thank Professors Roald Hoffmann and Charles Levin for making computer programs available to us.

## Appendix

Extended Hückel calculations[23] were performed by using the weighted $H_{ij}$ formula.[24] The atomic parameters used are listed in Table II with the molybdenum parameters taken from ref 25. A double-ζ expansion was used for the d orbitals. Geometrical parameters used to model the open doubly bridged and closed quadruply bridged dimers are given in Table III.

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# The $F_3NO^-$ Radical Anion. ESR Spectra, Structure, and Its Dissociation to $F_2NO$

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*Received October 14, 1980*

**Abstract:** The isotropic ESR spectrum of $F_3NO^-$ in the $SF_6$ matrix has been obtained under conditions which minimize interference from signals due to other radicals and expose additional lines to those previously observed. These results confirm the higher order analysis of the spectrum in terms of hyperfine interaction with one nitrogen and three equivalent fluorines, exact matrix diagonalization calculations yielding the parameters $^{14}a(1) = 148.5 \pm 1.5$ G, $^{19}a(3) = 194.5 \pm 0.5$ G, and $g = 2.014 \pm 0.001$. The $C_{3v}$ symmetry suggested by these results is supported by INDO calculations which indicate that this geometry is preferred to those of trigonal-bipyramidal ($C_s$) structures. In contrast, theoretical calculations of the $g$ factor provide no clear-cut basis for discriminating between these various structures. Evidence was obtained for the dissociation of $F_3NO^-$ to $F_2NO$ on annealing the $SF_6$ matrix through the phase transition at 94 K, and this reaction is interpreted with reference to the characteristics of the semioccupied molecular orbital of $F_3NO^-$.

Some time ago, two of us reported the discovery of the hypervalent radical anion $F_3NO^-$,[6] a species of considerable interest in being the first example of a 33 valence electron radical composed only of first-row elements to compare with the well-established family of phosphoranyl radicals, including the formally analogous $Cl_3PO^-$[7] and $F_3PO^-$[8] radical anions. Subsequently, the related hypervalent species $c$-$C_nF_{2n}^-$ ($n$ = 3–6)[9,10] and $CF_3X^-$ (X = Cl, Br, I)[10,11] were generated by electron addition to halides of saturated carbon. However, attempts in our laboratory[1] to produce the congeneric radicals $NF_4$ and $CF_4^-$ have met with failure although the methods used were exactly analogous to those which yield their second-row central atom counterparts $PF_4$[12] and $SiF_4^-$,[13] and, to the best of our knowledge, $F_3NO^-$ remains the only known member of the potential class of 33 valence electron radicals drawn from first-row elements. Since $F_3NO^-$ can also be regarded, in a formal sense, as having nine electrons accommodated around nitrogen, its uniqueness extends to an even larger class of electron-excess radicals based on first-row central atoms, including potentially important but hypothetical species such as $CH_4^-$, $NH_4$, $H_3O$, $NH_3^-$, and $H_2O^-$.

A thorough study of $F_3NO^-$ therefore appeared to be warranted, and this paper extends the earlier communication[6] in three respects. First, we report the detection of two spectral components which were masked by hydrogen atom signals in the previously reported ESR spectrum.[6] These additional lines have allowed a more stringent test of the spectral analysis in terms of hyperfine interaction with one $^{14}N$ and three $^{19}F$ nuclei. Second, the structure of $F_3NO^-$ has been probed by theoretical calculations, the aim being to see if the $C_{3v}$ structure naturally suggested by the experimental results is preferred to the alternative model of a trigonal-bipyramidal ($C_s$) structure in which there is rapid exchange of the fluorine ligands between the axial and equatorial sites on the ESR time scale. The structure of $F_3NO^-$ assumes particular importance in view of mounting evidence since 1975 that some phosphoranyl[14,15] and other hypervalent radicals of this type[10,11,16] assume local $C_{3v}$ symmetry rather than the more common quasi-trigonal-bipyramidal structure[7,17-20] originally

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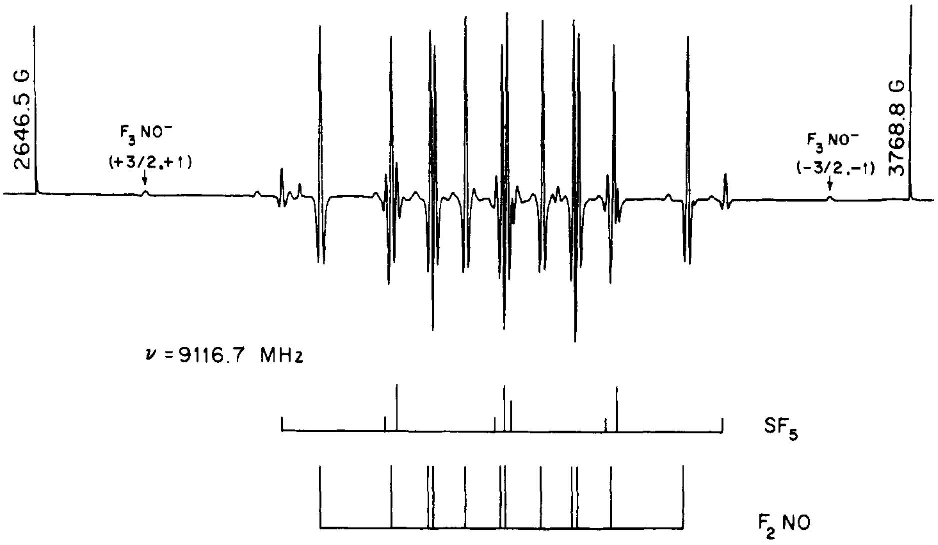

**Figure 1.** Second-derivative ESR spectrum of a γ-irradiated solid solution of 5 mol % of $F_3NO$ in $SF_6$ recorded at ca. 105 K. The sample was prepared in a Suprasil quartz tube and γ irradiated at 77 K.

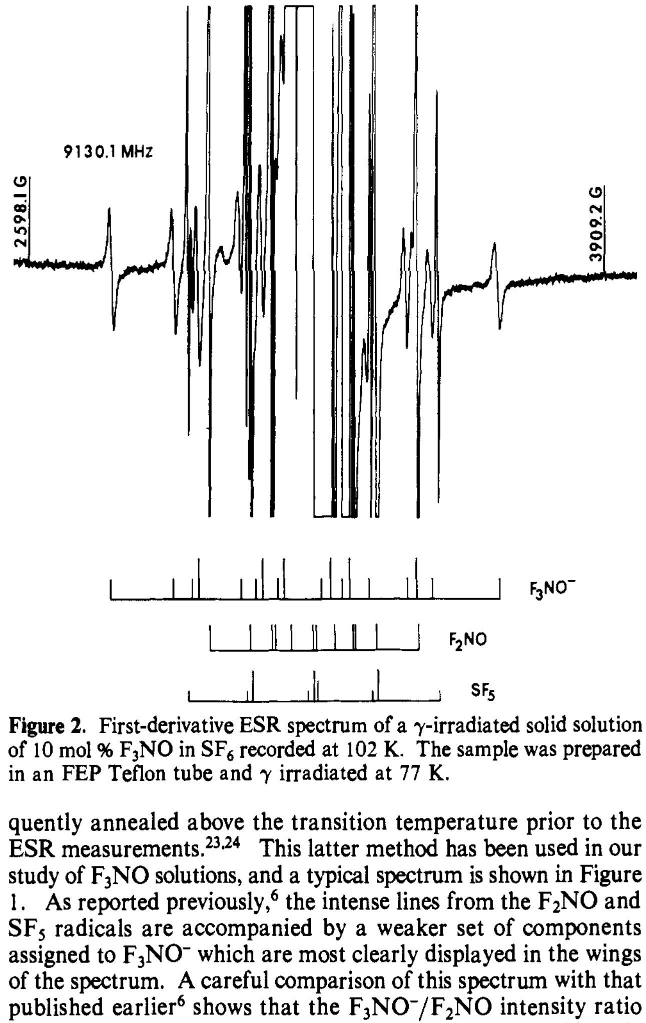

**Figure 2.** First-derivative ESR spectrum of a γ-irradiated solid solution of 10 mol % $F_3NO$ in $SF_6$ recorded at 102 K. The sample was prepared in an FEP Teflon tube and γ irradiated at 77 K.

thought to be characteristic of penta-atomic radicals possessing 33 valence electrons.[21]

Finally, in view of the large $F_2NO/F_3NO^-$ signal intensity ratio reported previously,[6] we have sought direct evidence for the dissociation of $F_3NO^-$ to $F_2NO$ under the annealing conditions which are commonly employed in ESR experiments with the $SF_6$ matrix.[6,12] This possible reaction is particularly interesting in terms of a $C_{3v}$ structure for $F_3NO^-$ since it would necessarily involve the elimination of a ligand from one of the trigonal sites rather than from the axial site, in contradistinction to the observed dissociation of $CF_3Cl^-$ into $CF_3$ and $Cl^-$.[10]

## Experimental Section

A sample of trifluoramine oxide was kindly supplied by Dr. F. Q. Roberto of the Air Force Rocket Propulsion Laboratory (MKPA), Edwards AFB, CA 93523. Solid solutions containing up to 10 mol % of $F_3NO$ in a sulfur hexafluoride (Matheson) matrix were prepared by standard vacuum techniques in Spectrosil (Thermal American Fused Quartz Company, Montville, NJ 07045), Suprasil (Heraeus-Amersil, Inc., Sayreville, NJ 08872), and FEP Teflon (Fluorocarbon Process Systems Division, Anaheim, CA 92803) tubes. The samples were irradiated at 77 K with γ-rays from a $^{60}Co$ source (Gammacell 200, Atomic Energy of Canada Ltd.), the typical dose being ca. 0.5 Mrad.

ESR measurements as described elsewhere[10] were carried out on the γ-irradiated samples at various temperatures. Sample temperatures in the range between 80 and 94 K were conveniently obtained by using a stream of cold nitrogen gas generated by an electric heater placed inside a 30-L LAB-30 storage dewar (Minnesota Valley Engineering, New Prague, MN 56071), the desired temperature being attained by adjusting the boil-off rate, while higher temperatures were obtained by using the standard V-4557 variable-temperature accessory and V-4540 controller units (Varian, Instrument Group, Palo Alto, CA 94303). ESR measurements at temperatures lower than 77K were carried out by means of the Heli-Tran LTD-3-110B1 liquid-helium-transfer refrigerator system (Air Products & Chemicals, Inc.).

## Results

**ESR Studies.** In order to obtain isotropic ESR spectra from trapped radicals in the $SF_6$ matrix, the spectra must usually be recorded with the radicals present in the rotator phase above the solid–solid transition temperature of 94 K.[12,22] Although the technique of in situ electron-beam irradiation originally employed by Fessenden and Schuler[12,22] for studies of solid $SF_6$ has obvious advantages for the detection of short-lived radicals, successful results have also been obtained with this matrix when the radicals are generated by γ irradiation at 77 K and the sample is subsequently annealed above the transition temperature prior to the ESR measurements.[23,24] This latter method has been used in our study of $F_3NO$ solutions, and a typical spectrum is shown in Figure 1. As reported previously,[6] the intense lines from the $F_2NO$ and $SF_5$ radicals are accompanied by a weaker set of components assigned to $F_3NO^-$ which are most clearly displayed in the wings of the spectrum. A careful comparison of this spectrum with that published earlier[6] shows that the $F_3NO^-/F_2NO$ intensity ratio is appreciably larger in the present case, suggesting that this ratio could be determined by the dissociation of $F_3NO^-$ under the annealing conditions which, of course, may not be exactly reproducible from one experiment to another. This question will

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Table I. Optimized Geometries and Energies for the $F_3NO^-$ Radical Anion[a]

| $\angle F_{ax}NF_{ax}$[b] | $E_{total}$ | N-O | N-$F_{ax}$ | N-$F_{eq}$ | $\angle ONF_{eq}$ | $\angle ONF_{ax}$ |
|---|---|---|---|---|---|---|
| 109.5 ($C_{3v}$) | −2946.244 | 1.256 | 1.295 | 1.295 | 109.5 | 109.5 |
| 130 ($C_s$) | −2946.050 | 1.260 | 1.307 | 1.279 | 109.6 | 107.2 |
| 150 ($C_s$) | −2945.339 | 1.266 | 1.311 | 1.281 | 111.2 | 101.2 |
| 180 ($C_s$) | −2943.027 | 1.278 | 1.323 | 1.288 | 116.5 | 90.0 |

[a] Bond distances in Å, bond angles in degrees, and total energy in eV. [b] This starting parameter was held constant in the energy minimization procedure.

be explored after we have given an analysis of the isotropic ESR spectrum assigned to $F_3NO^-$.

An unsatisfactory feature of the $F_3NO^-$ spectrum obtained from the samples prepared in synthetic quartz tubes is that the low-field line of the hydrogen atom obscures the resolution of the two 1:2 second-order components which should be associated with line 3 of $F_3NO^-$.[6] In the present study, we have removed this source of interference by using tubes made of FEP Teflon which, after exposure to $\gamma$ radiation, give rise to a very broad ESR signal at $g \approx 2.00$ but yield no detectable signals from hydrogen atoms. The advantage of using samples contained in FEP Teflon tubes is illustrated by the spectrum in Figure 2 which shows that the two ($M_I^F$, $M_I^N = +^1/_2, +1$) predicted components of line 3 in the $F_3NO^-$ spectrum are now clearly resolved between the outermost lines of $SF_5$ and $F_2NO$ at low field. The spectral analysis for $F_3NO^-$ is also confirmed by the partial resolution of the two ($M_I^F$, $M_I^N = -^1/_2, -1$) components from line 10 situated just inside the strong outermost component of $F_2NO$ at high field and by the fact that 10 out of the total of 12 lines are well-defined, the other two (lines 7 and 8) being masked by the strong signals from the sample tube in the center of the spectrum. The ESR parameters were derived by fitting the field positions of the transitions as computed by an exact diagonalization of the energy matrix constructed from the spin Hamiltonian[10] to the measured line positions, this procedure giving $g = 2.014 \pm 0.001$, $^{14}a(1) = 148.5 \pm 1.5$ G, and $^{19}a(3) = 194.5 \pm 0.5$ G as the best-fit values with the coupling constants having the same sign. As a further check on the equivalence of the three fluorines, the measured second-order splittings for lines 3 and 10 are 14.5 and 20.0 (±0.5) G, respectively, in excellent agreement with the corresponding values of 14.5 and 19.9 G calculated according to the above parameters. Thus, the spectral analysis in terms of hyperfine interaction with one $^{14}N$ and three equivalent $^{19}F$ nuclei has been verified both qualitatively and quantitatively.

We now return to consider the possible chemical changes which take place in the $\gamma$-irradiated $F_3NO/SF_6$ system when the $SF_6$ matrix is annealed from 77 K to above the phase transition at 94 K. In the earlier communication,[6] it was noted that the ESR spectrum of $F_2NO$ in $SF_6$ showed very little anisotropic broadening at 77 K, as judged by the retention of the second-order $^{19}F$ splittings characteristic of the isotropic spectrum. This observation has now been exploited to monitor changes in the $F_2NO$ radical concentration resulting from the annealing of the matrix, and the ESR spectra measured at 81 K before and after annealing are presented in Figure 3. It is clear from these spectra that while the $F_2NO$ radical is present initially at 81 K, this radical also grows in to a considerable extent on annealing. At the same time, there is a corresponding decrease in some of the outer spectral features. These broad anisotropic lines shown at high spectrometer gain in the upper spectrum are easily differentiated from the prominent features in the powder spectrum of the $SF_6^-$ radical[25,26] which can be observed at 81 K after $\gamma$ irradiation of pure $SF_6$ at 77 K. Also, they clearly do not belong to the anisotropic spectrum of the $SF_5$ radical[25] which is marked by arrows in the lower spectrum. Therefore, by elimination, we attribute these broad lines to the anisotropic spectrum of the $F_3NO^-$ radical. Accordingly, the irreversible spectral changes which take place on annealing the sample through the transition point and back (Figure 3) can be interpreted as arising from the thermal dissociation of the $F_3NO^-$ radical anion to give the neutral $F_2NO$ radical by loss of a fluoride anion.

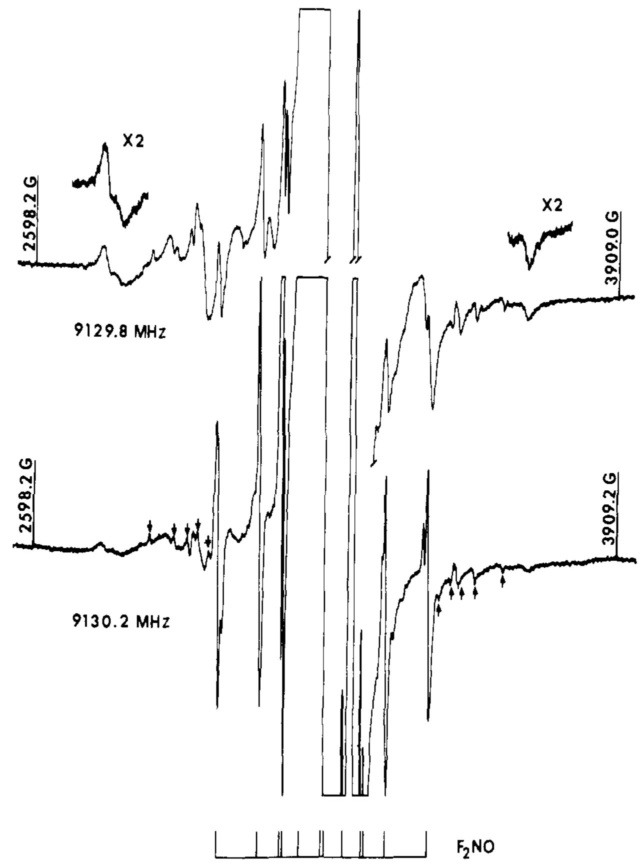

Figure 3. First-derivative ESR spectrum of a $\gamma$-irradiated solid solution of 10 mol % $F_3NO$ in $SF_6$ recorded with the same spectrometer settings at 81 K (a) before and (b) after annealing the sample to 102 K. The sample was prepared in an FEP Teflon tube and $\gamma$ irradiated at 77 K. The arrows in the lower spectrum (b) designate features belonging to the anisotropic spectrum of the $SF_5$ radical.

There is no trace of the $SF_6^-$ powder pattern[25,26] in the anisotropic spectrum of the $\gamma$-irradiated $F_3NO/SF_6$ solid solution observed at 81 K before annealing (Figure 3), and likewise there are no detectable signals from the isotropic spectrum of $SF_6^-$[23] in the spectra of these solutions recorded above the transition temperature (Figures 1 and 2). When one considers that $SF_6^-$ is readily observed under both conditions following $\gamma$ irradiation of the pure $SF_6$ matrix,[23-26] these results are remarkable in showing that $F_3NO$ undergoes electron capture almost exclusively despite the fact that $SF_6$ is present in a tenfold higher concentration and that it is generally considered to be an efficient electron scavenger.

**Theoretical Calculations.** The structure of the $F_3NO^-$ radical was examined theoretically by the INDO MO method. The total energy of $F_3NO^-$ was calculated by the INDO-UHF method[27] in which the $F_{ax}NF_{ax}$ angle was fixed at a certain value and the other geometrical parameters were optimized. The optimized structure and the total energy for each fixed $F_{ax}NF_{ax}$ angle are

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Table II. Calculated Spin Densities and *g* Factors for the $F_3NO^-$ Radical Anion

| | $C_{3v}$[a] | $C_s$[b,c] | | |
|---|---|---|---|---|
| $\angle F_{ax}NF_{ax}$ | 109.50 | 130° | 150° | 180° |
| $\rho_{2s(N)}$ | 0.2650 | 0.2426 | 0.2124 | 0.1619 |
| $\rho_{2s(F_{ax})}$ | 0.0153 | 0.0159 | 0.0128 | 0.0077 |
| $\rho_{2s(F_{eq})}$ | 0.0153 | 0.0072 | 0.0024 | −0.0032 |
| $g_1$ | 2.0059 | 2.0063 | 2.0071 | 2.0108 |
| $g_2$ | 2.0043 | 2.0054 | 2.0060 | 2.0064 |
| $g_3$ | 2.0043 | 2.0033 | 2.0031 | 2.0041 |
| $g_{av}$ | 2.0048 | 2.0050 | 2.0054 | 2.0071 |
| relative energy,[d] eV | 0.000 | 0.309 | 0.859 | 2.868 |

[a] For the $C_{3v}$ structure, the g tensor is axially symmetric with $g_1 = 2.0059$ being the principal value in the direction parallel to the N–O bond. [b] For the $C_s$ structures, the tensor components $g_1$ and $g_2$ have their directions in the $ONF_{eq}$ plane while $g_3$ is the component perpendicular to this plane. [c] Diagrams showing the principal directions of the g tensor components are given in the supplementary material filed with this paper. Also, a table showing the complete spin distribution calculated by the INDO-UHF method for the $C_{3v}$ and $C_s$ structures is included in this material. [d] These relative energies do not correspond to the energies listed in Table I and were obtained from the UHF energies for the corrected structures, as explained in the text.

listed in Table I. As shown in Table I, the $C_{3v}$ structure is more stable than the trigonal-bipyramidal $C_s$ structures. Actually, the full geometry optimization which starts from the $C_s$ structure gave the $C_{3v}$ structure as the most stable one for the $F_3NO^-$ radical. The INDO-UHF method therefore predicts the $C_{3v}$ structure for the $F_3NO^-$ radical.

It should be noted that the experimental structure for the neutral $F_3NO$ molecule ($C_{3v}$, N–O = 1.159 Å, N–F = 1.432 Å, and ∠ONF = 119.4°)[28] differs from the results of the closed-shell INDO calculation on $F_3NO$, the latter yielding values of 1.249 Å, 1.261 Å, and 115.0° for the N–O and N–F distances and the ONF angle, respectively. If the structural change from the neutral $F_3NO$ molecule to the $F_3NO^-$ radical anion is assumed to be estimated correctly by the INDO calculation, the N–O and N–F bond distances in the $F_3NO^-$ radical can be obtained from the values listed in Table I together with the calculated and observed values for the neutral $F_3NO$ molecule. In the following calculations of the spin distribution and *g* factors for $F_3NO^-$, the N–O and N–F bond distances corrected by this method were employed.

The spin densities on the 2s AO's of the N and F atoms calculated by INDO-UHF are listed in Table II. The spin distribution on the N and F atoms of the $C_{3v}$ structure agree quite well with the observed values $\rho_{2s(N)} = 0.27$ and $\rho_{2s(F)} = 0.011$,[29] although the values for the $C_s$ structure are also close to the experimental values. Thus, the similarity in the calculated spin distributions does not discriminate between the $C_{3v}$ and $C_s$ structures, as has been pointed out in the previous paper.[6]

Since the *g* factors of a radical correlate strongly with the structure of the radical, it was thought that a theoretical calculation of the *g* factors for $F_3NO^-$ might shed additional light on the present structural problem. We thus calculated the *g* factors of $F_3NO^-$ according to Stone's formula.[30] The restricted MO's which are necessary for the evaluation of the *g* factors were obtained by the approximate open-shell SCF version proposed by Longuet-Higgins and Pople.[31] The calculated *g* factors are listed in Table II. As may be seen from Table II, the difference in the calculated *g* factors for the $C_{3v}$ and $C_s$ structures of $F_3NO^-$ is not very large, and it is difficult to decide on the structure from the present *g* factor calculation. The $g_{av}$ value of the $C_s$ structure with $\angle F_{ax}NF_{ax} = 180°$ is closest to the experimental value ($g_{av} = 2.014$), but this structure possesses a total energy which is much higher than that of the optimized $C_{3v}$ structure (Table II). The calculated $g_{av}$ values (2.005–2.007) are much smaller than the observed value. This discrepancy may come partially from the INDO approximation which overestimates the excitation energies; if the MINDO/3 approximation[32] is employed, the value of $g_{av} = 2.010$ is obtained for the $C_{3v}$ structure. Hence, the present analysis of *g* factors does not indicate the preferred structure of the $F_3NO^-$ radical.

## Discussion

**Identification and Structure of $F_3NO^-$.** In addition to the structural arguments which are advanced in some detail below, chemical evidence also points to $F_3NO^-$ as the species under consideration. Electron capture by $F_3NO$ is clearly implicated by the virtual absence of $SF_6^-$, the primary product of electron capture in the pure $SF_6$ matrix,[23] among the radicals produced by the radiolysis of $F_3NO/SF_6$ solid solutions. Additional chemical evidence for the intermediacy of $F_3NO^-$ is provided by the large yield of $F_2NO$, the expected radical product from the dissociation of the radical anion, which grows in on annealing the sample after irradiation.

The analysis of the isotropic spectrum attributed to $F_3NO^-$ demonstrates unequivocally that the three fluorines are equivalent on the ESR time scale. This result implies that, unless $F_3NO^-$ is a fluxional molecule (vide infra), the radical anion retains the $C_{3v}$ symmetry of the parent molecule.

When $F_3NO^-$ was first reported, serious consideration was also given to the possibility of a trigonal-bipyramidal ($C_s$) structure since this geometry was thought at the time to be characteristic of the valence isoelectronic phosphoranyl radicals. Indeed, $F_3PO^-$ is known and assumes a $C_s$ structure.[8,33] More recently, however, it has become clear that certain phosphoranyl radicals such as $Ph_3PCl$ adopt a $C_{3v}$ structure,[14,15] so that in general there seems to be a delicate balance between the trigonal and trigonal-bipyramidal configurations for radicals of this generic type. As a further illustration of this dichotomy, $SO_2F_2^-$ possesses a trigonal-bipyramidal ($C_{2v}$) geometry with the two fluorines occupying the axial sites,[33] whereas the isoelectronic species $FClO_3^-$ prefers a $C_{3v}$ arrangement with the fluorine in the axial position.[34] In the light of these recent findings, we suggest that special justification for a $C_{3v}$ structure in the case of $F_3NO^-$ is no longer needed and that the choice between this and the fluxional $C_s$ structure should be considered only on the basis of the pertinent evidence.

Although the ESR measurements on $F_3NO^-$ were restricted to the temperature range between 10 and ca. 110 K, no evidence was obtained for fluxional behavior. That is, no substantial change occurred in the anisotropic ESR spectrum from 94 down to 10 K, while the isotropic spectrum also remained the same between 94 and 110 K. Since we have shown that the three fluorines are exactly equivalent in the isotropic spectrum, these results cannot be compatible with a fluxional $C_s$ structure unless the rate of fluorine ligand exchange between the axial and equatorial positions remains fast on the ESR time scale down to 10 K. This situation is very unlikely in view of studies showing that fluorophosphoranyl radicals undergo such rapid exchange only at temperatures above 200 K.[35] The above argument assumes, of course, that the $SF_6$ phase transition of itself does not bring about a sudden onset of fast exchange in $F_3NO^-$, and this possibility is thought to be remote.

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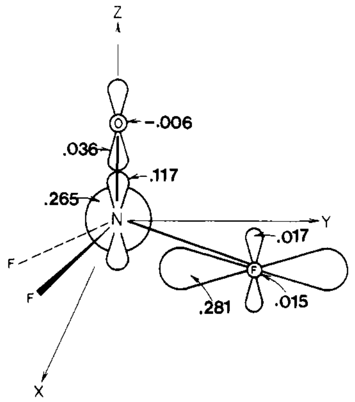

**Figure 4.** The spin density distribution obtained by INDO calculations for the energy-minimized $C_{3v}$ structure of $F_3NO^-$. The total spin density of 1.36 obtained from the values shown here can be explained by the presence of large negative spin densities in the other AO's.

Strong support for the $C_{3v}$ structure also comes from the INDO calculations (Table I) showing that this geometry corresponds to the energy minimum for the $F_3NO^-$ radical anion. At the same time, it must be admitted that the calculated values for the spin distribution and the isotropic $g$ factor (Table II) are relatively insensitive to the choice of structure, so that comparison of these INDO predictions with the experimental results does not discriminate between the two possibilities. It should be mentioned, however, that the experimental spin densities $\rho_{2s(N)} = 0.27$ and $\rho_{2s(F)} = 0.011$ are in very good agreement with the corresponding values of 0.265 and 0.015 predicted by the INDO calculations for the $C_{3v}$ structure, so that the limitation of the INDO method in this connection is simply one of structural discrimination.

The possibility that the spectrum has been misassigned may now be considered briefly. Given the spectral analysis and the observation of $F_2NO$ as a daughter product, the only other conceivable choice is $F_3NO^+$, although this species would seem to be an unlikely candidate as a precursor of $F_2NO$ by loss of $F^+$. Fortunately, this chemical intuition can be reinforced by a much more direct argument on the basis of the large value for the spin density in the nitrogen 2s orbital. For $F_3NO^+$, the unpaired electron would be expected to occupy one of the degenerate 6e orbitals in $C_{3v}$ symmetry,[36] and INDO calculations show that these orbitals are essentially lone pairs on the oxygen atom which are perpendicular to the threefold axis.[37] Consequently, only a small spin density on nitrogen would be expected for the radical cation, and this is clearly at variance with the experimental value. We also note here that the ESR parameters assigned to $F_3NO^-$ are quite different from those obtained for $NF_3^+$.[38]

It is interesting that while both $F_3NO^-$ and $CF_3Cl^-$ adopt a $C_{3v}$ geometry, their counterparts $F_3PO^-$[8,33] and $SiF_3Cl^-$[19c] with central atoms from second-row elements prefer to take up the trigonal-bipyramidal ($C_s$) configuration. Furthermore, the results for radical anions obtained from $CH_3X$ and $SiH_3X$ (X = Cl, Br, I) are noteworthy. ESR spectra of methyl radical–halide ion adducts were obtained when methyl halides were irradiated in acetonitrile matrices.[39] The adduct was considered to represent an intermediate stage in the dissociation process of a radical anion $CH_3X^-$ with $C_{3v}$ symmetry and to be composed of a planar methyl radical interacting weakly with an $X^-$ ion. In contrast to this result, the $SiH_3X^-$ radical anions detected in tetramethylsilane ($Me_4Si$) matrices were revealed to have a trigonal-bipyramidal structure with a halogen X and a hydrogen in the axial positions and two hydrogens in the equatorial positions.[19b] These comparisons all tend to suggest that trigonal-bipyramidal structures are less probable when the central atom is a first-row element rather than a second-row element. However, this conclusion should certainly not be construed to mean that $C_{3v}$ structures are never formed by hypervalent radicals of this class when the central atom is a second-row element, and examples have been mentioned earlier.[14,15,34]

**Dissociation of $F_3NO^-$.** We now consider whether the electronic structure of $F_3NO^-$ has a strong bearing on its preferred mode of dissociation into $F_2NO$. The spin distribution obtained by INDO calculations for the $C_{3v}$ structure is illustrated in Figure 4, and it can be seen that the semioccupied $a_1$ molecular orbital is composed largely of the 2s and $2p_z$ orbitals of nitrogen and of the $2p_\sigma$ orbitals of the trigonal fluorines. This combination is essentially antibonding between nitrogen and the three fluorines. In contrast, there is very little spin density in the $2p_z$ orbital of oxygen, and the combination of this orbital with the $2p_z$ orbital on nitrogen is bonding. It is natural to expect, therefore, that dissociation of the radical anion involves the scission of an N–F rather than an N–O bond, as observed.

It is also possible to visualize the evolution of the $F_2NO$ radical[6,40,41] in the course of $F_3NO^-$ dissociation by means of the orbital diagram (Figure 4). As one of the N–F bonds lengthens, so the $C_{3v}$ symmetry of the radical anion will be lost and the unpaired electron will increasingly reside in the 2s and 2p orbitals of nitrogen. In the limit of complete dissociation, the unpaired electron will be in an sp-hybrid orbital of pyramidal $F_2NO$[6,40,41] directed approximately along the broken N–F bond resulting from the expulsion of a fluoride anion.

As mentioned in the Introduction, the dissociation of $F_3NO^-$ differs from that of $CF_3Cl^-$ insofar as the ligand is expelled from the axial site in the latter.[10,11] However, this contrast in the dissociation behavior of $C_{3v}$ radical anions can be reconciled with the difference in detailed electronic structure between these two radical anions. Although the unpaired electron in $CF_3Cl^-$ also occupies an $a_1$ orbital, this is now concentrated along the symmetry ($z$) axis and is composed mainly of the antibonding combination of the 2s and $2p_z$ orbital of the central (carbon) atom with the $3p_z$ orbital of the (chlorine) ligand in the axial site. A similar description of the semioccupied orbital holds for $CF_3Br^-$,[10,11] $CF_3I^-$,[10,11] $Ph_3PCl$,[14] $O_3ClF^-$,[34] and, by extension, for the non $C_{3v}$ radicals $(MeO)_2P(S)Br^-$[15] and $CF_2(CONH_2)Br^-$[42] where bromine is the pseudo axial ligand. Thus, the fact that the $CF_3$ and $ClO_3$ radicals are produced by the dissociation of the $CF_3X^-$ (X = Cl, Br, I)[10,11] and $O_3ClF^-$[34] radical anions, respectively, with the release of the axial ligand can be easily rationalized in terms of the spin distribution and the antibonding character of the semioccupied orbital in these radical anions. Therefore, the dissociation of $F_3NO^-$ as well as of these other $C_{3v}$ radical anions is determined by electron distribution rather than by the forced withdrawal of the ligand from a particular geometrical site (trigonal or axial).

**Acknowledgment.** This research was supported at the University of Tennessee by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Report No. DOE/ER/02968-132). We thank Dr. G. Mamantov (University of Tennessee) and Dr. F. Q. Roberto (Edwards AFB, CA) for supplying us with a sample of trifluoramine oxide, and Dr. C. M. L. Kerr (National Research Council, Ottawa) for carrying out some of the matrix diagonalization calculations.

**Supplementary Material Available:** A table listing the INDO-UHF spin densities and diagrams showing the principal directions of the calculated **g** tensor components for the $C_{3v}$ and $C_s$ structures of the $F_3NO^-$ radical anion (3 pages). Ordering information is given on any current masthead page.

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