NF_5—Viable or Not?

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Abstract: The structure, bonding, harmonic vibrational frequencies, and decomposition reactions of NF_5 were studied employing complete active space SCF (CASSCF), multireference configuration interaction (MRCI), hybrid Hartree−Fock/density functional theory (B3LYP), second-order perturbation theory (MP2), and the coupled-cluster method with single, double (CCSD), and perturbative triple excitations [CCSD(T)] in conjunction with basis sets of up to triple-ζ quality. The overall $NF_5 \rightarrow NF_3 + F_2$ reaction is exothermic by 42 kcal mol^{-1} at the CCSD(T)/cc-pVTZ//CCSD/DZP level. Nevertheless, the trigonal-bipyramidal form of NF_5 (D_{3h}) is found to be a minimum at all levels of theory employed for harmonic vibrational frequency analysis [up to CCSD(T)/DZP]. The C_{4v} NF_5 stationary point is a 4 kcal mol^{-1} [CCSD(T)/cc-pVTZ// CCSD/DZP] higher lying transition structure for Berry rotation. No C_{3v} $NF_4^+F^-$ ion pair minimum could be found at correlated levels of theory. A natural bond orbital comparison of NF_5 and PF_5 revealed the much greater polarity of the PF than the NF bonds. NF_5 has one well-developed three center-two electron and three two center-two electron bonds. The weak ionic character and the relatively short FF separations, within the sum of the van der Waals radii, are responsible for the metastable nature of NF_5. The lowest energy transition state found, 16 to 23 kcal mol^{-1} above NF_5 at MRCI/cc-pVTZ//CASSCF(4,3)/DZP, MRCI/cc-pVTZ//UB3LYP/cc-pVTZ, or CCSDT-1/TZ2P//UHF-CCSD/DZP, corresponds to the 8.5 kcal mol^{-1} exothermic [CCSD(T)/cc-pVTZ//CCSD/DZP + ZPVE] decomposition into C_{3v} symmetric NF_4 and F radicals.

Introduction

"Let us not give up hope for hypercoordinated nitrogen", appealed Carl S. Ewig and John R. Van Wazer[1] in 1990 in *Chemical and Engineering News* to Karl O. Christe,[2] who doubted the existence of nitrogen(V) compounds with more than four fluorine substituents in a letter-to-the-editor. In two ab initio studies at levels up to MP2/6-31++G**, Ewig and Van Wazer[3,4] found NF_nH_{5-n} with $n = 3-5$ and even NF_6^- to be electronically and structurally stable; i.e., these species should be stable toward electron loss and correspond to local minima on the potential energy surfaces (PES). Hence, they suggested that these hypercoordinated nitrogen compounds might be prepared in the laboratory.

However, Christe et al. concluded earlier from ^{18}F radiotracer experiments "that the maximum coordination number of nitrogen (V) toward fluorine is four".[5] Indeed, stimulated by Christe's synthesis of the NF_4^+ cation in 1966,[6] several attempts to prepare the hypercoordinated conjugate base NF_5 turned out to be fruitless.[5,7−14] Although Ewig and Van Wazer[1] pointed out that the failure to observe ^{18}F exchange only showed that the experimental conditions were inadequate, it is generally accepted that nitrogen cannot accommodate five fluorine atoms in its first coordination sphere.[15] However, nitrogen coordination numbers of up to eight are found in solid metal nitrides.[16] In the crystal structure of Li_3N, for example, the N atom is hexagonal bipyramidally surrounded by eight Li atoms at distances of 1.94 and 2.13 Å.[16] Similarly, Li−Li bonding interactions could be identified in the experimentally unknown neutral NLi_5 molecule, which also is a trigonal-bipyramidal minimum on the PES.[17] Furthermore, in the recently discovered $[(Ph_3PAu)_5N]^{2+}$ dication, the nitrogen atom is in the center of an almost perfect trigonal-bipyramidal cluster of five gold atoms.[18] In the $\{[(Me_3PAu)_5N][Me_3PAuCl]_2\}^{2+}$ dication two of the three equatorial edges of the Au_5N trigonal bipyramid are bridged by gold atoms of the two Me_3PAuCl molecules.[19] Theoretical studies suggest that peripheral gold−gold interactions contribute significantly to the

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stability of these gold clusters, which are isolobal with NH_5^{2+} and with NLi_5^{2+}.[20-22] Interestingly, the tetragonal-pyramidal (C_{4v} point group) NH_5^{2+} dication is unknown and does not form in superacid medium, although the barrier for deprotonation of NH_5^{2+} is high [26 kcal mol^{-1} at G2(MP2)].[15]

The first theoretical studies (up to the HF/4-31G level) on D_{3h} symmetric NF_5 (**1**) agreed that the maximum coordination number of nitrogen in molecules is four.[23,24] The authors concluded that "there appears little chance for the existence of NF_5".[24] However, in more recent studies, not only Ewig and Van Wazer[3,4] but also Michels and Montgomery[25] regard the synthesis of NF_5 as possible. In the most thorough study of NF_5 to date, the latter group[25] investigated the effect of the basis set and of electron correlation at the MP2 level on the structure and harmonic vibrational frequencies of NF_5 systematically. The vibrational spectra of NF_5 and PF_5 (**2**) were found to be very similar and differ only in the relative strength of the asymmetric axial stretch (ω_3, a_2'') and of the symmetric out-of-plane bend (ω_4, a_2'').[25] The weaker ω_3 mode is poorly represented at the HF level and corresponds to an imaginary vibrational frequency when the DZP+ and 6-311+G* basis sets are employed.[25] In contrast, only real frequencies between 550 and 600 cm^{-1} are found for the ω_3 mode at all MP2 levels studied.[25] Topological atoms-in-molecules (Bader)[26] electron density analyses (see below) of the D_{3h} forms of NF_5 and PF_5 revealed five bond critical points for both molecules.[25] The axial bonds in NF_5 have more ionic character than the equatorial bonds, but are less ionic than the corresponding bonds in PF_5.[25] This charge distribution reflects the greater electronegativity of N compared to P. The NF bonds lack the high polarity that is essential for "hypervalence";[27-29] this is responsible for the metastable character of NF_5.[30] The Berry pseudorotation of D_{3h} NF_5 via a C_{4v} transition structure is very facile with a predicted barrier of only 8.8 kJ/mol (2.1 kcal mol^{-1}) at the MP2/6-31G* level of theory.[25]

On the basis of a Born–Haber cycle, Christe and Wilson[31] concluded that covalent D_{3h} NF_5 and crystalline $NF_4^+F^-$ are of similar energy. The exothermicity of the $NF_5 \rightarrow NF_3 + F_2$ reaction was computed by Michels and Montgomery to be about 33 kcal mol^{-1}. The mild exothermicity suggested that covalent NF_5 might be accessible from NF_3 and F_2 as well as from NF_4^+ and F^-. However, excessive ligand crowding around the small nitrogen atom is expected by some to preclude NF_5 formation,[5,32] as the axial and equatorial fluorine atoms would be closer (roughly 2.1 Å at MP2/6-311+G*[25]) than the sum of their van der Waals radii, which is 3.0 to 3.2 Å.[33] Christe and Wilson[31] argue that, due to the short N–F bond lengths in the precursors NF_3 (1.365 Å) and NF_4^+ (1.31 Å), there is not enough space to accommodate a fifth fluorine atom unless a significant bond lengthening takes place. Attempts of Christe and Wilson[31] to synthesize crystalline $NF_4^+F^-$, which should not suffer from steric problems and thus might be easier to prepare, were not successful. Instead of the metathesis reaction $NF_4^+BF_4^- + N(CH_3)_4^+F^- \rightarrow NF_4^+F^- + N(CH_3)_4^+BF_4^-$ in CHF_3 at −142 °C, a redox reaction yielding $NF_3 + F_2$ was observed.

The issue of crucial importance for the existence of covalent NF_5, the kinetic stability, has not yet been studied. How high are the barriers for the unimolecular decomposition of D_{3h} symmetric NF_5? Does decomposition involve loss of an F atom or a F_2 molecule? This research addresses these issues and presents barriers, reaction enthalpies, and harmonic vibrational frequencies computed at high levels of theory.

Methods

This study employed the following basis sets: (a) Pople's[34] 6-311+G* basis set; (b) DZP, constructed from Dunning's[35] double-ζ (9s5p/4s2p) contraction augmented with one set of *d* polarization functions with orbital exponents of $\alpha_d(N) = 0.902$ and $\alpha_d(F) = 1.58$; (c) TZ2P, constructed from Dunning's[36] triple-ζ (10s6p/5s3p) contraction augmented with two sets of *d* polarization functions with orbital exponents of $\alpha_d(N) = 1.6$ and 0.4 and $\alpha_d(F) = 2.0$ and 0.5; (d) TZ2Pf, obtained from the TZ2P basis set by augmenting with one set of *f* functions ($\alpha_f(N) = 1.0$ and $\alpha_f(F) = 1.85$); (e) TZ2P++, obtained from the TZ2P basis set by adding a diffuse *s* ($\alpha_s(N) = 0.06742$ and $\alpha_s(F) = 0.1164$) and one set of diffuse *p* functions ($\alpha_p(N) = 0.04959$ and $\alpha_p(F) = 0.07161$); and finally (f) Dunning's[37] correlation consistent cc-pVTZ basis set. Pure angular momentum functions were employed in all basis sets except for DZP.

We applied Becke's[38] three-parameter hybrid description of exchange together with the correlation functional of Lee, Yang, and Parr[39] as implemented in GAUSSIAN 94.[40] Furthermore, complete active space SCF (CASSCF), second-order Møller–Plesset perturbation theory (MP2), and multireference singles and doubles configuration interaction (MRCI) were utilized. We employed coupled cluster methods which included single and double (CCSD)[41] and perturbative contributions from connected triple excitations [CCSD(T)],[42,43] as well as some of the T_3 terms iteratively (CCSDT-1).[44-46]

As the breaking of an NF axial bond is of interest, the three molecular orbitals which comprise the 3c-4e bond in D_{3h} symmetric NF_5 (Scheme 2) were selected as the active space in the CASSCF computations. We

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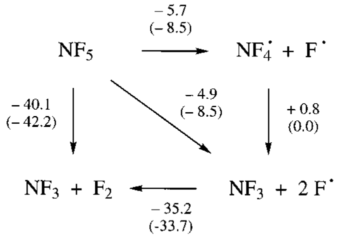
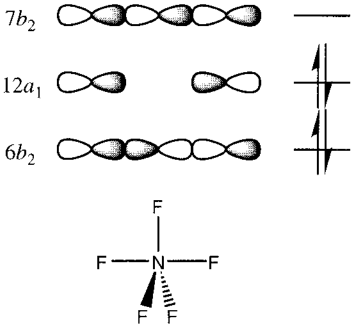
Scheme 1. Reaction Energies at 0 K Obtained at CCSD(T)/cc-pVTZ//CCSD/DZP[a]



[a] The zero-point corrected values (vibrational frequencies from B3LYP/cc-pVTZ) are given in parentheses.

Scheme 2. Symmetry Adapted Combination of a Nitrogen and Two Fluorine p Orbitals Generates the Three MO's of the Three Center-Four Electron Bond in D_{3h} Symmetric NF_5



determined the composition of the CISD wave function in terms of CI natural orbitals and selected the most important configuration state functions (CSFs) as reference functions in the MRCI runs. The B3LYP, CASSCF, and MP2 computations were performed with GAUSSIAN 94[40] the CCSD, CCSD(T), and CCSDT-1 calculations with ACES2,[47] and PSI2.0.8[48] was employed to obtain the MRCI wave functions. While all MP2 and MRCI calculations employed the frozen-core approximation, no such simplifications were used with the coupled cluster methods, unless noted otherwise.

Geometries were fully optimized and harmonic vibrational frequencies were computed analytically (B3LYP and MP2) or numerically [CCSD and CCSD(T)]. Zero-point vibrational energy corrections were obtained at the B3LYP/cc-pVTZ level for the coupled-cluster energies. The spin-unrestricted formalism was employed for geometry optimizations of the lowest energy transition state (homolytic NF cleavage, **TS1**) by using the UB3LYP and UHF-CCSD/DZP methods as well as for UB3LYP and UHF-CCSD(T) single energy calculations. The B3LYP/6-311+G* wave functions of the D_{3h} and C_{4v} NF_5 isomers were analyzed in terms of natural bond orbitals (NBO) with the G94NBO program.[40]

Results

Table 1. Bond Lengths (in Å) in D_{3h} Symmetric NF_5 (**1**), in C_{3v} Symmetric NF_3 (**3**), and in T_d Symmetric NF_4^+ at Various Levels of Theory

	NF_5			
theory	r_{ax}	r_{eq}	NF_3	NF_4^+
CASSCF(4,3)	1.602	1.307		
MP2/6-311+G*	1.583	1.383	1.369	1.306
MP2/TZ2P	1.578	1.399	1.382	
MP2/TZ2P++	1.582	1.396	1.382	
MP2/TZ2Pf	1.570	1.383	1.371	
MP2/cc-pVTZ	1.557	1.383	1.367	1.304
B3LYP/6-311+G*	1.608	1.381	1.382	1.318
B3LYP/TZ2P	1.597	1.386	1.385	
B3LYP/TZ2P++	1.599	1.384	1.384	
B3LYP/TZ2Pf	1.597	1.377	1.379	
B3LYP/cc-pVTZ	1.589	1.381	1.379	1.316
CCSD/DZP	1.568	1.384	1.371	1.311
CCSD/TZ2P	1.569	1.378		
CCSD(T)/DZP	1.586	1.399		
CCSD(T)/TZ2P	1.587	1.398		
experiment			1.371[a]	1.26−1.32[c]
			1.365[b]	1.31[d]

[a] MW: Sheridan, J.; Gordy, W. *Phys. Rev.* **1950**, *79*, 513. [b] ED: Otake, M.; Matsumura, C.; Morino, Y. *J. Mol. Spectrosc.* **1968**, *28*, 316. [c] X-ray structure of $[NF_4]^+[BF_4]^-$. [d] IR.

A. Geometry of NF_5. In agreement with earlier theoretical investigations,[3,24,25] we found that the axial and equatorial N−F bond lengths in D_{3h} symmetric NF_5 differ considerably (see Table 1, $r_{ax} = 1.56$ to 1.60 Å, $r_{eq} = 1.31-1.40$ Å), in contrast to PF_5 where they are more nearly equal in length ($r_{ax} = 1.575$ Å, $r_{eq} = 1.534$ Å).[49,50] Except at CASSCF(4,3)/DZP, the equatorial NF bond lengths are very similar at all the levels employed and are only slightly longer than the bonds in NF_3. In contrast, the axial NF distances depend to a greater extent on the method and the basis set. Three trends are noteworthy: First, CCSD underestimates the axial bond lengths by roughly 0.02 Å compared to CCSD(T), indicating the importance of triple excitations. Second, adding diffuse functions to the TZ2P basis set does not improve the geometries at MP2 and B3LYP significantly (and presumably also at coupled-cluster levels) as r_{ax} increases only marginally when going from TZ2P to TZ2P++. Third, with every basis set of TZ2P quality, the B3LYP method gives longer axial and shorter equatorial NF bonds than does MP2. The tightly contracted cc-pVTZ (4s3p2d1f) basis set results in significant r_{ax} bond shortening compared to the TZ2Pf basis set (5s3p2d1f) at both MP2 and B3LYP levels.

The repulsion between the fluorine atoms is minimized in the trigonal-bipyramidal D_{3h} arrangement and in the square-pyramidal C_{4v} conformation compared to nuclear arrangements of lower symmetry. The C_{4v} form corresponds to a saddle point on the NF_5 PES, similar to other AB_5 molecules, e.g. PF_5.[51] The apical NF bond in C_{4v} symmetric NF_5 is short (1.33 Å, see Figure 1). The four NF bonds defining the base of the square pyramid are significantly longer (1.50−152 Å, see Figure 1), although not as long as the axial NF bonds in the D_{3h} conformer. The optimized geometries for C_{4v} NF_5 at all the levels of theory employed are very similar.

B. Thermodynamics of the NF_5 System. NF_5 is thermodynamically unstable with respect to dissociation into NF_4 + F, into NF_3 + 2F, and into $NF_3 + F_2$ (Scheme 1 and Table 2). Whereas the reactions which yield fluorine radicals were only slightly exothermic (-8.5 kcal mol^{-1}), the $NF_5 \rightarrow NF_3 + F_2$ decomposition was exothermic by -40.1 kcal mol^{-1} at CCSD(T)/cc-pVTZ//CCSD/DZP. Correcting this value for zero-point vibrational contributions (determined at B3LYP/cc-pVTZ) gives a heat of reaction at 0 K, $\Delta H_r(0\ K)$, of -42.2 kcal mol^{-1}. Michels and Montgomery[25] predicted a slightly less exothermic

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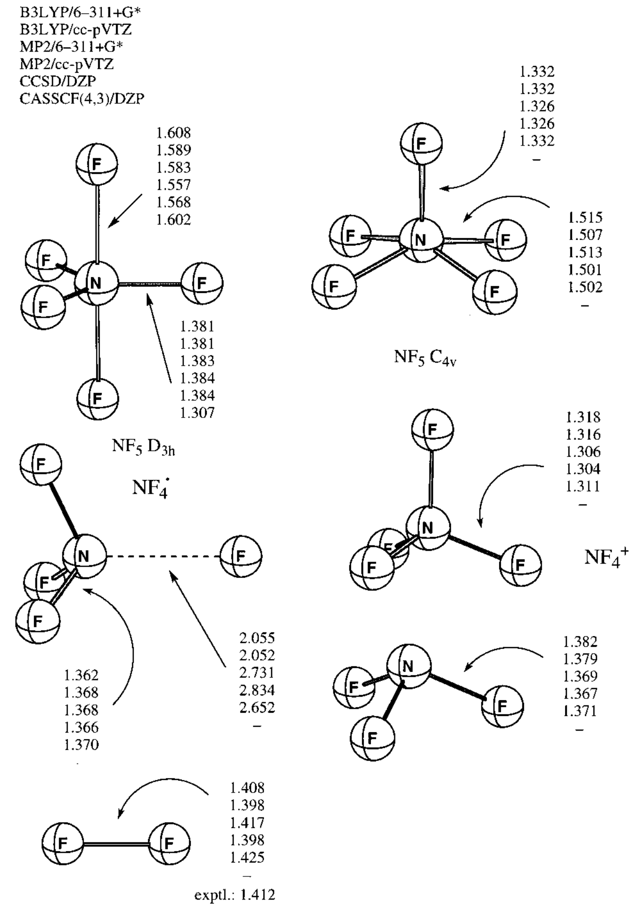

Figure 1. Ground states optimized with the B3LYP/6-311+G**, B3LYP/cc-pVTZ, MP2/6-311+G**, MP2/cc-pVTZ, CCSD/DZP, and CASSCF(4,3)/DZP (from top to bottom) methods. Bond lengths are in Å.

reaction, $\Delta H_r(0\ \mathrm{K}) = -35.1$ kcal mol^{-1} at MP2/6-311+G**. At finite temperatures the thermodynamic stability of NF_5 is even smaller due to the entropy increase associated with a dissociation reaction. We obtain $\Delta H°_{298} = -41.4$ kcal mol^{-1} and $\Delta G°_{298} = -53.7$ kcal mol^{-1} for the $NF_5 \rightarrow NF_3 + F_2$ reaction at CCSD(T)/cc-pVTZ//CCSD/DZP (with B3LYP/cc-pVTZ thermochemical corrections), in reasonable agreement with the results obtained by Ewig and Van Wazer ($\Delta H°_{298} = -30.1$ kcal mol^{-1} and $\Delta G°_{298} = -41.8$ kcal mol^{-1}).[3]

A C_{3v} symmetric $[FNF_3]^+F^-$ ion pair, where the fluoride ion is close to three fluorine atoms, could not be located on the B3LYP, MP2, and CCSD PES's in agreement with Michels and Montgomery.[25] The C_{3v} Hartree–Fock $NF_4^+F^-$ ion pair minimum of NF_5 collapsed into the D_{3h} symmetric form when reoptimized at correlated levels of theory. Note that the recently described $[(CH_3)_3NF]^+F^-$ ion pair is not the trimethyl derivative of the Hartree–Fock $NF_4^+F^-$ ion pair, as an N–F–F arrangement was deduced for $[(CH_3)_3NF]^+F^-$.[52]

The NF_4 radical is a C_{3v} symmetric minimum with an almost undisturbed NF_3 moiety and one long N–F distance at all levels of theory employed (see Figure 1). Whereas the NF_4^+ cation has a tetrahedral geometry, this conformation is a third-order stationary point for the NF_4 radical. Note that the D_{4h} structure of the NF_4 radical studied by Peters and Allen[24] in 1988 corresponds to a second-order stationary point at B3LYP and MP2.

The NBO analyses with the B3LYP/6-311+G** and MP2/6-311+G** density matrices all show the presence of two species which interact via the nitrogen lone-pair and a *p* fluorine orbital in a two center-three electron (2c-3e) fashion. Whereas NF_4 is bound relative to $NF_3 + F$ by almost 6 kcal mol^{-1} at B3LYP, it only is a very weakly bound complex (<1 kcal mol^{-1}) at MP2 and CCSD(T). Indeed, the N–F bond lengths in the B3LYP geometry of the NF_3 moiety of NF_4 are slightly shorter than those in free NF_3. The tighter binding at B3LYP also is shown by the distance to the fluorine atom (2.05 Å), which is 0.6–0.8 Å shorter than that at ab initio levels. The NF_4 radical is isoenergetic with separated NF_3 and F when zero-point corrections are included. The bond dissociation energy D_o of the isolated diatomic F_2 molecule at CCSD(T)/cc-pVTZ//CCSD/DZP is 33.7 kcal mol^{-1}, in reasonable agreement with the experimental value of 36.9 kcal mol^{-1}.[53]

C. Barriers for the Decomposition of NF_5. The D_{3h} NF_5 molecule may be expected to decompose into $NF_4 + F$ by homolytic cleavage of a longer and weaker axial NF bond. The heterolytic cleavage into NF_4^+ and F^- is unfavorable in the gas phase as there are no solvent molecules to assist ionization. In addition, no stationary point corresponding to a $NF_4^+F^-$ ion pair could be found on the NF_5 PES.

The correct descriptions of homolytic bond dissociation processes, which generate two radical species, are challenging problems in computational quantum chemistry.[54] Spin-restricted RHF methods fail completely to describe homolytic bond dissociations. Spin-unrestricted UHF theory, although giving the qualitatively correct dissociation, suffers from significant spin-contamination at large distances, i.e., the spin-unrestricted wave function is not a pure singlet.[54] Such problems with the UHF wave function often result in serious errors. However, coupled-cluster methods based on an UHF determinant, such as UHF-CCSD, reduce spin contamination significantly,[55–60] and describe single bond dissociations quite well.[61] The CCSDT-1 approach, which is superior to CCSD(T) when a very poor RHF reference is employed, gives dissociation curves in very good agreement with full CI.[57,61,62] The UB3LYP method also suffers siginificantly less from spin contamination than UHF wave functions.[63,64] Furthermore, Goldstein et al.[65] showed that UB3LYP gives an H_2 dissociation curve in good agreement with the exact Kolos–Wolniewicz potential.[66,67] These results encouraged us to study the geometry of the C_{3v} symmetric **TS1**

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Table 2. Relative Energies (in kcal mol^{-1}) and Reaction Enthalpies at 0 K (in kcal mol^{-1}, in parentheses) for NF_5 Decomposition Reactions at Various Levels of Theory[d] and $\Delta H°_{298}$ and $\Delta G°_{298}$ (in kcal mol^{-1}, in brackets) for the $NF_5 \rightarrow NF_3 + F_2$ Reaction at the CCSD(T)/cc-pVTZ//CCSD/DZP Level of Theory

level of theory	$NF_5 \rightarrow NF_3 + F_2$	$NF_5 \rightarrow NF_4 + F$	$NF_5 \rightarrow NF_3 + 2F$	$F_2 \rightarrow 2F$
B3LYP/6-311+G*	−34.9 (−36.9)	−9.7 (−12.2)	−3.1 (−6.5)	−31.8 (−30.4)
B3LYP/cc-pVTZ	−35.0 (−37.1)	−3.3 (−6.1)	+3.0 (−0.6)	−38.0 (−36.5)
MP2/6-311+G*	−32.6 (−34.7)	−4.3 (−7.5)	−3.4 (−6.8)	−29.2 (−27.9)
MP2/cc-pVTZ	−30.7 (−32.8)[a]	+8.9 (+5.7)[a]	+9.5 (+6.1)[a]	−40.1 (−38.8)[a]
CCSD/DZP	−51.6 (53.7)[b]	−30.4 (−33.2)[b]	−29.7 (−33.3)[b]	−21.9 (−20.4)[b]
CCSD(T)/cc-pVTZ//CCSD/DZP	−40.1 (−42.2)[b] [$\Delta H°_{298} = -41.4$; $\Delta G°_{298} = -53.7$][c]	−5.7 (−8.5)[b]	−4.9 (−8.5)[b]	−35.2 (−33.7)[b]
CCSD(T)/cc-pVTZ				−35.5 (−34.2)
experiment				(−36.9)[d]

[a] ZPVE correction at MP2/6-311+G*. [b] ZPVE correction at B3LYP/cc-pVTZ. [c] Thermochemical corrections at B3LYP/cc-pVTZ. [d] Reference 53.

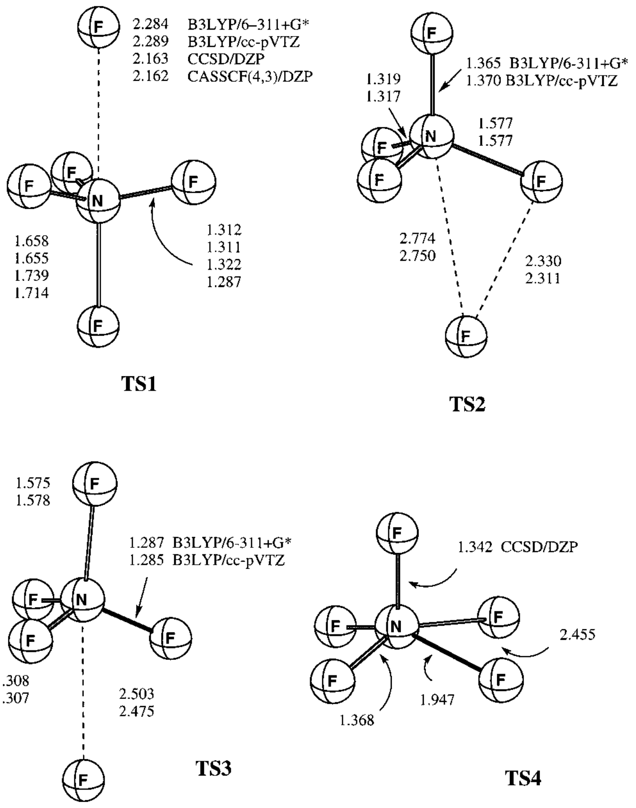

Figure 2. Transition structures optimized at various levels of theory. Bond lengths are in Å.

for NF bond breaking with UB3LYP and UHF-CCSD methods. Multiconfiguration zeroth-order wave functions give correct dissociation curves at large nuclear distances without the drawback of spin-contamination. Thus, we employed the CASSCF method with four electrons distributed among three active orbitals, i.e., CASSCF(4,3).

A transition structure **TS1** for homolytic axial NF bond cleavage was found at CASSCF(4,3)/DZP, UHF-CCSD/DZP, and UB3LYP levels. Whereas the CASSCF and UHF-CCSD geometries of **TS1** are very similar (see Figure 2), the dissociating axial NF bond is 0.13 Å longer at UB3LYP. The equatorial F atoms in **TS1** are bent toward the departing F atom and have significantly shorter (by 0.02 to 0.07 Å) distances to the N atom than in the ground state. Significant interaction between the developing NF_4 and F moieties in **TS1** may be deduced from the total atomic UB3LYP/6-311+G** spin densities, which are +0.51 on the departing F atom, −0.25 on the N, and −0.24 on the other former axial F atom.

The barrier for the homolytic NF cleavage varies considerably with the level of theory employed. Whereas the CCSD and CCSD(T) treatments predict classical barriers of roughly 30 kcal mol^{-1}, the CASSCF(4,3)/DZP barrier is only 4 kcal mol^{-1}. The UB3LYP, MRCI, and RHF-CCSDT-1 barriers of 16−22 kcal mol^{-1} lie between these estimates.

The extreme CCSD, CCSD(T), and CASSCF values arise from the insufficient treatment of nondynamic and dynamic electron correlation in these methods. The nondynamic correlation is not sufficiently taken into account in the coupled-cluster treatments, which are based on single UHF reference wave functions. The expectation value of the S^2 operator, 0.62, indicates a substantial amount of spin-contamination for the UHF-CCSD wave function. Thus, the UHF-CCSD wave function is only a poor approximation to the multiconfiguration zeroth-order wave function, which is necessary to describe **TS1** accurately, and even the highly correlated CCSD(T) treatment cannot remedy the inherent deficiencies of the UHF reference. Note that a good agreement between coupled-cluster theory and MRCI (see below) is obtained for the dissociation barrier when triple excitations are included iteratively. The CASSCF method takes nondynamic correlation into account, and it is therefore suited in principle to give a correct zeroth-order description of the homolytic bond-breaking process. However, the neglect of dynamic correlation in the CASSCF treatment can cause serious errors. Thus, methods such as MRCI, which take into account both dynamic and nondynamic correlation, have to be employed to predict the barrier for homolytic NF cleavage reliably.

We used both the CASSCF(4,3)/DZP and the UB3LYP/cc-pVTZ geometries of **TS1** and **1** in MRCI/cc-pVTZ single point computations. The second CSFs of the CISD/cc-pVTZ wave functions (with the UB3LYP/cc-pVTZ and CASSCF(4,3)/DZP geometries) for **1** and **TS1** do not correspond to the same type of excitation (Table 3). Whereas the second CSF for **TS1** corresponds to excitation from the former nonbonding into the antibonding 3c-4e MO, the second CSF for **1** is an excitation from the 3c-4e bonding $6b_2$ MO into the antibonding $7b_2$ 3c-4e MO. We decided to describe **TS1** with two CSF's and **1** with only one CSF, as the second CSF has a considerably higher weight in the **TS1** wave function than in **1** (−0.081 vs −0.048). Such a selection gives a lower limit of the barrier for NF cleavage as it is biased favoring **TS1**. The barrier for homolytic cleavage (Table 4) of an axial NF bond in D_{3h} symmetric NF_5 is 15.8 to 20.0 kcal mol^{-1} at MRCI/cc-pVTZ employing B3LYP/cc-pVTZ and CASSCF(4,3)/DZP geometries, respectively. These results are in very good agreement with the RHF-CCSDT-1/TZ2P//UHF-CCSD/DZP barrier of 22.6 kcal mol^{-1}.

The small separation of roughly 2.1 Å between the axial and equatorial fluorine atoms in D_{3h} NF_5 suggests that a concerted

Table 3. CISD/cc-pVTZ Wave Functions at the B3LYP/cc-pVTZ and CASSCF(4,3)/DZP (in parentheses) Geometries for D_{3h} NF$_5$, **TS1**, and **TS2** in Terms of the CISD Natural Orbitals

structure	CI coefficient	orbital occupation
D_{3h} NF$_5$	0.918 (0.920)	$\ldots(5b_1)^2\,(11a_1)^2\,(6b_1)^2\,(2a_2)^2\,(6b_2)^2\,(12a_1)^2$
	−0.048 (−0.048)	$\ldots(5b_1)^2\,(11a_1)^2\,(6b_1)^2\,(2a_2)^2\,(12a_1)^2\,(7b_2)^2$
	−0.048 (−0.047)	$\ldots(5b_1)^2\,(11a_1)^2\,(6b_1)^2\,(2a_2)^2\,(6b_2)\,(12a_1)\,(7b_2)\,(13a_1)$
TS1	0.919 (0.919)	$\ldots(7a'')^2\,(15a')^2\,(16a')^2\,(8a'')^2\,(17a')^2\,(18a')^2$
	−0.081 (−0.075)	$\ldots(7a'')^2\,(15a')^2\,(16a')^2\,(8a'')^2\,(17a')^2\,(19a')^2$
	−0.035 (−0.032)	$\ldots(7a'')^2\,(15a')^2\,(16a')^2\,(17a')^2\,(18a')^2\,(9a'')^2$
TS2	−0.919	$\ldots(15a')^2\,(7a'')^2\,(16a')^2\,(17a')^2\,(8a'')^2\,(18a')^2$
	−0.075	$\ldots(15a')^2\,(7a'')^2\,(16a')^2\,(17a')^2\,(8a'')^2\,(19a')^2$
	−0.036	$\ldots(15a')^2\,(7a'')^2\,(16a')^2\,(17a')^2\,(18a')^2\,(9a'')^2$

Table 4. Barriers for the Reaction NF$_5$ → NF$_4$ + F via **TS1**, at Various Levels of Theory (Energies in kcal mol^{-1})

method	classical barrier
UHF-CCSD/DZP	28.6
UHF-CCSD(T)/TZ2P//UHF-CCSD/DZP[a]	30.7
RHF-CCSDT-1/TZ2P//UHF-CCSD/DZP[a]	22.6
UB3LYP/6-311+G*	16.4
UB3LYP/cc-pVTZ	21.2
MRCI/cc-pVTZ//UB3LYP/cc-pVTZ[b]	15.8
CASSCF(4,3)/DZP	4.3
MRCI/cc-pVTZ//CASSCF(4,3)/DZP[b]	20.0

[a] Core and six highest virtual orbitals were deleted in the single point computation. [b] Core orbitals were held frozen.

elimination of F$_2$ might also be a plausible mechanism for the decomposition of NF$_5$. Its **TS2** is characterized by a long nonbonding axial NF distance (2.75 Å), a shortening of the other axial bond to 1.37 Å (Figure 2). The distance between the F$_2$ forming axial and equatorial F atoms is *increased* to 2.31 Å in the transition structure. Computation of the B3LYP/6-311+G* intrinsic reaction coordinate (IRC) confirms that **TS2** connects trigonal-pyramidal NF$_5$ with a C_{3v} symmetric complex of NF$_3$ and F$_2$. A pivoting motion of the developing F$_2$ moiety can be discerned from selected structures along the IRC (Figure 3). This motion is accompanied by a shortening of the F−F distance and continues until the linear N−F−F arrangement in the NF$_3$−F$_2$ complex is reached. The almost undistorted NF$_3$ and F$_2$ moieties are separated by 2.79 to 2.83 Å in the complex, which is accordingly only slightly bound (<0.2 kcal mol^{-1} at B3LYP/cc-pVTZ+ZPVE).

The nature of the multireference character was deduced for **TS2** (see Table 3) from CISD/cc-pVTZ//B3LYP/cc-pVTZ computations. For the same reason as **TS1**, two CSF's were included in the MRCI treatment of **TS2**, but only one CSF for **1**. The barrier for concerted F$_2$ elimination is around 35−40 kcal mol^{-1} (Table 5), and thus this reaction cannot compete with the lower energy homolytic NF bond cleavage via **TS1**.

Note that all attempts to optimize **TS2** with “full” triple-ζ basis sets of TZ2P quality rather than with the valence triple-ζ cc-pVTZ and 6-311+G* basis sets resulted in another transition state, **TS3** (Figure 2). The latter transition structure is C_s symmetric and roughly 6 kcal mol^{-1} lower in energy than **TS2**. The spin-restricted RB3LYP/6-311+G* **TS3** wave function was found to be triplet unstable (i.e., unstable toward becoming spin-unrestricted).[68] Subsequent re-optimization of **TS3** with the spin-unrestricted UB3LYP/6-311+G* method, instead of RB3LYP, yielded **TS1**, which is almost 10 kcal mol^{-1} lower in energy than **TS3**. Similarly, attempts to optimize **TS2** at the CCSD/DZP level resulted in **TS3** for which the RHF reference wave function was triplet unstable.

Another transition structure (**TS4**, Figure 2) on the NF$_5$ PES could be located only at the CCSD/DZP and MP2 levels of theory. The MP2/6-311+G* IRC computation reveals that **TS4**, which is 14 to 16 kcal mol^{-1} (MP2/cc-pVTZ and CCSD/DZP) above the D_{3h} form, describes the dissociation of two fluorine atoms from the C_{4v} form of NF$_5$. Analysis of the CISD/cc-pVTZ//CCSD/DZP wave function reveals that, besides the HF configuration (0.907), the closed-shell configuration obtained by exciting both HOMO electrons into the LUMO is extremely important (−0.187). The MP2 as well as the CCSD method are not capable of dealing with such an electronic configuration. Thus, we tried both the CASSCF(2,2)/DZP and CCSD(T)/DZP methods to locate **TS4** on the PES, but without success. Therefore, we assume that the existence of **TS4** as obtained with MP2 and CCSD/DZP is an artifact, which arises from the insufficient inclusion of dynamical electron correlation in these methods.

D. Harmonic Vibrational Frequencies and Berry Pseudorotation of NF$_5$. The D_{3h} symmetric structure of NF$_5$ corresponds to a minimum on the potential energy surface with all theoretical methods employed, and it is thus a viable chemical entity, at least as an isolated species. The harmonic vibrational frequencies for NF$_5$ (Table 6) obtained at various levels of theory are quite consistent and agree reasonably well with earlier lower level results reported by Ewig and Van Wazer[3] and Michels and Montgommery.[25] The strongest variations between B3LYP and MP2 vibrational frequencies are observed for the asymmetric axial stretch (ω_3 mode), which is poorly described at the HF level,[25] and the symmetric out-of-plane bend (ω_4 mode). Our CCSD(T)/DZP data are the most accurate prediction of the NF$_5$ vibrational spectrum to date and hopefully will facilitate the identification of the compound. The CCSD(T)/DZP harmonic vibrational frequencies are in good agreement with the scaled MP2/6-311G** force field of Michels and Montgomery,[25] except for the a_2'' symmetric ω_4 mode for which the CCSD(T)/DZP prediction is roughly 100 cm^{-1} smaller.

The similarity between the NF$_5$ and the PF$_5$ harmonic force field[69−72] was stressed by Michels and Montgomery.[25] The softest normal mode of PF$_5$,[69,73] the e' equatorial bend $\omega_7 = 180$ cm^{-1}, was found to be an in-phase combination of the equatorial and axial bending symmetry coordinates and it transforms one D_{3h} symmetric trigonal-bipyramid into another, thus enabling an exchange between axial and equatorial atoms. This type of rearrangement was suggested by Berry[74] to explain the facile stereomutation of trigonal-bipyramidal phosphorus compounds, and is now commonly known as Berry pseudorotation. The turnstile mechanism proposed by Ugi for cyclic phosphoranes proceeds on the slope of a valley of the PES

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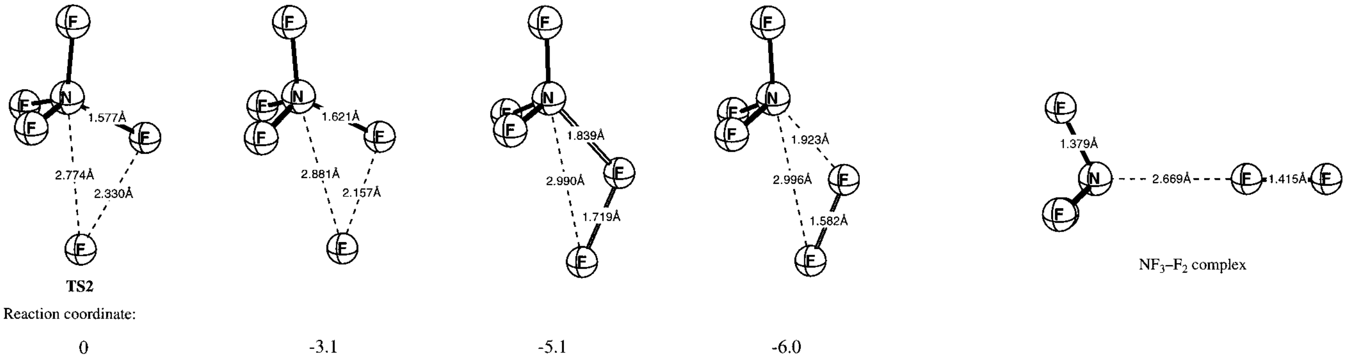

Figure 3. Selected structures along the B3LYP/6-311+G** intrinsic reaction coordinate (IRC) from **TS2** to the NF_3–F_2 complex.

Table 5. Barriers for the Reaction $NF_5 \rightarrow NF_3 + F_2$ via **TS2**, at Various Levels of Theory (Energies in kcal mol^{-1})

method	classical barrier
B3LYP/6-311+G*	30.9
B3LYP/cc-pVTZ	37.0
MRCI/cc-pVTZ//B3LYP/cc-pVTZ[a]	40.3

[a] Core orbitals were held frozen.

without a TS.[75,76] The transition vector of the square-pyramidal PF_2H_3 transition structure for pseudorotation, however, has transition vectors in agreement with both the Berry and the turnstile mechanism.[77] In analogy to PF_5, the deformation along the $\omega_7 = 186$ cm^{-1} normal mode of NF_5 leads to Berry pseudorotation: the angle between two equatorial F atoms increases from 120° to 180°, while at the same time the angle between the axial F atoms decreases from 180° to 120°.

A C_{4v} square pyramid is a transition structure for the pseudorotation of both PF_5 and NF_5.[25,51] The barrier for PF_5 pseudorotation has been estimated to be 3.8−5.1 kcal mol^{-1} from SCF and perturbation theory studies,[51,71,78] in good agreement with experimental estimates (2.8−5.0 kcal mol^{-1}).[73,79−81] Similarly, a low barrier of 8.8 kJ mol^{-1} (2.1 kcal mol^{-1}) was computed for the NF_5 pseudorotation by Michels and Montgomery at MP2/6-31G*.[25] We obtain slightly higher classical barriers between 4 and 5 kcal mol^{-1} (Table 7) with B3LYP, CCSD, and CCSD(T). Taking the difference in B3LYP/cc-pVTZ zero-point vibrational energies into account lowers the classical barrier by 0.4 kcal mol^{-1} to 3.7 kcal mol^{-1} at our highest level of theory (CCSD(T)/cc-pVTZ//CCSD/DZP). Thus, similar to PF_5, NF_5 is a highly fluxional molecule with extremely facile exchange between axial and equatorial F atoms.

Discussion

The work by Ewig and Van Wazer[3,4] and that by Michels and Montgomery[25] as well as our analysis strongly suggest that the coordination number of nitrogen toward fluorine should not be limited to four. However, the existence of compounds such as NF_5 and NF_6^- contradicts the rules for the formation of covalent bonds: "an atom can form an electron-pair bond for each stable orbital".[82] Thus, first row atoms cannot form more than four covalent bonds. Langmuir[83] and Lewis[84] recognized that achieving the eight valence electron configuration of noble gas atoms is the underlying principle of bond formation. Atoms with fewer than eight electrons in their valence shell tend to share electron pairs with other electron deficient atoms by forming localized two-electron covalent chemical bonds ("Lewis bonding pair"), to achieve an electron octet in their valence shell.

The well-known ability of some heavier main group elements to bind to five or more atoms or groups ("hypercoordination") was explained for many years by "octet expansion". Through promotion of electrons into vacant higher-lying atomic d orbitals, resulting in sp^3d and sp^3d^2 hybridization,[82] the octet rule is violated, but additional covalent bonds can be formed. Halgren et al.[85] classifies molecules as "hypervalent" only when the coordination number is larger than expected on the basis of the octet rule and when simultaneously the octet rule is violated. Pauling discussed the bonding in compounds such as PF_5, PCl_5, and SF_6 in terms of valence bond theory as superpositions of completely covalent, i.e., hypervalent, and ionic structures, which obey the octet rule.[82] Interestingly, Pauling assumed the completely covalent resonance structure of PF_5 to be of little significance, whereas for PCl_5 he assumed the covalent resonance structure to dominate.[82]

In the 1960s, the discovery of xenon compounds[86,87] popularized the 3 center-4 electron (3c-4e) bond model, which has been applied to interhalogen compounds originally.[88,89] It was realized that the 5p to 5d promotion energy of Xe was prohibitively large.[90−93] In the 3c-4e model one of the two bonding electron pairs is delocalized onto the two ligands resulting in a charge distribution of roughly +1.0 on the central atom and −0.5 on the ligands. An equivalent description of the bonding is possible with localized molecular orbitals (LMO's) for each bond which is one-half ionic and one-half covalent.[85,90] On the basis of the 3c-4e model, Rundle,[94] Musher[95] (who introduced nonorthogonal sp^x hybrids),[96] and

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Table 6. Harmonic Vibrational Frequencies (cm^{-1}) Obtained for D_{3h} Symmetric NF_5 at Various Levels of Theory

	frequencies, ω (cm^{-1})							
species	a_1'	a_1'	a_2''	a_2''	e'	e'	e'	e''
symmetry coordinate	sym eq stretch	sym ax stretch	asym ax stretch	sym out-of-plane bend	asym eq stretch	ax bend	eq bend	asym bend
normal mode	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
level of theory								
CASSCF(2,2)/DZP	876	441	501	774	1443	621	302	609
MP2/6-311+G*	678	347	567	877	962	536	193	569
MP2/TZ2P	664	373	584	892	926	529	179	563
B3LYP/6-311+G*	687	356	473	745	981	520	210	551
B3LYP/TZ2P	686	373	509	761	975	509	206	553
B3LYP/TZ2Pf	696	371	504	762	993	529	213	558
B3LYP/cc-pVTZ	700	382	525	779	998	534	208	564
CCSD/DZP	702	415	539	814	1039	599	210	587
CCSD(T)/DZP	645	382	492	790	956	522	186	561

Table 7. Pseudorotation of NF_5 via C_{4v} Structure (Energies in kcal mol^{-1})[a]

method	classical barrier
B3LYP/6-311+G*	5.3
B3LYP/cc-pVTZ	5.1
MP2/6-311+G*	2.6
MP2/cc-pVTZ	2.8
CCSD/DZP	4.8
CCSD(T)/cc-pVTZ//CCSD/DZP	4.1

[a] ΔZPVE = −0.4 at B3LYP/cc-pVTZ.

Coulson,[90] could explain hypercoordinate bonding without invoking the participation of d orbitals. However, whereas Musher[95] considered the octet rule to be violated in hypercoordinated compounds, Coulson[90] and later Halgren et al.[85] concluded that due to the partial ionic "fractional bonds"[85] of the 3c-4e bond model the octet rule is not violated.

The advances in computational quantum chemistry in the 1970s made the computation of reliable polyatomic wave functions possible[97,98] and, as reviewed by Kutzelnigg,[32] reinforced the 3c-4e picture of bonding. Interpretations of computed wave functions by means of shared electron number and occupation number analysis,[99−101] electron density analysis,[102−104] and natural population analysis (NPA)[105−109] reveal in the 1980s that the d orbital contribution to bonding in hypervalent molecules is far less than the traditional sp^3d and sp^3d^2 models demand.

For sulfur hexafluoride, SF_6, a well studied prototype hypercoordinated molecule, Reed and Weinhold[105] find that the d orbital contribution to the $sp^{1.7}d^{0.16}$ hybridized σ_{SF} natural localized molecular orbitals (NLMOs) is less than 6%, only about one-sixth of what is required by the sp^3d^2 ideal. The authors[105] suggest a highly polarized bonding model for SF_6 that agrees with the computed natural charges.

In addition, no qualitative difference in bonding could be found between the "normal valent" and "hypervalent" species in the series SF_2, SF_4, and SF_6,[110,111] although the population of the sulfur atoms increases along this series according to natural population analysis (NPA).[112] A similar conclusion is reached[27] for X_3AY-type molecules, e.g., F_3CO^-, F_3NO, and F_3PO, where short AY bonds suggest hypervalent bonding caused by $p_\pi-d_\pi$ double bonds. Reed and Schleyer concluded in 1990 that due to ionic bonding the octet rule was "*far from being violated*" in hypercoordinated compounds.[27a]

This point of view was unsuccessfully challenged by theoretical groups[113−119] applying Mayer's approach,[120−122] which is based on nonorthogonal orbitals and Mulliken population analysis (MMA), as well as by Patterson and Messmer[123−125] using strong orthogonality and perfect pairing approximation within the GVB model (SOPP-GVB). As pointed out by Reed and co-workers,[27,107] MMA overestimates the occupancy of high-energy atomic orbitals. Thus, d orbitals on the central atom "steal" electrons from ligand s and p orbitals resulting in overestimated valencies and greatly reduced ionic character for the hypercoordinated molecule. Cooper et al.[126,127] concluded that Messmer's[123−125] results are artifacts arising from the orthogonality constraint imposed in the GVB computations. The *full*-GVB calculations of Cooper et al. suggest,[126] in agreement with the NPA analyses,[27,105] that there is no qualitative difference in bonding between "normal" and hypercoordinated species.

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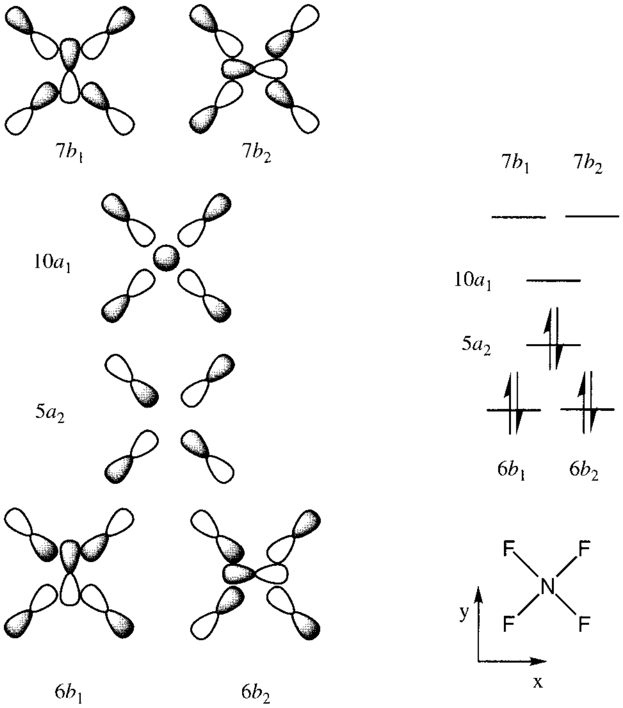
Table 8. Comparison of NF_5 and NF_3 with PF_5 and PF_3 at the B3LYP/6-311+G* Level of Theory

D_{3h} forms	X−F distances (Å)		natural charges			NLMO polarization toward F (%)	
	r_{ax}	r_{eq}	ρ_{ax}	ρ_{eq}	$\rho(X)$	axial	equatorial
NF_5	1.608	1.381	−0.3	−0.1	+0.9	64	57
PF_5	1.604	1.570	−0.6	−0.5	+2.6	81	80
C_{4v} forms	X−F distances (Å)		natural charges			NLMO polarization toward F (%)	
	r_{apical}	r_{base}	ρ_{apical}	ρ_{base}	$\rho(X)$	apical	base
NF_5	1.332	1.515	−0.1	−0.2	+0.9	59	59
PF_5	1.551	1.594	−0.5	−0.5	+2.5	80	80
NF_3	1.382		−0.2		+0.6	63	
PF_3	1.605		−0.6		+1.8	82	

Scheme 3. The Frontier Orbitals of C_{4v} Symmetric NF_5 Viewed along the 4-Fold Axis[a]



[a] The symmetry labels are given for the C_{2v} point group.

If the traditional sp^3d and sp^3d^2 models are invalid, what then is the role of d functions in molecular orbital computations of hypercoordinated molecules? Clearly, the inclusion of d functions into the basis set is essential for an adequate quantitative description of hypercoordinated systems.[128−130] But the earlier inference that this was due to the important role atomic d orbitals were expected to play in hypercoordinated bonding was incorrect. However, Mulliken[131] already pointed out in 1962 that "a linear combination of atomic orbitals as building blocks to construct molecular orbitals is merely a convenience", a fact emphasized also by Musher,[95,132,133] Coulson,[134] and others.[110,111,135] Thus d functions do not play a "chemical" role but their necessity arises from the formalism employed to solve the Schrödinger equation. The atomic d basis functions in Hartree−Fock and *full*-GVB wave functions are polarization functions for the orthogonal atomic s and p functions (in correlated wave function they provide angular correlation)[111] in "normal valent" and "hypervalent" molecules *irrespective of the coordination* of the central atom.[105,110]

We performed natural atomic and natural bond orbital (NAO and NBO, respectively) analyses of the B3LYP/6-311+G** density matrices to compare the bonding in NF_5 with that in PF_5 and NF_3 (Table 8).[105] The NBO procedure, which requires the linear combination of orthonormal natural hybrid orbitals (NHOs), gives a set of five two-center σ_{NF} bond orbitals which have low occupancy (1.76 electrons for axial and 1.90 electrons for equatorial NBOs) in analogy to the results for SF_6.[105] The two NBOs corresponding to the axial NF bonds are polarized more strongly (71%) toward fluorine than the three equatorial NBOs (60%). The five resulting hybrids on nitrogen are of sp^3d character, although the d orbital contribution to the original NHOs is only marginal. This result is an artifact caused by the *orthogonality constraint* in the NBO procedure and by the high symmetry of the molecular framework, as pointed out by Reed and Weinhold for SF_6.[105]

There is a set of five natural localized molecular orbitals (NLMOs), obtained by diagonalizing the NBO density matrix, corresponding to the five NF bonds. Besides the F p_σ lone pair and the N $sp^{3.51}d^{0.02}$ NHO, one p lone pair from each other F atom contributes almost 1% to the axial NLMO. The two axial NLMOs are polarized more strongly toward fluorine (64%) than are the equatorial NLMOs (57%). The latter, however, are less ionic than the NF bonds in NF_3, where the F atoms contribute 64% to the σ_{NF} NLMOs. This is further emphasized by the computed natural charges which are only −0.09 for the equatorial F atoms compared to −0.21 in NF_3. Even the axial F atoms are only moderately charged (−0.30), resulting in a natural charge of +0.89 for N in NF_5 compared to +0.63 in NF_3.

The axial and equatorial bonds in PF_5 are closer in length (r_{ax} = 1.604 Å, r_{eq} = 1.570 Å at B3LYP/6-311+G**, r_{ax} = 1.576 Å, r_{eq} = 1.530 Å experiment) than in NF_5,[81] due to the larger P atom. The bonds in PF_5, like those in SF_6,[105] are extremely polarized toward F (80.6% and 80.0% in axial and equatorial NLMOs, respectively), reflecting the large difference in electronegativity between P ($\chi = 2.06$) and F ($\chi = 4.10$).[136] The +2.63 charge on the P center is almost evenly distributed onto the five F atoms (−0.55 axial, −0.51 equatorial). Musher[95] acknowledged that the actual bonding configuration of PF_5 could lie anywhere between one axial 3c-4e bond and three covalent equatorial PF bonds on one hand and two axial PF bonds formed with two orthogonal P(sp) hybrids on the other hand. The NLMO data do not support the idea of partially ionic 3c-4e bonding involving the axial fluorine atoms in PF_5, but do support such a model with NF_5. Note that our NPA-based analysis of the bonding in NF_5 and PF_5 is in agreement with the picture which emerged from Mulliken and Bader analyses.[4,25]

The three F atoms in the equatorial plane are bonded to N with only slightly polarized covalent bonds (vide supra). The two axial F atoms interact with an N orbital of high p character along the C_3 symmetry axis to give one three center-four electron bond with its typical ionic character (Scheme 3). Strong electron donation from one bonding axial NLMO into the antibonding NLMO of the other axial bond reduces the axial bond order to

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the computed value of 0.5 in agreement with the canonical MO description (Scheme 2).

Two of the three MO's, which are generated by symmetry adapted combination of a nitrogen and two fluorine p orbitals, are doubly occupied in a 3c-4e bond. The lowest of them, $6b_2$, is one of the degenerate HOMO-1 in NF_5 and is bonding for both axial NF bonds. Double occupation of the nonbonding $12a_1$ orbital, the HOMO of NF_5, places the electrons on the fluorine atoms and thus results in ionic character. The antibonding $7b_2$ MO is the LUMO+1 in D_{3h} symmetric NF_5. The axial NF bonds are longer and weaker than their three equatorial counterparts, because there is only one bonding electron pair for two bonds.[90] Nonetheless, Michels and Montgomery[25] were able to locate five bond critical points for NF_5 using Bader's[135] atoms-in-molecules electron density analysis.

In analogy, the four long NF bonds in the C_{4v} conformation of NF_5 can be described with two orthogonal 3c-4e bonds. Symmetry adapted linear combination of two orthogonal nitrogen p orbitals with four F(p) orbitals yields the six frontier MO's displayed in Scheme 3. The two doubly occupied NF bonding ($6b_1$ and $6b_2$) MO's are degenerate and so are the empty NF antibonding ($7b_1$ and $7b_2$) MO's. The nonbonding MO's, $5a_2$ and $10a_1$, comprise the HOMO and LUMO of C_{4v} NF_5, respectively. Note the antibonding combination between the four F(p) orbitals and the N(s) orbital in the LUMO.

To summarize, the existence of hypercoordinated compounds depends mainly on the possibility of making sufficiently polar bonds, as already pointed out by several groups earlier.[27,101,105,126] For first and second row central atoms, d-orbital participation is not essential and should not be invoked to explain the differences between, e.g., NF_5 and PF_5. The octet rule is not violated in either molecule; there is no valence shell expansion. As the bonds are not completely covalent, conventional formal electron count procedures are misleading. The bonds drawn for hypercoordinated molecules do not correspond to Lewis electron pairs, but represent bonding interactions where fewer than two electrons are shared between atoms due to high ionic character. NF bonds are less ionic than PF bonds.

Conclusions

This investigation shows beyond any reasonable doubt that D_{3h} symmetric NF_5 corresponds to a local minimum even though the $NF_5 \rightarrow NF_3 + F_2$ reaction is exothermic by about 42 kcal mol^{-1} in the gas phase at 0 K. Thus, NF_5 could in principle be an observable chemical entity, at least as an isolated species. A thorough search of the potential energy surface identifies the 9 kcal mol^{-1} exothermic reaction to NF_4 and F along the 3-fold symmetry axis as the lowest barrier (16−20 kcal mol^{-1}) decomposition reaction of NF_5. The NF_4 radical is only weakly bound (0.1 kcal mol^{-1}) with respect to NF_3 and F. No lower energy transition structure could be found in this study, and we consider the existence of such a stationary point to be unlikely although we cannot rule it out completely.

Thus, the existence of an isolated D_{3h} symmetric NF_5 molecule in the gas phase seems possible. The elusive nature of the hitherto unobserved NF_5 can be ascribed to two factors. Due to the small size of the N atom the nonbonding FF distance is smaller than the sum of the fluorine van der Waals radii. However, this inhibits but does not preclude the existence of NF_5, as assumed earlier.[32] As a consequence of the significantly higher electronegativity of N vs P, the bonds in NF_5 are not as polar and the electrostatic attraction is less favorable than in PF_5.

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