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Commentationes

Ab initio Study of the Molecular Geometry and Properties of Nitrosyl Fluoride

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Ab initio SCF MO calculations employing a basis set of multi-component Gaussian orbitals are carried out for the FNO molecule at various internuclear angles and FN bond separations. The resulting total energy at the experimental FNO geometry is estimated to be in the range of 0.15 to 0.25 hartrees above the Hartree-Fock limit; the calculations find an internuclear equilibrium angle which is 1.1° higher than the experimental value (110°) and a FN bond distance which is 0.02 bohrs greater than that found experimentally (2.872 bohrs). The molecular charge density contours indicate that nitrosyl fluoride can be considered quite concisely as a loosely bound combination of a fluorine atom and an NO radical. Finally, a model is constructed on the basis of the SCF calculations which is capable of explaining rather anamolous features of the FNO molecular geometry and properties in a consistent manner.

Für das FNO-Molekül wurden bei verschiedenen Molekülwinkeln und FN-Abständen *ab initio* SCF–MO-Berechnungen durchgeführt, wobei als Basis Atomfunktionen, welche sich jeweils aus einer größeren Anzahl von Gaußfunktionen zusammensetzen, verwendet wurden. Dabei ergibt sich für das Molekül in der experimentellen Gleichgewichtsstruktur eine Gesamtenergie, welche als ungefähr 0,15 bis 0,25 Hartree über der Hartree-Fock Energie liegend abgeschätzt wird; die Berechnungen ergeben einen Wert für den Molekülwinkel, der 1,1° größer ist als der experimentelle (110°) und eine um 0,02 Bohr größere FN-Bindungslänge als experimentell ermittelt worden ist (2,872 Bohr). Die berechnete Elektronendichteverteilung im Molekül deutet darauf hin, daß FNO als Gebilde betrachtet werden kann, das aus einem Fluoratom und einem NO-Radikal besteht, welche nur locker aneinander gebunden sind. Auf Grund der SCF-Rechnungen wird weiterhin ein Modell entworfen, welches in der Lage ist, die Besonderheiten in der Struktur und den Eigenschaften des FNO-Moleküls auf konsequente Weise zu erklären.

La molécule FNO est calculée par la méthode ab-initio SCF MO, utilisant une base d'orbitales gaussiennes multiples, pour différents angles et différentes distances FN. L'énergie totale obtenue pour la géométrie expérimentale est considérée comme se trouvant à 0,15—0,25 hartrees au dessus de la limite Hartree-Fock; les calculs fournissent un angle d'équilibre supérieur de 1,1° à la valeur expérimentale (110°) et une distance F–N supérieure de 0,02 bohrs à la distance expérimentale (2,872 bohrs). Les contours de densité de charge montrent que le fluorure de nitrosyle peut être considéré avec précision comme une combinaison entre un radical NO et un atome F faiblement lié. Sur la base des calculs SCF on construit un modèle capable d'expliquer raisonnablement des caractères anormaux de la géométrie et des propriétés de FNO.

Introduction

Experimental studies of nitrosyl fluoride FNO employing the techniques of microwave spectroscopy have determined both the equilibrium geometry and the dipole moment of this molecule quite precisely [1 – 3]. These results are particularly interesting because the dipole moment and the FN bond length determined for this system are each considerably larger than corresponding values found in other FN compounds. Attempts have been made to explain these findings theoretically on a qualitative basis [4] but to the present no quantitative study of the electronic structure of FNO has been undertaken. Such a theoretical study seems desirable not only because of the anamolous position this molecule holds with respect to other fluoronitrogen compounds but also because it is a non-symmetric triatomic molecule of ABC type and previous work dealing with triatomic molecules has been restricted almost exclusively to the study of symmetric AB_2 systems [5 – 7]. *Ab initio* SCF calculations have therefore been carried out for the closed shell ground state of nitrosyl fluoride in order to investigate the geometry, properties and electronic structure of this system.

Calculations and Results

Energy

The basis set for the calculations discussed in this paper employs a fixed group set of gaussian lobe functions, which are quite good approximations to the Hartree-Fock AO's of fluorine, nitrogen and oxygen respectively [8], as can be seen from Tab. 1a; this table compares the total energies for the N, O and F atoms obtained by different methods: 1) the values obtained from a basis of single exponential (single zeta) functions, 2) the energies calculated from the gaussian lobe function

Table 1a. *Total energies (hartrees) for the* N, O *and* F *atoms obtained by different methods. (All values are taken from* Ref. *8)*

	N	O	F
Single exponential	−54.26890	−74.54036	−98.94211
Gaussian lobe functions	−54.38815	−74.79154	−99.3823
Hartree-Fock (Extended exponential)	−54.40091	−74.80936	−99.40929
Δ (Gaussian — Hartree-Fock)	0.0127	0.0179	0.0270

Table 1b. *Total energies (hartrees) for the* C_2, N_2 and F_2 *molecules (at their experimental equilibrium separation) obtained by different methods. (All values are taken from* Ref. *9)*

	C_2	N_2	F_2
Single exponential[a]	−75.2238	−108.6336	−197.8769
Fixed group gaussian lobe functions	−75.2823	−108.7225	−198.6804
Hartree-Fock (Extended exponential)	−75.4062[b]	−108.9928[c]	−198.7683[d]
Δ (Fixed group — single zeta)	− 0.0585	− 0.0889	− 0.8035
Δ (Fixed group — Hartree-Fock)	0.1239	0.2703	0.0978

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[a] Ransil, B. J.: Rev. modern Physics **32**, 239, 245 (1960).

[b] From data prepared by LMSS, University of Chicago.

[c] Cade, P. E., K. D. Sales, and A. C. Wahl: J. chem. Physics **44**, 1973 (1966).

[d] Wahl, A. C.: J. chem. Physics **41**, 2600 (1964).

basis and 3) the Hartree-Fock values obtained via an extended Slater type orbital basis. A diagram showing the coordinate system used for this calculation is given in Fig. 1. Total, kinetic and orbital energies obtained for the ground state of FNO in its experimental equilibrium geometry [1] (angle FNO = 110°, FN = 2.872 bohrs, NO = 2.135 bohrs) are found in Tab. 2, while the molecular orbital coefficients for the corresponding wavefunction are contained in the Appendix.

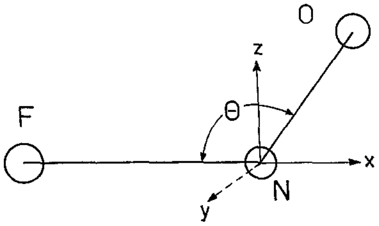

Fig. 1. Coordinate system for the FNO molecule

Table 2. *Total energy E_T, kinetic energy E_K and orbital energies for the ground state of* FNO (FN = 2.872 bohrs, NO = 2.135 bohrs and ∢ FNO = 110°)[a]

orbitals	energies
$1a$	− 26.2801
$2a$	− 20.8744
$3a$	− 16.0316
$4a$	− 1.7718
$5a$	− 1.5808
$6a$	− 1.0219
$7a$	− 0.8460
$8a$	− 0.7924
$1b$	− 0.7877
$9a$	− 0.6547
$2b$	− 0.6487
$10a$	− 0.5390
E_T	−228.3800
$-E_K/E_T$	0.9978

[a] Throughout this paper, unless otherwise specified, all energy values are given in hartrees.

Because of the relatively complicated nature of the gaussian wavefunctions obtained it is helpful to estimate the level of the present calculations with reference to the corresponding single zeta and molecular Hartree-Fock solutions; extrapolation of the results of a previous comparison between fixed group gaussian, single zeta and Hartree-Fock Roothaan treatments of N_2 and F_2 [9] presents one method of obtaining this information; these energies are listed for C_2, N_2 and F_2 in Tab. 1b. Also, since the experimental FNO total energy is known (mean experimental $E_T = -229.830$ hartrees) one can estimate the Hartree-Fock total energy by calculating a hopefully reliable value for its pair correlation energy. This, in turn, can be done in two ways: first, by combining experimental and calculated binding energies with known atomic correlation energies and secondly, by making use of a previously computed value for the correlation energy of isoelectronic ozone [6], i.e., by assuming this quantity to be equal for O_3 and FNO on the basis of an analogous comparison between isoelectronic N_2 [12], CO and BF [13]*. As a result of these various computations the Hartree-Fock energy for FNO is believed to lie between 0.15 and 0.25 hartrees lower than the fixed group

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* This value of 1.275 hartrees was obtained by a simple linear extrapolation based on the relative number of electron pairs for O_3 and O_2 (12 and 7 respectively) and the known correlation energy of O_2 (0.744 hartrees according to prepared data from the LMSS, University of Chicago, a value which is somewhat greater than one would expect from the correlation energy of N_2, CO and BF, beeing 0.593, 0.591 and 0.611 hartrees respectively (Ref. 12, 13); if the extrapolation would be based on one of the latter values — which could not be justified so easily, however, — the estimated correlation energy of O_3 and consequently of FNO would become smaller).

value of Tab. 1, the correlation energy being between 1.20 and 1.30 hartrees. At the same time they indicate that the single zeta total energy would be about 0.75 hartrees above the fixed group value, so that the present treatment is believed to account for roughly 80% of the expected difference between single zeta and Hartree-Fock total energies.

The binding energy calculated for FNO in its experimental geometry is −4.9 eV, well below the experimental range of this quantity of from 7.7 [10] to 8.9 eV [11], a discrepancy which must be expected from the assumed single determinental form of the wavefunction. The minimum ionization potential calculated from Koopmann's theorem is 14.6 eV; experience indicates that this value is 1.0 − 1.5 eV greater than the corresponding experimental quantity.

Geometry

Although the more anamolous features of the FNO molecular geometry occur with respect to its bond distances it is also important to investigate its angular potential surface by means of SCF calculations, especially since previous experience [5 − 7, 14] has indicated a rather precise agreement between calculated and experimental equilibrium angle. The FNO angular potential curve based on five calculations for angles ranging from 60° to 180° (assuming experimental FN and NO distances) is thus shown in Fig. 2. A polynomial fit to the data of this figure finds an equilibrium angle of 111.1° in very good agreement with the experimental value of 110°; the corresponding force constant is computed to be $23.2 \cdot 10^{-12}$ erg/rad^2, in fairly good agreement with the experimental value of $18.55 \cdot 10^{-12}$ erg/rad^2 [15]. Thus the present and previous calculations for triatomic molecules find FNO falling roughly midway between 26 electron F_2O and 24 electron O_3, both with respect to equilibrium angle and bending force constant (F_2O having the smallest equilibrium angle and largest force constant of the three).

The agreement between calculated and experimental results for the bond angle thus removes one ambiguity one might have thought present in determining a set of molecular parameters for the more interesting FN bond distance search; in what follows, however, the experimental equilibrium NO bond length in nitrosyl fluoride has simply been assumed (2.135 bohrs), since it agrees quite closely with the corresponding bond distance in nitric oxide (2.175 bohrs), and thus is not a

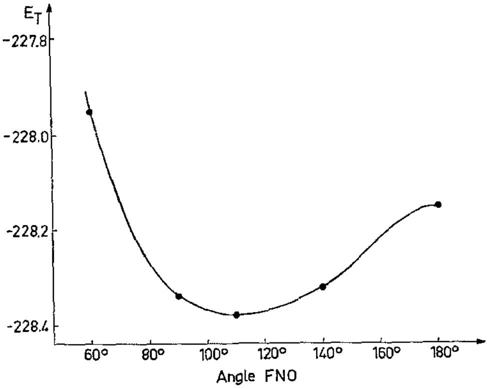

Fig. 2. Total energy E_T (in hartrees) as a function of internuclear angle for nitrosyl fluoride

particularly distinctive feature of the FNO molecular geometry. Two additional calculations were therefore carried out which allowed an increase and a decrease of 0.20 bohrs in the FN bond length relative to the experimental value already assumed in the angular search ($\sphericalangle$ FNO $= 110°$); the total energy data for these calculations given in Tab. 3 show that the SCF results for this bond distance again agree quite well with experiment, although somewhat less precisely than for equilibrium angles. Such a value for this particular geometrical parameter, in turn, is in marked contrast to that found for other FN compounds (in NF_3 2.598 bohrs; in FNO_2 2.5512 bohrs) [15]. Another most interesting feature of the data is the decided flatness of the potential curve; changes in total energy for comparable bond length variations around the equilibrium geometry are five times greater for CO_2 [7], for example, and even for BeF_2 [7] and Li_2O [5] with similarly large internuclear distances (2.702 and 3.13 bohrs) the respective energy variations are almost twice as large as in FNO. A parabolic fit to the data of Tab. 3 finds an equilibrium FN distance of 2.896 bohrs, 0.024 bohrs greater than that found experimentally, a discrepancy which is considerably smaller than that found for analogous CO_2 and BeF_2 calculations [7]. The calculated force constant for the FN stretch is 5.45 mdyn/Å, well above the experimental value of 2.09 mdyn/Å [16], although Tab. 4 shows that both calculations and experiment find a similar ordering among the stretching force constants of CO_2, BeF_2 (symmetric stretch) and FNO (FN stretch)*. Thus it is clear from both experiment and SCF calculation that nitrosyl fluoride exhibits a rather strong resistance to changes in its internuclear angle but is comparatively insensitive to variations in its FN bond length.

Molecular Properties and Interpretation

The F–N *bond*

The rather consistent picture of the FNO equilibrium geometry indicated by experiment and SCF calculations thus gives hope for finding a reliable explanation

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* It must be emphasized, however, that the calculated FN stretching force constant results from only a three point fit to the fixed group SCF potential curve and should therefore be taken only as a first approximation. Furthermore, neither of the wavefunctions for CO_2, BeF_2 and FNO is completely optimized at every internuclear separation R since each group orbital (i.e. the linear coefficients within each group orbital and the individual gaussian exponents) was left unchanged for the different R values; this method of calculation causes the potential well to rise too steeply on either side of the minimum and consequently leads to too large a force constant. But even after complete optimization a relatively large difference between calculated and experimental stretching force constant is expected to remain, particularly in light of the results obtained from true Hartree-Fock-Roothaan solutions (using Slater type orbitals) for diatomic non-hydride molecules: the calculated force constant of N_2 (Ref. 12) is in error by 34% [$(k_{\text{calc}} - k_{\text{exp}})/k_{\text{exp}}$], those of three different N_2^+ states by 36, 48 and 64% respectively, and in F_2 the deviation between calculated and experimental force constant is 87% [A. C. WAHL, J. chem. Physics **41**, 2600 (1964)]; it was concluded then that spectroscopic constants can be obtained with quite good accuracy (k in error by 4—20%) from a Hartree-Fock potential curve only for diatomic hydrides and not for A_2 or AB molecules, since for the hydrides the correlation energy apparently does not vary much with internuclear separation over the range of R values considered [P. E. CADE and W. M. HUO, J. chem. Physics **47**, 614 (1967)]. It should be pointed out, however, that the calculated force constants seem to be systematically in error in sign (they all are calculated too large), so that the calculated values, although incorrect in magnitude, might be very valuable for purposes of comparing different molecules.

Table 3. *Total energy E_T for the* FNO *ground state as a function of the* FN *distance* R

R (bohrs)	E_T (hartrees)
2.672	-228.3713
2.872	-228.3800
3.072	-228.3747

Table 4. *Calculated and experimental stretching force constants for* CO_2, BeF_2 *and* FNO (in mdyn/Å)

	k (calc)	k (exp)
CO_2	22.7	14.2 or 16.8[a]
BeF_2	9.0	5.0[b]
FNO	5.45	2.09

[a] HERZBERG, G.: Infrared and raman spectra, p. 173. Princeton, N.J. D. Van Nostrand Co., Inc. 1964.

[b] BUCHLER, A., and W. KLEMPERER: J. chem. Physics **29**, 121 (1958).

for the electronic structure of this system based upon a study of the SCF representation of its electronic charge density. A contour map showing the calculated total electronic charge distribution of FNO in its equilibrium geometry is therefore given in Fig. 3; this diagram, in turn, clearly suggests that the fluorine atom of FNO retains a substantial portion of its atomic character while the strong NO bond of nitric oxide appears to remain in tact.

This picture of a fluorine atom loosely bound to an NO complex can be more sharply defined by examining the various molecular orbital coefficients of the ground state wavefunction contained in the Appendix; for there it can be seen that each of the valence MO's in this system, with the important exception of the highest occupied $10a$, can be characterized quite, distinctly according to its AO constitution as either a predominantly fluorine or a predominantly NO orbital (these orbital descriptions are made explicit in Tab. 5). This pattern is broken only by the $10a$ MO, whose composition is almost equally divided among the three component atoms; this observation is made clearer by examining a plot of the $10a$ orbital charge density given in Fig. 4. Such an analysis seems to dictate a rather

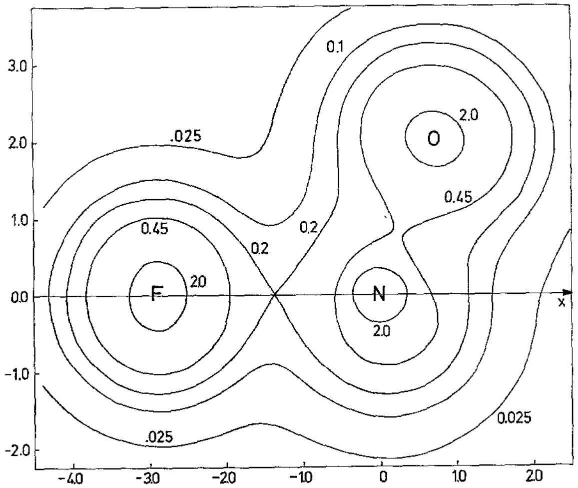

Fig. 3. Contours of the total electronic charge density calculated for FNO in its equilibrium geometry

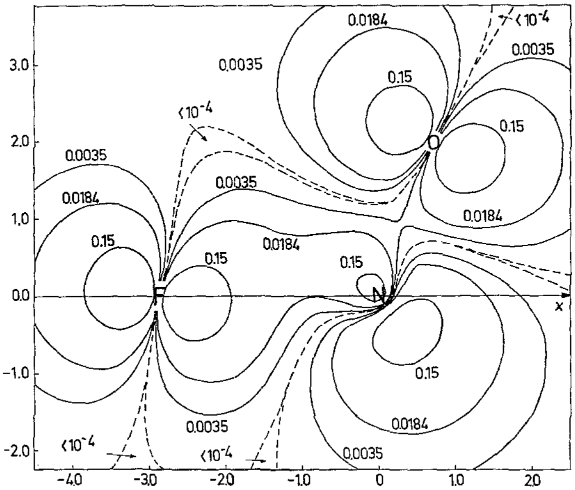

Fig. 4. Contours of the $10a$ orbital charge density of FNO in its equilibrium geometry

simple conception of the FNO molecule as a collection of unperturbed doubly occupied fluorine AO's ($1s, 2s$, two $2p$) and nitric oxide MO's ($1\sigma, 2\sigma, 3\sigma, 4\sigma, 1\pi, 5\sigma$) with only one truly FNO *molecular* orbital formed from an almost equal admixture of fluorine $2p$ and nitric oxide 2π orbital character. Apparently the lower lying orbitals of both of the radicals F and NO are stable entities in themselves with nothing particularly to gain from molecular formation; the existence of FNO as a stable compound can thus be traced directly to the advantage gained by pairing the odd electrons of both fluorine and NO in a single molecular orbital whose charge density is rather evenly distributed over the whole FNO molecule.

This simple conceptual picture of molecular binding in nitrosyl fluoride indicated by the SCF charge density contours is especially interesting because it puts one into the rather unique position of being able to discuss detailed features of the molecular geometry and properties of this system with reference to the behavior of a single molecular orbital with respect to various nuclear displacements. It is worthwhile therefore to consider the dynamics of a fluorine atom approaching a nitric oxide molecule from a relatively large distance and particularly to examine possible relative spatial orientations of the fluorine $2p$ AO and the highest occupied

Table 5. *Schematic description of the valence molecular orbitals of nitrosyl fluoride*

Orbital	Description
$4a$	3σ–NO (in phase)
$5a$	$2s$–F
$6a$	4σ–NO (out of phase)
$7a$	1π–NO (in phase)
$8a$	5σ–NO (in phase)
$1b$	1π–NO (in phase)
$9a$	p_z–F
$2b$	p_y–F
$10a$	2π–NO (out of phase) + p_x–F

Table 6. *Orbital energies ε of innershell orbitals in FNO and in its separated constituent atoms* [8]

	ε (molecule)	ε (atom)
F	−26.280	−26.380
O	−20.874	−20.666
N	−16.032	−15.630

2π MO of nitric oxide. In the first place then, since fluorine is the most electronegative of the three atoms under consideration, it is not at all surprising that it should be attracted more toward the nitrogen end of the diatomic radical because this is the more electropositive center of the molecule.

Closer examination of the SCF calculations are in accord with such an analysis, as can be seen from comparison of corresponding atomic and molecular innershell orbital energies, given in Tab. 6. Previous work [5] has quite clearly established the point that the charge distribution of these innershell orbitals with respect to their nuclei are unchanged upon their introduction into a molecular environment and consequently changes in their orbital energies,

$$\varepsilon_i = \langle \varphi_i \,|\, -\tfrac{1}{2}\nabla^2 - \sum \frac{Z_a}{r_a} \,|\, \varphi_i \rangle + \sum_{j=1}^{n} \{[ii \,|\, jj] - [ij \,|\, ji]\} ,$$

where the electron repulsion sum is over all the occupied spin orbitals of a given system, are caused solely by differences between the respective surrounding atomic and molecular fields. Thus the fact that the fluorine $1s$ orbital energy increases from atom to molecule (Tab. 6) is a clear indication that the fluorine environment is more negative when it is bound in nitrosyl fluoride than when it is a free atom. Conversely, the data stress the relatively positive nature of nitrogen and oxygen in this molecule since their $1s$ orbital energies are decreased in the transition from atoms to molecule*.

Once the two premises are established that the fluorine atom is attracted more to the nitrogen side of the NO dipole and that molecular formation of FNO is accomplished almost entirely by means of overlap of a fluorine $2p$ AO with the nitrogen end of the NO 2π molecular orbital, each of which is the most long range spatial function occupied in the respective separated species, it is not at all surprising that any resulting fluoronitrogen bond should be characterized by both an extremely shallow potential minimum and an unusually large equlibrium separation.

Equilibrium Angle

The pertinence of the present model to the explanation of the observed equilibrium angle in nitrosyl fluoride remains to be discussed. In this connection, it is quite important to recognize that for a linear FNO configuration the fluorine $2p$ atomic orbital which is to overlap with the nitric oxide 2π MO must necessarily approach it in a parallel position in order to preserve the overall symmetry of the resulting molecular orbital in the FNO complex. Inspection of the calculated representation of this orbital at 180°, however, finds it to be FN antibonding rather than bonding and with a relatively small contribution from the fluorine p atomic orbital; indeed, such a constitution of this orbital can only be expected because of the fact that it is the third highest occupied π MO (3π) in this molecule and thus should be distinctly antibonding in its character. The charge density contours of

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* Furthermore, experience indicates that improvement of the SCF wavefunction to Hartree-Fock accuracy results in a general increase in all orbital energies, so that improved calculations would indicate an even more negative environment for the fluorine, with the nitrogen and oxygen being less positive than in the present fixed group description of the nitrosyl fluoride total charge density. In this connection it should also be pointed out that the fixed group *atomic* orbital energies are relatively more accurate agreeing within 0.001 hartrees with the corresponding Hartree-Fock values.

Fig. 4, however, make it clear, that this situation is decidedly altered by decreasing the FNO angle since the decrease in symmetry from linear to bent geometry allows the fluorine and nitrogen $2p$ AO's to change from weakly FN antibonding to rather strongly FN σ *bonding*. Recalling again that the more stable fluorine and NO orbitals are essentially unperturbed by the mutual approach of these two systems it is apparent that one can point to the definite stabilization of the highest occupied FNO orbital upon bending as the factor which is almost solely responsible for the small equilibrium angle observed for nitrosyl fluoride. Also, since the constitution of the $10a$ molecular orbital is considerably more dependent upon the relative orientation of its component p AO's than it is upon the distance for which their optimum overlap is achieved, it is clear that the present model is quite adequate for explaining the decidedly greater resistence of FNO to changes in internuclear angle than to expansion or contraction of its FN separation.

The effect of the foregoing description of the electronic structure of nitrosyl fluoride upon its molecular properties is also an interesting subject, particularly since its dipole moment has been observed to have a rather large magnitude of 1.81 debyes [1]. In constrast measurement of the dipole moment for pyramidal NF_3 (angle FNF = 102.5° [17]) has found a value of 0.234 D [20], from which it has been concluded that each NF component dipole has a magnitude of only 0.18 D [1], so that once again it appears that nitrosyl fluoride is displaying abnormal behavior for a fluoronitrogen compound.

Dipole Moment

To further investigate these phenomena then, the dipole moment of FNO has been calculated using the fixed group SCF wavefunction and the results of this treatment (at $R = 2.872$ bohrs) are compared with experiment in Tab. 7. The most

Table 7a. *Calculated dipole moment* μ *and quadrupole tensor components for* FNO *as a function of the* FN *distance* R *(in bohrs) together with the corresponding experimental values.* ($\sphericalangle$ FNO = 110°)

	calculated			experimental
$R =$	3.072	2.872	2.672	2.872
$\mu(x)$	0.4260	0.2829	0.1329	0.7114
$\mu(z)$	0.0755	0.0523	0.0216	0.0629
$\langle xx \rangle$	-13.7250	-13.4362	-13.1971	
$\langle yy \rangle$	-11.0863	-11.0682	-11.0401	
$\langle zz \rangle$	-12.8793	-12.9357	-12.9972	
$\langle xz \rangle$	- 0.3154	- 0.3235	- 0.3398	
$\lvert \mu \rvert$	0.4326 (1.0996 D)	0.2877 (0.7312 D)	0.1346 (0.3421 D)	0.7142 (1.81 D)
θ_μ[a]	169° 57′	169° 31′	170° 47′	174° 57′

[a] θ_μ is, as defined in Fig. 1, the angle of the dipole masured from the negative x axis. All values, unless otherwise specified are given in atomic units. The quadrupole tensor components were calculated relative to the nitrogen nucleus as origin.

obvious feature in these data is the wide disagreement between calculated and experimental magnitudes. Such a discrepancy emphasizes the point made earlier by HUO [13] that calculated dipole moments (and presumably other one electron properties) are not reliable for SCF wavefunctions at least until the latter are very good approximations to the true Hartree-Fock solution (and not only with respect to a total energy criterion); her results for CO and BF clearly do not exclude possible fortuitous agreement in a given case but they certainly do not give hope of obtainin any consistent and general quantitative agreement between experimentg and SCF calculations employing only moderately large basis sets.

In spite of the quantitative inadequacies of the calculated molecular properties it is still possible to derive useful information from these results because of the additional insight they allow for the understanding of the molecular dynamics of nitrosyl fluoride. In this connection it is worthwhile to note that microwave measurements yield an unambiguous value only for the magnitudes of two perpendicular components, while the direction of the dipole moment vector must be deduced from chemical intuition (hence the experimental angle is believed to be 174° 57′) [1]. Thus it can be seen that both the SCF calculations and, perhaps more importantly, the accompanying electronic structure model under discussion substantiate the experimentalists' choice for the dipole moment angle, i.e. the dipole vector points almost directly along the FN axis with its negative end towards the fluorine. In other words, the more electronegative fluorine p AO attracts some of the electronic charge from the nitrogen end of the nitric oxide 2π MO leaving the NO complex more positive. It is possible to obtain a rough idea of the amount of this charge transfer by comparing the observed NO distance in nitrosyl fluoride (2.135 bohrs) to that found in the two diatomic species, NO (2.175 bohrs) and NO^+ (2.007 bohrs) [19]; from these data it seems clear that, despite the $N \rightarrow F$ charge transfer, the NO species in FNO is still more similar to neutral nitric oxide than to its positive ion.

The calculations also allow one to examine the spatial dependence of the FNO molecular properties, again at least in a qualitative manner. Thus Tab. 7a also gives the calculated dipole moments as a function of the FN distance. From these data the dipole moment is seen to increase with the FN bond length, indicating that the charge transfer from the NO complex is more favorable at distances larger than equilibrium. Such an analysis is also supported by innershell orbital energy data in Tab. 8a and by the distance dependence of the diagonal elements of the quadrupole tensor (Tab. 7a). Thus the fluorine $1s$ orbital energy is found to increase with the FN distance and the $\langle xx \rangle$ component of the quadrupole moment to become more negative, while the other two diagonal elements are roughly unchanged; together these observations clearly indicate that the centroid of electronic charge moves more closely to the fluorine atom than does that of the nuclear charge as the fluorine separates from the NO radical. This observation again emphasizes the long range nature of the FN bond in nitrosyl fluoride since it points up a definite decrease in the amount of charge transfer from the NO radical as the fluorine atom approaches beyond its equilibrium separation.

The dependence of the molecular properties of FNO upon bending around the equilibrium angle of 110° is considered in Tab. 7b; the magnitude of the dipole moment is observed to increase from 140° to 90°, particularly the FN component,

Table 7b. *Calculated dipole moment* μ *and quadrupole tensor components for* FNO *as a function of internuclear angle* (FN = 2.872 bohrs)

$\theta =$	140°	110°	90°
$\mu(x)$	0.1433	0.2829	0.3603
$\mu(z)$	0.2286	0.0523	0.0005
$\langle xx \rangle$	−13.5402	−13.4362	−13.3843
$\langle yy \rangle$	−11.0738	−11.0682	−11.0352
$\langle zz \rangle$	−12.5157	−12.9357	−12.9533
$\langle xz \rangle$	− 0.5007	− 0.3235	− 0.0862
$\lvert \mu \rvert$	0.2698 (0.6857 D)	0.2877 (0.7312 D)	0.3603 (0.9158 D)
θ_μ	122° 05′	169° 31′	179° 55′

and this fact is consistent with the increase in FN $p\sigma$ bonding with decreasing angle discussed earlier in connection with the angular behavior of the $10a$ orbital. In fact, at 140°, for which angle $p\sigma$ bonding is not particularly favored, the z component of the dipole is actually greater than that in the FN direction. Again, the fluorine $1s$ orbital energies (Tab. 8b) can be used to substantiate the fact that charge transfer to the fluorine is definitely favored by bending the molecule from the linear configuration.

Before concluding it is worthwhile to remark upon one other possible effect of the fluorine to nitrogen charge transfer with increasing internuclear angle. In linear geometry, as indicated previously, the 3π MO has so little fluorine charge available to it that there is considerable doubt that this MO is actually occupied for the FNO ground state at this angle. It may indeed be more energetically favorable to populate the 8σ orbital instead, since this MO is found to have a fairly large contribution from the fluorine AO's. No such ambiguity appears to be present in bent FNO configurations because both the 8σ and the in-plane component of the 3π belong to the same irreducible representation for C_s symmetry and

Table 8. *Energies for the* F, N *and* O *innershell orbitals of* FNO *as a function of internuclear distance* R *and as a function of internuclear angle* θ[a]

	$R =$	3.072	2.872	2.672
a	F	−26.252	−26.280	−26.320
	N	−16.047	−16.032	−16.039
	O	−20.880	−20.874	−20.836
	$\theta =$	140°	110°	90°
b	F	−26.310	−26.280	−26.255
	N	−16.010	−16.032	−16.038
	O	−20.858	−20.874	−20.846

[a] All energy values are given in hartrees, distances in bohrs.

consequently the SCF procedure is free to mix these orbitals in an optimum manner so that the most stable possible $10a$ orbital results. The present calculations have doubly occupied the 3π MO and the dipole moment calculated for this state in linear geometry (an open shell configuration) is found to be in the F^+N^- direction, reflecting the small amount of fluorine character in the 3π. The availability of the 8σ orbital, however, indicates that the most stable single determinental configuration for FNO may actually be a closed shell species and since the 8σ has a considerably larger amount of fluorine character than the 3π it seems likely that the dipole moment calculated for this closed shell wavefunction would possess the more conventional F^-N^+ direction. Essentially the same choice exists for isoelectronic ozone in its linear geometry (between the $2\pi_u$ and $5\sigma_g$ MO's) but since the nuclear charges for this system are all equal it is not possible for the lower π MO's to deprive the $2\pi_u$ of its stability to the extent found for the 3π in FNO; consequently it seems clear that the linear ozone ground state is an open shell configuration ($^3\sum_g^-$) which doubly occupies the $2\pi_u$ in preference to the $5\sigma_g$.

Finally, because the ambiguity of electronic states in FNO occurs only in the limit of linear geometry, i.e. relatively far from the experimental equilibrium angle the above considerations should have only a negligible effect upon the calculated angular potential curve around the equilibrium point; this view is also supported by the fact that the calculated equilibrium angle and bending force constant are quite insensitive to the inclusion of the 180° open shell energy in the range of values employed to compute the polynomial fit to the angular potential surface.

Appendix: Tabulation of the FNO Ground State Wavefunction

The following table presents the coefficients for the occupied molecular orbitals of the FNO ground state wavefunction. The atomic group functions centered at the N, F, and O nuclei are denoted as s or x, y and z according to spatial symmetry. Details concerning the group functions can be found in Ref. [8].

Orb.	$1a$	$2a$	$3a$	$4a$	$5a$	$6a$	$7a$	$8a$	$9a$	$10a$
N: $1s$	0.0001	0.0001	0.9794	−0.1354	0.0064	0.1656	−0.0172	0.0562	−0.0215	0.0667
s	0.0000	0.0000	0.0520	−0.0060	0.0002	0.0077	−0.0008	0.0029	−0.0011	0.0034
$2s$	−0.0006	−0.0017	0.0040	0.3832	0.0093	−0.6977	0.0709	−0.3539	0.1429	−0.3893
x	0.0006	−0.0003	−0.0002	0.0253	−0.1293	0.0489	0.4331	0.1320	0.0201	−0.3383
z	0.0000	−0.0008	0.0029	0.2043	−0.0820	0.0881	−0.1463	0.5288	−0.1671	0.3800
F: $1s$	0.9791	0.0000	0.0000	−0.0638	−0.2345	−0.0608	−0.0459	−0.0277	0.0044	0.0073
s	0.0517	0.0000	−0.0000	−0.0029	−0.0109	−0.0029	−0.0023	−0.0014	0.0002	0.0004
$2s$	0.0054	−0.0000	−0.0003	0.2356	0.9318	0.2888	0.2371	0.1369	−0.0177	−0.0424
x	0.0009	−0.0001	0.0000	0.0381	0.0578	−0.2021	−0.2732	−0.2563	0.1118	0.6158
z	0.0000	−0.0001	−0.0003	−0.0049	0.0107	0.0245	−0.1427	0.2525	0.9543	−0.1132
O: $1s$	0.0000	0.9794	−0.0003	−0.1721	0.0758	−0.1466	0.0126	0.0616	−0.0016	−0.0041
s	−0.0000	0.0511	−0.0000	−0.0076	0.0034	−0.0069	0.0006	0.0031	−0.0001	−0.0002
$2s$	−0.0000	0.0058	−0.0010	0.5756	−0.2755	0.6902	−0.0635	−0.3652	0.0235	−0.0004
x	0.0000	−0.0010	0.0002	−0.0850	0.0183	0.1113	0.5803	−0.2967	0.2943	0.5837
z	0.0000	−0.0027	−0.0003	−0.2136	0.0786	0.2994	−0.3245	−0.5008	0.0983	−0.3202

Orb.	$1b$	$2b$
N: y	0.5495	−0.1514
F: y	0.3357	0.9297
O: y	0.5850	−0.3650

Conclusion

The rather unique electronic structure of nitrosyl fluoride can be explained on the basis of a model derived from *ab initio* SCF calculations which considers the dynamics of a rather long range confrontation between a fluorine atom and a nitric oxide radical. The observation that the doubly occupied orbitals of both species are very nearly unperturbed by the process of chemical formation greatly simplifies the qualitative analysis so that attention can be focused almost entirely on the behavior of the highest occupied orbital of nitrosyl fluoride upon changes in the molecular geometry. In this way a nearly complete one-to-one correspondence may be drawn between the characteristics of the potential surface of one molecular orbital and that of the entire FNO molecule.

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