4974 *J. Phys. Chem. A* **2001,** *105,* 4974−4979

Parametrized Valence Bond Studies of the Origin of the N−F Bond Lengthenings of FNO_2 and FNO

Richard D. Harcourt* and P. Peter Wolynec

School of Chemistry, University of Melbourne, Victoria 3010, Australia

Received: December 11, 2000; In Final Form: February 28, 2001

The origins of the lengthening of the N−F bonds of FNO_2 and FNO relative to that of NH_2F are examined via STO-6G valence bond calculations. The calculations were parametrized to reproduce approximately the UHF/cc-pVQZ molecular orbital estimates for the nitrogen and oxygen spin densities of NO_2 and NO. This procedure was used in a recent valence-bond study of *asym* N_2O_3. The results of the calculations show that the N−F lengthening for FNO_2 arises from the delocalization of oxygen lone-pair electrons into the AOs of the N−F σ bond, whereas this effect and the presence of a "bent" N−F σ bond are primarily responsible for the N−F lengthening in FNO. For comparison with the experimental geometries of FNO_2, FNO, and NH_2F, B3LYP/6-31+G(d) molecular orbital estimates of their geometries and those for related systems are reported. Consideration is also given to a spin-coupled valence-bond representation of the electronic structure of FNO_2, and a valence-bond representation for the reaction $FNO_2 + O_3 \rightarrow FNO + 2O_2$ is provided via the use of increased-valence structures for the reactants.

Introduction

Experimental estimates (Table 1) of the geometries of FNO_2 and FNO show that the N−F bond lengths of these molecules (1.467 and 1.512 or 1.517 Å)[1,2] are longer than that for a "normal" N−F single bond, as in NH_2F (1.432 Å),[3] for example. Similar types of results have been obtained from GAUSSIAN 98 B3LYP/6-31+G(d) molecular orbital (MO) calculations[4] (Table 2). On the other hand, the geometries of the NO_2 and NO moieties of FNO_2 and FNO resemble (Tables 1 and 2) those for[5−7] NO_2, NO, and *asym* N_2O_3.

In ref 8, we used a parametrized valence-bond (VB) procedure to demonstrate that the origin of the long, weak N−N bond of *asym* N_2O_3 was associated with two electronic effects:

(a) some delocalization of lone-pair electrons—from the oxygen atoms of the $-NO_2$ moiety in particular—into the nitrogen atomic orbitals (AOs) that are involved in the formation of the N−N σ bond, and

(b) the orientation of the nitrosyl−nitrogen AO, which participates in the formation of the (fractional) N−N σ bond. Due to the noncollinearity of the axes of the AOs of this σ bond, it is designated as a bent bond.

The parametrization involved the construction of STO-6G VB wave functions for NO_2 and NO so that UHF/cc-pVQZ MO estimates[4] of 0.51 and 0.80 for their nitrogen odd electron spin densities were reproduced.

In the present paper, we employ the same parametrization method for NO_2 and NO to demonstrate that electronic effect a is responsible for the lengthening of the N−F bond of FNO_2, whereas both a and b together generate the N−F bond lengthening for FNO. We also give consideration to several types of VB structures for FNO_2, each of which involves an apparently pentavalent nitrogen atom.

TABLE 1: Experimental Estimates of Bond Lengths (*r*(AB)) and Bond Angles (∠ABC) for FNO_2, FNO, FNH_2, NO_2, NO, and *asym* N_2O_3[a]

	r(NF)	*r*(NO)	∠ONO	∠FNO
FNO_2[b]	1.467	1.180	135.9	112.0
FNO[b]	1.512	1.136		110.1
FNO[b]	1.517	1.131		109.9
FNH_2[b]	1.432			
NO_2[c]		1.193	135	
NO[c]		1.150		
$O'NNO_2$[c]		1.140 (O′N) 1.202, 1.207 (NO)		

[a] In all tables, the units for bond length, bond angle and energy (*E*) are Å, deg, and au, respectively. [b] Refs 1−3. [c] Refs 5−7

TABLE 2: B3LYP/6-31+G(d) Equilibrium Bond Lengths and Bond Angles for FNO_2, FNO, FNH_2, and Related Species.

	r_e(NF)	r_e(NO)	r_e(NC)	∠ONO	∠FNO	∠FNC
FNO_2	1.4861	1.1856		135.9	112.0	
$FN(CH_2)_2$ [a]	1.4052		1.3259			111.1
FNO	1.5295	1.1408			110.2	
$FNCH_2$	1.4282		1.2687			108.7
FNH_2	1.4396					
NO_2		1.2017		134.0		
NO		1.1578				

[a] Planar form is a transition state, with one imaginary frequency.

Valence Bond Structures for the Calculations

For FNO_2, we consider six "active space" electrons which are primarily responsible for the N−F σ−bond properties. These electrons occupy the oxygen $\bar{\pi}_1$ and $\bar{\pi}_3$ AOs, the nitrogen hybrid AO h_2, and the fluorine 2pσ AO, which overlaps with h_2. The orientations of these AOs and other valence-shell σ AOs are displayed in Figure 1a. The remaining 18 electrons of the $-NO_2$ moiety are located in nine relevant core-type orbitals described in ref 8. For the fluorine atom, eight core electrons doubly occupy the 1s, 2s, 2pπ, and 2p$\bar{\pi}$ AOs. For a given distribution of 26 core electrons, 10 canonical ($S = 0$ spin) Lewis structures (structures **1−10** of Figure 2) arise when six electrons are distributed among the four "active space" AOs. These structures were included in the VB calculations, together with two

---

* Corresponding author. E-mail: harcus@rubens.its.unimelb.edu.au.

10.1021/jp004459r CCC: \$20.00

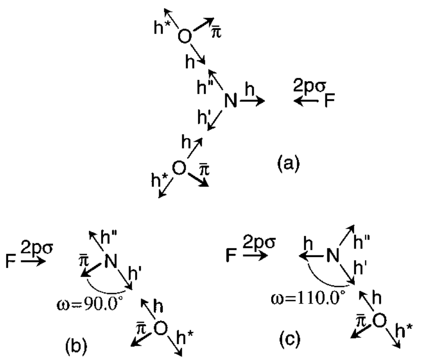

Figure 1. Orientation of the valence-shell σ AOs for (a) FNO_2, (b) FNO for nitrogen hybridization angle $\omega = 90°$, and (c) FNO for $\omega = 110°$. For FNO_2, atoms 1−4 are the oxygen, nitrogen, oxygen, and fluorine atoms.

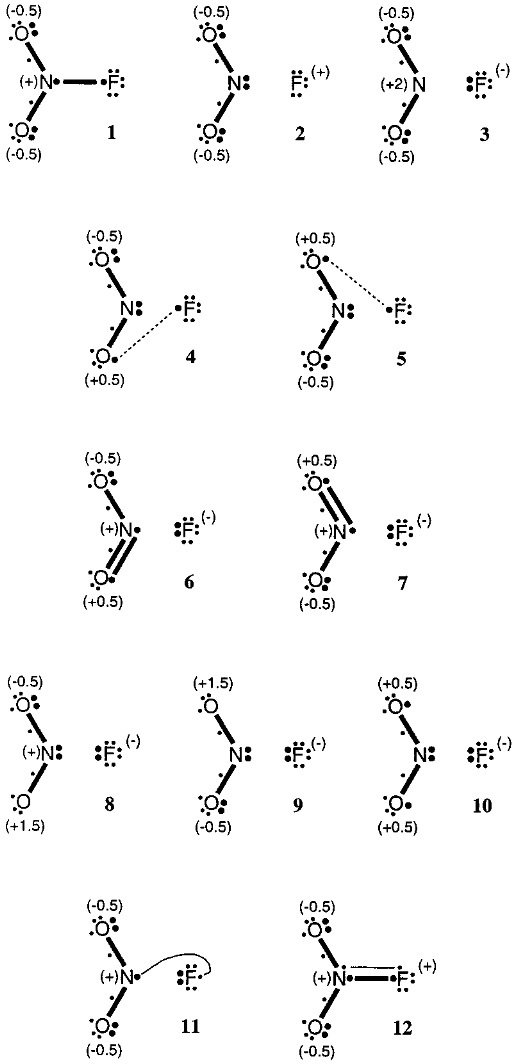

Figure 2. VB structures for FNO_2 that arise from the delocalization of 0, 1, and 2 oxygen $\bar{\pi}$ electrons.

additional structures, **11** and **12** in Figure 2, with N−F σ bonds. Structures **11** involves $2s_F$−h_N instead of $2p\sigma$−h_N σ bonding in structure **1**, and structure **12** involves N−F π bonding as well as $2p\sigma$−h_N σ bonding.

As was the case in ref 8, the NO_2, NO_2^+, and NO_2^- π electron distribution of the four π electrons in each of the structures **1**−**11** is represented as[9]

$$\dot{O}\cdot N\cdot\dot{O}$$

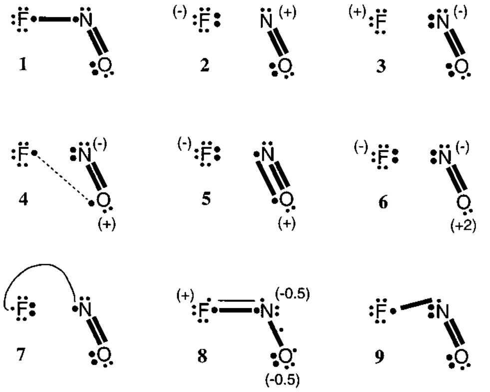

Figure 3. VB structures for FNO that arise from the delocalization of 0, 1, and 2 oxygen $\bar{\pi}$ electrons.

The NO_2^- moiety in structure **12** has five π electrons, and we have employed the following symbolism (cf. ref 10),

$$\dot{O}\cdot\dot{N}\cdot\dot{O}$$

which is equivalent to resonance between three Lewis structures,

$$\ddot{O}\ \dot{N}\ \ddot{O} \longleftrightarrow \ddot{O}\ \ddot{N}\ \dot{O} \longleftrightarrow \dot{O}\ \ddot{N}\ \ddot{O}$$

to represent the π electron distribution for this structure.

For FNO, four active-space electrons occupy the $2p\sigma_F$, h_N, and $\bar{\pi}_O$ AOs (cf. Figure 1b,c). For a given distribution of 20 core electrons, six canonical Lewis structures, **1**−**6** of Figure 3, arise when the four active-space electrons are distributed among the $2p\sigma_F$, h_N, and $\bar{\pi}_O$ AOs. As for FNO_2, we have included two additional VB structures, **7** and **8** of Figure 3, with N−F bond properties which are the same as those for the FNO_2 structures **11** and **12** of Figure 2. For some of the calculations, we have also included structure **9** of Figure 3. This structure is the FNO analogue of the asym N_2O_3 structure **1a** displayed in ref 8.

Whereas the h_N AO for FNO_2 is directed along the N−F internuclear axis (Figure 1a), for FNO, the optimum orientation of the h_N AO is not necessarily in this direction. The angle $\omega = \angle h_N{-}N{-}h'_N$ (Figure 1b,c), which determines this orientation, is calculated variationally for each N−F bond length (cf. calculations[8] for the N═O substituent of *asym* N_2O_3). For this purpose, we have used integer values of 92°−96° and 110° for ω, and have chosen the integer value of ω which gives the lowest energy.

Method of Calculation

The computational procedure follows essentially that which is described in ref 8. Roso's ab initio VB program[8,10a,b,11] was used to perform STO-6G VB calculations with "best atom" AO exponents. As discussed in the previous section, the electronic structures of the nonactive space cores for the NO_2 and NO moieties of FNO_2 and FNO were assumed to be identical to those described for N_2O_3.

Following ref 8, the π electrons of the $-NO_2$ moiety of FNO_2 were located in the orthogonal MOs, $b_1 = \pi_1 + k\pi_2 + \pi_3$, $a_2 = \pi_1 - \pi_3$, and $b_1^* = \pi_1 - k^*\pi_2 + \pi_3$, to give initially the $(b_1)^2(a_2)^2$ configuration for structures **1**−**11** and the $(b_1)^2(a_2)^2(b_1^*)^1$ configuration for structure **12**. Similarly, the N−O π electrons of FNO were located in the NO-parametrized orthogonal MOs $\pi_{NO} = \pi_N + l\pi_O$ and $\pi^*_{NO} = \pi_N - l^*\pi_O$. Values of 2.2 and 1.2 were chosen[8] for the MO parameters k and l so that VB calculations for NO_2 and NO, with $(b_1)^2(a_2)^2$ and $(\pi_{NO})^2$ π electron configurations respectively, reproduced approximately

TABLE 3: FNO_2 Equilibrium N−F Bond Lengths and Energies for Resonance between Sets of VB Structures from Figure 2

structures	r_e(NF)	*E*
1−**12**[a]	1.54_0	−301.97150
1−**12**[b]	1.48_0	−302.00343
1−**3**, **11**, **12**[c]	1.41_0	−301.92670
1, **4**, **5**	∞	−301.92480

[a] Excluding and [b]including π electron correlation for structures **2**, **3**, **6**−**10**, and **12**. [c] Including π electron correlation for structures **2**, **3**, and **12**.

the UHF/cc-pVQZ MO estimates[4] of 0.51 and 0.80 for the nitrogen odd electron spin densities of these molecules.

The $S = 0$ spin wave functions for structures **1**−**11** of Figure 2 and structures **1**−**7** and **9** of Figure 3 involve either one or two Slater determinants, viz, $|a^{\alpha}a^{\beta}|$ or $|b^{\alpha}b^{\beta}|$ and $|a^{\alpha}b^{\beta}| + |b^{\alpha}a^{\beta}|$, according to whether there are zero or two of the active-space AOs (a and b) which are singly occupied. In each of the structures **12** of Figure 2 and **8** of Figure 3, there are four singly occupied orbitals, namely, $a = h_2$, $b = 2p\sigma_F$, $c = b_1^*$ or π^*(NO), and $d = 2p\pi_F$, with $h_2{-}2p\sigma_F$, and $b_1^*{-}2p\pi_F$ spin pairings. With an h_2, $2p\sigma_4$, b_1^*, $2p\pi_F$ ordering of the spatial orbitals in the Slater determinants, the appropriate $S = 0$ spin wave function[12] is $|a^{\alpha}b^{\beta}c^{\alpha}d^{\beta}| + |a^{\beta}b^{\alpha}c^{\beta}d^{\alpha}| - |a^{\alpha}b^{\beta}c^{\beta}d^{\alpha}| - |a^{\beta}b^{\alpha}c^{\alpha}d^{\beta}|$.

For either molecule, interpolation via energy calculations for different values of the N−F internuclear separation was used to determine the value of the equilibrium bond length, r_e(NF). Corrections for basis set superposition error, which were found to be unimportant for *asym* N_2O_3, have not been included here.

In the following discussion for each molecule, we assume that when the r_e(NF) is similar to the experimental estimate, the VB wave function provides an appropriate (parametrized) VB representation[13] of the distribution of the active-space electrons that we have considered.

Results for FNO_2

In Table 3, we report the minimum energies and associated equilibrium bond lengths for several types of VB calculations for FNO_2. Resonance between structures **1**−**11** of Figure 2, each with a $(b_1)^2(a_2)^2(2p\pi_F)^2$ π electron configuration, and structure **12** with a $(b_1)^2(a_2)^2(b_1^*)^1(2p\pi_F)^1$ π electron configuration generates a minimum energy when $r_e(NF) = 1.54$ Å. This length is 0.07 Å longer than the experimental estimate of 1.47 Å (Table 1). Without changing the AO basis set, we have introduced more $F^-NO_2^+$ and $F^+NO_2^-$ ionic character into the VB resonance scheme to obtain a closer agreement between theory and experiment.

As indicated earlier, the (nonvariational) π electron MOs for NO_2 generate the noncorrelated π electron distribution which is needed to reproduce UHF/cc-pVQZ MO estimates[4] for the (σ electron) odd electron spin densities for free NO_2. To ensure that the ground-state of FNO_2 dissociates to generate these spin densities, the covalent structures **1**, **4**, and **5** must retain this π electron distribution at all N−F internuclear separations.[8] However, because the remaining structures do not contribute to the ground-state resonance scheme when the molecule dissociates, it is permitted to modify the π electron distributions for these structures.

Each of the ionic structures **2**, **3**, and **6**−**10** has a $(b_1)^2(a_2)^2(2p\pi_F)^2$ π electron configuration. The corresponding structures with $(b_1)^2(b_1^*)^2(2p\pi_F)^2$, $(a_2)^2(b_1^*)^2(2p\pi_F)^2$, and $(b_1)^1(a_2)^2(b_1^*)^1(2p\pi_F)^2$ π electron configurations can also be constructed.[14] The polar structure **12** has a $(b_1)^2(a_2)^2(b_1^*)^1(2p\pi_F)^1$ π electron configuration. We can also construct a polar structure with a $(b_1)^1(a_2)^2(b_1^*)^2(2p\pi_F)^1$ π electron configuration. When these additional structures are included, the VB calculations involve 34 $S = 0$ spin configurations. The resulting energy minimum (Table 3) occurs at 1.48 Å, which is now close to the experimental estimate of 1.47 Å. When no oxygen $\bar{\pi}$ electron delocalization occurs, a VB calculation with VB structures **1**−**3**, **11**, and **12**, together with those for the π electron excited configurations for structures **2**, **3**, and **12** included, gives an N−F bond length of 1.41 Å. This length is now substantially shorter than the experimental estimate of 1.47 Å and similar to the N−F length of 1.43 Å for NH_2F with a “normal” N−F single bond (Table 1). Therefore, the delocalization of the oxygen $\bar{\pi}$ electrons into the AOs that form the N−F σ bond of structure **1** is calculated to be responsible for lengthening of the N−F bond.

TABLE 4: Chirgwin−Coulson Weights[15] at *r*(NF) = 1.48 Å for FNO_2 VB Structures 1−12 of Figure 2

	a	*b*		*a*	*b*
1	0.5416	0.5077	**8** = **9**	0.0004	0.0006
2	0.1129	0.1252	**10**	0.0036	0.0050
3	0.0803	0.1057	**11**	0.0078	0.0086
4 = **5**	0.0877	0.0795	**12**	0.0089	0.0077
6 = **7**	0.0344	0.0399			

[a] Excluding and [b]including π electron correlation in structures **2**, **3**, **6**−**10**, and **12**.

The results of B3LYP 6-31+G(d) calculations (Table 2) provide support for this conclusion. The N−F bond lengths for FNO_2 and isoelectronic $FN(CH_2)_2$ are 1.4861 and 1.4052 Å, respectively. For the latter species with a shorter N−F bond, there are no oxygen $\bar{\pi}$ electrons to delocalize.

In Table 4, we report structural weights[15] for structures **1**−**12** at *r*(NF) = 1.48 Å, excluding and including π electron correlation for structures **2**, **3**, **6**−**10**, and **12**. As expected, the covalent structure **1** with a $2p\sigma_F{-}h_N$ electron-pair bond, is the primary VB structure. The next most important structures are the ionic structures **2** and **3** and the “long-bond” covalent structures **4** and **5**. The remaining seven structures are calculated to have a substantially smaller importance, especially structures **8**−**12**. The somewhat larger weight for the $F^+NO_2^-$ structure **2** compared with that for the $F^-NO_2^+$ structure **3** is perhaps surprising, but it is in accord with qualitative expectations based on formal charge considerations. A similar type of result was obtained[8] for *asym* N_2O_3, namely, that $O_2N^-NO^+$ is more important than $O_2N^+NO^-$.

The results of NQR studies[16] indicate that the N−F bond is polarized in the sense $N^+{-}F^-$. Although the $F^+NO_2^-$ structure **2** alone is more important than the $F^-NO_2^+$ structure **3**, the sum of the weights for the four $F^-NO_2^+$ structures **3**, **6**, **7**, and **10** (0.192) is larger than the sum of weights for the $F^+NO_2^-$ structures **2** and **12** (0.133).

Results for FNO

(a) Resonance between VB Structures 1−8 of Figure 3. In Table 5, we report the energies and equilibrium N−F bond lengths for a variety of VB calculations for FNO. (For recent MO studies, see ref 17.) With a $(2p\pi_F)^2(\pi_{NO})^2$ π electron configuration for each of structures **1**−**7** of Figure 3 and a $(2p\pi_F)^1(\pi^*_{NO})^1(\pi_{NO})^2$ for structure **8** of the same figure, the minimum energy occurs when *r*(NF) = 1.60 Å for $\omega = 93°$. Allowance for π electron correlation via the inclusion of additional ionic configurations of the types $(2p\pi_F)^2(\pi^*_{NO})^2$ and $(2p\pi_F)^2(\pi^*_{NO})^1(\pi_{NO})^1$ for the ionic structures **3**−**6** and $(2p\pi_F)^1(\pi^*_{NO})^2(\pi_{NO})^1$ for structure **8** shortens the equilibrium

TABLE 5: FNO Hybridization Angles ω, Minimum Energies, and Equilibrium N−F Bond Lengths for Resonance between Sets of VB Structures from Figure 3[a]

structures	ω	r_e(NF)	E	ω	r_e(NF)	E
1−**8**	94	1.52_5	−227.66931	110	1.40_4	−227.52617
1−**3**, **7**, **8**	94	1.47_4	−227.62937	110	1.37_1	−227.49052
1−**9**	95	1.53_3	−227.67046	110	1.61_9	−227.63442
1−**3**, **7**, **8**, **9**	95	1.47_0	−227.63014	110	1.51_1	−227.59282
1, **4**	90	∞	−227.61032			

[a] π electron correlation included in structures **2**, **3**, **5**, **6**, and **8**.

TABLE 6: Equilibrium N−F Bond Lengths, Minimum Energies, and Approximately Optimum Values of the N−O Nitrogen Hybridization λ' for Resonance between Sets of FNO VB Structures (Figure 3) with Hybridization Angle ω = 110°

	r(NF)	E	λ'
1−**8**	1.42_4	−227.61194	1.5
1−**3**, **7**, **8**	1.39_2	−227.58028	1.5
1−**9**	1.52_5	−227.64414	2.0
1−**3**, **7**, **8**, **9**	1.45_8	−227.60642	2.0

[a] π electron correlation included in structures **2**, **3**, **5**, **6**, and **8**.

bond length to 1.525 Å with $\omega = 94°$, which is close to the experimental estimates[2] of 1.51−1.52 Å (cf. ref 17a for a careful MO study with extended basis sets, in which only eight of 35 different calculations with correlation give N−F bond lengths that range between 1.50 and 1.53 Å).

When no delocalization of oxygen $\bar{\pi}$ electrons occurs, i.e., structures **4**−**8** are omitted, the calculations with π electron correlation generate a shorter N−F length of 1.47 Å when $\omega = 94°$. Therefore, delocalization of the oxygen $\bar{\pi}$ electrons does generate some lengthening of the N−F bond. However, 1.47 Å is still longer than the 1.43 Å for a "normal" N−F single bond, as in NH_2F and CH_2NF (cf. Table 2). This lengthening is associated with the nature of the orientation of the h_N AO; for $\omega = 110°$, which orients this AO along the N−F bond axis (cf. Figure 1(c)), $r_e(NF) = 1.40$ and 1.37 Å with and without $\bar{\pi}_O$ electron delocalization.

(b) Resonance between VB Structures 1−9 of Figure 3. When structure **9** is included, together with π electron correlation in the ionic structures, resonance between structures **1**−**9** generates an equilibrium bond length of 1.53 Å when $\omega = 95°$. This length shortens to 1.47 Å, also for $\omega = 95°$, when structures **4**−**6** are omitted. These results are similar to those obtained when structure **9** is omitted. However, when ω is equal to the bond angle of 110°, these two types of calculations give equilibrium N−F bond lengths of 1.625 and 1.51 Å respectively. Similarly, for *asym* N_2O_3, when ω is equal to the N−N=O bond angle of 105°, inclusion of VB structure **1a** of ref 8 lengthens the N−N bond. In both cases, the value of 3.0 that has been used for the nitrogen hybridization parameter λ' for the N−O σ bond is far from energy-optimized when ω is equal to the bond angle. (3.0 is appropriate for $\omega = 90°$.) To demonstrate the effect of energy-optimizing the value of λ' when $\omega = 110°$, we have performed additional calculations, the results for which are reported in Table 6. With structures **4**−**6** omitted, optimization of the nitrogen hybridization shortens the N−F bond length from 1.51 Å when $\lambda' = 3.0$ to 1.46 Å when $\lambda' = 2.0$. However, 1.46 Å is still substantially longer than the 1.39 Å for $\lambda' = 3.0$ when structures **4**−**6** and **9** are omitted. Further investigation is needed to ascertain why the inclusion of structure **9** lengthens substantially the F−N bond when $\omega = 110°$.

(c) VB Structural Weights. In Table 7, we report structural weights for FNO for several sets of calculations, each at the optimum value for its N−F bond length and hybridization angle.

TABLE 7: Chirgwin−Coulson Weights[15] for FNO VB Structures 1−9 of Figure 3

	a	*b*	*b*
r_e(NF)/Å	1.60	1.525	1.525
ω/deg	93	94	95
1	0.6701	0.6186	0.6212
2	0.0994	0.1346	0.1353
3	0.0740	0.0899	0.0888
4	0.1055	0.0840	0.0847
5	0.0386	0.0464	0.0471
6	0.0004	0.0008	0.0008
7	0.0014	0.0111	0.0108
8	0.0107	0.0146	0.0141
9	−	−	−0.0029

[a] Excluding and [b]including π electron correlation in structures **2**, **3**, **5**, **6**, and **8**.

As is the case for FNO_2, the primary canonical structures are the covalent structure **1**, its ionic partners **2** and **3**, and the covalent structure **4** with a long or formal F−O bond. The latter structure arises from the delocalization of one oxygen $\bar{\pi}$ electron into the nitrogen h_N AO. (For FNO_2, there are two structures of this type, namely, structures **4** and **5** of Figure 2.) Structure **4** is usually omitted from qualitative VB descriptions of FNO and replaced by the ionic structure **5** of Figure 3. Structure **5** is calculated to have a substantially smaller weight, as have the FNO_2 analogues, structures **6** and **7** of Figure 2.

Because the covalent canonical Lewis structures for both FNO_2 and FNO have larger weights than the corresponding ionic canonical Lewis structures (cf. Tables 4 and 7), the primary F + NO_2 and F + NO bonding processes involve the spin pairings of the two unpaired electrons for each pair of reactants. When only these spin pairings occur, the nitrogen odd electron spin densities of 0.51 and 0.80 for NO_2 and NO give N−F bond numbers of 0.51 and 0.80 for FNO_2 and FNO. These values of the bond numbers suggest that FNO should have the shorter N−F bond. But the nature of the AO orientations which overlap to form this (fractional) bond leads to its lengthening.

Increased-Valence and Spin-Coupled Valence-Bond Structures

The results of spin-coupled VB calculations[19] for FNO_2 and $ClNO_2$ have been interpreted to imply that the nitrogen atoms participate "unambiguously in five bonds".[19] However, without expansion of the nitrogen valence shell to permit a $(2s)^1(2p)^3(3d)^1$, V_5 valence-state configuration, as in structure **I** of Figure 4, for example, true pentavalence (or quinquevalence) for a nitrogen atom in a VB structure cannot occur. The spin-coupled study indicates that nitrogen 3d AOs make very minor contributions to bonding, and therefore, the primary spin-coupled VB structure will involve an apparent rather than a true nitrogen pentavalence. Apparent pentavalence arises from the contribution of singlet diradical structures to an equivalent Lewis structure resonance scheme.[20]

In the spin-coupled calculations of ref 19, no allowance was made for the delocalization of oxygen $\bar{\pi}$ electrons in the active space. (These types of delocalization will of course arise in the core for the active space electrons, but no explicit attention was given to them.) Therefore, the appropriate spin-coupled VB structure is **II** of Figure 4, in which the N−O π bonds are fractional electron-pair bonds.[8,10,11,20−22] Thin bond lines are used to represent these types of bonds, whose bond orders are less than unity (cf. structure XX of ref 22 for HCO_2^-, with an apparently pentavalent carbon atom).

When allowance is made for the delocalization of oxygen $\bar{\pi}$ electrons, VB structures **III** and **IV** of Figure 4, with apparent

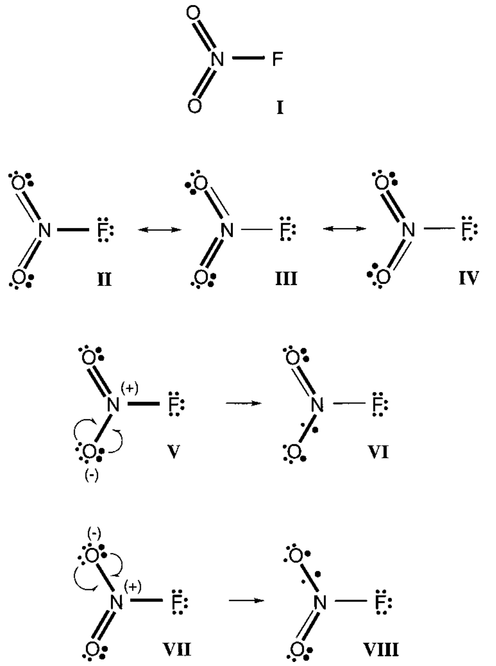

Figure 4. Lewis octet VB structures and VB structures with apparently pentavalent nitrogen atoms.

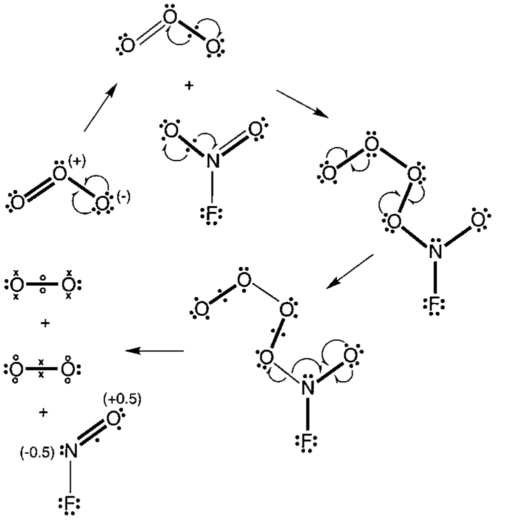

Figure 5. VB representation for the reaction $FNO_2 + O_3 \rightarrow FNO + 2O_2$, using increased-valence structures.

pentavalence for the nitrogen atom, will participate in resonance with VB structure **II**. In structures **III** and **IV**, the thin N−F bond lines imply that the bond is fractional[8,10,11,20−22] and therefore its length is longer than a "normal" N−F single bond.

On a number of occasions,[21,23] resonance between increased-valence structures **VI** and **VIII** of Figure 4, each with an apparently pentavalent nitrogen atom, has been used to represent the electronic structures of FNO_2. These VB structures can be derived from the standard Lewis structures **V** and **VII** of Figure 4 via one-electron delocalizations of oxygen π and $\bar{\pi}$ electrons, as indicated. Increased-valence structures **VI** and **VIII** make explicit the presence of singlet diradical character, and therefore, they are better suited than structures **I**−**IV** for helping to formulate the electronic reorganization that occurs for reactions that involve 1,3-dipolar molecules.

Ionic $F^-NO_2^+$ increased-valence structures, which participate in resonance with the covalent increased-valence structures of **VI** and **VIII**, are displayed in ref 21a. Increased-valence structures have been derived for FNO in refs 21a, 24, and 25 (cf. Figure 4 here also) and for F_3NO in refs 21a, 26, and 27.

In Figure 5, we show how increased-valence structures for FNO_2 and O_3 may be used to indicate how electronic reorganization could proceed for the reaction $FNO_2 + O_3 \rightarrow FNO + 2O_2$, which has been studied[28] with regard to its possible implications for atmospheric chemistry. The increased-valence structure for O_3 is derived from a standard Lewis structure, via one-electron delocalizations of O^- π and $\bar{\pi}$ electrons, as indicated. Two O_2 molecules are generated in their $S = 1$ spin ground states, (cf. for example, $O_4(S = 0) \rightarrow O_2(S = 1) + O_2(S = 1)$),[11e,29] and the mechanism displayed exploits the presence of singlet diradical character in each of the reactants. It should be noted that if one uses the familiar Lewis structures for the reactants, together with the familiar electron-pair transfers via double-headed arrows, an $S = 0$ spin excited state for each O_2 molecule (O═O) is generated in the VB representation for the reaction. There is no evidence that the reaction provides a source of singlet oxygen.

Conclusions

The results of the VB calculations presented here provide support for the hypothesis that the lengthenings of the N−F bonds of FNO_2 and FNO are associated with oxygen $\bar{\pi}$ electron delocalization for both molecules, together with the presence of a "bent" N−F σ bond in the latter molecule. Although we have not performed the calculations, it is probable that the existence of long N−Cl bonds in $ClNO_2$ and ClNO (1.840 Å, 1.975 Å)[30,31] (cf. Pauling's estimate[32] of 1.73 Å for the length of an N−Cl single bond) may be similarly rationalized. On the other hand, the C−N bond lengths for CH_3NO_2 and CH_3NO (1.489 Å, 1.480 Å)[33,34] (cf. Pauling's estimate[32] of 1.47 Å for the length of a C−N single bond) imply that these effects manifest themselves only slightly for these molecules. No doubt electronegativity and hybridization factors are responsible for the differences.

For each of FNO_2 and FNO, covalent structures that arise from the delocalization of an oxygen $\bar{\pi}$ electron into a nitrogen AO (to generate a "long" or formal O−F bond in each structure) are calculated to have weights that are substantially larger than are those for more familiar ionic structures (as $F^-NO_2^+$ and F^-NO^+) which also involve the delocalization of one oxygen $\bar{\pi}$ electron.

Acknowledgment. We are indebted to and thank Dr. W. Roso for his ab initio VB program, Dr. F. L. Skrezenek for installing it, and the MARC Centre at the University of Melbourne for access to a farm of DEC workstations through a RAS grant.

Appendix: Dissociation Energies for FNO and FNO_2

The calculations with π electron correlation for the ionic structures give values of 37.7 and 49.3 kcal mol^{-1} for the equilibrium dissociation energies (D_e) of FNO and FNO_2, respectively. With $D_e - D_o$ (zero point energy) estimates of 1.8 and 3.0 kcal mol^{-1} for these molecules,[17a,18a] the resulting values for the spectroscopic dissociation energies (D_o) are 35.9 and 46.3 kcal mol^{-1}. These D_o values do not compare well with experimental estimates of 55.0 and 51.7 kcal mol^{-1} (cf. refs 17a, 18a) or with some recent ab initio MO estimates (55.5 and 55.9 kcal mol^{-1} for FNO and 54.77 and 55.79 kcal mol^{-1} for FNO_2)[17a,18a] with better basis sets. An improvement for FNO would arise if the value of the nitrogen hybridization parameter λ′ for the ionic structures of Figure 3—for structures **2**, **3**, and **5** in particular—were energy-optimized.

References and Notes

(1) Legon, A. C.; Millen, D. J. *J. Chem. Soc. A* **1968**, 1736.

(2) (a) Buckton, K. S.; Legon, A. C.; Millen, D. J. *Trans. Faraday Soc.* **1969**, *65*, 1975. (b) Cazzoli, G.; Degli Esposti, C.; Favero, P. G.; Palmieri, P. *Nuovo Cimento* **1984**, *D3*, 627.

(3) Christen, D.; Minkwitz, R.; Nass, R. *J. Am. Chem. Soc.* **1987**, *109*, 1736. See also Palmer, M. H. *Z. Naturforsch. A* **1986**, *41A*, 147.

(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(5) Bird, G. R.; Baird, J. C.; Jache, A. W.; Hodgeson, J. A.; Curl, R. F.; Kunkle, A. C.; Bransford, J. W.; Rastrup-Andersen, J.; Rosenthal, J. *J. Chem. Phys.* **1964**, *40*, 3378.

(6) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(7) Brittain, A. H.; Cox, P. A.; Kuczkowski, R. L. *Trans. Faraday Soc.* **1969**, *65*, 1963.

(8) Harcourt, R. D.; Wolynec, P. P. *J. Phys. Chem. A* **2000**, *104*, 2138, 2144.

(9) This structure is used solely to provide a compact VB representation for a symmetrical distribution for the four π electrons. Its wave function does not correspond to the C_{2v} symmetry MO wave function $(b_1)^2(a_2)^2$, which has been used in the calculations.

(10) (a) Harcourt, R. D. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1089. (b) *J. Phys. Chem.* **1993**, *97*, 1351. (c) In *Pauling's Legacy-Modern Theory (Modelling) of Chemical Bonding*; Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: New York, 1999, p 449. (d) *Eur. J. Inorg. Chem.* **2000**, 1901.

(11) (a) Harcourt, R. D.; Roso, W. *Can. J. Chem.* **1978**, *56*, 1093. (b) Skrezenek, F. L.; Harcourt, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3934. (c) Harcourt, R. D. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1119. (d) Harcourt, R. D. *Theor. Chim. Acta* **1991**, *78*, 267. (e) Harcourt, R. D.; Pyper, N. C. *Int. J. Quantum Chem.* **1998**, *68*, 129.

(12) When there are four singly occupied orbitals in any of the resulting VB structures, the spin theory will be of the same type as that described above for structure **12**, with a $(b_1)^2(a_2)^2(b_1{}^*)^1(2p\pi_F)^1$ π electron configuration.

(13) For FNO_2 and, to a smaller extent, for FNO, the VB structural weights of Tables 4 and 7 indicate that there is substantial delocalization of oxygen lone-pair electrons into the AOs that are associated with N−F σ bond formation. Electronic delocalization could be evidenced in MO calculations either by performing a density analysis within the atoms-in-molecule framework (Bader, R. F. W. *Atoms in Molecules: a Quantum Theory*; O.U.P.: Oxford, 1990) or by using the electron localisation procedure (Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683) which works with the electron localisation function (ELF) as a potential function (Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397).

(14) The unimportant covalent structures **11** of Figure 2 and **7** of Figure 3 (cf. Tables 4 and 7), each with a $2s_F-2p\sigma_N$ electron-pair bond, have not been treated in this manner. Because the N−N bond length of 1.86 Å for asym N_2O_3 is substantially longer than the N−F bond length of 1.47 Å for FNO_2, the ionic character is smaller for *asym* N_2O_3. Therefore, π electron correlation in the ionic structures should have a smaller effect on the N−N bond length of *asym* N_2O_3 than it has for the N−F bond of FNO_2.

(15) Chirgwin, B. H.; Coulson, C. A. *Proc. R. Soc. London, Ser. A* **1950**, *201*, 1805. See Bachler, V. *Theor. Chem. Acc.* **1997**, *92*, 223 and refs 55 and 56 therein for an alternative expression for a structural weight.

(16) Styger, C.; Gatehouse, B.; Heinefing, N.; Jager, W.; Gerry, M. C. L. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1899.

(17) (a) Dibble, T. S.; Francisco, J. S. *J. Chem. Phys.* **1993**, *99*, 397. (b) Lee, T. J. *J. Chem. Phys.* **1993**, *99*, 9783. See ref 18 below for MO studies of FNO_2.

(18) (a) Thümmel, H. T.; Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **1997**, *101*, 1188. (b) Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 4223.

(19) Cunningham, T. P.; Cooper, D. L.; Gerratt, J.; Karadakov, P. B.; Raimomdi, M. *Int. J. Quantum Chem.* **1996**, *60*, 393. See also: Cooper, D. L.; Gerratt, J.; Raimondi, M. In *Pauling's Legacy-Modern Theory (Modelling) of Chemical Bonding*; Maksić, Z. B., Orville-Thomas, W. J., Eds.; Elsevier: New York, 1999, p 537.

(20) (a) Harcourt, R. D. *THEOCHEM* **1992**, *259*, 155. (b) *J. Mol. Struct.* **1993**, *300*, 243.

(21) (a) Harcourt, R. D. *J. Mol. Struct.* **1971**, *9*, 221. (b) Harcourt, R. D. Qualitative Valence-Bond Descriptions of Electron-Rich Molecules. *Lecture Notes in Chemistry*; Springer-Verlag: Berlin, 1982; Vol. 30, p 131.

(22) Harcourt, R. D. *Aust. J. Chem.* **1969**, *22*, 279. See also: Harcourt, R. D.; Schulz, A. *J. Phys. Chem. A* **2000**, *104*, 6510 and refs therein. (In ref 25 on p. 6516, replace 1.24 with 1.20.)

(23) Klapötke, T. M.; Harcourt, R. D. *J. Fluor. Chem.* **2000**, *106*, 7.

(24) Harcourt, R. D.; Roso, W. *Int. J. Quantum Chem.* **1979**, *16*, 1033.

(25) Harcourt, R. D. Qualitative Valence-Bond Descriptions of Electron-Rich Molecules. *Lecture Notes in Chemistry*; Springer-Verlag: Berlin, 1982; Vol. 30, p 117.

(26) Harcourt, R. D.; Bowden, J. A. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1115.

(27) Harcourt, R. D. Qualitative Valence-Bond Descriptions of Electron-Rich Molecules. *Lecture Notes in Chemistry*; Springer-Verlag: Berlin, 1982; Vol. 30, p 185.

(28) Wallington, T. J.; Schneider, W. F.; Szente, J. J.; Nielsen, O. J.; Ole, J.; Sehested, J. *J. Phys. Chem.* **1995**, *99*, 984.

(29) Harcourt, R. D. In *Quantum Chemical Methods in Main-Group Chemistry*; Klapötke, T. M.; Schulz, A., Eds.; Wiley: Chichester, 1998; p 232.

(30) Millen, D. J.; Sinnott, K. M. *J. Chem. Soc.* **1958**, 350.

(31) Millen, D. J.; Pannell, J. *J. Chem. Soc.* **1961**, 1322.

(32) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 229.

(33) Turner, P. H.; Cox, A. P. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 533.

(34) Cox, A. P.; Waring, S. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1060.