J|A|C|S
COMMUNICATIONS

The Electric Dipole Polarity of the Ground and Low-Lying Metastable Excited States of NF

Gerard S. Harbison*

Department of Chemistry University of Nebraska at Lincoln, Lincoln, Nebraska 68588-0304

Received March 30, 2001

Fluorine is the most electronegative of the elements, and therefore in covalent compounds the fluorine atom almost invariably carries a net negative charge. The sole exceptions known to date are the molecule BF, stable in the gas phase or at low temperatures under matrix isolation, and the radical CF•. The experimental dipole moment of BF (±0.5 ± 0.2 D)[1] has been shown convincingly, by ab initio methods,[2,3] to have a negative sign.[4] This phenomenon is readily explained by boron's Lewis acidity, which leads to π donation from the fluorine, and an electronic structure resembling the isoelectronic carbon monoxide and dinitrogen. CF•, similarly, has an experimental dipole moment of ±0.645 D,[5] which high-level theory[6] suggests should be negative. Carbon monoxide is of course the best known example of a diatomic with a negative dipole moment.

NF (nitrogen monofluoride, fluoroimidogen) is of comparable stability to BF. It was first prepared by photolytic decomposition of FN_3 in an argon matrix at 4 K, and characterized by infrared spectroscopy.[7] It has subsequently been studied in the gas phase by electronic,[8,9] infrared,[10] microwave,[11,12] and EPR[13] spectroscopy. Its ground-state electron configuration is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^2$$

The twin degenerate 2π orbitals are occupied by two electrons, resulting in six configurations. The $X\ {}^3\Sigma^-$ ground state of NF is a triplet, like dioxygen, with which it is isoelectronic. There are two metastable low-lying excited singlet states—the two-fold degenerate $a\ {}^1\Delta$ state, whose radiative lifetime at room temperature is 5.6 s, and the $b\ {}^1\Sigma^+$ state (lifetime 22 ms). Both have been well characterized by microwave spectroscopy.[11,12] NF in the $a\ {}^1\Delta$ state can readily be prepared from the near-stoichiometric reaction of NF_2 with hydrogen atoms, which two reactants can in turn be obtained by electrical discharge through an NF_3/H_2 mixture.[14] Chemically generated metastable NF can transfer energy to other gas-phase molecules, and this process has been proposed as the basis of a chemical laser.[15]

The dipole moment of the $a\ {}^1\Delta$ state was measured by Stark effect electron paramagnetic resonance at 0.37 ± 0.06 D;[13] since early Hartree−Fock *ab initio* calculations[16] had predicted a small positive dipole moment, that polarity was assumed in the experimental study. More recent configuration interaction calculations[17] have noted that the dipole moment of NF becomes more positive with increasing bond length (a common characteristic of diatomics)[18] but have not definitively established the polarity in the equilibrium or vibrational ground-state configuration of any of the electronic states.

Diatomics such as NF can now be modeled to very high accuracy by modern electronic structure methods. In particular, multireference perturbation theory, which starts from a set of reference configurations obtained by using multiconfigurational self-consistent field methods to optimize an active set of molecular orbitals,[19] and then second order quasidegenerate perturbation theory (MCQDPT)[20] to calculate perturbation corrections for the remainder of the basis, can with a reasonable basis set reproduce bond potentials and electrostatic properties such as the dipole moment and nuclear quadrupole coupling constant with a high degree of accuracy. It has been shown[19] that MCQDPT has an accuracy comparable to second-order multireference configuration interaction methods, and it is computationally considerably cheaper. It is a reasonable assumption that, if known experimental parameters such as the equilibrium bond-length r_e, the equilibrium vibrational frequency ω_e, the ^{14}N nuclear quadrupole coupling constant e^2qQ/h, and the magnitude of the dipole moment $|\mu|$ have been calculated accurately, then the computed sign of the dipole moment, which has not yet been determined experimentally, is correct.

Calculations employed the program GAMESS,[21] using the standard triple-ζ[22] valence basis set including diffuse functions, and three *d* and one *f* polarization functions. MCSCF wave functions were calculated using the Ames determinantal multiconfigurational self-consistent field algorithm, at bond distance intervals of 0.02 Å for ±0.28 Å around the experimental equilibrium bond lengths. For the MCSCF calculations, the 1s orbitals of nitrogen and fluorine were frozen and the remaining electrons calculated over an active set comprising the next lowest 14 Hartree−Fock orbitals, which included 6 orbitals of A_1 symmetry, four of B_1 symmetry and four of B_2 symmetry, in the Abelian C_{2v} subgroup of C_v. This included all orbitals through the nominal $3p\pi^*$ antibonding pair. Second order perturbation corrections to the energies were computed using these wave functions, using the MCDQPT method employing second-order configuration interaction. Computed bond potentials for the three lowest-energy nondegenerate states, identified by their symmetries and their spin multiplicities, were fit to order-8 polynomials, and the vibrational Schrödinger equation was solved by an eigenvalue method using a harmonic oscillator eigenbasis. The dipole moment μ and the electric field gradient at the nitrogen nucleus $eq = (\nabla E)_{zz}$ were computed at all distances and averaged over the ground-state MCDQPT vibrational wave function. A ^{14}N quadrupole moment Q of 20.5×10^{-30} m^2 was assumed[23] in calculating e^2Qq/h.

Values for important computed parameters are compared with experiment in Table 1. It should be noted that these values are more accurate than those obtained from a MCSCF calculation using the same active set ($r_e = 1.3362$ Å, $\omega_e = 1095$ cm^{-1}, $\mu = 0.154$ D, $e^2qQ/h = 4.447$ MHz for the $^3\Sigma^-$ state; $r_e = 1.3060$ Å, $\omega_e = 1208$ cm^{-1}, $\mu = -0.391$ D, $e^2qQ/h = 3.960$ MHz for the $^1\Delta$ state) and far more accurate than restricted open-shell Hartree−Fock results. The computed quadrupole coupling constants coincide with experiment within the experimental accuracy of the ^{14}N quadrupole

10.1021/ja0159261 CCC: $22.00

Table 1. Selected Experimental and Calculated Molecular Properties of the Three Low-Lying States of NF

	$X\,^3\Sigma^-$		$a\,^1\Delta$		$b\,^1\Sigma^+$	
	exptl	calcd	exptl	calcd	exptl	calcd
T_e (cm^{-1})			11435[a]	11979	18877[b]	19393
(kcal/mol)			32.7	34.2	54.0	55.4
r_e (Å)	1.3170[b]	1.3204	1.3040[c]	1.3067	1.2998[d]	1.2977
ω_e (cm^{-1})	1141[e]	1135	1182[d]	1162	1198[d]	1221
μ_0(D)		0.076	$\pm0.37 \pm 0.06$[f]	-0.388		-0.483
e^2qQ/h (MHz)		4.439	4.037[d]	4.024	4.267[d]	4.309

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 12. [e] Reference 10b. [f] Reference 13.

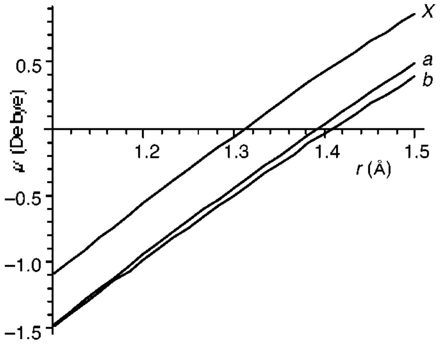
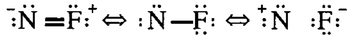


Figure 1. Computed variation in dipole moment with bond distance, for the three lowest-energy states of NF.

moment, while the vibrational frequencies and equilibrium bond lengths are satisfactorily close to experimental values.

Figure 1 shows the variation in computer dipole moment with bond distance for the three states, computed by MCSCF methods. As has previously been reported,[3] the dipole moment increases with increasing r. This increase can be rationalized from a simple electron-dot picture:



$$^{-}{:}\ddot{N}{=}\ddot{F}{:}^{+} \Leftrightarrow {:}\ddot{N}{-}\ddot{F}{:} \Leftrightarrow {}^{+}{:}\ddot{N}\quad {:}\ddot{F}{:}^{-}$$

which suggests that as the bond-order increases (with decreasing NF bond length) negative charge should shift from the fluorine to the nitrogen.

The dipole moments at the equilibrium bond distance of both of the metastable states are clearly negative; averaged over the ground vibrational state, the computed moment of the $^1\Delta$ state falls well within the error limits of the experiment, as long as the moment is negative in sign. Our calculations predict that the $b\,^1\Sigma^+$ state should have a dipole moment of −0.45, more negative than the $a\,^1\Delta$ by about 0.06 D.

The driving force for this counterintuitive molecular polarity can be rationalized as the desire for nitrogen to complete its octet, which is achieved by the lefthand-most Lewis structure. It is intriguing that the nitrogen atom in this compound is acting as a strong Lewis acid, in a similar way to boron, and unlike a nitrogen acting as a Lewis base.

The dipole moment for the triplet state is significantly more positive over the entire range of bond lengths. Our calculations predict a small positive moment of 0.07 D, which will probably be difficult to measure. The more positive ground-state moment can again be rationalized from a simple Lewis dot picture; the triplet state, since it is not spin-paired, cannot be reconciled with octet configurations around nitrogen and fluorine, and thus will tend to disfavor the left-hand Lewis structure and concentrate less negative charge on the nitrogen.

Therefore, while triplet NF is almost non-polar, with a slightly positive dipole moment, both of the low-lying singlet states have significant negative dipole moments. This study adds yet another member to the already substantial set of anomalously polar first and second row diatomics, which has so far included BF, CO, and the radical CF•.[18]

Acknowledgment. This work was supported by NSF (MCB-9605421).

References

(1) Lovas F. J.; Johnson, D. R. *J. Chem. Phys.* **1971**, *55*, 41.
(2) Yoshimine, M.; McLean, A. D. *Int. J. Quantum Chem.* **1967**, *S1*, 313.
(3) Kurtz, H. A.; Jordan, K. D., *Chem. Phys. Lett.* **1981**, *81*, 104.
(4) A dipole moment whose sign disagrees with predictions from standard electronegativity values is defined as negative.
(5) Saito, S.; Endo, Y.; Takami, M.; Hirota, E. *J. Chem. Phys.* **1971**, *55*, 41.
(6) Rendell, A. P.; Bauschlicher, C. W.; Langhoff, S. R. *Chem. Phys. Lett.* **1989**, *163*, 354−358.
(7) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1964**, *40*, 2461.
(8) Jones, W. E. *Can. J. Phys.* **1966**, *45*, 21.
(9) Douglas, A. E.; Jones, W. E. *Can. J. Phys.* **1966**, *44*, 2251.
(10) (a) Davies, P. B.; Hamilton, P. A.; Okumura, M.*J. Chem. Phys.* **1981**, *75*, 4294. (b) Davies, P. B.; Rothwell, W. J. *Proc. R. Soc. London, Ser. A* **1983**, *389*, 205.
(11) Yamamoto, S.; Saito, S. *J. Chem. Phys.* **1987**, *86*, 102.
(12) Kobayashi, K.; Saito, S. *J. Chem. Phys.* **1998**, *108*, 6606.
(13) Curran, A. H.; Macdonald, R. G.; Stone, A. J.; Thrush, B. A. *Proc. R. Soc. London, Ser. A* **1973**, *332*, 355.
(14) Malins, R. J.; Setser, D. W. *J. Phys. Chem.* **1981**, *85*, 1342.
(15) Benard, D. J. *J. Phys. Chem.* **1996**, *100*, 8316−8322.
(16) O'Hare, P. A. G. *J. Chem. Phys.* **1973**, *59*, 3842.
(17) Yarkony, D. R. *J. Chem. Phys.* **1986**, *85*, 7261.
(18) Huzinaga, S.; Miyoshi, E.; Sekiyat, M. *J. Comput. Chem.* **1993**, *14*, 1440.
(19) Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233.
(20) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983.
(21) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(22) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.
(23) Cummins, P. L.; Bacskay, G. B.; Hush, N. S.; Ahlrichs, R. *J. Chem. Phys.* **1987**, *86*, 6908.

JA0159261