9 (1)	-0.7	2.6	2.5
$M_{aa}(\mathbf{F})$	7.5 (27)	-1.9	9.4	2.1
$M_{bb}(\mathbf{F})$	62.9 (6)	-9.5	72.4	39.9
$M_{cc}(\mathbf{F})$	32.5 (6)	-6.0	38.5	21.1

" The numbers given under 'proportionality' are the values of the right-hand side of eqn. (2), calculated using p-density matrix elements from INDO calculations with the molecular geometries of ref. 1 and 4.

tions. In eqn. (4) and (5), e and m are the charge and mass of the electron,  $\mu_N$  is the nuclear magneton,  $g_{Nk}$  is the g factor of the kth nucleus, and  $Z_l$  is the atomic number of nucleus lwhich is a distance  $r_{kl}$  from nucleus k. In eqn. (4),  $\Sigma_i r_i^{-1}$  is over all electrons.

For FNO and FNO<sub>2</sub> the paramagnetic contributions  $\sigma_p$ were calculated for the F atoms using eqn. (5). The second term was obtained using the published geometries.<sup>1,4</sup> The resulting values are for FNO,  $\sigma_p^{(F)} = -874$  ppm, and for FNO<sub>2</sub>,  $\sigma_p^{(F)} = -775$  ppm. From the published chemical shifts,  $\sigma_d^{(F)}$  can now be estimated. For FNO, Holmes *et al.*<sup>24</sup> obtained  $\delta = -479 \pm 1$  ppm relative to CCl<sub>3</sub>F. With the absolute shielding  $\sigma = 188.7$  ppm for F in CCl<sub>3</sub>F,<sup>25</sup> the average shielding  $\sigma_{av}^{(F)}$  is thus -290 ppm, making  $\sigma_{d}^{(F)} = 584$ ppm. A similar procedure was used for FNO<sub>2</sub>; however, there are two widely divergent values in the literature for the chemical shifts. Drago<sup>26</sup> gives - 394 ppm and Mason and van Bronswijk<sup>27</sup> give -221 ppm for  $\delta$ , both with respect to CCl<sub>3</sub>F. The resulting values for  $\sigma_d^{(F)}$  are 570 and 743 ppm, respectively. The first value is similar to that of FNO, whereas the second is widely divergent from it. Since there are no grounds for assuming the FN bonds to be drastically different in the two molecules, the first value is probably the correct one.

The diamagnetic shielding,  $\sigma_d^{(F)}$ , provides a measure of the electron density at the F atom. The values obtained for FNO and FNO<sub>2</sub>, 584 and 570 ppm, respectively, are somewhat larger than those of  $F_2$  (512.9 ppm)<sup>28</sup> and OCF<sub>2</sub> (560 ppm).<sup>29</sup> The implication is that electron densities at F are rather bigger in FNO and FNO<sub>2</sub> than in F<sub>2</sub> and OCF<sub>2</sub>, consistent with the greater ionic character of the NF bond. This is entirely consistent with the results of the analysis of the <sup>14</sup>N nuclear quadrupole coupling constants given above for FNO<sub>2</sub>.

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