1914 *Inorg. Chem.* **2011**, *50*, 1914–1925
DOI: 10.1021/ic102310v

Inorganic Chemistry
Article

F^+ and F^- Affinities of Simple N_xF_y and O_xF_y Compounds

Daniel J. Grant, Tsang-Hsiu Wang, Monica Vasiliu, and David A. Dixon*

*Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa,
Alabama 35487-0336, United States*

Karl O. Christe

*Loker Research Institute and Department of Chemistry, University of Southern California, Los Angeles,
California 90089-1661, United States*

Received November 18, 2010

Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for the neutral and ionic N_xF_y and O_xF_y systems using coupled cluster theory with single and double excitations and including a perturbative triples correction (CCSD(T)) method with correlation consistent basis sets extrapolated to the complete basis set (CBS) limit. To achieve near chemical accuracy (±1 kcal/mol), three corrections to the electronic energy were added to the frozen core CCSD(T)/CBS binding energies: corrections for core−valence, scalar relativistic, and first order atomic spin−orbit effects. Vibrational zero point energies were computed at the CCSD(T) level of theory where possible. The calculated heats of formation are in good agreement with the available experimental values, except for FOOF because of the neglect of higher order correlation corrections. The F^+ affinity in the N_xF_y series increases from N_2 to N_2F_4 by 63 kcal/mol, while that in the O_2F_y series decreases by 18 kcal/mol from O_2 to O_2F_2. Neither N_2 nor N_2F_4 is predicted to bind F^-, and N_2F_2 is a very weak Lewis acid with an F^- affinity of about 10 kcal/mol for either the cis or trans isomer. The low F^- affinities of the nitrogen fluorides explain why, in spite of the fact that many stable nitrogen fluoride cations are known, no nitrogen fluoride anions have been isolated so far. For example, the F^- affinity of NF is predicted to be only 12.5 kcal/mol which explains the numerous experimental failures to prepare NF_2^- salts from the well-known strong acid HNF_2. The F^- affinity of O_2 is predicted to have a small positive value and increases for O_2F_2 by 23 kcal/mol, indicating that the $O_2F_3^-$ anion might be marginally stable at subambient temperatures. The calculated adiabatic ionization potentials and electron affinities are in good agreement with experiment considering that many of the experimental values are for vertical processes.

Introduction

Compounds with fluorine atoms adjacent to other atoms with lone pairs pose problems for computational chemistry. However, one can make reliable estimates of many of their thermomdynamic properties by the judicious use of various approaches. We are especially interested in the F^+ and F^- affinities[1−6] of a broad range of compounds to make reactivity predictions. Given the limited experimental data available for the fluorides of nitrogen and oxygen, we have performed high accuracy theoretical calculations to determine thermodynamic properties of these molecules, namely, their heats of formation and F^+ and F^- affinities.

There have been numerous experimental investigations of nitrogen−fluorine and oxygen−fluorine compounds, and Klapötke recently reviewed several classes of nitrogen−fluorine compounds.[7] The experimental heats of formation of NF,[8] NF_2,[8] NF_3,[8] *cis*- and *trans*-N_2F_2,[8] N_2F_4,[8] and O_2F_2[9,10] are available. The vibrational frequencies of NF_2,[11,12] HNF_2

---

*To whom correspondence should be addressed. E-mail: dadixon@bama.ua.edu.

(1) Christe, K. O.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 2978.

(2) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J.; Boatz, J. A. *J. Fluor. Chem.*, **2000**, *101*, 151. *Chem. Eng. News* **2003**, 48−49.

(3) Dixon, D. A.; Grant, D. J.; Christe, K. O.; Peterson, K. A. *J. Inorg. Chem.* **2008**, *47*, 5485.

(4) Grant, D. J.; Dixon, D. A.; Camaioni, D.; Potter, R. G.; Christe, K. O. *Inorg. Chem.* **2008**, *48*, 8811.

(5) Grant, D. J.; Wang, T.-H.; Dixon, D. A.; Christe, K. O. *Inorg. Chem.* **2010**, *49*, 261.

(6) Dixon, D. A.; Wang, T.-H.; Grant, D. J.; Peterson, K. A.; Christe, K. O.; Schrobilgen, G. J. *Inorg. Chem.* **2007**, *46*, 10016.

(7) Klapotke, T. M. *J. Fluor. Chem.* **2006**, *127*, 679.

(8) Chase, M. W., Jr. *NIST-JANAF Tables*, 4th ed.; *J. Phys. Chem. Ref. Data*, Mono. 9, Suppl. 1, 1998.

(9) Lyman, J. L. *J. Phys. Ref. Data* **1989**, *18*, 799.

(10) Kirshenbaum, A. D.; Grosse, A. V.; Aston, J. G. *J. Am. Chem. Soc.* **1959**, *81*, 6398.

(11) Harmony, M. D.; Myers, R. J.; Schoen, L. J.; Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1961**, *35*, 1129.

(included for its acidity), [13]NF_3,[13] NF_4^+,[14] *trans*-FN=NF, [13,15] *cis*-FN=NF, [16] N_2F^+, [17] $N_2F_3^+$, [18] N_2F_4,[19] and FN_3[20] have been reported. The molecular structures of NF_2,[21] *cis*-[22,23] and *trans*-N_2F_2,[22] and *gauche*[21,24,25] and *trans*-N_2F_4[21,24,25] based on electron diffraction studies have been reported. For gaseous[26] and liquid[27,28] N_2F_4, infrared spectroscopic experiments have indicated the existence of an equilibrium mixture of two rotational isomers, trans (C_{2h} symmetry) and gauche (C_2 symmetry), that differ slightly in energy. The conformational stability of gaseous N_2F_4 has been studied by far-infrared and low-frequency Raman spectroscopy.[19] The molecular structure of N_2F_4 has been reported from microwave rotational spectroscopy studies.[29,30] The rotational spectrum of the NF_2 free radical in the millimeter-wave region[31] and its microwave[32] and absorption[33] spectra have been reported. The photodissociation of NF_3 has been studied by vacuum-ultraviolet fluorescence spectroscopy.[34] The crystal structures of several N_2F^+ and NF_4^+ salts have been reported.[17,35,36] The structure of the free gaseous ion N_2F^+ has also been determined using millimeter-wave spectroscopy.[37] The experimental structure[38,39] and anharmonic vibrational frequencies[40−42] of FOOF have also been reported.

There have been several theoretical investigations into some of the compounds under study. FOOF has proven to be a troublesome molecule for traditional single reference ab initio methods, because of the presence of a large number of nominally inactive lone pairs that can interact with each other at short distances. Thus, several theoretical approaches have been employed at describing FOOF accurately.[43−45] The heats of formation and structures of five small oxygen fluoride molecules have been determined with coupled cluster theory incorporating at least quadruple excitations given that the wave functions of several systems have large multiconfiguration character requiring correlation recovery beyond CCSD(T) to achieve accurate results.[43] The $\Delta H_{f,298\mathrm{K}}$ of FOOF was predicted to be 6.4 ± 0.7 kcal/mol, which is the best available computational value so far.[43] Feller et al. previously reported coupled cluster and multireference configuration interaction calculations of FOOF.[44,45] Martin and co-workers have also reported W4.n calculations on the fluorine oxides.[46] They performed CCSDT(Q)/cc-pVDZ calculations to estimate the higher order correlation corrections for the geometry of FOOF. Their best value for $\Delta H_{f,298\mathrm{K}}$(FOOF) at the W4 level is 7.84 ± 0.18 kcal/mol using the CCSD(T)/cc-pVQZ geometry. FOOF was also studied using the analytic gradient technique at the CCSD(T)(FC)/[5s,3p,3d,1f] level.[47] Lee et al.[48] reported $\Delta H_{f,0\mathrm{K}}$(FOOF) = 9.7 ± 2.0 kcal/mol at the CCSD(T)(FC) level with a triple-ζ atomic natural orbital basis set. Ventura and Keininger studied FOOF with B3LYP/6-311++G(3df,3pd) density functional theory (DFT) obtaining $\Delta H_{f,0\mathrm{K}}$(FOOF) = 8.2 kcal/mol based on an average of two procedures.[49] The geometry of FOOF was reported at the DFT level within the local density approximation (LDA).[50] Several DFT methods were used to investigate the structures FOOF and three other small oxygen fluorides.[51] Keininger et al.[52] studied a collection of oxygen fluoride molecules at the DFT-B3PW91 level with the cc-pVQZ or aug-cc-pVQZ basis sets, and report $\Delta H_{f,298\mathrm{K}}$(FOOF) = 7.3 and 4.1 kcal/mol at the DFT and Gaussian-2 levels, respectively. Kraka et al. reported the geometry of FOOF at the CCSD(T)/CBS level based on extrapolating the values obtained with the aug-cc-pVTZ and aug-cc-pVQZ basis sets.[53]

Zhang and co-workers have studied the low-lying electronic states of NF_2 at the MP2 level.[54] High level calculations at the CCSD(T)/CBS level on the structures and thermodynamic properties of N_2F^+, N_2F_2 (cis and trans), and F_2NN have recently been reported,[36] and the results are consistent

---

(12) Harmony, M. D.; Myers, R. J. *J. Chem. Phys.* **1962**, *37*, 636.

(13) (a) Shimanouchi, T. Tables of Molecular Vibrational Frequencies Consolidated, Volume *II*, *J. Phys. Chem. Ref. Data* **1972**, *6*, 993. (b) Shimanouchi, T. Tables of Molecular Vibrational Frequencies Consolidated, Volume *I*; National Bureau of Standards: Gaithersburg, MD, **1972**; pp 1−160.

(14) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1977**, *16*, 849.

(15) Shimanouchi, T. *NIST Chemistry WebBook, NIST Standard Reference Database*, Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD; http://webbook.nist.gov.

(16) King, S. T.; Overend, J. *Spectrochim. Acta A* **1967**, *23*, 61.

(17) Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3795.

(18) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1978**, *17*, 2749.

(19) (a) Durig, J. R.; Shen, Z. *J. Phys. Chem. A* **1997**, *101*, 5010. (b) Durig, J. R.; MacNamee, R. W. *J. Raman Spectrosc.* **1974**, *2*, 635.

(20) Christen, D.; Mack, H. G.; Schatte, G.; Willner, H. *J. Am. Chem. Soc.* **1988**, *110*, 707.

(21) Bohn, R. K.; Bauer, S. H. *Inorg. Chem.* **1967**, *6*, 304.

(22) Bohn, R. K.; Bauer, S. H. *Inorg. Chem.* **1967**, *6*, 309.

(23) Kuczkowski, R. L.; Wilson, E. B., Jr. *J. Chem. Phys.* **1963**, *39*, 1030.

(24) Cardillo, M. J.; Bauer, S. H. *Inorg. Chem.* **1969**, *8*, 2086.

(25) Gilbert, M. M.; Gundersen, G.; Hedberg, K. *J. Chem. Phys.* **1972**, *56*, 1691.

(26) Oskam, A.; Elst, R.; Duinker, J. C. *Spectrochim. Acta* **1970**, *26A*, 2021.

(27) Miller, F. A.; Koster, D. F. *Spectrochim. Acta* **1968**, *24A*, 1487.

(28) Shchepkin, D. N.; Zhygula, L. A.; Belozerskaya, L. P. *J. Mol. Spectrosc.* **1978**, *49*, 265.

(29) Kaushik, V. J.; Venkateswarlu, F. *Chem. Phys. Lett.* **1977**, *46*, 426.

(30) Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1959**, *31*, 1129.

(31) Müller, H. S. P.; Löblein, K.; Hübner, H.; Hüttner, W.; Brown, J. M. *J. Mol. Spectrosc.* **2008**, *251*, 185.

(32) Brown, R. D.; Burden, F. R.; Godfrey, P. D.; Gillard, I. R. *J. Mol. Spectrosc.* **1974**, *25*, 301.

(33) Goodfriend, P. L.; Woods, H. P. *J. Mol. Spectrosc.* **1964**, *13*, 63.

(34) Seccombe, D. P.; Tuckett, R. P.; Jochims, H -W.; Baumgärtel, H. *Chem. Phys. Lett.* **2001**, *339*, 405.

(35) Haiges, R.; Gerken, M.; Iuga, A.; Bau, R.; Christe, K. O. *Inorg. Chem.* **2006**, *45*, 7981.

(36) Christe, K. O.; Dixon, D. A.; Grant, D. J.; Haiges, R.; Tham, F. S.; Vij, A.; Vij, V.; Wang, T.-H.; Wilson, W. W. *Inorg. Chem.* **2010**, *49*, 6823.

(37) Botschwina, P.; Sebald, P.; Bogey, M.; Demuynck, C.; Destombes, J. L. *J. Mol. Spectrosc.* **1992**, *153*, 255.

(38) Jackson, R. H. *J. Chem. Soc.* **1962**, 4585.

(39) Hedberg, L.; Hedberg, K.; Eller, P. G.; Ryan, R. R. *Inorg. Chem.* **1988**, *27*, 232.

(40) Kim, K. C.; Campbell, G. M. *Appl. Spectrosc.* **1985**, *39*, 625.

(41) Gardiner, D. J.; Lawrence, N. J.; Turner, J. J. *J. Chem. Soc.* **1971**, 400.

(42) Spratley, R. D.; Turner, J. J.; Pimentel, G. C. *J. Chem. Phys.* **1966**, *44*, 2063.

(43) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Phys. Chem. A* **2010**, *114*, 613.

(44) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204105.

(45) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 9641.

(46) Karton, A.; Parthiban, S.; Martin, J. M. L. *J. Phys. Chem. A* **2009**, *113*, 4802.

(47) Scuseria, G. E. *J. Chem. Phys.* **1991**, *94*, 442.

(48) Lee, T. J.; Rice, J. E.; Dateo, C. E. *Mol. Phys.* **1996**, *89*, 1359.

(49) Ventura, O. N.; Kieninger, M. *Chem. Phys. Lett.* **1995**, *245*, 488.

(50) Dixon, D. A.; Andzelm, J.; Fitzgerald, G.; Wimmer, E.; Jasien, P. *J. Phys. Chem.* **1991**, *95*, 9197.

(51) Jursic, B. S. *J. Mol. Struct.* (*Theochem*) **1996**, *366*, 97.

(52) Kieninger, M.; Segovia, M.; Ventura, O. N. *Chem. Phys. Lett.* **1998**, *287*, 597.

(53) Kraka, E.; He, Y.; Cremer, D. *J. Phys. Chem. A* **2001**, *105*, 3269.

(54) Cai, Z. L.; Sha, G. H.; Zhang, C. H.; Huang, M. B. *Chem. Phys. Lett.* **1991**, *178*, 273.

with other high quality calculations.[37,55] The electron affinity of NF has been calculated at R(U)CCSD(T), icMRCI(+Q), and MR-ACPF levels with the (d)-aug-cc-pV*n*Z basis sets up to $n = 6$.[56] The calculated value of 0.247 eV is 0.25 eV lower than the reported experimental value of 0.5 eV; however, no experimental details were given.[57]

Computational Methods

Modern computational chemistry methods can now provide reliable predictions of thermodynamic properties to within about 1 kcal/mol for most compounds that are not dominated by multireference character.[58] We use the approach that we have been developing at The University of Alabama and Washington State University for the prediction of accurate molecular thermochemistry to determine the atomization energies and the heats of formation of these compounds.[43−45] Our approach is based on calculating the total atomization energy (TAE) of a molecule and using this value with known heats of formation of the atoms to calculate the heat of formation at 0 K. The approach starts with coupled cluster theory with single and double excitations and including a perturbative triples correction (CCSD(T)),[59−61] combined with the correlation-consistent basis sets[62] extrapolated to the complete basis set (CBS) limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence and relativistic effects, both scalar and spin−orbit. The zero point energy can be obtained from experiment, theory, or a combination of the two. Corrections to 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor-harmonic oscillator approximation[63] and appropriate corrections for the heat of formation of the atoms.[64]

The standard aug-cc-pV*n*Z basis sets were used for N, O, and F and abbreviated as aV*n*Z. Only the spherical component subsets (e.g., 5-term *d* functions, 7-term *f* functions, etc.) of the Cartesian polarization functions were used. All CCSD(T) calculations were performed with the MOLPRO-2006[65] program system on an SGI Altix, a Cray XD-1, or the dense memory Linux cluster at the Alabama Supercomputer Center, or on the Dell Linux cluster at The University of Alabama, or on the massively parallel HP Linux cluster in the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory.

For the open shell atomic calculations, we used the restricted method for the starting Hartree−Fock wave function and then relaxed the spin restriction in the coupled cluster portion of the calculation. This method is conventionally labeled R/UCCSD(T).[66−68] Our CBS estimates use a mixed exponential/Gaussian function of the form[69]

$$E(n) = E_{\mathrm{CBS}} + B\mathrm{e}^{-(n-1)} + C\mathrm{e}^{-(n-1)^2} \qquad (1)$$

where $n = 2$ (aVDZ), 3 (aVTZ), and 4 (aVQZ).

To achieve thermochemical properties within ±1 kcal/mol of experiment, it is necessary to account for core−valence correlation energy effects beyond whatever treatment is used for the valence electron correlation. Core−valence (CV) calculations were carried out with the weighted CV basis set cc-pwCVTZ.[70] Relativistic effects are included at the scalar relativistic level, ΔE_{SR}, plus the spin orbit corrections for atoms. The atomic spin−orbit corrections are $\Delta E_{\mathrm{SO}}(\mathrm{O}) = 0.22$, $\Delta E_{\mathrm{SO}}(\mathrm{F}) = 0.39$, and $\Delta E_{\mathrm{SO}}(\mathrm{F}^+) = 0.48$ kcal/mol, respectively, taken from the tables of Moore.[71] We evaluated ΔE_{SR} by using expectation values for the two dominant terms in the Breit-Pauli Hamiltonian, the so-called mass-velocity and one-electron Darwin (MVD) corrections from configuration interaction singles and doubles (CISD) calculations. The quantity ΔE_{SR} was obtained from the CISD wave function with aVTZ basis set at the appropriate optimized geometry.

The geometries of the diatomic molecules were optimized up through the CCSD(T)/aVQZ level. Bond distances, harmonic frequencies, and anharmonic constants for the diatomics were obtained from a fifth order Dunham fit[72] of the potential energy curve at the CCSD(T)/aVQZ level. For $NF_2^{0/\pm}$, HNF_2, $NF_3^{0/\pm}$, $NF_4^{\pm}$, NH_5, NF_5, $N_2F^{0/\pm}$, N_2F_2 isomers, FN_3, $F_2N_3^{\pm}$ (except for $F_2N_3^{+}$ (B, C_1), which was optimized at the MP2/aVTZ level), OF_2, and $OF_3^{\pm}$, the geometries were optimized up through the CCSD(T)/aVTZ level. The aVTZ geometries were then used in single point CCSD(T)/aVQZ calculations. Zero point energies (ΔE_{ZPE}) were calculated at the CCSD(T)/aVTZ level without scaling. For FN_3, ΔE_{ZPE} was calculated at the CCSD(T)/VTZ level without scaling, and for the $F_2N_3^{\pm}$ions at the MP2/aVTZ level. For the remaining molecules, geometry optimizations were performed and ΔE_{ZPE}'s were calculated at the MP2/aVTZ level; this geometry was used in single point CCSD(T) calculations with the aVDZ, aVTZ, and aVQZ basis sets for these molecules.

By combining our computed $\sum D_0$ values, given by the following expression,

$$\sum D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} \qquad (2)$$

with the known heats of formation at 0 K for the elements, we can derive $\Delta H_{f,0\mathrm{K}}$ values for the molecules under study. The heats of formation of H, N, O, and F are well-established as

---

(55) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III *Theor. Chim. Acta* **1989**, *75*, 81.

(56) Fišer, J.; Polák, R. *Collect. Czech. Chem. Commun.* **2005**, *70*, 923.

(57) Sidorov, L. N. *Russ. Chem. Rev.* **1982**, *51*, 356.

(58) Dunning, T. H., Jr. *J. Phys. Chem.* **2000**, *104*, 9062.

(59) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(60) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(61) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(62) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. (c) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (d) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244. (e) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *110*, 7667.

(63) McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Sausalito, CA, 2001.

(64) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(65) MOLPRO, a package of ab initio programs designed by: Werner, H.-J.; Knowles, P. J. version 2006.1, Universität Stuttgart, Stuttgart, Germany, University of Birmingham, Birmingham, U.K., Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H., Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J.

(66) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033.

(67) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1994**, *99*, 5219.

(68) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(69) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(70) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(71) Moore, C. E. *Atomic energy levels as derived from the analysis of optical spectra*, Vol. 1, H to V; U.S. National Bureau of Standards: Gaithersburg, MD; Circular 467, U.S. Department of Commerce, National Technical Information Service: Washington, D.C., 1949; COM-72−50282.

(72) Dunham, J. L. *Phys. Rev.* **1932**, *41*, 721.

Table 1. Optimized MP2/aVTZ and CCSD(T) Bond Lengths (Å) and Bond Angles (deg)[a,b]

molecule	$R_{NF/OF}$	$R_{NN/OO/FF}$	∠FNN/FOO	∠FNF/FOF/NNN	dihedral
NF^+ ($^2\Pi$, $C_{\infty v}$)	1.1854				
NF ($^3\Sigma^-$, $C_{\infty v}$)	1.3192				
	1.317[76]				
NF^- ($^2\Pi$, $C_{\infty v}$)	1.4919				
OF^+ ($^3\Sigma^-$, $C_{\infty v}$)	1.2337				
OF ($^2\Pi$, $C_{\infty v}$)	1.3536[43]				
	1.3541[84]				
OF^- ($^1\Sigma^+$, $C_{\infty v}$)	1.5170				
F_2^+ ($^2\Pi_g$, $D_{\infty h}$)		1.3075			
F_2 ($^1\Sigma^+{}_g$, $D_{\infty h}$)		1.4130			
		1.4119[76]			
F_2^- ($^2\Sigma_u{}^+$, $D_{\infty h}$)		1.9225			
NF_2^+ ($^1A_1$, C_{2v})	1.2504			107.8	
NF_2 ($^2B_1$, C_{2v})	1.3536			103.1	
	1.34691[31]			*103.1 ± 0.02*[31]	
	1.363 ± 0.008[21]			*102.5 ± 0.9*[21]	
NF_2^- ($^1A_1$, C_{2v})	1.4965			99.4	
HNF_2 ($^1A'$, C_s)	1.0272 (1,2)			103.0	102.5 (2,1,3,4)
	1.3997 (1,3)				
NF_3^+ ($^2A_1$, C_{3v})	1.2858			113.7	132.3 (2,1,4,3)
NF_3 ($^1A_1$, C_{3v})	1.3702			101.8	
	1.371[74,75]			*102.9*[74,75]	
NF_3^- ($^1A'$, C_s)	1.3823 (1,3)			101.6 (3,1,4)	98.5 (2,1,3,4)
	2.2391 (1,2)			96.9 (2,1,3)	
NF_4^+ (^1A_g, T_d)	1.3112			109.5	120.0
	1.3076[35]			*109.5*[35]	
NF_4 ($^2A_1$, C_{3v})	2.7017 (1,3)			101.9 (2,1,4)	120.0 (2,1,3,4)
	1.3688 (1,2)			116.2 (2,1,3)	
NF_4^- ($^1A_1$, C_{2v})	1.800 (1,2)			171.0 (2,1,4)	−173.1 (2,1,3,4,)
	1.3720 (1,3)			101.8 (3,1,5)	−93.5 (2,3,1,5)
				92.8 (2,1,3)	
NH_5 ($^1A_1'$, D_{3h})	1.6778_{ax}			90.0	120.0
	1.0006_{eq}				
NF_5 ($^1A_1'$, D_{3h})	1.5778_{ax}			90.0	120.0
	1.3817_{eq}				
N_2 ($^1\Sigma^+{}_g$, $D_{\infty h}$)		1.1005			
		1.0977[76]			
N_2F^+ ($^1\Sigma_g$, $C_{\infty v}$)	1.2357	1.1246	180.0		
	1.217[17]	*1.099*[17]			
N_2F ($^2\Sigma_g$, $C_{\infty v}$)	2.8263	1.1138	180.0		
N_2F^- ($^1A'$, C_s)	2.8759	1.1143	79.6		
	2.8911				
cis-N_2F_2 ($^1A_1$, C_{2v})	1.3872	1.2248	114.2		0.0
	1.410 ± 0.009[22]	*1.214 ± 0.008*[22]	*114.4 ± 1.0*[22]		
	1.384 ± 0.010[23]	*1.214 ± 0.005*[23]	*114.5 ± 0.5*[23]		
trans-N_2F_2 (^1A_g, C_{2h})	1.3860	1.2321	104.7		180.0
	1.396 ± 0.008[22]	*1.231 ± 0.010*[22]	*105.5 ± 0.7*[22]		
$N_2F_3^+$ ($^1A'$, C_s)	1.2880 (1,4)	1.2526	127.4 (4,1,2)	113.6 (4,1,5)	0.0 (3,2,1,4)
	1.2836 (1,5)		119.0 (5,1,2)		180.0 (3,2,1,5)
	1.3140 (2,3)				
			108.2 (3,2,1)		
N_2F_3 (^2A, C_1)	1.3853 (1,4)	1.4188	102.2 (3,2,1)	103.1 (4,1,5)	176.1 (3,2,1,5)
	1.3755 (1,5)		105.2 (4,1,2)		69.2 (3,2,1,4)
	1.3440 (2,3)		100.6 (5,1,2)		
$N_2F_3^-$ (^1A, C_1)	2.2192 (1,4)	1.2413	103.8 (3,2,1)	91.9 (4,1,5)	−90.4 (3,2,1,4)
	1.3943 (1,5)		102.1 (4,1,2)		174.7 (3,2,1,5)
	1.4073 (2,3)		103.3 (5,1,2)		
N_2F_4 (^1A_g, C_{2h})	1.3741	1.5016	99.8	102.8	75.0 (3,2,1,6)
	1.375 ± 0.004[24]	*1.489 ± 0.007*[24]	*100.6 ± 0.6*[24]	*102.9 ± 0.75*[24]	
N_2F_4 (^1A, C_2)	1.3767 (1,5)	1.4628	100.7 (3,2,1)	102.9 (3,2,4)	−174.1 (3,2,1,6)
	1.3737 (1,6)		107.1 (4,2,1)		40.3 (4,2,1,5)
	1.375 ± 0.004[24]	*1.489 ± 0.007*[24]	*100.1 ± 1*[24]	*105.1 ± 1*[24]	
	1.393 ± 0.008[21]	*1.53 ± 0.02*[21]	*104.3 ± 1*[21]	*103.7 ± 0.9*[21]	
$N_2F_5^+$ ($^1A'$, C_s)	1.3136 (6,7)	1.6504	107.8 (3,6,1)	109.2 (2,6,7)	174.4 (4,1,6,2)
	1.3084 (6,2)		99.9 (4,1,6)	109.6 (2,6,3)	−67.4 (4,1,6,3)
	1.3280 (1,4)		133.3 (7,6,1)	104.7 (4,1,5)	53.5 (4,1,6,7)
$N_2F_5^-$ (^1A, C_1)	1.4876 (1,4)	3.0258	64.3 (4,1,6)	99.4 (4,1,5)	−82.1 (4,1,6,3)
	1.4796 (1,5)		80.4 (5,1,6)	100.5 (3,6,2)	175.8 (4,1,6,2)
	1.4075 (6,2)		142.3 (2,6,1)	100.2 (2,6,7)	18.7 (4,1,6,7)
	1.3589 (6,3)		86.0 (3,6,1)	101.5 (3,6,7)	172.5 (5,1,6,3)
	1.3773 (6,7)		115.0 (7,6,1)		70.4 (5,1,6,2)
					−86.8 (5,1,6,7)
FN_3 ($^1A'$, C_s)	1.4294	1.1375 (1,2)	103.9	172.1	180.0

Table 1. Continued

molecule	$R_{NF/OF}$	$R_{NN/OO/FF}$	∠FNN/FOO	∠FNF/FOF/NNN	dihedral
		1.2671 (1,3)			
	1.444[20]	*1.132(1,2)*[20]	*103.8*[20]	*170.9*[20]	
		1.253(1,3)[20]			
$F_2N_3^+$ ($^1A'$, C_s, A)	1.2550	1.1036 (1,3)	97.6	107.4	125.6 (4,2,1,3)
		2.4677 (1,2)			
$F_2N_3^+$ (^1A, C_1, B)	1.2977 (2,5)	1.2051 (1,2)	135.3 (5,2,1)	87.3 (1,2,3)	179.3 (5,2,3,4)
	1.3254 (3,4)	1.4221 (2,3)	105.2 (4,3,2)		−98.6 (4,3,2,1)
$F_2N_3^+$ (^1A, C_2, C)	1.3293	1.2251	111.2	152.7	135.8
$F_2N_3^-$ ($^1A'$, C_s, B)	2.0019 (1,3)	1.2851 (1,2)	98.8 (3,1,2)	160.6	180.0 (5,2,1,3)
	1.5298 (2,5)	1.1409 (2,4)	86.0 (5,2,1)		0.0 (3,1,2,4)
$F_2N_3^-$ ($^1A'$, C_s, C)	1.5082 (2,4)	1.2708 (1,2)	103.0 (4,2,1)	129.9	180.0 (4,2,1,3)
	1.6082 (3,5)	1.2330 (1,3)	108.6 (5,3,1)		0.0 (5,3,1,2)
OF_2 ($^1A_1$, C_{2v})	1.4033			102.9	
	1.412[85]			*103.1*[85]	
OF_3^+ ($^1A_1$, C_{3v})	1.3768			103.5	107.8 (4,1,3,2)
OF_3^- ($^1A_1$, C_{2v})	1.4567 (1,3)			100.3 (2,1,3)	180.0 (2,1,3,4)
	1.7432 (1,2)			159.5 (2,1,4)	
O_2F^+ ($^1A'$, C_s)	1.4639	1.1291	112.9		
O_2F^+ ($^3A''$, C_s)	1.3270	1.2589	108.6		
O_2F ($^2A''$, C_s)	1.6414[43]	1.1959[43]	110.9[43]		
	1.649[83]	*1.200*[83]	*111.2*[83]		
O_2F^- ($^3A''$, C_s)	2.8437	1.2275	177.6		
O_2F^- ($^1A'$, C_s)	1.9662	1.2655	109.4		
O_2F_2 (^1A, C_2)	1.6188	1.1662	110.5	104.4	−88.7 (3,2,1,4)
	1.575 ± 0.003[38]	*1.217 ± 0.003*[38]		*109.5 ± 0.5*[38]	
	1.586 ± 0.002[39]	*1.216 ± 0.002*[39]		*109.2 ± 0.2*[39]	
$O_2F_3^+$ ($^1A'$, C_s)	1.3605 (1,4)	1.6533	104.6 (4,1,2)	103.2 (3,2,5)	−54.6 (3,2,1,4)
	1.4054 (2,5)		103.7 (3,2,1)		
$O_2F_3^-$ ($^1A'$, C_s)	1.8386 (2,3)	1.1866	111.8 (3,2,1)	86.0 (3,2,5)	−132.7 (3,2,1,4)
	2.0733 (1,4)		129.0 (4,1,2)		

[a] Experimental values are given in italics. [b] Geometrical parameters for $NF_2^{0/\pm}$, HNF_2, $NF_3^{0/\pm}$, $NF_4^\pm$, NH_5, NF_5, $N_2F^{0/\pm}$, N_2F_2 isomers, FN_3, $F_2N_3^\pm$, OF_2, and $OF_3^\pm$ were calculated at the CCSD(T)/aVTZ level and for the diatomics at the CCSD(T)/aVQZ level.

$\Delta H_{f,0K}(H) = 51.63$ kcal/mol, $\Delta H_{f,0K}(B) = 135.1$ kcal/mol,[73] $\Delta H_{f,0K}(N) = 112.53$ kcal/mol, $\Delta H_{f,0K}(O) = 58.99$ kcal/mol, and $\Delta H_{f,0K}(F) = 18.47$ kcal/mol.[8] Heats of formation at 298 K were obtained by following the procedures outlined by Curtiss et al.[64]

Results and Discussion

The calculated and experimental geometries for the molecules under study are given in Table 1, including their electronic states and symmetry labels. The optimized molecular structures are depicted in Figure 1. The total CCSD(T) energies and calculated CCSD(T) or MP2 harmonic frequencies for the molecules are given as Supporting Information in Table SI-1 and Table SI-2, respectively, where they are compared with the available experimental values. The component reaction energies are also provided in the Supporting Information (Table SI-3).

Geometries. The experimental geometry of NF_2 has been reported from rotational spectroscopy[31] and electron diffraction experiments,[21] and our CCSD(T)/aVTZ value for the r(NF) distance is in excellent agreement, within |0.009| Å, of the two experimental values. Our CCSD(T)/aVTZ geometry of NF_3 is in good agreement with the experimental structures from microwave[74] and electron diffraction studies.[75]

The cationic and anionic forms of N_2F exhibit very different structures with N_2F^+ predicted to be linear[35] and N_2F^- predicted to be bent with an ∠FNN of ~80°. The r(NN) distance of N_2F^- is only slightly longer than that in N_2 ($^1\Sigma_g^+$)[76] and slightly shorter than that in N_2F^+. The the r(NF) distance is longer by 1.640 Å in N_2F^- than in N_2F^+ so, N_2F^- is best considered as a weak complex of F^- with N_2.

The structures of $N_2F_3^+$ and $N_2F_3^-$ also differ significantly with $N_2F_3^+$ being planar with 3 tightly bound fluorines and $N_2F_3^-$ being nonplanar with one very loosely bound fluorine. As predicted for the $N_2F^\pm$ pair, the r(NN) distance in the anion is predicted to be slightly shorter than in the cation. The values for r(NN) in $N_2F_3^+$ and $N_2F_3^-$ are typical N=N double bond values and are only slightly longer than that in *trans*-N_2F_2. Similarly, the r(NF) distances in the N_2F_2 subunit are predicted to be only slightly longer than that in *trans*-N_2F_2, but the N_2F_2--F^- distance is again very long (2.219 Å). Therefore, the structure of $N_2F_3^-$ can also be considered as a weak complex of F^- loosely interacting with *trans*-N_2F_2 from above the plane of the molecule.

There are two rotational isomers of N_2F_4, gauche (C_2 symmetry) and trans (C_{2h} symmetry), that are close in energy.[24,27,28] Bauer and Cardillo[24] determined the trans rotamer to be more stable than the gauche rotamer by 0.3−0.5 kcal/mol with a 47% gauche−53% trans mixture below room temperature. At the CCSD(T)/CBS level plus the additional corrections, we predict the trans rotamer to be more stable than the gauche rotamer by 0.1 kcal/mol at 298 K, completely consistent with the experimental

---

(73) Karton, A.; Martin, J. M. L. *J. Phys. Chem. A* **2007**, *111*, 5936.
(74) Sheridan, J.; Gordy, W. *Phys. Rev.* **1950**, *79*, 513.
(75) Schomaker, V.; Lu, C. *J. Am. Chem. Soc.* **1950**, *72*, 1182.
(76) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules. Molecular Spectra and Molecular Structure*, Vol. *IV*, Van Nostrand: Princeton, 1979.

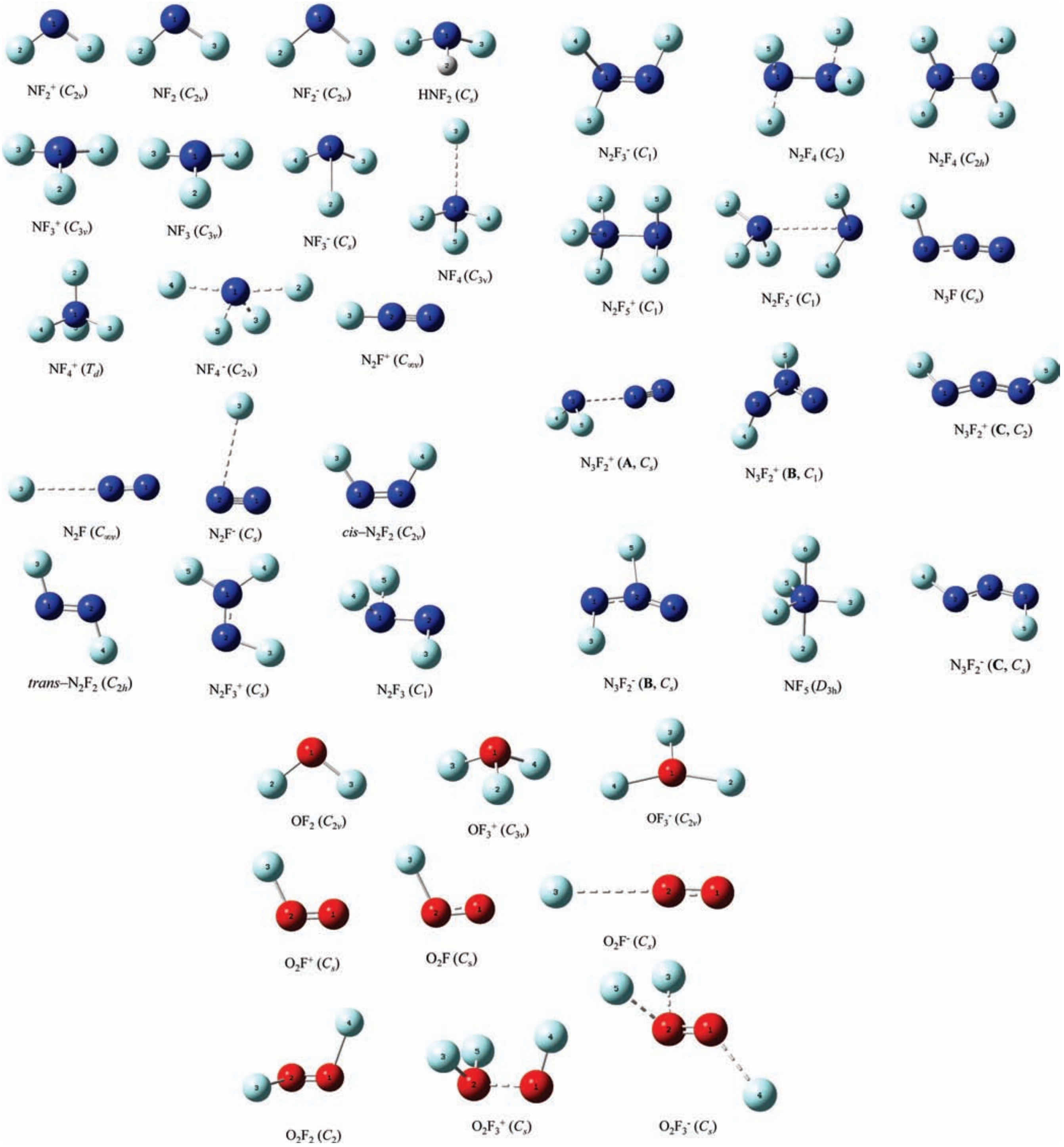

Figure 1. Optimized molecular structures for NF_2^+, NF_2, NF_2^-, NF_3^+, NF_3, NF_3^-, NF_4^+, NF_4, NF_4^-, N_2F^+, N_2F, N_2F^-, *cis*-N_2F_2, *trans*-N_2F_2, $N_2F_3^+$, N_2F_3, $N_2F_3^-$, N_2F_4, $N_2F_5^+$, $N_2F_5^-$, N_3F, $N_3F_2^+$, $N_3F_2^-$,NF_5, OF_2, OF_3^+, OF_3^-, O_2F^+, O_2F, O_2F^-, O_2F_2, $O_2F_3^+$, and $O_2F_3^-$.

product ratio. At just the CCSD(T)/CBS level based on the valence electronic energies, the trans rotamer is more stable than the gauche by 0.2 kcal/mol. The experimental structure of the gauche[21,24] and trans[24] rotamers have been reported from electron diffraction studies. The MP2/aVTZ geometry parameters for the trans rotamer are in excellent agreement with the most recent electron diffraction structure,[24] with the largest discrepancy predicted for the *r*(NN) distance, which was calculated to be too long by 0.013 Å. Reasonable agreement is also found for the gauche rotamer with the *r*(NN) distance predicted to be shorter by 0.026 Å. The large difference in *r*(NN) between N_2F_4 (C_{2h}) (1.502 Å) and *trans*-N_2F_2 (1.232 Å) is due to N_2F_4 having an N−N single bond and N_2F_2 having an N═N double bond. The *r*(NF) distances in N_2F_4 (C_{2h}) and N_2F_2 are within 0.006 Å of each other.

Addition of F^+ and F^- to N_2F_4 gives the $N_2F_5^+$ and $N_2F_5^-$ ions with C_s and C_1 symmetry structures, respectively. Whereas the N−F bonds of ∼1.31 Å in $N_2F_5^+$ are relatively short and stable, the *r*(NN) distance of 1.650 Å is relatively long, implying that $N_2F_5^+$ might at best have marginal stability at low temperatures. For example, N_2F_4 with an N−N bond length of 1.502 Å dissociates already at room temperature to NF_2 radicals. The predicted instability of the $N_2F_5^+$ cation is in accord with previous literature reports. In 1976, Toy and Stringham[77] reported the isolation of a stable solid which they attributed to $[N_2F_5]^+[(CF_3)_3CO]^-$ but which was subsequently reassigned by Christe and co-workers[78] to $(NO)_2SiF_6$. In a second report,[79] Stringham and Toy also claimed the synthesis of $N_2F_5^+BF_4^-$ which was again refuted by Christe and co-workers. By analogy with N_2F^- and $N_2F_3^-$, the $N_2F_5^-$ anion is also unstable. Its predicted N−N bond distance of 3.026 Å is only slightly shorter than the sum of its van der Waals radii ($r_{VDW}(N) = 1.55$ Å).[80]

There has been substantial interest in the existence of hypercoordinated nitrogen(V) compounds with more than three substituents. We predict NF_5 (D_{3h}) to be a local minimum from a harmonic vibrational analysis at the CCSD(T)/aVTZ level, in agreement with the results of Bettinger et al.[81] who found a minimum at all levels of theory employed, up through CCSD(T)/DZP. However, as discussed below in more detail, NF_5 is thermodynamically unstable by 42 kcal/mol with respect to decomposition to NF_3 and F_2, and the barrier to the loss of an F atom is only about 16 kcal/mol.[72]

The structure of FN_3 is planar with C_s symmetry and the two r(NN) distances are both longer by 0.040 and 0.169 Å as compared to r_e (N_2 $^1\Sigma_g^+$) = 1.0977 Å.[76] The fact that the two N−N bond distances differ significantly is in accord with the high covalency of the azido ligand in FN_3. High covalency facilitates the breakage of the longer N_α-N_β bond and favors the elimination of N_2, explaining the high shock sensitivity of these azides. There are three possible binding sites for the addition of F^+ to FN_3, with the most favorable one being that of F^+ binding to the α-position of FN_3 forming a C_s structure with a long F_2N−N_2 bond of 2.468 Å and an $-NF_2$ out-of-plane angle of 126° at the CCSD(T)/aVTZ level. The very long N−N bond of 2.468 Å indicates that $[F_2N{-}N_2]^+$ would readily lose N_2 and, therefore, would be a very unstable species. F^+ addition to the β- and γ-positions form structures of C_1 and C_2 symmetry, which are even less stable by 79.7 and 43.7 kcal/mol, respectively. Similarly, F^- can bind to FN_3 in three possible positions. Unlike the F^+ addition, the most favorable one is that of F^- binding to the γ-position of FN_3 forming a planar C_s structure (C) with N−F bond lengths of 1.608 and 1.508 Å suggesting that this anion might have marginal stability at low temperatures. F^- addition to the β-position forms structure (B) with C_s symmetry, and this structure is slightly less stable by 3.0 kcal/mol with a very long N(1)−F(3) bond length of 2.002 Å. F^- addition to the α-position leads to a dissociated structure in which F^- does not bind at the MP2/aVTZ level.

The geometry of FOOF has been reported from microwave spectroscopy[38] and electron diffraction[39] studies, as well as high-level theoretical calculations performed at the CCSD(T)(FC)/CBS[43] and the CCSD(T)/aV5Z[46] levels, both including additional corrections for higher order correlation and core−valence effects. Our MP2/aVTZ values are in reasonable agreement with the experimental and high-level computational values to within about 0.05 Å with r(O−O) being too short and r(O−F) too long.

The cationic and anionic forms of O_2F are structurally very different. The O_2F^+ cation is strongly bent ($\angle OOF = 112.9°$), has relatively short O−F and O−O bonds, and may have been experimentally observed at low temperatures.[82] The O_2F^+ cation is isoelectronic to the ozone molecule ($\angle OOO = 117.8°$),[83] consistent with the predicted bent structure. The first excited $^3A''$, state of O_2F^+ is only 4.8 kcal/mol higher in energy than the ground $^1\acute{A}$ state at 0 K. In contrast, the O_2F^- anion is a triplet, almost linear, and is best considered as a very weak complex of F^- with O_2 with a very long O−F bond distance of 2.844 Å. The triplet state results from binding the closed shell F^- to the ground state of O_2, which is a triplet. The first excited singlet state of O_2F^- is 19.9 kcal/mol higher in energy, consistent with this result and the $^3\Sigma_g^-{-}^1\Delta_g$ splitting of 22.6 kcal/mol in diatomic O_2.[76] The neutral radical O_2F has a C_s structure[43,84] with a bond angle similar to that of the O_2F^+ cation. The O−O and O−F bond distances in the neutral O_2F radical are 0.07 Å and 0.18 Å, respectively, longer than in the cation, suggesting that the radical could be less stable than the cation. The r_e of O_2 ($^3\Sigma_g^-$) is 1.2075 Å[76] and falls in between those of O_2F^+ (1.129 Å) and O_2F^- (1.228 Å).

The structure of OF_2 is of C_{2v} symmetry, and r(OF) is slightly longer by 0.040 and 0.049 Å than r(OF) of FO ($^2\Pi$) at the CCSD(T)/aVTZ level[43] and the experimental value,[85] respectively, but in good agreement with the experiment for OF_2.[86] The addition of F^+ to OF_2 results in a structure of C_{3v} symmetry with r(OF) slightly shorter than that in OF_2 by 0.027 Å at the CCSD(T)/aVTZ level, suggesting that OF_3^+ might be a marginally stable cation. Addition of F^- to OF_2 results in a planar T-shaped structure of C_{2v} symmetry with two long r(OF) distances of 1.743 Å indicating that the OF_3^- anion could readily lose an F^- anion and therefore be of low stability.

Addition of F^+ and F^- to O_2F_2 gives the compounds $O_2F_3^+$ and $O_2F_3^-$ with both structures having C_s symmetry. The $O_2F_3^+$ cation has relatively short and strong O−F bonds of about 1.38 Å but a weak O−O bond of 1.653 Å which would limit its thermal stability and could result in dissociation into OF_2 and OF fragments. In contrast, the corresponding $O_2F_3^-$ anion has a very short O=O double bond of 1.187 Å, but long and very weak O−F bonds of 1.839 and 2.073 Å, suggesting a very unstable species which could easily decompose to O_2 and fluorine.

---

(77) Toy, M. S.; Stringham, R. S. *J. Fluor. Chem.* **1976**, *7*, 229.

(78) Christe, K. O.; Schack, C. J.; Wilson, R. D. *J. Fluor. Chem.* **1978**, *11*, 183.

(79) Stringham, R. S.; Toy, M. S. Paper 74, presented at the 172nd ACS National Meeting, San Francisco, CA, Sept **1976**.

(80) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(81) Bettinger, H. F.; Schleyer, P. v. R.; Schaeffer, H. F., III *J. Am. Chem. Soc.* **1998**, *120*, 11439.

(82) Griffiths, J. E.; Edwards, A. J.; Sunder, W. A.; Falconer, W. E. *J. Fluor. Chem.* **1978**, *11*, 119.

(83) *Structure of Free Polyatomic Molecules−Basic Data*; Kuchitsu, K., Ed.; Springer-Verlag: Berlin, 1998; p77.

(84) Yamada, C.; Hirota, E. *J. Chem. Phys.* **1984**, *80*, 4694.

(85) Tamassia, F.; Brown, J.; Saita, S. *J. Chem. Phys.* **2000**, *112*, 5523.

(86) Pierce, L.; DiCianni, N.; Jackson, R. H. *J. Chem. Phys.* **1963**, *38*, 730.

Table 2. Components for Calculated Atomization Energies in kcal/mol

reactions	CBS[a]	ΔE_{ZPE}[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	ΔE_{SO}[e]	$\sum D_0(0\ K)$[f]
$NF^+ + e^- \rightarrow N + F$	−204.46	2.23	−0.34	−0.15	−0.39	−207.57
$NF \rightarrow N + F$	77.06	1.63	0.06	−0.25	−0.39	74.85
$NF^- \rightarrow N + F + e^-$	81.86	1.07	0.10	−0.26	−0.39	80.24
$OF^+ + e^- \rightarrow O + F$	−241.30	1.85	−0.30	−0.06	−0.61	−244.12
$OF^- \rightarrow O + F + e^-$	104.62	1.08	0.08	−0.23	−0.61	102.78
$F_2^+ + e^- \rightarrow 2F$	−324.57	1.60	−0.41	0.07	−0.78	−327.29
$F_2^- \rightarrow 2F + e^-$	107.35	0.64	0.14	−0.13	−0.78	105.93
$NF_2^+ + e^- \rightarrow N + 2F$	−121.90	4.65	−0.33	−0.41	−0.78	−128.07
$NF_2 \rightarrow N + 2F$	145.07	3.74	0.03	−0.51	−0.78	140.08
$NF_2^- \rightarrow N + 2F + e^-$	169.73	2.76	0.07	−0.51	−0.78	165.76
$HNF_2 \rightarrow H + N + 2F$	226.69	12.26	0.19	−0.61	−0.78	213.23
$NF_3^+ + e^- \rightarrow N + 3F$	−84.80	7.47	0.05	−0.85	−1.17	−94.24
$NF_3 \rightarrow N + 3F$	205.61	6.55	0.01	−0.67	−1.17	197.23
$NF_3^- \rightarrow N + 3F + e^-$	232.39	4.20	0.14	−0.71	−1.17	226.45
$NF_4^+ + e^- \rightarrow N + 4F$	−16.67	10.19	−0.02	−1.10	−1.56	−29.55
$NF_4 \rightarrow N + 4F$	204.33	6.70	0.02	−0.89	−1.56	195.20
$NF_4^- \rightarrow N + 4F + e^-$	298.82	6.01	−0.19	−0.84	−1.56	281.22
$NH_5 \rightarrow N + 5H$	300.51	27.38	0.52	−0.21	0.00	273.43
$NF_5 \rightarrow N + 5F$	205.76	9.94	−0.10	−1.32	−1.95	192.45
$N_2F^+ + e^- \rightarrow 2N + F$	−42.70	5.46	0.61	−0.36	−0.39	−47.70
$N_2F \rightarrow 2N + F$	227.79	3.49	0.65	−0.16	−0.39	224.40
$N_2F^- \rightarrow 2N + F + e^-$	306.50	3.55	0.75	−0.34	−0.39	306.50
cis-$N_2F_2 \rightarrow 2N + 2F$	250.89	7.27	0.38	−0.69	−0.78	242.53
trans-$N_2F_2 \rightarrow 2N + 2F$	249.45	7.12	0.40	−0.71	−0.78	241.25
TS-$N_2F_2 \rightarrow 2N + 2F$	180.82	5.78	0.71	−0.75	−0.78	174.22
$N_2F_2\ (^3B) \rightarrow 2N + 2F$	189.02	4.97	0.27	−0.69	−0.78	182.85
$F_2N = N \rightarrow 2N + 2F$	236.31	6.97	0.68	−0.73	−0.78	228.51
$N_2F_3^+ + e^- \rightarrow 2N + 3F$	24.98	10.54	0.53	−0.90	−1.17	12.89
$N_2F_3 \rightarrow 2N + 3F$	251.70	8.82	0.31	−0.88	−1.17	241.13
$N_2F_3^- \rightarrow 2N + 3F + e^-$	339.28	7.60	0.49	−0.91	−1.17	330.09
$N_2F_4\ (C_{2h}) \rightarrow 2N + 4F$	314.36	11.25	0.19	−1.11	−1.56	300.63
$N_2F_4\ (C_2) \rightarrow 2N + 4F$	314.16	11.27	0.26	−1.15	−1.56	300.45
$N_2F_5^+ + e^- \rightarrow 2N + 5F$	104.90	12.51	0.09	−1.25	−1.95	89.28
$N_2F_5^- \rightarrow 2N + 5F + e^-$	380.48	9.89	0.02	−1.35	−1.95	367.31
$FN_3 \rightarrow 3N + F$	283.76	7.91	1.00	−0.67	−0.39	275.79
$F_2N_3^+\ (\mathbf{A}, C_s) + e^- \rightarrow 3N + 2F$	112.15	9.03	0.30	−0.62	−0.78	102.02
$F_2N_3^+\ (\mathbf{B}, C_1) + e^- \rightarrow 3N + 2F$	33.68	9.90	0.21	−0.87	−0.78	22.34
$F_2N_3^+\ (\mathbf{C}, C_2) + e^- \rightarrow 3N + 2F$	68.95	10.07	0.67	−0.43	−0.78	58.33
$F_2N_3^-\ (\mathbf{B}, C_s) \rightarrow 3N + 2F + e^-$	383.94	9.21	0.99	−0.86	−0.78	378.01
$F_2N_3^-\ (\mathbf{C}, C_s) \rightarrow 3N + 2F + e^-$	386.44	8.51	0.84	−0.94	−0.78	377.05
$OF_2 + e^- \rightarrow O + 2F$	92.66	3.24	−0.10	−0.31	−1.00	88.02
$OF_3^+ \rightarrow O + 3F + e^-$	−193.54	5.42	−0.54	−0.19	−1.39	−201.08
$OF_3^- \rightarrow O + 3F + e^-$	188.37	3.65	−0.23	−0.42	−1.39	182.68
$O_2F^+\ (^1A', C_s) + e^- \rightarrow 2O + F$	−152.13	3.90	−0.31	−0.11	−0.83	−157.28
$O_2F^+\ (^3A'', C_s) + e^- \rightarrow 2O + F$	−155.25	5.64	−0.10	−0.22	−0.83	−162.04
$O_2F^-\ (^3A'', C_s) \rightarrow 2O + F + e^-$	201.19	2.18	0.30	−0.46	−0.83	198.02
$O_2F^-\ (^1A', C_s) \rightarrow 2O + F + e^-$	182.46	2.94	0.09	−0.59	−0.83	178.19
$O_2F_2 \rightarrow 2O + 2F$	149.90	5.08	−0.10	−0.46	−1.22	143.04
$O_2F_3^+ + e^- \rightarrow 2O + 3F$	−140.69	6.77	−0.60	−0.34	−1.61	−150.01
$O_2F_3^- \rightarrow 2O + 3F + e^-$	256.53	8.08	−0.12	−0.65	−1.61	246.07

[a] Extrapolated by using eq 1 with the aVnZ, n = D, T, Q basis set. [b] The zero point energies were obtained as described in the text. [c] Core−valence corrections were obtained with the cc-pwCVTZ (N, O, and F) at the optimized CCSD(T) or MP2 geometries. [d] The scalar relativistic correction is based on a CISD(FC)/VTZ MVD calculation and is expressed relative to the CISD result without the MVD correction. [e] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables, ref 71. [f] The theoretical value of the dissociation energy to atoms $\sum D_0(0\ K)$.

Frequencies. The anharmonic vibrational frequencies of NF_2,[11,12] HNF_2,[13] NF_3,[13] *cis*-N_2F_2,[16] and *trans*-N_2F_2,[13,15] N_2F_4,[19] NF_4^+,[14] $N_2F_3^+$,[18] and N_2F^+[17] have been experimentally observed, and our current and previously calculated CCSD(T)/aVTZ harmonic frequencies are in excellent agreement with them (see Supporting Information). The largest discrepancies are found for the F−N=N bend (π mode) of N_2F^+ which was calculated to be 20 cm^{-1} higher than the experimental value and the N−H stretch of HNF_2 which was calculated to be 175 cm^{-1} (a′ mode) larger than the experimental anharmonic value of 3193 cm^{-1}; the latter difference is due to the large anharmonicity correction of an N−H bond stretch. The anharmonic vibrational frequencies of FN_3 have also been reported,[20] and our calculated CCSD(T)/VTZ harmonic frequencies are in very good agreement, with a maximum discrepancy of 33 cm^{-1}, except for the N=N stretching vibration (a′ mode) which is predicted to be larger by 62 cm^{-1} than the reported gas-phase experimental value of 2037 cm^{-1}. We note that there is a small imaginary frequency at the CCSD(T)/aT level for NF_4^-, but that at the analytic MP2/aT level, the frequencies are all real for the C_{2v} structure.

Heats of Formation. The energetic components for predicting the total molecular dissociation energies are given in Table 2. We first discuss some general trends in the atomization energy components. The ΔE_{CV} corrections are small and may be positive or negative with most being less than |1.0| kcal/mol. The ΔE_{SR} corrections are all small and negative, ranging from −0.06 (OF^+) to −1.35 ($N_2F_5^-$) kcal/mol, except for F_2^+ (0.07 kcal/mol). We estimate that the error bars for the calculated heats of formation are ±1.5 kcal/mol (except for FOOF), considering errors in the energy extrapolation, frequencies, and other electronic energy components. An estimate of the potential for significant multireference character in the wave function can be obtained from the T_1 diagnostic[87] for the CCSD calculation. The values for the T_1 diagnostics (Supporting Information, Table SI-4) are small showing that the wave functions are dominated by single configurations.

The calculated heats of formation at 0 and 298 K are given in Table 3, and we use the values at 298 K in our discussion below. The heats of formation of NF_2 and NF_3 have been reported in the NIST-JANAF[8] tables, and our calculated values are in excellent agreement within 1.3 kcal/mol and within the reported error bars. Our calculated value for the heat of formation of NF is predicted to be 3.4 kcal/mol more stable than the JANAF value of 59.5 kcal/mol and within the ±7.9 kcal/mol error bars.[8] Our calculated value for the heat of formation of N_2F_4 is 2.0 kcal/mol more stable than the JANAF value of −2.0 kcal/mol,[8] and within the ±2.5 kcal/mol error bars.

Our composite CCSD(T)/CBS value for the $\Delta H_{f,298K}$(FOOF) is given simply because we needed it for the F^+ and F^- affinities. It differs from the experimental value adopted by the NIST-JANAF tables of 4.59 ± 0.5 kcal/mol[8] by 5 to 6 kcal/mol and from the best calculated value of 6.4 ± 0.7 kcal/mol by 4.5 kcal/mol, and the reasons for this have been discussed in detail.[43]

The structure, bonding, harmonic vibrational frequencies, and decomposition reactions of NF_5 have been predicted by Bettinger et al.[81] employing various correlated levels of theory up through the CCSD(T) level with basis sets of triple-ζ quality. They predict the overall reaction of $NF_5 \rightarrow NF_3 + F_2$ to be exothermic by 42.2 kcal/mol at the CCSD(T)/VTZ//CCSD/DZP level, in excellent agreement with our higher level value of 41.7 kcal/mol. We predict the decomposition of NF_5 into NF_4 (C_{3v} symmetry) and an F radical to be exothermic by 2.7 kcal/mol at the CCSD(T)/CBS//MP2/aVTZ level plus additional corrections (Table 5). The value of 8.5 kcal/mol obtained at the CCSD(T)/VTZ//CCSD/DZP + ZPVE level[81] is in qualitative agreement with our higher level value. The NF_4 radical is predicted to be unbound with respect to NF_3 + F by 2.0 kcal/mol (Table 5) at the CCSD(T)/CBS level plus additional corrections, whereas Bettinger et al.[81] find it to be weakly bound by only 0.1 kcal/mol at the CCSD(T)/VTZ//CCSD/DZP + ZPVE level. Thus, NF_5 would also readily decompose to NF_3 with the generation of two fluorine radicals in an exothermic reaction (−4.8 kcal/mol). Unlike the analogous fluorine counterpart, the trigonal bipyramidal form of NH_5 (D_{3h}) is not predicted to be a minimum at the CCSD(T)/aVTZ level with an imaginary frequency of 982.4 cm^{-1} (a_2'' mode). Given $\Delta H_{f,0K}(NH_3)$[8,88] the decomposition pathway of $NH_5 \rightarrow NH_3 + H_2$ is predicted to be highly exothermic by 106.9 kcal/mol which is greater than the bond energy[8] in H_2, so two H atoms will be readily formed.

Table 3. Calculated Heats of Formation (kcal/mol) at 0 and 298 K

molecule	$\Delta H_f(0\ K)_{theory}$	$\Delta H_f(298\ K)_{theory}$	$\Delta H_f(298\ K)_{expt}$
NF^+ ($^2\Pi$, $C_{\infty v}$)	338.6	338.6	
NF ($^3\Sigma^-$, $C_{\infty v}$)	56.1	56.1	59.5 ± 7.9[8]
NF^- ($^2\Pi$, $C_{\infty v}$)	50.8	50.8	
OF^+ ($^3\Sigma^-$, $C_{\infty v}$)	321.6	321.6	
OF^- ($^1\Sigma^+$, $C_{\infty v}$)	−25.3	−25.3	
F_2^+ ($^2\Pi_g$, $D_{\infty h}$)	364.2	364.2	
F_2^- ($^1\Sigma^+{}_g$, $D_{\infty h}$)	−69.0	−69.0	
NF_2^+ ($^1A_1$, C_{2v})	277.5	276.8	
NF_2 ($^2B_1$, C_{2v})	9.4	8.8	10.1 ± 1.9[8]
NF_2^- ($^1A_1$, C_{2v})	−16.3	−16.8	
HNF_2 ($^1A'$, C_s)	−12.1	−13.7	
NF_3^+ ($^2A_1$, C_{3v})	262.2	260.8	
NF_3 ($^1A_1$, C_{3v})	−29.3	−30.7	−31.6 ± 0.3[8]
NF_3^- ($^2A'$, C_s)	−58.5	−58.9	
NF_4^+ (^1A_g, T_d)	216.0	213.8	
NF_4 ($^2A_1$, C_{3v})	−8.8	−9.6	
NF_4^- ($^1A_1$, C_{2v})	−94.5	−93.4	
NH_5 ($^1A_1'$, D_{3h})	97.3	93.7	
NF_5 ($^1A_1'$, D_{3h})	12.4	10.1	
N_2F^+ ($^1\Sigma_g$, $C_{\infty v}$)	291.2	290.6	
N_2F ($^2\Sigma_g$, $C_{\infty v}$)	19.1	19.5	
N_2F^- ($^1A'$, C_s)	−63.0	−62.8	
cis-N_2F_2 ($^1A_1$, C_{2v})	19.5	18.1	16.4 ± 1.2[8]
trans-N_2F_2 (^1A_g, C_{2h})	20.8	19.5	19.4 ± 1.2[8]
TS-N_2F_2 ($^1A'$, C_s)	87.8	86.8	
N_2F_2 (^3B, C_2)	79.1	78.0	
$F_2N = N$ ($^1A_1$, C_{2v})	33.5	32.4	
$N_2F_3^+$ ($^1A'$, C_s)	267.6	265.6	
N_2F_3 (^2A, C_1)	39.3	37.6	
$N_2F_3^-$ (^1A, C_1)	−49.6	−50.8	
N_2F_4 (^1A_g, C_{2h})	−1.7	−4.0	−2.0 ± 2.5[8]
N_2F_4 (^1A, C_2)	−1.5	−3.9	
$N_2F_5^+$ ($^1A'$, C_s)	228.1	230.6	
$N_2F_5^-$ (^1A, C_1)	−49.9	−51.1	
FN_3 ($^1A'$, C_s)	80.3	79.0	
$F_2N_3^+$ ($^1A'$, C_s, **A**)	272.5	271.8	
$F_2N_3^+$ (^1A, C_1, **B**)	352.2	350.4	
$F_2N_3^+$ (^1A, C_2, **C**)	316.2	314.5	
$F_2N_3^-$ ($^1A'$, C_s, **B**)	0.5	−1.1	
$F_2N_3^-$ ($^1A'$, C_s, **C**)	−2.5	−4.0	
OF_2 ($^1A_1$, C_{2v})	7.9	7.4	
OF_3^+ ($^1A_1$, C_{3v})	315.5	314.2	
OF_3^- ($^1A_1$, C_{2v})	−68.3	−68.9	
O_2F^+ ($^1A'$, C_s)	293.7	293.3	
O_2F^+ ($^3A''$, C_s)	298.5	298.4	
O_2F^- ($^3A''$, C_s)	−61.6	−62.3	
O_2F^- ($^1A'$, C_s)	−41.7	−42.0	
O_2F_2 (^1A, C_2)	11.9	10.9	4.6 ± 0.5[8] 5.9 ± 0.4[9] 4.6 ± 0.2[9] 4.7 ± 0.3[10]
$O_2F_3^+$ ($^1A'$, C_s)	323.4	321.4	
$O_2F_3^-$ ($^1A'$, C_s)	−72.7	−74.0	

Ionization Potentials and Electron Affinities. The ionization potentials (IP) and electron affinities (EA) for a number of the molecules are given in Table 4. For the diatomics, the agreement with experimental data[89−93] is

---

[87] Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

[88] Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129.

[89] (a) Dyke, J. M.; Jonathan, N.; Mills, J. D. *Mol. Phys.* **1980**, *40*, 1177. (b) Zhang, Z.; Kuo, S.-C.; Klemm, R. B.; Monks, P. S. *Chem. Phys. Lett.* **1994**, *229*, 377.

[90] Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *J. Chem. Phys.* **1992**, *96*, 8012.

[91] Van Lonkhuyzen, H.; De Lange, C. A. *Chem. Phys.* **1984**, *89*, 313.

[92] Wenthold, P. G.; Squires, R. R. *J. Phys. Chem.* **1995**, *99*, 2002.

[93] Dyke, J. M.; Jonathan, N.; Lewis, A. E.; Morris, A. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1445.

Table 4. Calculated Ionization Potentials (IP) and Electron Affinities (EA) of the N_xF_y and O_xF_y Compounds in eV at 0 K

molecule	IP (eV)	IP expt	EA eV	EA expt
F_2	15.79	15.697 ± 0.003[90]	2.99	3.005 ± 0.071[91]
FO	12.80	12.77[88]	2.24	2.2720 ± 0.0060[89]
NF	12.25	12.26 ± 0.01[92]	0.23	0.50[57]
NF_2	11.63	11.63 ± 0.01[93]	1.11	1.21 ± 0.20[94] 1.10 ± 0.10[95]
NF_3	12.64	12.94 ± 0.01[97]	1.27	
NF_4	9.75		3.72	
N_2F	11.80		3.56	
N_2F_3	9.90		3.86	
trans-N_2F_2	12.69	12.8[96]		
cis-N_2F_2	13.28			

Table 5. Calculated A−F Bond Dissociation Energies (BDE) of the N_xF_y and O_xF_y Compounds in kcal/mol at 0 K

molecule	product	BDE
NF	N + F	74.9
NF_2	NF + F	65.2
NF_3	NF_2 + F	57.2
NF_4	NF_3 + F	−2.0
NF_5	NF_4 + F	−2.7
N_2F	N_2 + F	−0.6
N_2F_2	N_2F + F	18.1
$F_2N{=}N$	N_2F + F	4.1
N_2F_3	N_2F_2 + F	57.8
N_2F_4	N_2F_3 + F	59.5
OF	O + F	51.2
OF_2	OF + F	36.9

good with the largest error in the ionization potential being 0.1 eV for F_2 and the largest error in the electron affinity being ~0.25 eV for NF. Our calculated value for EA(NF) is in excellent agreement within 0.02 eV of the value of 0.247 eV reported using even larger basis sets with double diffuse functions.[56] There are no experimental details[57] reported for the experimental value of 0.5 eV so this value needs to be remeasured. The difference in the IP of F_2 is most likely due to the difference in the vertical and adiabatic values. At the CCSD(T)/CBS level with the aug-cc-pV*n*Z basis sets for n = D, T, Q, the difference in the vertical and adiabatic IPs (ΔE_{elec}) is 0.17 eV, consistent with this argument. This suggests that there may be differences in the calculated and experimental IPs because the calculated value is an adiabatic value and the experimental value is an extrapolation of a vertical value to the adiabatic value.

The calculated adiabatic IP and EA for NF_2 are in excellent agreement with experiment.[94−96] The calculations show that the predicted adiabatic IP for *trans*-FNNF agrees within 0.1 eV with the experimental value[97] of 12.8 eV which is only given to one decimal place accuracy. The calculated IP of 13.28 eV of the *cis*-N_2F_2 is substantially higher. This difference in the ionization potentials for the cis and trans isomers is considerably larger than those in *cis*- and *trans*-1,2-difluoroethylene where the IPs are within 0.02 eV of each other.[98] The calculated IP for NF_3 is 0.3 eV below the experimental value.[99] Examination of the spectra shows a broad photoionization peak. We calculated the ΔE_{elec} component of the difference for the vertical and adiabatic ionization potentials of NF_3 at the CCSD(T)/CBS level and predict a substantial difference of 1.19 eV. The large difference in the adiabatic and vertical IPs is due to the substantial changes in the geometry of ~0.1 Å in r(N−F) and of ~12° in the F−N−F bond angle. We further checked this by calculating the ionization potential of NH_3. The difference in the adiabatic and vertical values is 0.74 eV. The calculations show that it is very difficult to extrapolate from the vertical to the adiabatic value for NF_3. At the CCSD(T)/CBS level, the vertical and adiabatic ionization potentials for *cis*- and *trans*-N_2F_2 are also predicted to have large differences of 0.77 and 0.82 eV, respectively.

The electron affinity of NF_3 of 1.27 eV is surprisingly large for a closed shell molecule. The electron affinities of NF_4, N_2F, and N_2F_3 are all comparable and up to 0.5 eV larger than that of 3.40 eV for the F atom.[8]

A−F Bond Dissociation Energies. The adiabatic bond dissociation energies (BDEs) at 0 K, in which dissociation of the reactant occurs to the ground states of the separated product species, are given in Table 5. The series NF, NF_2, NF_3 exhibits a moderate substituent effect. The addition of one F atom results in a decrease of the BDE from 74.9 kcal/mol in NF to 57.2 kcal/mol in NF_3. NF_4 and NF_5 are predicted to have negative bond energies and are metastable species as discussed above. For N_2F, there are two possible dissociation pathways with the formation of N_2 + F being favored by 150 kcal/mol over that resulting in NF + N. The N−N BDE in N_2F is 149.6 kcal/mol, about 75 kcal/mol less than that in N_2.[44,76] The N−F BDE in N_2F_2 is predicted to be 18.1 kcal/mol, that is, to be 57 kcal/mol lower than that in diatomic N−F. The N−F BDE in the $F_2N{=}N$ isomer has a small value of 4.1 kcal/mol and is 14.0 kcal/mol less than that in N_2F_2. The N−F BDEs in N_2F_3 and N_2F_4 are predicted to have moderately high values of about 59 kcal/mol, to be within 2 kcal/mol of each other, are bracketed by the N−F BDEs of NF_2 and NF_3, and are 17.1 and 15.4 kcal/mol less, respectively, than that of diatomic NF. The O−F BDEs in OF_2 and OF have intermediate values of 36.9 and 51.2 kcal/mol, respectively, and the BDE of OF_2 is predicted to be 14.3 kcal/mol lower than that in diatomic OF.[45]

F^+ and F^- Affinities. Given the experimental $\Delta H_{f,0\mathrm{K}}$(F^+) = 419.40 and $\Delta H_{f,0\mathrm{K}}$(F^-) = −59.96 kcal/mol, we can predict the F^+ and F^- affinities of the N_xF_y and O_xF_y compounds defined as $-\Delta H$ for the representative reactions of N_2F_y:

$$N_2F_y + F^+ \rightarrow N_2F_{y+1}{}^+ \tag{3}$$

$$N_2F_y + F^- \rightarrow N_2F_{y+1}{}^- \tag{4}$$

The calculated F^+ and F^- affinities at 0 K are given in Table 6. The F^+ cation affinity (FCA) within the N_2F_y series increases from N_2 to N_2F_4 with the FCA of N_2F_2 being 44 kcal/mol higher than that of N_2, and FCA(N_2F_4) being 18 kcal/mol larger than FCA(N_2F_2). The FCA(N_2F_2) and FCA(N_2F_4) are toward the more positive end of the previously reported oxidizer strength scale[1] with values comparable to those of XeF_2O (173 kcal/mol) and ClFO (193 kcal/mol), respectively, indicating that the corresponding cations are only moderately strong oxidizers. The FCA(N_2F_4) is 4 kcal/mol lower and the FCA(NF) is 4.6 kcal/mol higher than that of the N atom. The FCA(N_2) falls in the less positive range of the oxidizer scale[1] with a value that is bracketed by FCA(O_2)

Table 6. Calculated F^+ and F^- Affinities of the N_xF_y and O_xF_y Compounds in kcal/mol at 0 K

molecule	F^+	F^-
N	193.4	1.8
O	156.8	24.3
F	73.6	27.5
NF	198.0	12.5
NF_2	166.6	7.9
NF_3	174.1	5.2
N_2	127.0	−1.5
cis-N_2F_2	171.3	9.1
trans-N_2F_2	172.6	10.4
FN_3	227.2	22.8
N_2F_4	189.6	−11.8
O_2	125.7	1.6
OF_2	111.8	16.2
O_2F_2	107.9	24.6

(126 kcal/mol) and FCA(BrF_3O) (131 kcal/mol). Therefore, N_2F^+ is a relatively strong oxidative fluorinator. The FCA(NF_2) and FCA(NF_3) are comparable to FCA(N_2F_2) and are in the more positive end of the oxidizer strength scale,[1] making NF_3^+ and NF_4^+ only moderately strong oxidizers. With FCA(FN_3) of 227.2 kcal/mol, $F_2N_3^+$ is predicted to be the weakest oxidizer of the compounds studied.

Although FCA(O_2) and FCA(N_2) are very similar and differ only by 1.3 kcal/mol, FCA(O_2F_2) is very different from FCA(N_2F_2), with $O_2F_3^+$ being a considerably stronger oxidizer than $N_2F_3^+$. The oxidizing power of $O_2F_3^+$ also exceeds that of O_2F^+ by 18 kcal/mol, contrary to the large decrease of 44 kcal/mol in oxidizing power predicted for going from N_2F^+ to $N_2F_3^+$. The oxidizing power of OF_3^+ falls between those of O_2F^+ and $O_2F_3^+$, while OF^+ is predicted to be the weakest oxidizer among the group of oxygen fluoride cations studied.

Neither N_2 nor N_2F_4 is predicted to bind F^-, and for N_2, this is consistent with the expected interaction between the closed-shell atomic anion F^- and the very stable N_2 molecule. As would be expected as well, there is no place for F^- to interact with N_2F_4 without encountering an electron pair, so it too does not bind F^-. N_2F_2 is a very weak Lewis acid with an F^- affinity (FA) of about 10 kcal/mol for either the cis or trans isomers; structurally, $N_2F_3^-$ is a weakly bound complex of N_2F_2 and F^-. NF_2 and NF_3 are also predicted to be very weak Lewis acids, as is NF with FA(NF) $\sim$ 13 kcal/mol. The FA(FN_3) is the largest compared to the other N_xF_y compounds studied and at 23 kcal/mol is almost two times that of NF. However, its value is still too low for the probable existence of a room-temperature stable $N_3F_2^-$ salt. The FA(NF_3) of 5.2 kcal/mol is one of the smallest for the NF_x compounds, and 2.7 kcal/mol smaller than FA(NF_2) and only 3.4 kcal/mol larger than FA(N).

Unlike N_2, O_2 is predicted to have a small, but positive F^- affinity, indicating a weak complex of O_2 with F^- that is slightly more stable than the separated $O_2 + F^-$ reactants. The F^- affinities of O_2 and N are essentially the same, but FA(O) is predicted to be 23 kcal/mol higher than those of O_2 and N. The FA(O_2F_2) is positive and its Lewis acidity increases by 23 kcal/mol upon F_2 addition to O_2. OF_2 is a very weak Lewis acid and its FA falls in between FA(O_2) and FA(O_2F_2). Of all the molecules and atoms of this study, F has the highest F^- affinity, slightly above those of O and O_2F_2, but none can be considered to exhibit significant Lewis acidity.

NF_4 Radical. The lowest unoccupied molecular orbital (LUMO) of NF_4^+ (T_d symmetry) is an a_1 orbital so the addition of an electron to give neutral NF_4 does not necessarily lead to a distortion. The equivalent C_{2v} structure of NF_4 is not a minimum based on a harmonic vibrational analysis at the MP2/aVTZ level (one imaginary frequency of 628.1 cm^{-1} (b_1 mode)). A search for the minimum of NF_4 led to a C_{3v} structure with a long N−F bond of 2.702 Å along the C_3 axis and an N−F distance in the NF_3 moiety of 1.369 Å, 0.002 Å shorter than the N−F distance in NF_3 ($^1A_1$) at the MP2/aVTZ level. The C_{3v} structure of NF_4 is best described as a loose complex of an F atom weakly interacting with NF_3, and is predicted to be minimum at the MP2/aVTZ level with two low frequencies of 15.3 cm^{-1} (e mode), corresponding to an N−F wag, and 56.0 cm^{-1} (a_1 mode), corresponding to the unique N−F stretch. The IP of NF_4 is predicted to be 9.75 eV, substantially lower than that in other NF compounds consistent with the formation of a more stable NF_4^+ ion.

Bronsted Acidity of HNF_2 and the Elusive NF_2^- Anion. The gas phase acidity ($HNF_2 \rightarrow NF_2^- + H^+$) can be predicted ($\Delta H_f(H^+, 0\ K) = 365.22$ kcal/mol),[8,100] and the enthalpic contribution to the deprotonation energy is 361.1 kcal/mol. There have been many unsuccessful attempts to isolate the corresponding NF_2^- anion.[101] A likely explanation for these failures is the ease with which NF_2^- can lose an F^- anion to form NF, which can then readily dimerize in a highly exothermic reaction (92.8 kcal/mol at the CCSD(T)/CBS level plus additional corrections) to form N_2F_2 with the formation of an N═N double bond. We predict the enthalpy of the reaction $NF_2^- \rightarrow NF + F^-$ (-FA(NF), Table 6) to be only 12.5 kcal/mol at 0 K, showing that NF_2^- is only marginally stable toward F^- loss. The possibility of NF_2^- dissociating to $NF^- + F$ radicals is much less likely because this pathway is highly endothermic by 85.5 kcal/mol.

Conclusions

We have predicted the heats of formation of a number of small neutral and ionic N_xF_y and O_xF_y systems at the CCSD(T) level plus additional corrections. The calculated heats of formation and stabilities are in good agreement with the available experimental values, except for FOOF because of the exclusion of higher order correlation effects in this

---

(94) Berkowitz, J.; Greene, J. P.; Foropoulos, J., Jr.; Neskovic, O. M. *J. Chem. Phys.* **1984**, *81*, 6166.

(95) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S. Z.; Hu, L. Q.; Sung, K. S.; Desmarteau, D. D.; Yagupolskii, L. M. *J. Am. Chem. Soc.* **1994**, *116*, 3047.

(96) Ruckhaberle, N.; Lehmann, L.; Matejcik, S.; Illenberger, E.; Bouteiller, Y.; Periquet, V.; Museur, L.; Desfrançois, C.; Schermann, J.-P. *J. Phys. Chem. A* **1997**, *101*, 9942.

(97) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451.

(98) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*(Supplement 1), 83.

(99) Ruede, R.; Troxler, H.; Beglinger, C.; Jungen, M. *Chem. Phys. Lett.* **1993**, *203*, 477.

(100) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 2576.

(101) Lawless, E. W.; Smith, I. C. *Inorganic High-Energy Oxidizers, Synthesis, Structure, and Properties*; Marcel Decker, Inc.: New York, 1968.

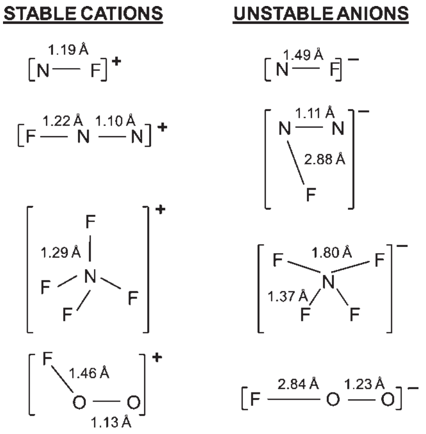

Figure 2. Summary of structures of the stable cations and unstable anions.

molecule. The cations are in general more stable than the anions (Figure 2). The F^+ affinities of the N_2F_y molecules increase by 44 kcal/mol from N_2 to N_2F_4 whereas those of the O_2F_y molecules exhibit an opposite trend with a notable decrease of 18 kcal/mol from O_2 to O_2F_2. Neither N_2 nor N_2F_4 are predicted to bind F^-, whereas N_2F_2 is a very weak Lewis acid with an F^- affinity of about 10 kcal/mol for either the cis or trans isomer. O_2 is predicted to have a small but positive F^- affinity while that of O_2F_2 is also positive and increases by 23 kcal/mol upon F_2 addition to O_2.

Acknowledgment. This research was supported, in part, by the U.S. Department of Energy, Office of Basic Energy Research, Chemical Sciences, in the catalysis program and by the National Science Foundation (CTS-0608896) through the NIRT program. The Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory is a national user facility funded by the Office of Biological and Environmental Research in the U.S. Department of Energy. The Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute. K.O.C. is indebted to the Air Force Office of Scientific Research, the Office of Naval Research, the Defense Threat Reduction Agency, and the National Science Foundation for financial support.

Supporting Information Available: Total CCSD(T) energies (Table SI-1) as a function of basis set; calculated CCSD(T)/aVTZ and MP2/aVTZ frequencies (cm^{-1}) (Table SI-2); components for calculated reactions energies in kcal/mol (Table SI-3); and T_1 diagnostics calculated at the CCSD(T)/aVQZ level (Table SI-4). This material is available free of charge via the Internet at http://pubs.acs.org.