Theoret. Chim. Acta (Berl.) 63, 161–175 (1983)

THEORETICA CHIMICA ACTA

Ab initio Studies on ONH_3, ONF_3 and OCF_3^-, Using Polarization Functions and Configuration Interaction Methods

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SCF geometry optimizations, using double-zeta basis sets with polarization functions, either as *d*-orbitals or bond functions, were performed on ONH_3, ONF_3, and OCF_3^-. The bonding in these molecules is discussed with the help of orbital density plots and Mulliken population analyses. ONF_3 can be explained as donor-acceptor product of O with NF_3. For OCF_3^-, diffuse functions have also been added to the basis set. The *CF* distance is predicted to be 1.39 Å, in qualitative agreement with the known infrared spectrum. With the best basis set, the NF distance of ONF_3 is too short by 0.08 Å at the SCF level. A geometry optimization by the configuration-interaction method gives the NF distance as well as the ON distance in excellent agreement with experimental results.

Key words: SCF and CI calculations – Polarization functions – Geometry optimizations – Discussion of bondings – ONH_3 – ONF_3 – OCF_3^-.

1. Introduction

Many qualitative bonding schemes involve *d*-functions for explaining bonds between atoms that have no formal *d*-orbital occupation. Most interesting are bonds formed by second row atoms such as P and S. But there are also cases of bonds between first row atoms which lend themselves to an explanation involving *d*-orbitals. For example, in ONF_3 the NO bond is similar to an NO double bond, whereas the NF bonds are like elongated single bonds. The structure

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(C_{3v} symmetry) was determined by electron diffraction [1], with the NO distance being 1.159 Å (compared with 1.15 Å for the NO molecule) and the NF distance 1.43 Å (compared with the NF distance in NF_3 of 1.364 Å [2]). Qualitatively, one can say that nitrogen has expanded its valence shell by using *d*-orbitals, allowing it to be pentavalent, in violation of the octet rule [1, 3].

For many years theoretical chemists have tried to confirm the need for *d*-functions by using *ab initio* quantum chemical methods, and by comparing results obtained without and with *d*-functions. Although many studies were performed, and much work is still being done, no clear picture has yet emerged. The general impression among theoretical chemists is that *d*-orbitals become unnecessary when a good basis set, such as a double-zeta (DZ) basis, is used. Experimental chemists, who work with minimal basis sets for qualitative bond interpretations, continue to use *d*-functions, and confrontations between the two groups are commonplace.

The problem is further complicated by the dual role ascribed to *d*-orbitals. Coulson [4] distinguished between two situations of *d*-orbital participation. In one case, at least one *d*-orbital is clearly involved in the bonding, such as in sp^3d^2 octahedral hybrids. In the other case, the *d*-orbitals have the purpose of polarizing the *p*-orbitals, however little or no chemical significance can be attributed to such *d*-participation.

Recently, Ratner and Sabin [5, 6] discussed a criterion based on symmetry considerations for characterizing the need for the addition of *d*-orbitals to basis sets. According to their criterion, for each occupied MO there should be at least one basis orbital per atomic center, of a symmetry appropriate to contribute to the molecular orbital. This may necessitate the introduction of *d*-orbitals (e.g. the $1a_2$ orbital in SO_2 is localized on the oxygens unless *d*-orbitals are placed on the sulphur atom).

None of the above criteria suggest a direct *d*-orbital participation for ONH_3, OCF_3 and OCF_3^-, and therefore the only effect of using *d*-orbitals should result in the polarization of other atomic orbitals.

It has been known for some time that bond functions can effectively replace *d*-orbitals in their role as polarization functions. Bond functions (BF) are located in the bond region, rather than on the nuclei. Commonly one uses a set of *s*- and *p*-orbitals per bond. It is generally assumed that in situations where BF's give results very similar to *d*-orbitals, the polarization nature of the *d*-orbitals is proven, and the *d*-orbitals should not be ascribed a role as independent additional atomic orbitals. (This assumption must be considered with caution, since the *p*-orbitals in BFs could be arranged in such a way that they effectively duplicate *d*-orbitals.)

In the following, geometry optimizations will be performed on ONH_3, ONF_3 and OCF_3^-, using DZ basis sets, DZ basis sets with *d*-orbitals and DZ basis sets with bond functions. A comparison of the results obtained for various basis sets will allow to clarify the need for *d*-orbitals in these molecules. Aspects of the bonding in these molecules will be discussed by using density plots and Mulliken population analysis data.

2. Methods

The 4-31G [7] (abbreviated 4G) and the Huzinaga–Dunning $(9s5p/4s2p)$ [8] (abbreviated DZ) basis sets with the $4s/2s$ contraction for hydrogen were used with additional d-orbitals or bond functions as indicated. Short notations such as 4G-d or DZ-B should be obvious. For d-orbitals, an exponent of 0.8 was taken for C, N, O, F [9]. All bond function exponents were set as $\alpha_s = \alpha_p = 1$ [10]. They were located at the center of mass for bonds between first row atoms, and at the optimized distance of 0.25 Å from N for the NH bond. In the calculations on OCF_3^-, diffuse functions on all atoms were added [11]. The HONDO program [12] was used for basis sets containing d-functions, otherwise a modified version of GAUSSIAN70 [13] was employed. Geometry optimizations were done to an accuracy of 0.01 Å or 0.5 degree.

3. Results for ONH_3

Ammonia oxide ONH_3, is unknown, but its structure is expected to be similar to that of $ON(CH_3)_3$, for which an NO distance of 1.404 Å was determined by X-ray crystallography [14].

ONH_3 has been the subject of two recent papers. Radom et al. [15] optimized its geometry using STO-3G, 4-31G, 6-31G and Dunning's $(10s6p/5s4p)$ basis sets, without and with d-orbitals on N and O. Their results are given in Table 1. The NO distance without d-orbitals is found to be 1.52–1.53 Å, but is lowered by the addition of d-orbitals to 1.377 Å, a decrease of about 0.14 Å. Electron correlation was found to have little effect on bond lengths. Due to the significant drop of the optimized NO bond distance caused by the addition of d-orbitals, and the fact that the bond length without d-orbitals is by far too long, the authors

Table 1. Geometry optimizations on ONH_3

Basis set	R_{NO} (Å)	R_{NH} (Å)^a	$O\hat{N}H$ $(dg)^a$	E (hartree)
4G^b	1.531	(1.01)	(109.5)	−130.7596
6G^b	1.52	(1.01)	(109.5)	−130.8937
4G-d_N^{c}	1.45	1.001	108	—
4G-B_{NO}	1.43	(1.01)	(109.5)	−130.7786
4G-B_{all}	1.40	1.01	111.0	−130.8057
6G-$d_{N,O}$^{b}	1.377	1.009	111.6	−130.9332
expt.	1.404^d			

[a] Values in parentheses were not optimized
[b] Radom et al. [15].
[c] Olsen et al. [16].
[d] Experimental NO distance of $ON(CH_3)_3$, Ref. [14].

concluded that *d*-orbitals are important for the description of the ONH_3 molecule.

The other paper, by Olsen and Howell [16], is based on similar calculations. However, *d*-orbitals were only located on N. The optimized bond distance then becomes 1.45 Å (Table 1), about halfway between the results without *d*-orbitals and with *d*-orbitals on both N and O. Although the effect of *d*-orbitals on the optimized NO distance is big, the authors conclude on the basis of orbital interpretations, Mulliken population analyses and orbital energy lowerings that *d*-orbitals are not important to describe the bonding in ONH_3. For example, the total energy lowering was only 0.02 hartree, and the overlap populations as well as charges changed only slightly. Since the charge on O increased in the presence of *d*-orbitals, the authors concluded that *d*-orbitals polarize the lone pair on nitrogen, making it a better σ-donor, but do not influence the π-back donation from O in any significant way.

Our geometry optimization results, assuming C_{3v} symmetry, are given in Table 1. Repetition of the 4G and 4G-*d* series was not necessary due to the previous work.

The new contributions to the study of ONH_3 consisted in adding bond functions to the 4G basis set. In the first case, BFs were added to the NO bond only, in the second case to the NH bonds as well. The 4G-B_{NO} basis gives a smaller NO distance than the 4G-d_N basis. With BFs on all bonds, an NO distance of 1.40 Å is obtained, not as low as the 6G-$d_{N,O}$ distance, but quite reasonable, and in good agreement with the experimental NO distance in $ON(CH_3)_3$. It is seen from Table 1 that the NH distance is not affected by changes in the basis set, and that the optimized bond angles of the 4G-B_{all} and 6G-$d_{N,O}$ series are nearly identical.

From our results, it can be concluded that BFs are similar to *d*-orbitals as far as geometry optimizations and lowerings of the total energy are concerned. This means that ONH_3 has no need for the addition of independent atomic orbitals of *d*-type, as suggested also by the qualitative models put forward by Coulson and others, but that orbital polarization is important, in particular in the NO bond region.

Orbitals density plots (Fig. 1) are given for the three highest occupied molecular orbitals $1e$, $5a_1$, and $2e$ (the electronic configuration of ONH_3 is $4a_1^2 1e^4 5a_1^2 2e^4$), obtained from the calculations with the 4G-B_{all} basis set. It is seen that $1e$ and $5a_1$ are mainly responsible for the ON and NH bonding. The $1e$-orbital is a truly delocalized bonding type molecular orbital having in addition to ON and NH also bonding OH contours. The orbital $2e$, on the other hand, is essentially an oxygen lone pair, and is ON antibonding.

Mulliken population analysis data for the ON and NH bonds, as well as atomic charges, are given in Table 2 for the 4G and the 4G-B_{all} basis sets. With bond functions at center X between N and O, the overlap population for the NO bond was calculated as $P_{NO}+P_{NX}+P_{OX}+P_{XX}$. A corresponding expression was

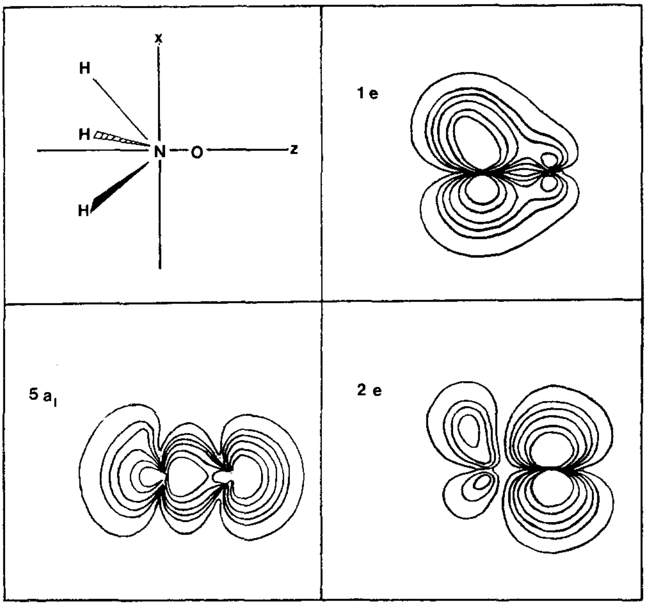

Fig. 1. Molecular orbitals of ONH_3 (contour values used are 0.10, 0.050, 0.020, 0.010, 0.0050 and 0.00010)

used for the NH bond, and in calculations of the following molecules. In the 4G basis, ON is antibonding, but it becomes bonding by the addition of bond orbitals, which also strengthen the NH bond (Olsen and Howell obtained a negative ON overlap population, even with *d*-orbitals.) In terms of charges, the

Table 2. Mulliken population analysis for ONH_3[a]

	4-31G basis			4-31G-B_{all} basis		
MO	ON		$NH^{b,c}$	ON		$NH^{b,c}$
$3a_1$	0.40		0.06	0.49		0.11
$4a_1$	−0.15		0.10	−0.03		0.13
$1e$	0.06		0.21	0.08		0.18
$5a_1$	−0.48		−0.02	−0.41		−0.02
$2e$	−0.06		0.02	0.01		0.02
Total	−0.23		0.59	0.23		0.74
	O	N	H	O	N	H
Charges	−0.60	−0.54	0.38	−0.57	−0.42	0.33
π els	3.91	2.65	—	2.88	2.58	—

[a] For both basis sets, the 4-31G-B_{all} optimized geometry was used. The results at the 4-31G optimized geometry are very similar.

[b] For degenerate orbitals average values are given.

[c] The gross orbital charges of the ON bond functions are 0.29, and of each set of NH bond functions 0.08.

improved bonding is accomplished by making oxygen and nitrogen less negative and thereby the hydrogens less positive. According to Table 2, the MO $3a_1$ is mainly responsible for the ON bond, and $1e$ for the NH bond. $5a_1$, which from the orbital plot, Fig. 1, appears to be ON bonding, is strongly ON antibonding. Disagreements between orbital plot and Mulliken population bond interpretations have been reported on many occasions. Although it is our tendency to place greater weight on orbital plots, the changes in overlap populations by adding bond functions to the basis set provide valuable information. The reversal of the ON bonding character, and the increased NH bonding in the 4G-B_{all} case, are accomplished by increased overlap populations of most MOs listed in Table 2, a notable exception being $1e$, which becomes slightly less NH bonding.

According to Table 2, bond functions cause a decrease in π electron population both on O and N, and an additional σ reduction on N. The net beneficiaries are the hydrogens.

Since standard basis sets, including polarization functions, give a good geometry for ONH_3 at the SCF level, no need for configuration-interaction studies was seen for this molecule.

4. Results for ONF_3 and Comparison with NF_3

Olsen and Howell [16] performed 4-31G geometry optimizations on trifluoroamine oxide ONF_3, resulting in an NO bond distance of 1.187 Å (vs. the experimental distance of 1.159 Å[1]), an NF distance of 1.412 Å (experimentally 1.43 Å), and an ONF angle of 117.2° (vs. 117.4° experimentally). They subsequently added a set of d-orbitals to nitrogen, and obtained an optimized NO distance of 1.156 Å, in excellent agreement with experiment. However, they did not attempt to optimize the NF distance with the 4G-d_{N} basis set. By detailed population analysis studies and molecular orbital plots they investigated the effects of the added d-orbitals, concluding that d-orbitals are more important in ONF_3 than in ONH_3, and that they can interact with the oxygen lone pairs, thereby shortening the NO bond and lengthening the NF bond. On the other hand, the d-orbitals in ONF_3, although essential, are not as important as in OPF_3, where the PO bond length is shortened even more, and the energy lowering is greater than in ONF_3.

Olsen and Howell found that the $6e$ orbital is the only one that lowers in energy upon addition of d-orbitals to the basis set, indicating a strong d-component in this orbital. Their population analysis data show that this orbital is about 50% p_π-d_π bonding.

Our geometry optimization results are given in Table 3. C_{3v} symmetry was always assumed. Bond functions for all bonds, and d-orbitals on all atoms were added to the 4G basis. Furthermore, optimizations were performed with the DZ and DZ-B_{all} basis sets, leading to slightly larger NO distances than the corresponding 4G basis sets. The 4G-B_{all} and 4G-d_{all} basis sets give 1.17 Å for R_{NO}, however

Table 3. Geometry optimization results and calculated dipole moment for ONF_3

Basis Set	R_{NO} (Å)	R_{NF} (Å)	O$\hat{N}$F (deg.)	E (hartree)	μ (Debye)
4G[a]	1.187	1.412	117.2	−426.7288	0.88
4G-d_N[a]	1.156	(1.412)[b]	(177.2)[b]	—	—
4G-B_{all}	1.17	1.36	116.6	−426.9059	1.20
4G-d_{all}	1.17	1.35	116.6	−426.9231	—
DZ	1.21	1.42	116.6	−427.2679	1.12
DZ-B_{all}	1.18	1.36	116.9	−427.4232	1.23
Experimental[c]	1.159	1.432	117.4	—	0.039

[a] Ref. [16].
[b] Values in parentheses were not optimized.
[c] Ref. [1].

they shorten the NF distance much below the experimental value (1.35/1.36 Å vs 1.43 Å experimentally).

This shows that the good agreement with the experimental NO distance, obtained by Olsen and Howell using the 4G-d_N basis set, is an artifact of the basis set, and not substantiated by improved methods. The calculated dipole moments, also shown in Table 2, are much too big, and worsen upon addition of polarization functions (0.88 Debye for the 4G basis).

Before discussing the bonding in ONF_3, a set of similar geometry optimization will be reported for NF_3. The purpose of these calculations was to relate the NF_3 to the ONF_3 orbitals, as will be discussed below. Table 4 gives the geometry optimization results for NF_3. Experimental values [2] are also given. Without polarization functions the NF distance is too long, with polarization functions too short. The addition of polarization functions lowers the NF distance by 0.05 to 0.06 Å, which is the same as obtained for ONF_3. The DZ-B_{all} basis set gives a dipole moment closest to the experimental value.

In Fig. 2, density plots of the valence molecular orbitals of ONF_3 and NF_3 are given as obtained from the DZ basis set. (The electronic configuration of ONF_3 is $6a_1^2 3e^4 7a_1^2 4e^4 8a_1^2 1a_2^2 5e^4 6e^4$.) The atoms are located as shown in Fig. 1, with the F_3 group on the left hand side. An attempt will be made to explain ONF_3

Table 4. Geometry optimization results and calculated dipole moment for NF_3

Basis set	R_{NF} (Å)	F$\hat{N}$F (deg.)	E (hartree)	μ (Debye)
4G	1.38	102.5	−352.0761	0.42
4G-B_{all}	1.32	103.0	−352.2016	0.14
4G-d_{all}	1.33	102.6	−352.2126	—
DZ	1.38	102.8	−352.5251	0.48
DZ-B_{all}	1.33	102.7	−352.6318	0.27
Experimental[a]	1.364	102.37		0.234

[a] Ref. [2].

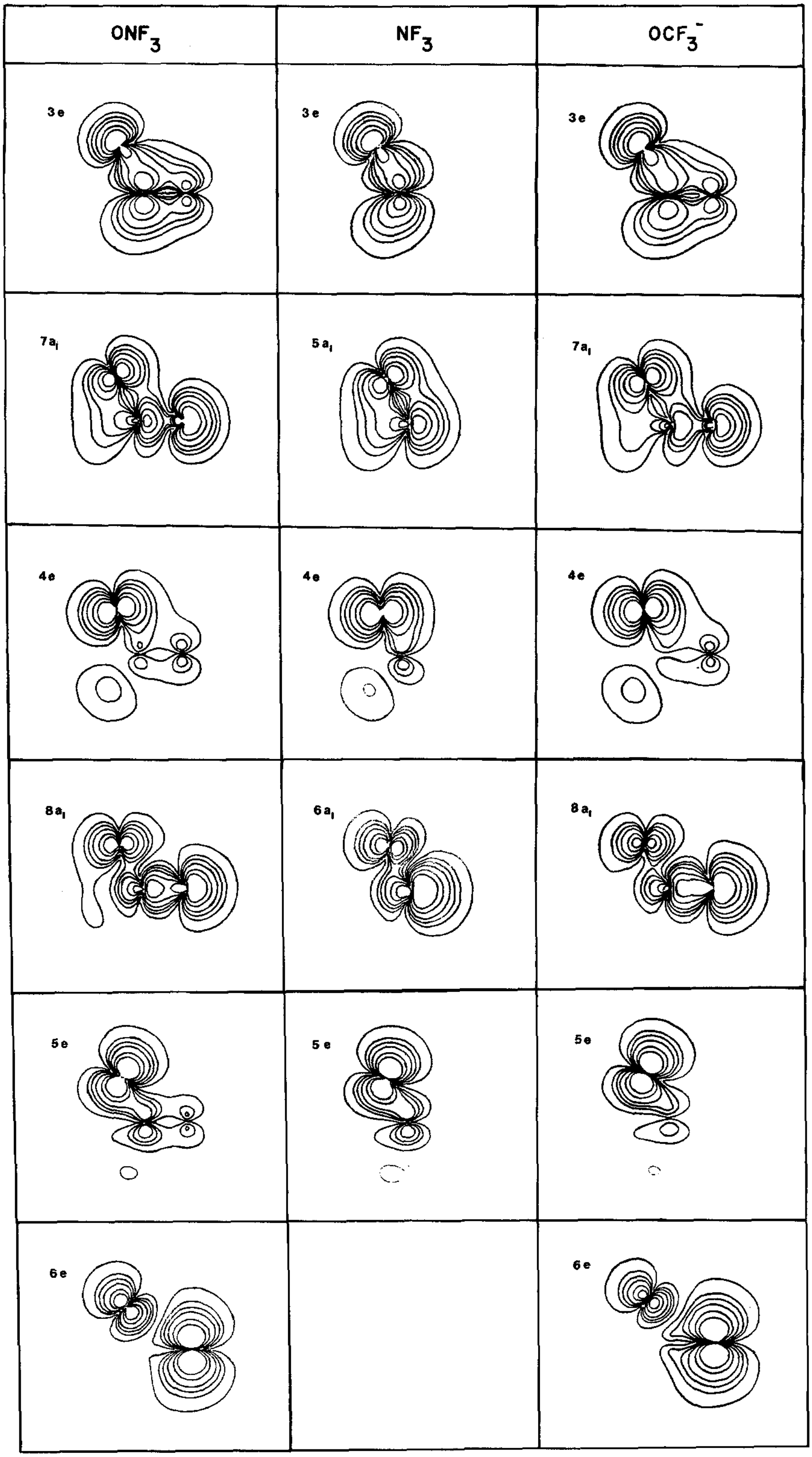

Fig. 2. Molecular orbitals of ONF$_3$, NF$_3$ and OCF$_3^-$ (the same contour values are used as in Fig. 1)

as a donor-acceptor product of O with NF_3. A similar scheme was used to explain the bonding in OPF_3 [17]. In the case of ONF_3, back donation of oxygen lone pair electrons into empty d-orbitals on nitrogen can be ruled out. The electron donor (σ-donor) properties of NF_3 are associated with the lone pair on nitrogen, which is a $2s$-$2p_z$ hybrid transforming according to the a_1 irreducible representation of the C_{3v} group. Inspection of the valence molecular orbitals of NF_3 indicates that $5a_1$ and $6a_1$ fit this criterion. In particular, $6a_1$ retains most of the lone pair on nitrogen, and looks like a good σ-donor orbital. Those orbitals on NF_3 which will act as acceptor orbitals (π-acceptor) should have a large $2p_x$-$2p_y$ component on nitrogen, and therefore e-symmetry. Of the qualifying orbitals, $3e$ is the best acceptor orbital. Both the $4e$ and $5e$ orbitals have large contributions from lone pairs on the fluorines which are directed towards the incoming oxygen.

From Fig. 2 it can be seen that those ONF_3 molecular orbitals which form the NO bond ($3e$ and $8a_1$) correlate very well with the above selected orbitals ($3e$ and $6a_1$) of NF_3. The NO σ bond in ONF_3 results from a combination of the $7a_1$ and $8a_1$ orbitals, with the latter having the larger contribution as predicted by the corresponding NF_3 orbitals. The NO π bond is due to the $3e$ orbital, with much smaller contributions from the $4e$ and $5e$ orbitals, as predicted.

A comparison of those molecular orbitals in ONF_3 and NF_3 which are responsible for NF bonding ($3e$, $5a_1$ and $5e$ in NF_3; $3e$, $7a_1$ and $5e$ in ONF_3) shows that the electron density in the NF region is reduced by delocalization into the NO bond. This explains why the NF bond in ONF_3 is longer than in NF_3. The lengthening of the NF bond in ONF_3 cannot be explained as being due to four coordinate nitrogen, since the calculated NF bond distance in the isoelectronic NF_4^+ cation is only 1.34 Å (4G basis set, FNF angle kept at 109.7°, total energy of −450.8823 hartree).

In Table 5 population analysis data for ONF_3 are given , again comparing the 4G with the 4G-B_{all} set. The use of bond functions permits large charge accumulations in the bond regions, leading to otherwise uncommon bond populations of 1.2 for the ON, and 1.06 for the NF bond. If one uses d-orbitals, then most of their charge is counted towards the atomic net population and not towards the bonds. Most of the molecular orbital contributions to overlap populations increase on account of the bond functions. The ON overlap of the $3e$ and $8a_1$ orbitals, mentioned earlier in connection with the donor-acceptor model, increases slightly in the 4G-B_{all} basis. A look at the atomic charges shows that while N and the F's become less charged, the negative charge on oxygen increases slightly upon the addition of bond functions. As expected, the calculated dipole moment increases, and thereby moves further away from the experimental value. Olsen and Howell report a charge decrease on oxygen when adding d-orbitals to N. (Their population analysis was performed at the experimental geometry, not at the optimized one as ours). The $8a_1$ orbital has a large ON overlap population, in agreement with the above prediction that this orbital accomplishes the σ-donation from NF_3 to the ON bond. Of the π-type back donation orbitals,

Table 5. Mulliken population analysis for ONF_3[a]

	4-31G basis			4-31G-B_{all} basis		
MO	ON		NF[b,c]	ON[d]		NF[d]
$3e$	0.10		−0.04	0.12		0.08
$7a_1$	−0.90		0.10	−0.55		0.09
$4e$	0.01		0.00	0.02		0.05
$8a_1$	0.13		−0.02	0.15		−0.02
$5e$	0.00		0.01	0.00		0.04
$6e$	0.22		−0.07	0.34		0.12
Total	0.21		0.06	1.20		1.06
	O	N	F	O	N	F
Charges	−0.31	+0.90	−0.20	−0.33	+0.77	−0.15

[a] The 4-31-B_{all} optimized geometry was used in both cases.
[b] For degenerate orbitals average values are given.
[c] The MO $4a_1$ has an NF overlap population of 0.15.
[d] The gross orbital charges on the ON bond functions are 0.47, and 0.32 on each set of NF bond functions.

$3e$ has the largest NF overlap population (besides $6e$, which has no equivalent orbital in NF_3).

Configuration interaction calculations for ONF_3 will be described in section 6.

5. Results for OCF_3^-

The trifluoromethoxide anion OCF_3^- was reported by Redwood and Willis [18] in 1965. The structure has not been determined. The vibrational spectrum supports the assumption of a pseudotetrahedral structure of C_{3v} symmetry [19]. The vibrational frequencies are comparable to those of ONF_3. The CO frequency, 1560 cm^{-1}, is about 500 cm^{-1} higher than in singly bonded CO, whereas the CF_3 frequencies have decreased by about 350 cm^{-1} with respect to CF_4 [19].

Minimal basis *ab initio* SCF calculation were performed by So [20], who reached the conclusion that the structure of OCF_3^- is similar to that of ONF_3. He found the CO distance to be 1.368 Å, with an estimated bond order of 1.45. The CF distance was found to be 1.454 Å, and the OCF angle 116.6°.

We performed geometry optimizations (in C_{3v} symmetry) using the 4G and DZ basis sets as before, with diffuse orbitals [11] added to the DZ basis set because of the negative charge. The results are given in Table 6. The CO bond distance drops by 0.01 to 0.02 Å upon addition of polarization functions, whereas the CF bond distance lowers by 0.03 to 0.04 Å. Again, bond functions and d-orbitals give essentially the same results. The results differ strongly from the minimal basis values cited above. The calculated CF bond distance is larger than usual

Table 6. Geometry optimization results for OCF_3^-

Basis set	R_{CO} (Å)	R_{CF} (Å)	$O\hat{C}F$ (deg.)	E (hartree)
4G	1.23	1.42	116.5	−410.5690
4G-B_{all}	1.22	1.39	116.9	−410.6835
4G-d_{all}	1.21	1.39	116.9	−410.7058
DZ-Diff	1.24	1.43	117.0	−411.0840
DZ-B_{all}-Diff	1.22	1.39	116.9	−411.2034
Minimal[a]	1.368	1.454	116.6	

[a] Ref. [20].

(1.32 Å in CF_2 [21], 1.317 Å in CF_4 [22]) while the CO bond distance is similar to distances in other CO double bonds (1.203 Å in H_2CO [21]).

The unusually large calculated CF distance is in qualitative agreement with infrared spectra, where a decrease of the CF frequencies by 350 cm^{-1} relative to CF_4 has been reported [19]. Many examples show that double zeta plus polarization basis sets lead to optimized bond distances which are about right or too short, but rarely too long [10]. This situation would again parallel that found for ONF_3, where the experimental NF distance is larger than that found in NF_3 and NF_4^+. Whereas the CF frequency of OCF_3^- decreased by 350 cm^{-1} relative to CF_4, the NF frequency of ONF_3 decreased by only 24.1 cm^{-1} relative to NF_4^+ [19, 23], with a corresponding increase in the NF bond distance by 0.09 Å (using the calculated NF_4^+ distance).

The molecular orbitals of OCF_3^-, whose density plots are also given in Fig. 2, have a striking similarity to those of ONF_3, indicating the close relationship between the structures of these two molecules. The electron configuration of

Table 7. Mulliken population analysis for OCF_3^- [a]

	4-31G basis			4-31G-B_{all} basis		
MO	OC		CF[b]	OC		CF
$3e$	0.06		0.08			
$7a_1$	−0.40		0.09			
$4e$	0.00		0.00			
$8a_1$	0.28		−0.01			
$5e$	0.00		0.03			
$6e$	0.26		−0.13			
Total	0.93		0.29	1.53		0.71
	O	C	F	O	C	F
Charges	−0.77	1.29	−0.51	−0.74	1.04	−0.43

[a] The 4-31-B_{all} optimized geometry was used in both cases.

[b] Average values are given for degenerate orbitals.

OCF_3^- is the same as that given for ONF_3, except that the orbitals $5e$ and $8a_1$ are interchanged. $8a_1$ is the second highest occupied MO of OCF_3^-.

In Table 7 Mulliken population results are given for OCF_3^-. Molecular orbital values in the 4G-B_{all} basis are not available. The effect of added bond functions is to increase the bond population, and to decrease the charges on all atoms. The extra negative charge is seen to reside mainly in the OC region, on O, and on the F's. With bond functions, the CF population is smaller than the corresponding NF population of ONF_3. Despite the negative molecular charge, carbon is more positive than N in ONF_3.

Since the experimental geometry of OCF_3^- is not known, and the theoretical results look reasonable, no CI calculations were performed on this molecule.

6. Configuration Interaction Studies on ONF_3

For ONF_3, the optimized NF bond distance, using a polarized DZ basis set, is 0.08 to 0.09 Å shorter than the experimental distance, depending on the details of the basis set. The NO bond distance is 0.01 to 0.02 Å too long. For ONH_3, the optimized NO distance is probably within 0.02 Å of the exact value, although experimental numbers for this molecule are not available. Similarly, the calculated OCF_3^- results at the SCF level are assumed to be good.

This leaves the NF distance of ONF_3 as the only geometry parameter that needs a correlation correction. A similar situation occurred for ONF [24], where the best polarized basis set gave an NF bond distance too short by 0.12 Å at the SCF level, and configuration-interaction methods were required in order to correct this error.

For the following studies, the CI program by Buenker and Peyerimhoff [25] was used, and CI calculations were performed on ONF_3 with the DZ-B_{all} basis set. The calculations were centered around the experimental values. In the first series, the NO distance was kept fixed at 1.16 Å, and the NF distance varied from 1.41 to 1.43 to 1.45 Å. In the second series, the NF distance was fixed at 1.43 Å, and the NO distances of 1.14 and 1.18 Å were selected. The ONF angle was always kept constant at 117.4°. The nine lowest-energy occupied orbitals (to $7a'$, $2a''$ in C_s symmetry), up to an orbital energy of about −1.6 hartree, were frozen (i.e. always doubly occupied), still leaving 24 valence electrons available for excitations. The 16 highest-energy virtual orbitals (34-44a' and 18–22a''), with orbital energies above 3.1 hartree, were discarded. The number of possible single and double excitations from the ground state Hartree–Fock configuration was 30 715. After the configuration selection, using an energy threshold of 20 μh, about 5000 configurations remained for the final diagonalization. Since the extrapolation error was about 0.002 h, and the number of selected configurations was virtually constant, unextrapolated CI energies were used for the optimization. Extrapolated energies showed the same trends as the actual CI energies. The CI energies are given in Table 8. The interpolated NF distance is about 1.425 Å, in good agreement with the experimental value. The

Table 8. CI energies obtained for ONF_3[a]

R_{ON} (Å)	R_{NF} (Å)	E_{CI} (hartree)	No. of CFs[b]
1.16	1.41	−427.763 094	5046
1.16	1.43	−427.763 321	4995
1.16	1.45	−427.761 745	5059
1.14	1.43	−427.762 752	4971
1.18	1.43	−427.762 726	5015

[a] At $R_{ON} = 1.16$ Å and $R_{NF} = 1.43$ Å, the extrapolated energy (for energy threshold 0) was −427.820 h, and the full-CI energy −427.863 h.

[b] The number of configurations selected with energy threshold above 20 μhartree.

interpolated NO distance is very close to 1.16 Å. These calculations confirm that the short NF and the slightly too long NO distance at the SCF level is due to the lack of electron correlation, and can be easily corrected without the need to further increase the basis set.

The dipole moment at $R_{NO} = 1.16$ Å and $R_{NF} = 1.43$ Å is 0.53 D at the SCF level, and 0.52 D by CI. Correlation appears to have a negligible effect on the dipole moment in this case. The experimental value is 0.039 D [1]. The large discrepancy at the CI level is somewhat disappointing, and can in general terms be explained by the lack of high-order angular momentum functions in the basis set, and the severe restrictions introduced due to configuration selection, which may have eliminated most of the single excitations (see discussion of the dipole moment of CO [26]). Also, the relatively large frozen part of the orbital space may have contributed to the 0.5 D error in dipole moment.

The excited configurations which make the most significant, however still very small, contributions to the SCF configuration are $6a_1 3e \rightarrow 9a_1 7e$ (0.004) and $6e^2 \rightarrow 7e^2$ (0.002), with the square of the CI coefficients given in parentheses. A simple generalization of the ONF interpretation is not possible. There, it could be shown that the correlating configurations replaced orbitals bonding in NF by NF antibonding orbitals, in order to accomplish a lengthening of the NF bond distance. While the $3e$ orbital of ONF_3 is definitely NF bonding, and both $7e$ and $9a_1$ are NF antibonding, the role of the $6a_1$ and $6e$ orbital replacement is not quite clear. These orbitals appear to be NF antibonding.

7. Discussion and Conclusion

In Table 9 SCF geometry optimization results are compared for the three molecules. The effect of polarization functions is strongest for the ON bond of ONH_3, with a shortening of 0.13 Å, followed by the NF bond of ONF_3 which is shortened by 0.05 Å. The latter is the only bond distance in considerable disagreement with the experimental value, as far as available. It is found to be too small by 0.07 Å with bond functions on all bonds. There is a definite need

Table 9. Comparative geometry optimization results[a]

Bond	ONH_3	ONF_3	OCF_3^-
ON/ON/OC	1.53/1.40(1.40?)	1.19/1.17(1.16)	1.23/1.22
NH/NF/CF	1.01/1.01	1.41/1.36(1.43)	1.42/1.39

[a] Bond distances in Å. First number for 4-31G, second for 4-31G-B_{all} basis set. Experimental values in parentheses.

Table 10. Comparative population results[a]

	ONH_3	ONF_3	OCF_3^-
ON/ON/OC	−0.23/0.23	0.21/1.20	0.93/1.53
NH/NF/CF	0.59/0.74	0.06/1.06	0.29/0.71
charge on O	−0.60/−0.57	−0.31/−0.33	−0.77/−0.74
charge on N/C	−0.54/−0.42	0.90/0.77	1.29/1.04
charge on H/F	0.38/0.33	−0.20/−0.15	−0.51/−0.43

[a] First number for 4-31G, second for 4-31G-B_{all} basis set.

for electron correlation. It was shown [24] that for ONF the NF distance dropped from 1.47 to 1.38 Å upon the addition of bond functions, and that electron correlation raised it to 1.52 Å, in agreement with the experimental value. A similar situation, although not as drastic, applies to ONF_3. CI calculations, performed with the DZ-B_{all} basis set, restore the NF bond distance to about 1.425 Å. For NF_3, bond functions cause a lowering of the optimized NF distance by 0.06 Å, 0.04 Å below the experimental distance. There is no doubt that a CI treatment would give a very good NF distance. On the other hand, optimized bond angles usually remain almost unchanged under the effect of polarization functions.

In Table 10 population analysis data are compared for the molecules under discussion. As expected, for ONH_3 O and N are negative, H positive, whereas for ONF_3 and OCF_3^- the F's are negative and N or C positive. The addition of bond functions to the 4-31G basis set increases all bond populations, most for the ON and the NF bonds of ONF_3. The use of *d*-orbitals instead of bond functions leads to very similar optimized geometries. This point was made with respect to fluorine bonds in an earlier paper [10]. Bond populations and charges on atoms obtained from *d*-orbital basis sets differ strongly from those obtained by bond functions, due to the fact that *d*-orbitals are located on the nuclei, whereas bond functions are located in the bond region.

Acknowledgments. This work was supported by an operating grant from the Natural Sciences and Engineering Research Council of Canada, and by a grant of computer time from this University.

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Received January 12, 1983