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Molecular Structure of Fluorine Nitrate: Dangerous for Experiment and Theory

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Abstract: A general valence force field for $FONO_2$ is deriverd from Ne-matrix infrared spectra together with ^{15}N and ^{18}O isotopic shifts. A gas electron diffraction study results in a planar structure with the following geometric parameters (r_a distances and $\angle_\alpha$ angles with 3σ uncertainties): $N{=}O = 1.184(2)$ Å, $N{-}O = 1.507(4)$ Å, $O{-}F = 1.409(5)$ Å, $O{-}N{=}O_c = 117.1(9)^\circ$, $O{-}N{=}O_t = 108.4(18)^\circ$, $O_c{=}N{=}O_t = 134.5(21)^\circ$, and $N{-}O{-}F = 106.0(11)^\circ$. O_c and O_t are the oxygen atoms cis and trans to the O—F bond. The N—O single bond in fluorine nitrate is ca. 0.1 Å longer than those in nitric acid and methyl nitrate. Various ab initio calculations predict rather different N—O bond distances between 1.384 and 1.609 Å, depending on the level of theory (HF, MP, CC, or CI). Local density functional theory reproduces the experimental geometry perfectly. Nonlocal corrections, however, make the results drastically worse.

Introduction

Fluorine nitrate, $FONO_2$, was synthesized for the first time ca. 60 years ago by G. H. Cady.[2] Its structure has a long and controversial history. Already in 1937 Pauling and Brockway reported a gas electron diffraction study.[3] These authors remarked that the quality of their recorded intensities was not optimum, but the experiment could not be repeated because the sample had exploded. From the diffraction data it was concluded that $FONO_2$ possesses a nonplanar structure with the O–F bond perpendicular to the NO_3 plane and with an N–O single bond length of 1.39(5) Å. Around 1960, microwave spectroscopy clearly indicated planar structures for nitric acid, $HONO_2$,[4] and for methyl nitrate, CH_3ONO_2.[5] Primarily on the basis of these results, infrared spectra for $FONO_2$ were interpreted in terms of a planar structure.[6,7] From polarization data of the Raman spectra, it was concluded that the structure is nonplanar.[8,9] On the other hand, analysis of band contours in the infrared spectrum shows fluorine nitrate to be planar.[10] In the past five years, ab initio calculations have been performed by several groups.[11] All calculations clearly result in planar structures for $FONO_2$. The values reported for the N–O single bond length, however, differ strongly and vary from 1.384 to 1.558 Å. Molecules which consist of strongly electronegative atoms, such as F, O, and N, often cause problems for quantum chemical calculations. Well-known examples are FOOF[12] and FONO,[13] where various ab initio and local density functional theory calculations lead to drastically different results. In such cases the calculational method which reproduces the experiment correctly can be determined only by comparison with experimental data, such as geometric structures or vibrational frequencies. The published ab initio results for $FONO_2$ indicate that this molecule is another example of such a problematic case.

In the present publication we report the determination of the geometric structure of fluorine nitrate by gas electron diffraction and a harmonic force field derived from matrix spectra of various isotopic species. Furthermore, we present theoretical results obtained by various ab initio and local density functional theory methods which will be compared with the experimental structure. Attempts to record and assign the microwave spectrum in the frequency range 18–25 GHz were unsuccessful. The reason for this failure is most likely the very small dipole moment of this molecule and partial decomposition in the absorption cell. Various quantum chemical calculations predict dipole moments between 0.05 and 0.5 D, with the component in direction of the *a* axis smaller than that in the *b* direction. Some observed strong absorption lines were obviously due to decomposition products.

Vibrational Spectra

Several vibrational studies of $FONO_2$ have been performed in the past, including extensive infrared[7] and Raman[8] spectroscopic analyses. From the fundamentals of natural and ^{15}N-enriched $FONO_2$, a general valence force field was derived.[7] In order to improve this force field, more isotopic data and precise band positions are needed. Therefore, we reinvestigated the vibrational spectrum and measured from fundamentals of ^{18}O-enriched $FONO_2$. All new and prominent vibrational data are collected in Table 1. The most intense component of each band is given. The low ^{18}O content of $FONO_2$ (~4%) permits observation of only a few vibrations of monosubstituted *cis*- and *trans*-FONO*O. Since the planar structure is now established (see below), the assignment of the nine fundamentals is straightforward and according to ref 7. The matrix spectra allow precise measurements

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Table 1. Vibrational Wavenumbers of $FONO_2$ and Their Assignments

IR (gas)	nitrogen-14 Ne matrix	nitrogen-15 Ne matrix	oxygen-18 Ne matrix cis[a]	oxygen-18 Ne matrix trans[a]	Raman (solid (−196 °C))	assignment according to C_s symmetry
(s)	1762.5					$\nu_2 + \nu_6$
1760.9 (vs)	1758.4	1719.7	1744.0	1746.7	1745 (w)	ν_1 (a′)
1603 (vw)	1604.2					$2\nu_4$
(vw)	1600.1					$\nu_2 + \nu_7$
1417.8 (w)	1421.8				1415 (vw)	$2\nu_8$
(vw)	1364.5					$\nu_3 + \nu_6$
1301.2 (vs)	1300.9	1288.6	1276.8	1274.6	1310 (s)	ν_2 (a′)
1248.2 (m)	1256.2					$\nu_4 + \nu_6$
932 (m)	934.6					$\nu_5 + \nu_7$
927 (s)	929.8	929[b]	925.9[c]	924.4[c]	927 (m)	ν_3 (a′)
914 (m)	914.1				921 (w)	$2\nu_6$
803.4 (vs)	802.7	790.5	790.5	790.5	813 (w)	ν_4 (a′)
707.3 (s)	710.0	691.7[b]	706.1	706.1	706 (vw)	ν_8 (a″)
632.9 (w)	635.0	633.5[b]	629.0[c]	625.3[c]	638 (s)	ν_5 (a′)
458.5 (ms)	459.9	459.9[b]	455.8[c]	452.3[c]	465.5 (vs)	ν_6 (a′)
349.6[d] (vw)	341.9				353 (vw)	$\nu_4 - \nu_6$
302.6[d] (w)	300.0	399.0[b]	294.5[c]	299.5[c]	308 (ms)	ν_7 (a′)
151.6[d] (vw)	161.0	160.6[b]	160.6[c]	159.3[c]	181 (w)	ν_9 (a″)

[a] $N{=}^{18}O$ cis to OF and $N{=}^{18}O$ trans to OF. [b] Isotopic shift transferred from ref 7. [c] Calculated with the force field from Table 2. [d] Reference 7.

Table 2. Force Constants (10^2 N m^{-1}) and Potential Energy Distribution (PED) of $FONO_2$

	force constants[a]		PED								
	b	*c*	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
f_{rt}[d]	(13.1)	10.94	0.46	0.60							
f_{rc}[e]	(13.4)	11.48	0.64	0.33							
f_R[f]	(4.7)	3.60			0.53		0.56				
f_r[g]	(1.8)	2.48				0.47		0.69			
f_β[h]	(2.6)	2.60			0.19	0.49		0.13			
f_α[i]	(2.4)	2.37			0.22		0.18	0.33	0.29		
f_γ[j]	(1.5)	1.29			0.11			0.15	0.94		
f_{oop}[k]		0.39								0.99	
f_τ[l]		0.127									0.99
f_{rtc}	(0.24)	1.36	−0.14	0.11							
$f_{R\gamma}$	(0.27)	0.40			−0.11				−0.11		
f_{rR}	(0.15)	0.59					−0.13				
$f_{r\gamma}$	(0.56)	0.50						−0.14	0.14		
$f_{r\alpha}$	(0.43)	0.30						0.13			
$f_{\alpha\gamma}$	(0.26)	0.40			0.11			−0.15	−0.36		

[a] Further force constants contributing less than 0.1 to the PED are the following: $f_{rcr} = 0.46$ (0.60); $f_{r\alpha} = 0.099$ (0.81); $f_{\beta\alpha} = 0.16$ (1.22); $f_{rt\beta} = -0.82$ (−0.65); $f_{rtr} = 1.47$ (0.70); $f_{rt\gamma} = 0.29$ (0.25); $f_{rc\alpha} = -0.70$ (−0.72); $f_{rc\beta} = 0.59$ (−0.13); $f_{rc\gamma} = 0.29$ (−0.22); $f_{\beta\gamma} = 0.32$ (0.16); $f_{R\alpha} = 0.36$ (0.23); $f_{R\beta} = 0.36$ (−0.17). [b] MP2/6-31G*. [c] Experimental. [d] rt: N=O(trans). [e] rc: N=O(cis). [f] R: O—F. [g] r: N—O. [h] β: ∠O=N(cis/N—O). [i] α: ∠O=N(trans/N—O). [j] γ: ∠N—O/O—F. [k] oop: out of plane. [l] τ: torsion about the N—O bond.

of band positions and isotopic shifts and make the perturbation of some fundamentals by Fermi resonance easily visible. Such perturbation is important between $\nu_1/(\nu_2 + \nu_6)$ and $(\nu_5 + \nu_7)/\nu 3/2\nu_6$. In these cases, the observed isotopic shifts must be corrected before they are used in the force field calculation.

Normal Coordinate Analysis

The electron diffraction structural parameters (see below) together with the wavenumbers of the fundamentals (rounded average values between gas-phase and Ne-matrix values, Table 1) and the isotopic shifts, corrected for Fermi resonance and anharmonicity, were taken as input data in the calculation of a general force field with the program NORCOR.[14] The isotopic shifts were enlarged in general by 2% for anharmonicity and corrected for Fermi resonance as follows: The position of ν_1 is shifted to lower wavenumbers by Fermi resonance with $(\nu_2 + \nu_6)$. This shift is more prominent in the ^{14}N than in the ^{15}N species. Hence, the perturbed isotopic shift $\Delta\nu_1$(measured) = 38.7 cm^{-1} must be enlarged by about 3 cm^{-1}, yielding 42 ± 1 cm^{-1}. ν_2 is only little perturbed by $(\nu_4 + \nu_6)$. Because both ν_2 and $(\nu_4 + \nu_6)$ are shifted by ^{15}N substitution in the same way, no correction for Fermi resonance is needed and $\Delta\nu_2$ is set to 12.5 ± 0.1 cm^{-1}. ν_3 is strongly perturbed by $(\nu_5 + \nu_7)$ and by $2\nu_6$. The observed ^{15}N isotopic shift of about 1 cm^{-1} is very uncertain (±1 cm^{-1}). All other measured isotopic shifts are quite reliable because no combinations are in the vicinity of these fundamentals and the uncertainties arise from the precision of the measurements only: $\Delta\nu_4 = 12.4 \pm 0.1$, $\Delta\nu_5 = 1.5 \pm 0.5$, $\Delta\nu_6 \sim 0$, $\Delta\nu_7 = 1 \pm 0.5$, $\Delta\nu_8 = 18.7 \pm 0.5$, and $\Delta\nu_9 = 0.5 \pm 0.5$ cm^{-1}. Using the product rule in a′ and a″, it can be shown that the isotopic frequencies are correct to within the given uncertainties.

The fundamental wavenumbers and the ^{15}N isotopic shifts were used together with the force constants from the literature[7] and from ab initio calculations (MP2/6-31G*, see Table 2) to derive a preliminary force field. The iteration procedure was finished when all vibrational data were reproduced within their experimental uncertainties. With this force field, the wavenumbers of the ^{18}O-monosubstituted *cis*- and *trans*-FONO*O were calculated, allowing a correct assignment of the ^{18}O satellites in the Ne-matrix spectra (Table 1). The ^{18}O shifts were corrected similarly to the procedure described above, resulting in $\Delta\nu_1$(cis) = 16 ± 1, $\Delta\nu_1$(trans) = 14 ± 1, $\Delta\nu_2$(cis) = 25.0 ± 0.5, $\Delta\nu_2$(trans) = 27.2 ± 0.5, $\Delta\nu_4$(cis) = 12 ± 1, $\Delta\nu_4$(trans) = 12 ± 1, $\Delta\nu_8$(cis) = 4.0

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Table 3. Results of Electron Diffraction Analysis

Geometric Parameters[a]

N=O	1.184(2)	(p_1)	O—N=O$_c$	117.1(9)	(p_4)
N—O	1.507(4)	(p_2)	O—N=O$_t$	108.4(18)	(p_5)
O—F	1.409(5)	(p_3)	O$_c$=N=O$_t$	134.5(21)	
			N—O—F	106.0(11)	(p_6)

Interatomic Distances and Vibrational Amplitudes a_k from Electron Diffraction and Spectroscopic Data

	distance	a (ED)		a (spectr.)
N=O	1.184(2)	0.039(4)	(a_1)	0.038
O—F	1.409(5)	0.050[5][b]		0.050
N—O	1.507(4)	0.061(4)	(a_2)	0.059
O$_c$···O$_t$	2.184(17)	0.050[c]		0.049
O$_t$···O	2.191(25)			0.062
O$_c$···O	2.302(12)	0.061(9)	(a_3)	0.062
N···F	2.328(17)			0.070
O$_c$···F	2.453(31)	0.090[c]		0.093
O$_t$···F	3.358(20)	0.065(8)	(a_4)	0.060

[a] r_a distances in Å and $\angle_\alpha$ angles in degrees. Atom numbering is indicated in Figure 1. Error limits are 3σ values and include possible systematic errors due to the constraint for the O—F vibrational amplitude. [b] Not refined but varied in the given range to estimate possible systematic errors.[c] Not refined.

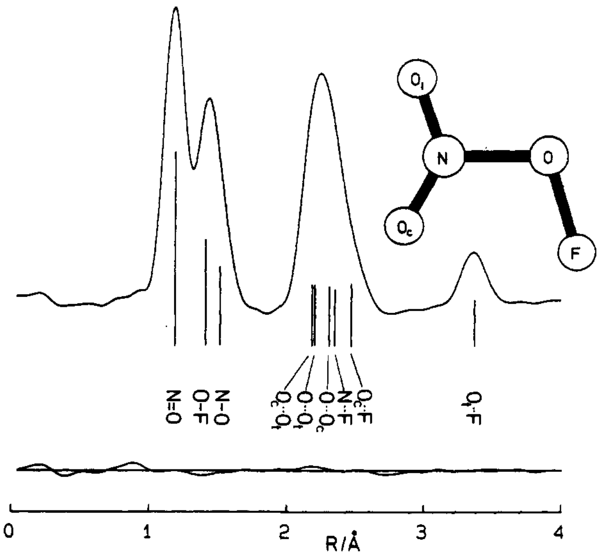

Figure 1. Experimental radial distribution function and difference curve.

± 0.5, and $\Delta\nu_8$(trans) = 4.0 ± 0.5 cm^{-1}. In the final refinement of the force field, the ^{18}O shifts were included in the input data and all vibrational data were fitted within the given uncertainties. It was, however, not possible to reproduce the experimental values for $\Delta\nu_1$(trans) and $\Delta\nu_4$(trans). The calculated isotopic shifts are $\Delta\nu_1$(trans) = 11.0 and $\Delta\nu_4$(trans) = 6.4 cm^{-1}. The results are presented in Table 2 together with the potential energy distribution (PED). Whereas the a″ vibrations are very characteristic, $\nu_8 = \delta$(oop) and $\nu_9 = \tau$(N—OF), all a vibrations are strongly coupled, except ν_7, which is a quite pure FON bending mode. Both ν_1 and ν_2 have strong terminal N=O stretching character, ν_3 and ν_4 are mixtures between O—F stretching and in-plane bending modes, and ν_4 and ν_6 show N—O stretching and in-plane bending character.

Gas-Phase Structure

The presence of two different F···O distances in the radial distribution curve (Figure 1) at 2.45 and 3.36 Å, which correspond to F···O$_c$ and F···O$_t$ (c = cis, t = trans), clearly demonstrates that the structure of FONO$_2$ is planar. For a nonplanar structure with the O—F bond perpendicular to the NO$_3$ plane, a strong peak near 2.90 Å would occur. Slight deviations from planarity with F—O—N=O$_c$ dihedral angles up to ca. 15° are compatible with the electron diffraction intensities. Such structures, however, are very unlikely and can be excluded on the basis of the ab initio calculations (see below). In the least squares refinement, the molecular intensities were modified with a diagonal weight matrix and known scattering amplitudes and phases were used.[15] The N=O double bond lengths were set equal (N=O$_c$ = N=O$_t$). If the difference between these two bond lengths is constrained to the ab initio values (0.004–0.010 Å, see below), the fit of the experimental intensities does not improve and the refined geometric parameters are affected less than their standard deviations. Constraints for vibrational amplitudes are evident from Table 3. With these assumptions, six geometric parameters p_i and four vibrational amplitudes a_k were refined simultaneously. Strong correlations (Table 4) exist between some refined parameters and cause large uncertainties, especially for the bond angles. The final results are summarized in Table 3.

Table 4. Correlation Coefficients (×100)

p_1	100									
p_2	–6	100								
p_3	14	0	100							
p_4	22	–13	–11	100						
p_5	–4	–26	–28	73	100					
p_6	–15	–3	0	–87	–75	100				
a_1	2	5	40	–5	–11	–1	100			
a_2	7	–1	78	–8	–21	0	38	100		
a_3	7	–8	–18	54	77	–77	–7	–16	100	
a_4	–1	–2	–1	–1	–1	1	0	–1	–1	100

Theoretical Calculations

Ab initio geometry optimizations of FONO$_2$ with various basis sets and different approximations for electron correlation were performed with the GAUSSIAN 92 program system.[16] The geometry, including out of plane coordinates, was completely relaxed in all calculations and the residual forces were below 3 × 10^{-4} au. Furthermore, various density functional theory calculations were done with the programs DGAUSS,[17] DMOL,[18] and ADF 1.0.1.[19] These calculations were initially carried out at the local density functional level (LDFT) with the local potentials of Vosko et al.[20] (DGAUSS and ADF 1.0.1) and of Barth et al.[21] (DMOL). In some cases the Stoll correction (*S*) was applied.[22] Subsequently, calculations were performed also at the nonlocal level with Becke (*B*)[23] and/or Perdew (*P*)[24] gradient corrections.

Results and Discussion

Despite the controversial results of an early electron diffraction analysis and various spectroscopic studies, the planarity of FONO$_2$, which is demonstrated in the present study, is not unexpected, considering the planar structures of nitric acid[4] and other nitrates XONO, with X = CH$_3$,[5] Cl,[25] and Br,[25] and the clear results of published ab initio calculations. The experimental value obtained for the N—O single bond length, however, is

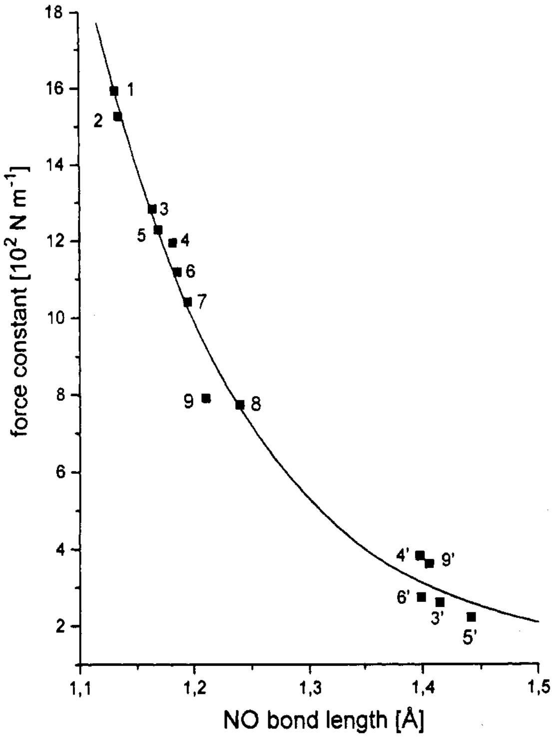

Figure 2. Force constants vs bond lengths for NO bonds in various molecules: **1**, ONF (refs 26 and 27); **2**, ONCl (refs 26 and 27); **3** and **3′**, *t*-CH_3ONO (ref 28); **4** and **4′**, *c*-CH_3ONO (ref 28); **5** and **5′**, *t*-HONO (ref 29); **6** and **6′**, *c*-HONO (ref 29); **7**, NO_2 (ref 30); **8**, NO_2^- (ref 30); **9** and **9′**, HNO_3 (ref 28).

surprising. This bond in $FONO_2$ (1.507(4) Å) is about 0.1 Å longer than those in $HONO_2$ (1.406(5) Å)[4] and CH_3ONO_2 (1.402(5) Å).[5] On the other hand, a similarly long N—O bond was recently determined for $ClONO_2$ (1.493(3) Å) and an intermediate value occurs in $BrONO_2$ (1.457(5) Å).[25]

It is interesting to compare the valence force constants (Table 2) with the respective bond lengths. For this purpose, a relationship between NO force constants and bond lengths from literature data is presented in Figure 2. From this curve, one can estimate an average N═O double bond length of 1.185 ± 0.005 Å and an N—O single bond length of 1.47 ± 0.05 Å. Both values are in good agreement with the electron diffraction results. The $N{=}O_t$ bond ($f_{rt} = 10.94 \times 10^2\ Nm^{-1}$) is weaker than the $N{=}O_c$ bond ($f_{rc} = 11.84 \times 10^2\ Nm^{-1}$), and the bond length difference of 0.008 Å estimated from the force constants is in accordance with ab initio results (see below). Little is known about O—F bonds in the literature. The OF force constant of $3.6 \times 10^2\ Nm^{-1}$ can be compared to the data for OF_2: $f_r = 3.97 \times 10^2\ Nm^{-1}$, O—F = 1.405 Å.[31] From this comparison a slightly longer O—F bond length than the electron diffraction result (1.409(5) Å) is expected. However, the force field supports one unusual structural feature of $FONO_2$: the central O atom is very weakly bound between N and F.

For clearness only, the N—O and O—F single bond lengths which were obtained by different quantum chemical methods are listed in Table 5. These two bonds show the strongest dependence on the calculational procedures. Tables of all optimized geometric parameters are included as supplementary material. The N═O double bonds vary between 1.162 and 1.211 Å, and the $N{=}O_t$ bond is predicted to be longer than the $N{=}O_c$ bond by 0.004–0.010 Å. In all cases the bond angles agree with the experimental values to within ±3°. In order to allow a direct comparison with the theoretical results, r_e values for the two single bond distances were derived from the experimental r_a values, using the approximate expression for diatomic molecules.[32] A surprisingly close agreement with the experimental structure is obtained with the most simple method (1), but the predicted vibrational frequencies deviate from the experimental values by up to ±300 cm^{-1}. The two widely applied standards methods 2 and 3 yield N—O distances which are 0.12 Å too short or 0.05 Å too long and O—F distances which deviate by −0.05 or +0.03 Å from the experimental value. Higher order perturbation theories 4 and 5 do not converge smoothly but show strong fluctuations for the two bond lengths. Larger basis sets (6-311G* or 6-31G*(2d)) in methods 2–5 have only small effects on the geometry. The two coupled cluster methods 6 and 7 result in nearly identical bond lengths. The calculated N—O distance is too short by about 0.03 Å, and the O—F distances agree very well with the experiment. The low-level CI method 8 predicts the N—O bond too short by 0.07 Å. The higher level calculation 9 reproduces the N—O bond length very well but results in an O—F bond which is too long by 0.04 Å.

LDFT calculations in its basic version reproduce the experimental bond lengths very well with method 12 and excellently with methods 10 and 14. The Stoll correction 15 has only a small effect. The application of nonlocal gradient corrections, however,

Table 5. Calculated N—O and N—F Bond Lengths

method	N—O	O—F
experiment (r_e values)	1.500(6)	1.402(7)
(1) HF/3-21G	1.494	1.421
(2) HF/6-31G*	1.385	1.350
(3) MP2/6-31G*	1.551	1.429
(4) MP3/6-31G*	1.458	1.409
(5) MP4SDTQ/6-31G*	1.609	1.447
(6) CCD/6-31G*	1.467	1.413
(7) CCSD/6-311G(2d)	1.467	1.403
(8) CISD//6-31G*	1.427	1.382
(9) QCISD(T)/6-31G*	1.518	1.440
(10) LDFT/TZP[a]	1.494	1.401
(11) NLDFT/TZP[a]	1.567	1.428
(12) LDFT/num[b]	1.485	1.417
(13) NLDFT/num[b]	1.583	1.462
(14) LDFT/TZP[c]	1.500	1.403
(15) LDFT/TZP (S)[c]	1.518	1.415
(16) NLFDT/TZP (S, B)[c]	1.656	1.476
(17) NLDFT/TZP (S, P)[c]	1.582	1.434
(18) NLDFT/TZP (S, B, P)[c]	1.600	1.446

[a] Program DGAUSS, TZP basis (Gaussian functions).[17] [b] Program DMOL, double numerical basis with d and f functions.[18] [c] Program ADF 1.0.1, TZP basis (Slater functions).[19] *S* = Stoll correction, *B* = Becke correction, and *P* = Perdew correction.

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leads to lengthening of the N—O bond by 0.07–0.16 Å and of the O—F bond by 0.03–0.07 Å and makes the agreement with the experimental data drastically worse. It is unsatisfactory that higher level calculations with ab initio or local density functional theory methods do not necessarily lead to closer agreement with the experiment.

Conclusion

Gas electron diffraction and ab initio calculations at various levels demonstrate that $FONO_2$ has a planar structure. The experimental N—O bond is unusually long, and this property is reflected in the respective force constant. Various ab initio methods predict rather different values for this bond length, and none of the applied methods reproduce the experimental structure very well. Local density functional theory calculations result in very good agreement with the experiment, but nonlocal gradient corrections make the agreement much worse.

Experiments

Caution! Fluorine nitrate is shock sensitive. Volatile materials were manipulated in a glass vacuum line equipped with PTFE valves (Young) and a capacitance manometer (Setra Type 280 E). Fluorine nitrate was prepared by direct fluorination of KNO_3 in a stainless steel cylinder.[33] KNO_3, 4% enriched in ^{18}O, was prepared from NO_2 (Baker), O_2, $H_2{}^{18}O$ (Prochem), and KOH. The crude fluorine nitrate was purified by repeated trap to trap condensation (−196 °C) through a trap held at −120 °C. The purity was checked by infrared spectroscopy. Neon (99.9999 %, Linde) was used as matrix material without further purification and mixed with $FONO_2$ (500:1) in a well-passivated (with ClF_3) stainless steel vacuum line. Details about the matrix isolation apparatus are given elsewhere.[34]

Neon-matrix infrared spectra were recorded on a Bruker IFS 66v FT spectrometer in reflectance mode using a transfer optic (Bruker). A DTGS detector together with a KBr beam splitter operated in the region 5000–400 cm^{-1}. In this region, 64 scans were coadded for each spectrum using an apodized resolution of 0.35 cm^{-1}. A liquid helium-cooled Si bolometer (Infrared Laboratories) together with a 6-μm Mylar beam splitter was used in the region 550–80 cm^{-1}. In this region, 256 scans were coadded for each spectrum using a apodized resolution of 0.25 cm^{-1}. Gas-phase infrared spectra were recorded on an FTIR spectrometer MX-1 (Nicolet) operating between 4800 and 400 cm^{-1} at a resolution of 2 cm^{-1} using a glass cell of 20-cm path length fitted with silicon windows (Wacker Chemie). Raman spectra of solid $FONO_2$ at −196 °C were recorded with a resolution of 2 cm^{-1} on a Bruker FRA 106 FT Raman spectrometer using the 1064-nm exciting line of a narrow-band Nd-YAG laser (ADLAS, DPY 301).

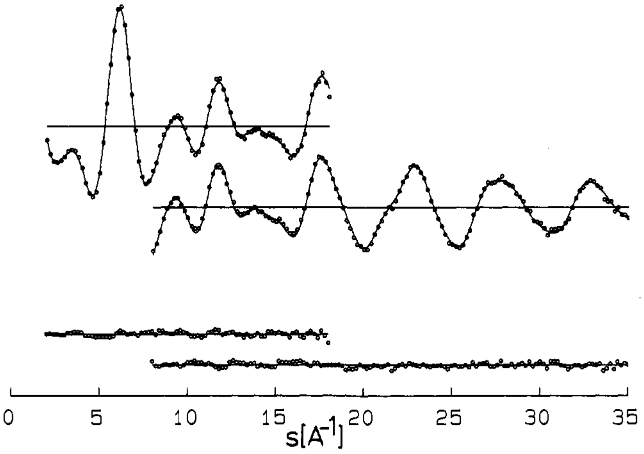

Figure 3. Experimental (dots) and calculated (full line) molecular intensities and differences.

A sample was transported to Tübingen in liquid nitrogen. The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2 at 25- and 50-cm camera distances and with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated by ZnO powder diffraction. The sample was kept at −105 °C, and the inlet system and nozzle were at room temperature. The camera pressure during the experiment was 10^{-5} Torr. The photographic plates were analyzed by the usual procedures,[35] and averaged molecular intensities in the scattering ranges 2–18 and 8–35 $Å^{-1}$ in steps of Δs = 0.2 $Å^{-1}$ are shown in Figure 3. Numerical values of the total scattering intensities are available as supplementary material.

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Supplementary Material Available: Tables of total electron diffraction intensities for $FONO_2$ and optimized geometric parameters obtained with different ab initio methods and LDFT and NLDFT calculations (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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