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Ab initio Studies on Several Species of the Formula X_3YO and X_3YOH

Geometries and Electronic Structure

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Ab initio molecular orbital calculations using both minimal and extended basis sets have been applied to two isoelectronic sets of molecules. One set corresponds to the 18 electron species H_3NO, H_3CO^- and H_3COH while the second set contains the 42 electron fluorinated molecules F_3NO, F_3CO^- and F_3COH. The geometries of these molecules have been optimized, using both the minimal STO-3G and the extended 4-31G basis sets. These comparative calculations reveal that the 4-31G basis produced structural parameters in much better agreement with experiment. The effect of including *d*-orbitals in the basis set was also investigated. For the fluorinated oxides it has been found that the optimized 4-31G structures were only slightly altered by the addition of *d*-orbitals. For H_3NO, on the other hand, the inclusion of *d*-orbitals considerably shortens the N–O bond distance. Both H_3NO and CF_3OH, which are unknown experimentally, are theoretically predicted to be capable of existence. The electronic structures of these molecules have also been examined using electronic partitioning according to the Mulliken scheme.

Key words: Electronic structure of X_3YO type compounds

1. Introduction

Ab initio molecular orbital theory has been rather successful in reliably predicting molecular geometries [1–3]. Pople's work on neutral molecules [4–8] and carbonium ions [9–11] has amply demonstrated that reliable predictions of geometry are obtained at both the minimal or STO-3G basis set level [12] and the split-valence (extended) or 4-31G basis [13]. Fewer studies on anions have been reported [14] but Radom [15] has completed STO-3G and 4-31G calculations on the geometries of 18 anions. His general conclusion was that while the STO-3G

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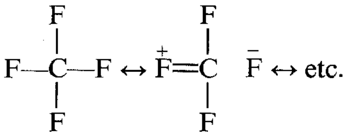
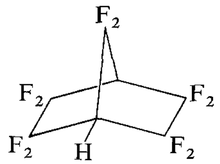
basis is less reliable for anions than it is for neutral molecules, the extended basis gives calculated structures in much better agreement with experiment.

We wish to report herein the results of *ab initio* molecular orbital calculations (employing a variety of basis sets) on four oxides (H_3NO, F_3NO, H_3CO^- and F_3CO^-) and two alcohols (H_3COH and F_3COH). Two of the oxide structures are anions corresponding formally to the loss of a proton from the alcohol. The molecules without fluorine form an isoelectronic set, each molecule containing 18 electrons while the fluorinated molecules all contain 42 electrons. In the latter series of molecules we will examine the effect of fluorine substitution on the electronic structures of these molecules. Experimentally, fluorine is known to alter both the physical and chemical properties of organic compounds in unusual and interesting ways [16]. A simple example of the unusual effect of fluorine substitution in methanes is the shortening of the C–F bond distance as one proceeds from CH_3F (1.385 Å) to CF_4 (1.328 Å). A number of rationalizations [16] have been advanced for this trend, the most popular, but not necessarily the best, is the fluorine hyperconjugation or double bond – no bond theory of resonance [17]:



$$\mathrm{F{-}\overset{\displaystyle F}{\underset{\displaystyle F}{C}}{-}F} \leftrightarrow \mathrm{\overset{+}{F}{=}\overset{\displaystyle F}{\underset{\displaystyle F}{C}}\ \ \overset{-}{F}} \leftrightarrow \text{etc.}$$

Hine [18] has suggested that each C–F bond is increased in stability by 3.2 kcal/mol for each resonance form available to it. Streitwieser [19], on the other hand, argues against fluorine hyperconjugation since he finds the bicyclic molecule



to be more acidic than $(CF_3)_3C$–H.

Because of Bredt's rule the double bond resonance structures arising from fluorine hyperconjugation cannot form at the bridgehead position and the acidity is simply explained by the inductive effect of fluorine [19].

The effect of fluorine on the structure of the amine oxides is well known experimentally [20]. While the trialkylamine oxides are salt-like in character, trifluoramine oxide has the properties of a covalent substance. Spectroscopic studies [21] suggest the molecule has close to a tetrahedral structure (C_{3v}) with a very short N–O bond as revealed by electron diffraction studies [22]. Christie *et al.* [23] have recently analyzed the vibrational spectrum of the isoelectronic CF_3O^- species and assigned it a pseudo-tetrahedral structure of C_{3v} symmetry. The vibrational frequencies for these two isoelectronic molecules were quite similar so that Christie *et al.* [23] suggested that the electronic structure of F_3NO and F_3CO^- should be rather similar.

Although F_3CO^- is known [24], it cannot be prepared conventionally from the parent alcohol since trifluoromethanol is unknown and is thought to be incapable of existence due to the ease of elimination of HF in compounds having a fluorine atom in a position α to an hydroxyl group.

It is our desire, with the aid of *ab initio* molecular orbital theory, to shed further light on the electronic structures of these interesting molecules.

2. Calculations

All of the calculations reported in this paper are of the SCF-LCAO-MO type with no empirical parameters being utilized. The majority of the computations were performed using the single determinant theory of the GAUSSIAN 70 series of programs [25]. The basis sets we have employed are described as follows:

Minimal. The smallest basis set used is STO-3G [12] where each STO was expanded as a linear combination of three Gaussians.

Extended. In the split-shell basis two functions, an inner and an outer part, are used for each valence shell orbital. We used the 4-31G basis [13] which is comparable to double zeta [26] in accuracy. Typical discrepancies between optimized geometries at this level of theory and experiment are 0.01 Å bond distances and 4^0 for bond angles. Complete geometry optimizations on the molecules considered in this study have been carried out using both the minimal STO-3G basis and the extended 4-31G basis.

Extended and Polarization. We have improved the 4-31G basis by adding a set of five pure *d*-type functions with an exponent, of 0.8, a value suggested by Pople and Hariharan based on optimization studies [27]. The *d*-orbitals were only admitted to the central atom (C or N). We refer to this basis as the 4-31G(d) basis and we have only carried out optimizations of the C–O or N–O bond leaving the other geometric parameters fixed at their optimized values found using 4-31G theory. The calculations using the 4-31G(d) basis set were carried out using the POLYATOM program [28]. For the 42 electron fluorine oxides the full basis set consists of 106 primitive Gaussians, contracted to 51 basis functions.

3. Results and Discussion

3.1. Geometries

Table 1 compares the results of the geometry optimization studies for the six molecules studied, with experimental data where available. The first four oxides in the table are predicted to be pseudo-tetrahedral having C_{3v} symmetries. The two alcohols are predicted to have a C_s geometry with the staggered conformations being favored (1–2 kcal/mol) over the eclipsed form.

H_3NO: Both the minimal STO-3G and the extended 4-31G basis predicts a rather long N–O bond distance (1.58 Å [10] and 1.54 Å, respectively). An even longer bond length (1.69 Å) was predicted by Hart [29] using a minimal basis set of

Table 1. Geometry predictions vs basis sets for X_3YO and X_3YOH

Molecule	Basis	$r_{(Y-O)}{}^a$	$r_{(X-Y)}{}^a$	$r_{(OH)}{}^a$	$\theta_{(OYX)}{}^b$	$\phi_{(YOH)}{}^b$	Energy (hartrees)
H_3NO	STO-3G	1.58	1.038	—	112.8	—	−129.1697
	4-31G	1.543	1.00	—	108	—	−130.7601
	4-31G(d)	1.45	1.00	—	108	—	−130.7830
H_3CO^-	STO-3G	1.363	1.122	—	115.6	—	−112.7055
	4-31G	1.36	1.12	—	115.8	—	−114.2185
F_3NO	STO-3G	1.32	1.41	—	116	—	−421.4644
	4-31G	1.19	1.412	—	117.2	—	−426.7287
	4-31G(d)	1.16	1.41	—	116	—	−426.8169
	Expt'l.	1.16	1.432	—	117.1	—	—
F_3CO^-	STO-3G	1.276	1.423	—	117.0	—	−405.2064
	4-31G	1.233	1.417	—	116.7	—	−410.5690
	4-31G(d)	1.210	1.417	—	116.7	—	−410.6407
H_3COH	STO-3G	1.432	1.094	0.991	110.8	103.3	−113.5486
	Expt'l.	1.434	(1.09)^c	0.94	109.5	105.9	—
F_3COH	STO-3G	1.401	1.380	0.991	110.4	104	−405.9571
	4-31G	1.346	1.347	0.947	110.9	115.6	−411.0982

^{a}Bond distances in Å. ^{b}Bond angles in degrees. ^{c}Not determined experimentally.

Gaussian lobe functions. The addition of polarization functions to the 4-31G basis shortens the N–O bond distance considerably to 1.45 Å. The magnitude of the N–O bond length reduction is similar to that found for hypervalent molecules [30]. However, the total energy lowering due to the inclusion of *d*-orbitals is only 0.023 hartrees whereas the energy lowering in hypervalent molecules is usually an order of magnitude larger than that found for H_3NO. The N–O potential curve of ammonia oxide is found to be rather flat; for example, structures with N–O bond distances of 1.39 Å and 1.59 Å are only 1.2 and 1.3 kcal/mol, respectively, higher in energy than the minimum energy 4-31G(d) geometry. We note from the results of Table 1, that the optimized N–O bond distance in H_3NO is strongly basis set dependent. The optimized N–H bond distances reported in Table 1 are in good agreement with each other and are close to the experimental value found in ammonia. The ONH pyramidal angle is seen to be close to the tetrahedral value (4-31G basis).

Although H_3NO is predicted to be thermodynamically bound it is unstable with respect to its tautomeric form, hydroxylamine, H_2NOH. 4-31G theory predicts hydroxylamine to be 19 kcal/mol more stable than H_3NO. Hart [29] finds a difference of 30 kcal/mol, while Trindle and Shillady [31] using STO-4G theory find a much larger difference of 114 kcal/mol. These latter authors also conclude that H_3NO should enjoy kinetic stability since the barrier to rearrangement to H_2NOH was found to be considerable.

H_3CO^-: Both the minimal and extended basis set calculations give essentially the same optimized structure: [$r_{(CO)} = 1.36$ Å and $r_{(CH)} = 1.12$ Å]. Methoxide ion is predicted to be considerably more pyramidal than both H_3NO and methanol. Compared to the corresponding bonds in methanol, the C–H bond is longer and the C–O bond is shorter. These bond length variations are consistent with the higher energy of the oxygen lone pairs in CH_3O^- with a resultant greater donation into the C–Hσ^* orbitals of appropriate symmetry. Thus, the electron populations in the $2py$ AO for H_3NO, CH_3OH and CH_3O^- is 1.99, 1.97 and 1.90e$^-$, respectively, while the corresponding NO(CO)π overlap populations are 0.003, 0.016 and 0.084e$^-$, respectively. The longer C–H bonds in methoxide relative to methanol, allows for a larger H–H separation resulting in a more pyramidal methyl group.

F_3NO: The computed bond lengths [$r_{(NO)}=1.33$ Å (STO-3G), 1.19 Å (4-31G), and 1.16 Å (4-31G(d)) and $r_{(NF)}=1.41$ Å (STO-3G) and 1.41 Å (4-31G)] reveal that the minimal basis set results for the N–O bond distance deviate considerably from experiment [22] (1.156 Å). Significant improvement is obtained at the 4-31G level while the admission of *d*-orbitals to the basis has only a modest effect on improving the 4-31G results. Both minimal and extended basis sets predict an N–F distance slightly shorter than the experimental value [22]. The ONF pyramidal angle is reproduced well at all levels of theory. Recent calculations by Collins *et al.* [32], on the valence isoelectronic F_3PO molecule showed behavior similar to that found here with the important exception that the long P–O distance predicted using the minimal basis set is only moderately improved upon going to the extended 44-31G basis. Only when polarization functions are incorporated into the basis (STO-3G(d)) in our notation or STO-3G* in Collins [32] however is there agreement with experiment. This is perhaps not too unexpected since *d*-orbitals would be expected to play a more important role in phosphorus compounds than in nitrogen compounds. We will return to the function of *d*-orbitals in F_3NO in Sect. 3.2.

F_3CO^-: The optimized bond lengths [$r_{(CO)}=1.28$ Å (STO-3G), 1.23 Å (4-31G) and 1.21 Å (4-31G(d)) and $r_{(CF)}=1.42$ Å (minimal and extended)] together with the optimized pyramidal angle of about 117° indicate that the geometric structure of this anion is rather similar to that of the isoelectronic trifluoramine oxide consistent with the observations of Christie, *et al.* [23]. It is interesting to note that the 4-31G theory predicts essentially identical B–F, C–F and N–F bond distances in the isoelectronic species BF_4^-, CF_3O^- and NF_3O. Radom [15] finds BF_4^- to have a B–F distance of 1.416 Å in good agreement with experimental values [33] for this parameter. The effect of including *d*-orbitals in the basis set is similar to that found for F_3NO and results in only a modest decrease in the C–O bond distance. The total energy lowering due to the inclusion of *d*-orbitals for the fluorine oxides is larger than for the ammonia oxide molecule being 0.072 hartrees for F_3CO^- and 0.088 hartrees for F_3NO. However, these energy lowerings are not of the magnitude expected for significant *d*-orbital participation [32].

H_3COH: The minimal basis set calculations give rise to geometric parameters in good agreement with experiment [34] and previous *ab initio* results [35].

F_3COH: The optimized bond lengths [$r_{(CO)}=1.40$ Å (STO-3G), 1.35 Å (4-31G); $r_{(CF)}=1.38$ Å (STO-3G), 1.35 Å (4-31G); $r_{(OH)}=0.99$ Å, (STO-3G) 0.95 Å (4-31G)] show that use of the extended basis set yields shorter bond lengths than the minimal basis. Using the 4-31G basis set results in a C–O bond length reduction of 0.08 Å compared to the corresponding bond in methanol. The C–F bond is seen to be considerably shorter than the corresponding bond in CF_3O^- and is predicted to be only slightly longer than the C–F bond distance found [16] in CF_4 (1.32 Å) or the C–F bond distance in CF_3SH (1.335 Å) [36]. The bond shortening as a result of fluorine substitution is due in part [16] to a contraction of the carbon valence orbitals as found by Pople *et al.* [37] where the optimized carbon exponent changed from 1.76 in CH_4 to 1.84 in CF_4.

As far as the angles are concerned we find for the pyramidal OCF angle a value of 110° (STO-3G and 4-31G).

However, the HOC angle is seen to be rather different according to the two basis sets: 104° (STO-3G) and 116° (4-31G). With the exception of the OH bond distance and the HOC bond angle the 4-31G geometric parameters presented in Table 1 are consistent with an earlier INDO calculation on this molecule [38]. INDO finds a rather long OH bond distance (1.04 Å) with a rather "normal" HOC bond angle of 107°. The long OH bond distance found by the INDO method is suggestive of the weakness of this bond and offers a possible reason for the non-existence of F_3COH. Bearing in mind the known inadequacies [26] of simple SCF methods when applied to chemical reactions we have nevertheless gone ahead and performed STO-3G and 4-31G optimizations on HF and F_2CO, the expected products from the decomposition of CF_3OH. According to minimal basis set theory the alcohol is predicted to be ~42 kcal/mol more stable than the products of decomposition while 4-31G theory reduces this value to ~20 kcal/mol. Correlation effects could of course reverse the stabilities but it appears that F_3COH should be capable of existence. The atomization energy of CF_3OH (294.7 kcal/mol) is not much different from that of methanol (331 kcal/mol) at the 4-31G level. The atomization energies were obtained by subtracting the molecular energy of the separated isolated atoms [13]. The energy for the isodesmic reaction

$$CF_3OH + 3CH_4 \longrightarrow CH_3OH + 3CH_3F$$

is computed to be +48 kcal/mol. This compares favorably with the value computed for the reaction $CF_4 + 3CH_4 \rightarrow 4CH_3F$ (47.5 kcal/mol). Experimentally [39], heptafluorocyclobutanol, for instance, has been prepared and isolated from the reaction of hexafluorocyclobutanone and HF. The arguments presented herein are in favor of the existence of CF_3OH.

3.2. Electronic Structures

According to extended basis set calculations (4-31G, 4-31G(d)) the ground state for the isoelectronic species ammonia oxide and methoxide ion corresponds to the electronic configuration:

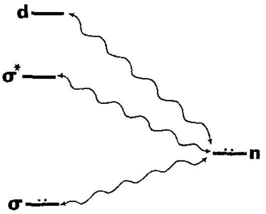
$$1a_1^2 2a_1^2 3a_1^2 4a_1^2 1e^4 5a_1^2 2\mathrm{e}^4 : ({}^1A_1).$$

The corresponding ground state electronic configuration for F_3NO is

$$1a_1^2 1e^4 2a_1^2 3a_1^2 4a_1^2 2e^4 5a_1^2 6a_1^2 3e^4 7a_1^2 4e^4 8a_1^2 1a_2^2 5e^4 6e^4 : ({}^1A_1).$$

Isoelectronic F_3CO^- is predicted to have a ground state configuration similar to that given above with the single exception of an inversion in the $8a_1$ and $5e$ levels. Consistent with previous calculations on anions [14, 15], we find the highest occupied level ($2e$ in CH_3O^- or $6e$ in CF_3O^-) to be unbound if the minimal STO-3G basis is used. Use of the more flexible extended basis however, brings the highest occupied orbitals in these anions into binding range.

Before proceeding further we present in Scheme I an interaction diagram for the interplay of the oxygen lone pairs with N–F (C–F)σ and σ^* bonds as well as the *d*-orbitals on the nitrogen (carbon). Donation into the nominally empty σ^* and *d*-orbitals is a stabilizing interaction which will increase the strength of the N–O (C–O) bond and allow for charge drift towards the nitrogen (carbon). Electronegative substituents such as fluorine will lower the energy of the σ^* orbitals and polarize them so as to favor interaction with the adjacent oxygen lone pairs. Additionally, such substituents will have the effect of decreasing the energy of the *d*-orbitals making them also more available for accepting electron density.



Scheme I

In Table 2 we summarize the results of a Mulliken population analysis [40] for the six optimized species presented in Table 1. We compare gross charges, overlap populations, and dipole moments as computed using STO-3G and 4-31G wavefunctions in Table 2. Perhaps the most glaring feature of Table 2 is the large charge polarization upon going from the minimal basis to the extended 4-31G basis set. This charge polarization is also reflected in the dipole moments as obtained for the 4-31G basis set relative to the STO-3G (the 4-31G dipole moment for methanol is 2.36D). The 4-31G dipole moments are also seen to be substantially larger than the experimental moments, an observation noted previously by Pople, *et al.* [7].

The large dipole moment in H_3NO and the low N–O overlap population (the negative overlap population recorded in Table 2 for the 4-31G basis occasionally is encountered and not much meaning should be attached to it) both speak for a classical N–O dative bond ($H_3N^+–O^-$) with little back-bonding of the oxygen lone pairs. The STO-3G overlap population of 0.12 for the NO bond in H_3NO is only slightly (using equal N–O bond lengths) less than the corresponding N–O overlap population (0.16) in $(CH_3)_3NO$.

In methoxide ion the charge is more localized on the oxygen according to extended basis set calculations, whereas the minimal basis set results spreads the negative

Table 2. STO-3G and 4-31G population analysis for X_3YO and X_3YOH (optimized forms)

		Gross charges				Overlaps			
Molecule	Basis	Q_x	Q_y	Q_0	Q_H	X–O	X–Y	O–H	μ^c
H_3NO	STO-3G	+0.24	−0.38	−0.33	—	0.12	0.68	—	4.29
	4-31G	+0.39	−0.67	−0.48	—	−0.15	0.61	—	5.38
H_3CO^-	STO-3G	−0.10	−0.05	−0.65	—	0.54	0.67	—	—
	4-31G	−0.04	+0.06	−0.95	—	0.61	0.64	—	—
F_3NO	STO-3G	−0.01	+0.32	−0.28	—	0.37	0.28	—	2.20
	4-31G	−0.19	+0.86	−0.28	—	0.20	0.12	—	0.51[d]
F_3CO^-	STO-3G	−0.29	+0.45	−0.58	—	0.73	0.35	—	—
	4-31G	−0.51	1.29	−0.77	—	0.88	0.29	—	—
H_3COH	STO-3G	+0.06[a]	−0.06	−0.29	+0.17	0.50	0.75[a]	0.51	1.48[e]
F_3COH	STO-3G	−0.15[b]	+0.52	−0.28	+0.22	0.51	0.41[b]	0.51	1.79
	4-31G	−0.39	+1.42	−0.72	+0.46	0.44	0.43	0.52	2.67

[a] The three hydrogen charges and three C–H bonds were averaged to a single value.

[b] The three fluorine charges and three C–F bonds were averaged.

[c] Dipole moment in Debyes.

[d] Experimental value 0.04D: Kirchhoff, W. H., Lide, D. R.: J. Chem. Phys. **51**, 467 (1969).

[e] Experimental value = 1.69D (Ref. [7], p. 15).

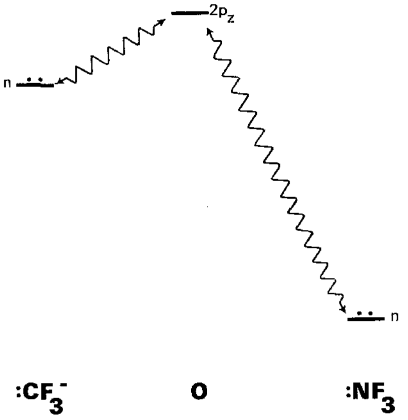
charge more onto the hydrogens. Comparing methoxide with methanol in the STO-3G basis we see, using overlaps as a criterion of bond strength, that the C–O bond is stronger while the C–H bond is weaker in the anion. This results from the higher energy of the lone pair electrons in CH_3O^- interacting more effectively with the C–Hσ^* orbitals leading to a stronger C–O and a weaker C–H bond.

Comparing methanol with trifluoromethanol in the STO-3G basis reveals that the C–O and O–H bonds are predicted to be virtually identical based on overlaps and that the gross charges on the oxygen in these alcohols is also seen to be practically identical. The hydroxylic proton is predicted to be more positive and thus more acidic in CF_3OH as might be anticipated. The C–F bond in trifluoromethanol is predicted to have the same overlap population as the C–F bond in carbonyl fluoride (C–F bond distance is 1.42 Å in CF_2O). The geometric parameters presented in Table 1 and the population analysis presented in Table 2 save perhaps the large positive charge on carbon indicate nothing unusual about the bonding in CF_3OH nor do we find any indications for its apparent instability.

For F_3NO experimental [21, 22] indications are that the NO bond is exceedingly short with a rather high IR stretching frequency (1690 cm^{-1}). The N–F bonds, on the other hand, are observed to be rather long. Christie, *et al.* [23] have recently obtained the IR and Raman spectra of F_3CO^- with the finding that the vibrational spectra of this anion closely resembles the vibrational spectra of the isoelectronic F_3NO molecule. Frost *et al.* [41] concluded that calculations on F_3NO and related molecules will probably need the addition of *d*-orbitals in the basis. In order to examine the electronic structures of the isoelectronic species F_3NO and F_3CO^-

in more detail we present in Table 3 the results of a Mulliken population analysis, of the 4-31G(d) wavefunctions.

The $1a_1$–$3a_1$ levels are the core orbitals, while the remaining sixteen filled valence orbitals describe the bonding in these molecules as well as the lone pair orbitals on oxygen and fluorine. The $5a_1$ orbital and to a lesser extent $8a_1$ orbital constitute the N–O (C–O) sigma bonding in these fluorine oxides. The C–O total overlap population is seen to be considerably larger than the N–O overlap population. An examination of the individual molecular orbitals of Table 3 reveals this difference in magnitude of total overlaps is primarily due to a substantial reduction in the C–O antibonding interactions present in the $6a_1$ and $7a_1$ molecular orbitals. The larger absolute magnitude of the C–O overlap population compared to the N–O overlap population can also be rationalized by the interaction diagram presented in Scheme II, where we show the interaction between the lone pair orbital on :CF_3^- (:NF_3) with the acceptor orbital of the valence state of the oxygen atom. Not only is the $6a_1$ lone pair (n) orbital of :CF_3^- much closer in energy to the oxygen acceptor orbital, but the carbon atomic orbital coefficients in this MO are larger than the corresponding nitrogen AO coefficients in the $6a_1$ MO of NF_3. Both these factors favor a stronger C–O bond. According to 4-31G calculations there is a transfer of $0.75e^-$ from NF_3 to oxygen in the σ system and $0.65e^-$ back-donated when one compares F_3N with F_3NO. The corresponding quantities for the $F_3C{:}^-$–F_3CO^- pair are $1.10e^-$ (σ) and $0.50e^-$ (π).



Scheme II

The effect of including d-orbitals in the basis set can be seen by comparing the total population values presented at the bottom of Table 3 where the parenthetic values refer to the without d calculations. There is seen to be a remolding of electron density with a drift of electronic charge from oxygen towards nitrogen (carbon) giving rise to a less extreme charge distribution and a strengthening of both the N–O (C–O) and N–F (C–F) bonds. The effect of adding d-orbitals to the basis appears to be more important for the F_3NO molecule where the inclusion of d-orbitals in the

Table 3. Mulliken population analysis of F_3NO and F_3CO^- according to the 4-31G (d) basis

	Gross population						Overlap population			
Orbital	C	N	O	O′	F_1	F'_1	C–O	N–O	C–F_1	N–F_1
$1a_1$	0.005	0.004	0.000	0.000	0.673	0.673	0.000	0.000	0.002	0.002
$1e$	0.003	0.002	0.000	0.000	1.325	1.325	0.000	0.000	0.001	0.001
$2a_1$	0.005	0.005	1.995	1.995	0.000	0.000	0.008	0.008	0.000	0.000
$3a_1$	2.002	1.995	0.001	0.002	0.000	0.001	−0.002	0.004	−0.001	0.001
$4a_1$	0.138	0.630	0.054	0.235	0.603	0.378	0.020	0.179	0.049	0.123
$2e$	0.146	0.212	0.004	0.006	1.282	1.260	0.002	0.002	0.079	0.093
$5a_1$	0.451	0.534	1.429	0.860	0.040	0.202	0.518	0.515	−0.005	−0.027
$6a_1$	0.451	0.752	0.125	0.296	0.475	0.318	−0.026	−0.323	0.079	−0.091
$3e$	0.846	1.484	0.204	0.468	0.984	0.683	0.114	0.282	0.162	0.080
$7a_1$	0.195	0.303	0.450	0.996	0.452	0.234	−0.293	−0.679	0.082	0.062
$4e$	0.076	0.068	0.088	0.116	1.280	1.272	0.015	0.026	0.027	0.018
$8a_1$	0.296	0.164	1.093	0.458	0.204	0.459	0.221	0.066	−0.015	−0.008
$1a_2$	0.000	0.000	0.000	0.000	0.667	0.667	0.000	0.000	0.000	0.000
$5e$	0.110	0.122	0.000	0.042	1.296	1.280	0.000	0.026	0.050	0.002
$6e$	0.252	0.182	3.196	2.610	0.184	0.402	0.492	0.298	−0.087	−0.011
Total	4.976 (4.709)	6.458 (6.137)	8.637 (8.767)	8.083 (8.282)	9.462 (9.508)	9.153 (9.194)	1.071 (0.890)	0.399 (0.198)	0.415 (0.292)	0.243 (0.120)

Primes correspond to the F_3NO molecule. Parenthetic values correspond to 4-31G wavefunctions.

basis is seen to double the N–O overlap population while for F_3CO^- there is only a 19% increase in the C–O overlap population. The 3*d* carbon–oxygen overlap contributes 0.187 to the total C–O overlap population. The *d*-orbitals make their presence felt to the greatest extent in the degenerate pair of 6*e*-orbitals. The 6*e*-orbitals are largely oxygen lone pair orbitals with some N–O (C–O)π bonding. For F_3NO, the N–Oπ bond is essentially 50% *p–p* and 50% *p–d*. In CF_3O^-, however, the C–Oπ bond is largely (75%) a *p–p* bond. Of the 4.976e on carbon, 0.243e are in *d*-orbitals or about 5% of the carbon electron population is due to occupancy of *d*-orbitals. The occupancy of the *d*-orbitals in F_3NO is 0.3e which is also about 5%.

The 4-31G overlap population of the C–O bond in F_3CO^- is predicted to be about 90% of the C–O overlap population in F_2CO, where a formal C=O double bond is expected. A similar calculation reveals the N–O bond in F_3NO is about 80% of the N–O overlap population in F_2NO^+ and 65% of the value in FNO using the equal bond length approximation. This is consistent with the IR analysis of Fox *et al.* [21b], where they find the NO stretching frequency in F_3NO to be closer to that of the N=O double bond in FNO than to that of the nonfluorinated amine oxides. They find the N–O bond in F_3NO to possess 75% double bond character. The mass spectral cracking pattern for F_3NO also reveals a much stronger N–O bond compared to the N–F bond [42]. The overlap populations presented in Table 3 are consistent with these observations.

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References

1. Radom, L., Pople, J. A.: M.T.P. International review of science (Theoretical chemistry), W. Byers Brown, Ed. London: Butterworths 1972
2. Schaefer, H. F.: Ann. Rev. Phys. Chem. **27**, 261 (1976)
3. Pople, J. A.: Modern theoretical chemistry, H. F. Schaefer, Ed. New York: Plenum Press 1976; Hehre, W. J.: Accts. Chem. Res. **9**, 399 (1976)
4. Newton, M. D., Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **52**, 4064 (1970)
5. Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **93**, 808 (1971)
6. Random, L., Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **93**, 5339 (1971)
7. Lathan, W. A., Radom, L., Hariharan, P. C., Hehre, W. J., Pople, J. A.: Fortschr. Chem. Forsch. **40**, 1 (1973)
8. Ditchfield, R., Hehre, W. J., Pople, J. A., Radom, L.: Chem. Phys. Letters **5**, 13 (1970)
9. Lathan, W. A., Hehre, W. J., Curtiss, L. A. and Pople, J. A.: J. Am. Chem. Soc. **93**, 6377 (1971)
10. Lathan, W. A., Curtiss, L. A., Hehre, W. J., Lisle, J. B., Pople, J. A.: Progr. Phys. Org. Chem. **11**, 175 (1974)
11. Radom, L., Hariharan, P. C., Pople, J. A., Schleyer, P. v. R.: J. Am. Chem. Soc. **98**, 10 (1976)
12. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
13. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971)

14a. Bernardi, F., Csizmadia, I. G., Mangini, A., Schlegel, H. B., Whangbo, M-H., Wolfe, S.: J. Am. Chem. Soc. **97**, 2209 (1975)
14b. Wolfe, S., Schlegel, H. B., Csizmadia, I. G., Bernardi, F.: Can. J. Chem. **53**, 3365 (1975)
14c. Radom, L., Pople, J. A.: Org. Chem. Ser. One **71**, (1972)
14d. Williams Jr., J. E., Streitwieser Jr., A.: J. Am. Chem. Soc. **97**, 2634 (1975)

15. Radom, L.: Aust. J. Chem. **29**, 1635 (1976)
16a. Sheppard, W. A., Sharts, C. M.: Organic fluorine chemistry. Menlo Park, Calif.: W. A. Benjamin 1969
16b Holtz, D.: Progr. Phys. Org. Chem. **8**, 1 (1971)
17. Brockway, L. O.: J. Chem. Phys. **41**, 185, 747 (1937)
18. Hine, J.: J. Am. Chem. Soc. **85**, 3239 (1963)
19. Streitwieser Jr., A., Holtz, D.: J. Am. Chem. Soc. **89**, 692 (1967); Streitwieser Jr., A., Marchand, A. P., Pudjaatmaka, A. H.: J. Am. Chem. Soc. **89**, 639 (1967)
20. Fox, W. B., MacKenzie, J. S., McCarthy, E. R., Holmes, J. R., Stahl, R. F., Juurik, R.: Inorg. Chem. **7**, 2064 (1968), and references therein
21a. Curtis, E. C., Pilipovich, D., Moberly, W. H.: J. Chem. Phys. **46**, 2904 (1967)
21b. Hirschmann, R. P., Harnish, D. F., Holmes, J. R., MacKenzie, J. S., Fox, W. B.: Appl. Spectry. **23**, 333 (1969)
21c. Aminadav, N., Selig, H., Abramowitz, S.: J. Chem. Phys. **60**, 325 (1974)
22. Plato, V., Hartford, W. D., Hedberg, K.: J. Chem. Phys. **53**, 3488 (1970)
23. Christie, K. O., Curtis, E. C., Schak, C. J.: Spectrochim. Acta **31A**, 1035 (1975)
24. Redwood, M. E., Willis, C. J.: Can. J. Chem. **43**, 1893 (1965)
25. Program available from QCPE (#236), Chemistry Dept., Indiana University, Bloomington, Indiana
26. Schaefer III, H. F.: The electronic structure of atoms and molecules: A survey of rigorous quantum mechanical results. Reading, Ma.: Addison-Wesley 1972
27. Hariharan, P. C., Pople, J. A.: Theoret. Chim. Acta (Berl.) **28**, 213 (1973)
28. POLYATOM (Version 2), QCPE (#199), Chemistry Dept., Indiana University, Bloomington, Indiana
29. Hart, B. T.: Aust. J. Chem. **29**, 231, 240 (1976)
30. Radom, L., Schaefer III, H. F.: Aust. J. Chem. **28**, 2069 (1975); Ungemach, R., Schaefer III, H. F.: Chem. Phys. Letters **38**, 407 (1976)
31. Trindle, C., Shillady, D. D.: J. Am. Chem. Soc. **95**, 703 (1973)
32. Collins, J. B., Schleyer, P. v. R., Binkley, J. S., Pople, J. A.: J. Chem. Phys. **64**, 5142 (1976)
33. Bellanca, A., Sgarlata, F.: Rend. Soc. Mineral, Ital. **7**, 42 (1951); Pendred, D., Richards, R. E.: Trans. Faraday Soc. **51**, 468 (1955)
34. Ivash, E. V., Denninson, D. M.: J. Chem. Phys. **21**, 1804 (1953); Kimura, K., Kubo, M.: J. Chem. Phys. **30**, 151 (1959)
35. Radom, L., Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **93**, 289 (1971); Lathan, W. A., Radom, L., Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **95**, 699 (1973)
36. Marsden, C. J.: J. Mol. Struct. **12**, 168 (1973)
37. Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **92**, 2191 (1970)
38. Gordon, M. S., Pople, J. A.: J. Chem. Phys. **49**, 4643 (1968)
39. Andreades, S., England, D. C.: J. Am. Chem. Soc. **83**, 4670 (1961)
40. Mulliken, R. S.: J. Chem. Phys. **23**, 1833 (1955)
41. Frost, D. C., Herring, F. G., Mitchell, K. A. R., Stenhouse, I. A.: J. Am. Chem. Soc. **93**, 1596 (1971)
42. Diebeler, V. H., Walker, J. A.: Inorg. Chem. **8**, 1728 (1969)

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