Neon Matrix ESR and CI Theoretical Investigation of AlF⁺; Photoionization of AlF from Thermal and Laser Sputtering Generation Methods

Lon B. Knight, Jr.,*1 Edward Earl,† A. R. Ligon,‡ D. P. Cobranchi,‡ J. R. Woodward,* J. M. Bostick,* E. R. Davidson,† and David Feller†

Contribution from the Chemistry Department, Furman University, Greenville, South Carolina 29613, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. Received February 27, 1986

Abstract: The high-temperature AlF⁺ radical cation has been generated by the photoionization of AlF(g) produced both by a laser sputtering method and high-temperature vaporization reactions. This represents the first spectroscopic study of AlF⁺ and establishes its ground electronic state as \( \text{^2}S \). The ESR spectrum of the AlF⁺ radical, isolated in a neon matrix at 4 K, has been analyzed in detail, and the experimental magnetic parameters obtained show excellent agreement with the results of an extensive \( \alpha \)-initio theoretical calculation. The AlF⁺ magnetic parameters in a neon matrix are the following: \( g_\perp = 2.08 \), \( g_\parallel = 2.65 \), \( A_{\perp} = 2782 \pm 1 \) MHz, \( A_{\parallel} = 473 \pm 6 \) MHz, \( D_{\perp} = 90 \pm 5 \) MHz. The electronic structure of AlF⁺ is compared to the isoelectronic series \( ^{26}\text{SiO}^+ \), AlO, and MgF utilizing both experimental and theoretical findings. Orbital populations for the unpaired electron were obtained from the commonly applied free atom comparison method (FACM) and from a Mulliken type population analysis of a CI wave function which yielded magnetic parameters in close agreement with experiment. The effect of "core-other valence overlap" was studied in detail for this isoelectronic series. This AlF⁺ study and a previous one for SiO⁺ are apparently the first ESR investigations of high-temperature inorganic cation radicals.

Generation and trapping techniques have been developed to permit the ESR (electron spin resonance) investigation of small, highly reactive cations having relatively large electron affinities in neon matrices near 4 K. Examples of cations recently studied by ESR with these neon matrix trapping techniques include \( \text{CO}^+ \), \( \text{NH}_2^+ \), \( \text{N}_2^+ \), \( \text{H}_2\text{O}^+ \), \( \text{Cd}^+ \), \( \text{CH}_4^+ \), \( \text{C}_2\text{H}_5^+ \), and the high-temperature cation radical \( ^{26}\text{SiO}^+ \). Experimental results have also been obtained for a few anion radicals trapped in neon matrices as free ions including \( \text{F}^- \), \( \text{HF}^- \), \( \text{H}_2\text{O}^- \), \( \text{Cd}^- \), \( \text{CH}_4^- \), \( \text{C}_2\text{H}_5^- \), and \( \text{H}_2\text{CO}^- \), and \( \text{N}_2H^+ \). The \( \text{Cl}_2^- \) and \( \text{HCl}^- \) radicals have been previously studied by ESR as chemically bonded ion pairs, \( \text{M}^+\text{X}^- \), in argon matrices.\(^{1,2}\) The inert nature of the neon host, its low polarizability, and large ionization energy (21.6 eV) allow free or gas-like properties of ions to be obtained. Cations having electron affinities much greater than 10–11 eV apparently cannot be stabilized in other matrix materials such as argon or freon matrices. Paramagnetic ions trapped in frozen ionic solutions or crystalline hosts can be highly perturbed, and the information obtained might not accurately represent the inherent properties of the trapped species.

This AlF⁺ study illustrates that the matrix isolation trapping method could be applied to a wide range of charged and neutral chemical systems produced by reactive laser sputtering processes. The reactive intermediates produced by such laser induced gas-surface reactions could be characterized by the wide range of spectroscopic methods currently used with the matrix isolation technique. Current research efforts in our laboratory are using this laser technique to produce metal nitride neutral and cation radicals for ESR matrix studies. The feasibility of combining high-temperature vaporization and various ion generation techniques with the neon matrix isolation method for ESR spectroscopy has been demonstrated in a recent report.\(^{29}\) \( ^{26}\text{SiO}^+ \) was the first high-temperature (>1000 K) cation radical studied by ESR with any experimental approach.\(^{3}\) Many high-temperature neutral radicals have been investigated via the ESR matrix method, and the results have been presented in a recent monograph on the subject.\(^{13}\) This AlF⁺ study, which also utilizes high-temperature vaporization, extends the experimental capabilities to laser sputtering generation of the desired neutral species (AlF⁻). Vibration studies of AlF in neon, argon, and krypton matrices were reported in earlier work.\(^{14}\) High-temperature vaporization

1 Furman University.
2 Indiana University.

---

References:

(10) Knight, L. B., Jr.; Cobranchi, D. P.; Ligon, A. R., to be published.

© 1986 American Chemical Society

0002-7863/86/1508-5065$01.50/0
cryostat (Air Products) was used to cool a thin copper matrix deposition of AlF₃(s). The KrF excimer laser (Lumonics) sputtering technique developed for these ESR matrix studies was described in previous reports.¹,² The electron bombardment ion generation procedure used in combination with a high-temperature Knudsen effusion oven was described in previous reports.¹,²* The high-temperature vaporization reduction reaction of AlF₃(s) plus Al(s) was conducted in resistively heated tantalum IR matrix apparatus. Exactly the same vaporization conditions were repeated in the ESR apparatus with the same Knudsen cell. The major differences were that neon matrices were formed with the neon resonance photolization lamp operating during deposition and the trapping surface was copper rather than the CsI window employed in the IR matrix apparatus.

Results
ESR Spectral Analysis of AlF⁺. Neon matrix deposition of AlF⁺ from either the laser or high-temperature source under ionizing conditions (either electron bombardment or photolization) produced the same ESR spectra that consisted of a sextet of doublets for both the perpendicular (θ = 90°) and parallel (θ = 0°) directions. This is the expected pattern for AlF⁺ since I = 1/2 for ²⁷Al and I = 1/2 for ¹⁹F. The large amount of ¹⁹F A tensor anisotropy caused “extra” or off-angle features that for some transitions were more intense than the usually dominant θ = 0° lines where θ is the angle between the applied magnetic field and the molecular symmetry axis of AlF⁺.

Given the extremely large magnitude of the Al hfs, A₁ = 994 (2) G, the various ESR transitions extended from 323 to 5770 G for the X-band microwave frequency of 9570 MHz. Second-order approximations are not appropriate for such large hfs, and

ANgULAR DEPENDENCE
ALLOWED AIF TRANSITIONS

Figure 2. Angular dependence of the allowed ESR hyperfine lines of AIF\(^+\) obtained from an exact diagonalization treatment is shown by using the magnetic parameters listed in Tables I and II for a neon matrix sample. The angle plotted (\(\theta\)) is the angle between the molecular axis of AIF\(^+\) and the applied magnetic field. The field position corresponding to the free spin value is denoted by \(g_e\). See Figure 3.

an exact diagonalization treatment of the following axially symmetric spin Hamiltonian had to be used to extract the magnetic parameters from the observed ESR line positions listed in Table I. The inclusion of nuclear Zeeman and \(^{27}\text{Al}\) quadrupole terms

\[ H = g_e \beta H S_z + g_e \delta (H S_x + H S_y) + \left[ A_2 S_x S_z + A_1 (I_x S_z + I_z S_x) + A_1 (I_y S_z + I_z S_y)\right]_{\text{Al}} \]

did not affect the excellent agreement between calculated and observed lines for quadrupole constants in the range predicted by the ab initio CI calculations. See Table IV.

The resulting 24 \(\times\) 24 spin energy determinants were solved as a function of \(\theta\) and the applied magnetic field for a given set of input parameters with the assistance of various quadratic interpolation schemes whose accuracy was checked at numerous specific points. The 24 \(\theta\)-dependent magnetic energy levels obtained from these determinants were combined in all reasonable combinations and weighted according to calculated transition probabilities. These angular and field-dependent transitions were then coupled to a first derivative Lorentzian line shape function for direct comparison with the experimental ESR spectra. To assist in the assignment of off-angle or extra transitions, \(\theta \text{ vs. } H_{\text{RES}}\) plots were also generated from the diagonalization process. As shown by the data in Table I, all of the expected ESR lines were observed, and their positions, phases, and relative intensities exhibited agreement with the calculated positions well within the experimental uncertainties. Figures 2 and 3 present the overall spectral characteristics of AIF\(^+\), showing line positions, \(\theta \text{ vs. } H_{\text{RES}}\) dependencies, and simulated first derivative spectra of all transitions. Figures 4–6 present various spectral regions in a more expanded scale format where direct comparison between simulated and experimental spectra are made. The lowest field transitions

\[ \Delta M = 0, \quad \Delta M = 1 \]

\(\theta = 0^\circ\) lines
(parallel)
\(\theta = 90^\circ\) lines
(perpendicular)

<table>
<thead>
<tr>
<th>(\theta = 0^\circ) lines</th>
<th>(\theta = 90^\circ) lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{obsd}^a)</td>
<td>(\text{calcd}^b)</td>
</tr>
<tr>
<td>AI</td>
<td>(M_z = \frac{1}{2})</td>
</tr>
<tr>
<td>F</td>
<td>(M_z = \frac{1}{2})</td>
</tr>
</tbody>
</table>

\*All calculated line positions in gauss were obtained from an exact diagonalization analysis using the \(g\) and \(A\) values listed in Table II. See text. \*Note: strong off-angle (69 \(\pm\) 5\(^\circ\)) feature observed and calculated at 1132 (2) which partially obscures this perpendicular line. \*Note: strong off-angle (74 \(\pm\) 3\(^\circ\)) feature observed and calculated at 2156 which obscures this perpendicular line. \*Note: strong off-angle (74 \(\pm\) 3\(^\circ\)) feature observed and calculated at 3722 (1) which obscures this perpendicular line. \*Note: strong off-angle (72 \(\pm\) 3\(^\circ\)) feature observed and calculated which obscures this perpendicular line.

(Al: \(M_z = \frac{1}{2}\) and \(\frac{3}{2}\)) in the 300–800-G region are shown in Figure 4B and compared with simulated spectra in Figure 4A. The dashed lines superimposed over Figure 4A give the \(\theta \text{ vs. } H_{\text{RES}}\) dependence of these two hyperfine transitions. Note that for the \(M_z = \frac{1}{2}\) transition, the most intense feature occurs not at \(\theta = 90^\circ\) but at the intermediate angle of approximately 59\(^\circ\) for the higher field component of the \(^{19}\text{F}\) doublet (\(^{19}\text{F} M_z = \frac{1}{2}\)). The lower field \(^{19}\text{F}\) component (\(M_z = \frac{1}{2}\)) for this \(M_z = \frac{1}{2}\) Al transition does not have an infinite slope at any intermediate angle along the \(\theta \text{ vs. } H_{\text{RES}}\) curve. Thus no "extra" or off-angle features are predicted nor observed in this spectral region. Neither of the \(^{19}\text{F}\) components of the Al \(M_z = \frac{1}{2}\) transition show extra features, and the spectrum in this region exhibits a classical line shape and phase pattern with observed lines occurring at the \(\theta = 0^\circ\) and 90\(^\circ\) limits. A and B in Figure 5 present a similar comparison between simulated and observed spectra for the Al \(M_z = \frac{1}{2}\) transition.

Figure 3. The computer simulated first derivative ESR spectrum for a powder sample of AIF\(^+\) is shown for all allowed hyperfine transitions. On the same magnetic scale above each transition is presented the \(\theta \text{ vs. } H_{\text{RES}}\) dependence. See Figures 4–6 for expanded scale presentations of various spectral regions. The magnetic field for \(g_e\) is 3420 G and the magnetic parameters employed are listed in Tables I and II.
Figure 4. Simulated (A) and experimental (B) first derivative ESR spectra of AlF⁺ in neon matrix at 4 K for the two lowest field Al hyperfine lines are shown. The dashed curves superimposed over the simulated spectrum show the θ vs. H dependence. Note that the higher field ¹⁹F (MI = -1/2) component of the Al MI = 1/2 transition exhibits a pronounced off-angle feature at θ ≈ 59° which is the most prominent feature for this entire spectral region. See Table I for exact line positions and magnetic parameters employed.

Figure 5. Simulated (A) and experimental (B) ESR spectra of AlF⁺ in neon matrix for the Al MI = 1/2 transition is presented. The dashed curves show the θ vs. H dependence. An intense off-angle line is observed for the lower field ¹⁹F component that overlaps the normally dominant θ = 90° (perpendicular transition). See Figure 4 and Table I for exact line positions and magnetic parameters employed.

As indicated in Table I, the exact position of the perpendicular transition (θ = 90°) for the low-field ¹⁹F (MI = 1/2) component is obscured by the intense off-angle feature at θ = 69°. The highest field transition, Al MI = -1/2, is shown in Figure 6B and compared with a simulated spectrum in Figure 6A. Again the exact position of the θ = 90° transition for ¹⁹F MI = 1/2 is obscured by a strong off-angle feature. For all of the six major spectral regions, the six MI values for Al, the agreement between observed and simulated spectra using the magnetic parameters given in Table I is excellent in every detail. However, the spectra recorded on the first set of experiments was difficult to recognize since it does deviate considerably from an obvious sextet of equally intense doublets for the parallel and perpendicular lines. Also, higher order effects cause the internal ¹⁹F doublet splittings for the six Al transitions to be unequal. Without access to exact simulated spectra and θ vs. H results for comparative purposes, it would have been impossible to assign the ESR spectral details of AlF⁺ and extract accurate magnetic parameters.

**Laser Sputtering.** The laser sputtering method developed for these matrix experiments was originally tried for the purpose of generating a cleaner source of AlF(g) for subsequent photionization. The thermal method of AlF(g) generation employing AlF₃ produced an impurity species discussed below that made the AlF⁺ ESR spectral assignment especially difficult. The laser method produced only the AlF⁺ radical (in addition to trace amounts of normally observed impurities such as CH₃, HCO, N, and H atoms) whose magnetic parameters obtained from the ESR spectra show excellent agreement with ab initio CI calculations.

The major “trial and error” phase of the laser sputtering experiment was to find a geometrical arrangement for the aluminum target such that reflected UV laser radiation would not strike the neon matrix deposition sample. Experiments with previously studied ions such as H₂O⁺ and N₂⁺ demonstrated that only a few pulses of such UV light were sufficient to photobleach nearly all cation radicals. The photobleaching process has been described previously for ESR, electronic, and vibrational matrix studies of charged species. Apparently, electrons are photoionized from the anion traps in the matrix and travel throughout the lattice neutralizing cations. The spectra of most neutral species are not affected, and hence the photobleaching process can be a useful technique in distinguishing between charged and uncharged matrix isolated species. To prevent photobleaching an arrangement was finally found that allowed laser sputtered species to impinge on the matrix deposition target without the reflected laser radiation. The hole burning reactive sputtering process that was successful has been described in the Experimental Section. It was necessary to locate the matrix deposition target slightly off the line defined by the laser beam. Apparently the molecules that were laser sputtered off the opposite side (matrix side) once a hole formed vaporized over a relatively large solid angle and could strike the off-line matrix target. The laser light traveled more directly through the hole and hence did not strike the matrix target. In this arrangement sputtered molecules could be matrix isolated without the deleterious photobleaching effect of direct or reflected laser radiation striking the deposited matrix sample. As the laser sputtered AlF(g) was being deposited in the neon matrix, con-

Neon Matrix ESR and CI Theoretical Investigation of AlF*  


Table II. Magnetic and Electronic Structure Comparisons of AlF* with Other Isoelectronic $\Sigma^+$ Radicals; 4 K Neon Matrix Data

<table>
<thead>
<tr>
<th>AlF*</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$A_1^\parallel$</th>
<th>$A_1^\perp$</th>
<th>$A_2^\perp$</th>
<th>$A_{a,b}$</th>
<th>$A_{a,c}$</th>
<th>$A_{b,c}$</th>
<th>neutral AlF*</th>
<th>AlF*</th>
<th>neutral AlF*</th>
<th>AlF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F)</td>
<td>2.0015</td>
<td>2.0000</td>
<td>2893 (8)</td>
<td>2782 (6)</td>
<td>2819 (6)</td>
<td>37 (5)</td>
<td>(72)</td>
<td>(44)</td>
<td>30</td>
<td>26</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td>(AI)</td>
<td>2.0015</td>
<td>2.0000</td>
<td>872 (1)</td>
<td>713 (1)</td>
<td>766 (2)</td>
<td>53.0 (7)</td>
<td>(20)</td>
<td>(64)</td>
<td>43</td>
<td>38</td>
<td>43</td>
<td>38</td>
</tr>
<tr>
<td>MgF</td>
<td>2.0020</td>
<td>2.0010</td>
<td>333 (1)</td>
<td>143 (3)</td>
<td>206 (3)</td>
<td>63 (2)</td>
<td>(0.39)</td>
<td>(3.6)</td>
<td>35</td>
<td>27</td>
<td>35</td>
<td>27</td>
</tr>
</tbody>
</table>

$^a$Values in MHz. $^b$% $s$ and $p$ (valence orbitals) were calculated by the ratio of observed molecular values of $A_{a,b}$ and $A_{a,c}$, respectively, to various neutral and charged atomic values of $A_{a,b}$ and $A_{a,c}$. See notes $c$–$e$ below. $^c$Neutral AlF* and AlF* values used were 3911 and 83 MHz, respectively. Reference 24. $^d$For AlF* = 4590 MHz was calculated from a small basis set CI wave function—their calculation of Al for $^e$the “real” AlF* radical to be approximately 920 G not 330 G. Subsequent vaporization experiments involving more careful handling of AlF(s) did show (in addition to this impurity radical) the presence of another radical whose identity is now clearly established as AlF* with $A_{1s}$ = 994 (3) G and $A_{1p}$ = 1033 (3) G for its Al hfs. The theoretical results were definitely a compelling prompt to generate AlF* by an alternative and independent experimental method.

Table II are the observed magnetic parameters for these diatomic radicals and the results of the free atom comparison method (FACM) for calculating % $s$ and $p$ character utilizing neutral and charge corrected atomic Al values of $A_{a,b}$ and $A_{a,c}$. The commonly applied set of atomic $A_{a,b}$ and $A_{a,c}$ parameters tabulated by Morton and Preston25 for neutral Al yields 72% $s$ and 28% $p$, character; for $^p$F the results are 40% $s$, 25% $p$, and 35% $d$. Obviously, the total spin density of 124% obtained in this manner should be corrected for the extreme ionic character of formal charge that exists on Al in AlF*. Formal charge analysis of the CI wave function indicates that the charge is approximately −1 on fluorine and +2 on aluminum. The AlF$^+$ model for AlF* readily accounts in a qualitative manner for the observed ESR nuclear hyperfine structure for both atoms. The Al(3p$^2$) ground state loses two electrons to form the $^3$S state for AlF* ($^3$S$^0$), and the near unit charge gained by fluorine produces a nearly closed shell ($^F$) which should yield only small $^1$F hfs in AlF*. The observed nuclear hfs for Al ($\approx$1000 G) in AlF* is the largest reported for any molecular Al radical, and the small $^1$F hfs resembles closely the magnetic

In the early stages of these vaporization depositions and before conducting the laser sputtering experiments, we thought that this impurity species must be AlF$^+$ although in hindsight there were no problems for the ESR line fitting process that did not seem proper for an axial symmetric radical. After these initial experiments were completed, other, more extensive computer calculations of Davidson and Feller became available which predicted the Al hfs in the “real” AlF* radical to be approximately 920 G not 330 G. Subsequent vaporization experiments involving more careful handling of AlF(s) did show (in addition to this impurity radical) the presence of another radical whose identity is now clearly established as AlF* with $A_{1s}$ = 994 (3) G and $A_{1p}$ = 1033 (3) G for its Al hfs. The theoretical results were definitely a compelling prompt to generate AlF* by an alternative and independent experimental method.

The possibility that the impurity radical could be AlOF$^+$ is interesting since this species has not been previously observed. Laser sputtering experiments on aluminum involving the simultaneous introduction of O$_2$ and F$_2$ are planned in order to produce a sufficiently intense ESR spectrum for detailed analysis. If this procedure is successful, it would be straightforward to utilize $^1$O$_2$ ($I = 1/2$) for isotopic confirmation.

**Discussion**

**Electron Structure of AlF* from ESR Data.** The valence electronic structure of AlF* for the unpaired electron will be analyzed by different methods and compared with previous findings for the $\Sigma$ isoelectronic radicals AlO, MgF$^+$, and SiF$^+$.$^6$ The results of highly approximate methods commonly applied to ESR data for obtaining orbital occupancies and hybridization ratios will be compared with those of a Mulliken type population analysis conducted on an ab initio CI wave function that reproduces within 10% the observed molecular values of $A_{a,b}$ and $A_{a,c}$ for Al in the neon isolated AlF* radical.

Presented in Table II are the observed magnetic parameters for these diatomic radicals and the results of the free atom comparison method (FACM) for calculating % $s$ and % $p$ character utilizing neutral and charge corrected atomic Al values of $A_{a,b}$ and $A_{a,c}$. The commonly applied set of atomic $A_{a,b}$ and $A_{a,c}$ parameters tabulated by Morton and Preston$^2$ for neutral Al yields 72% $s$ and 28% $p$, character; for $^p$F the results are 40% $s$, 25% $p$, and 35% $d$. Obviously, the total spin density of 124% obtained in this manner should be corrected for the extreme ionic character and formal charge that exists on Al in AlF*.

Formal charge analysis of the CI wave function indicates that the charge is approximately −1 on fluorine and +2 on aluminum. The AlF$^+$ model for AlF* readily accounts in a qualitative manner for the observed ESR nuclear hyperfine structure for both atoms. The Al(3p$^2$) ground state loses two electrons to form the $^3$S state for AlF* ($^3$S$^0$), and the near unit charge gained by fluorine produces a nearly closed shell ($^F$) which should yield only small $^1$F hfs in AlF*. The observed nuclear hfs for Al ($\approx$1000 G) in AlF* is the largest reported for any molecular Al radical, and the small $^1$F hfs resembles closely the magnetic

parameters observed for the highly ionic alkaline earth monofluoride neutral radicals (MgF, CaF, etc.) which can be described as $M^+ F^-$. The large amount of $3s/3p$ hybridization that occurs is also consistent with previous MF radical studies. Using an atomic $A_{iso}$ value of 4590 MHz obtained from a small basis set CI calculation of $Al^+$ reduces the % $3s$ character to 61% from 72% which was based on an Al neutral value of 3911 MHz. Likewise, the % $3p$ character is reduced from 44% for an Al neutral $A_{iso}$ of 83 MHz to 30% for an $Al^+$ $A_{iso}$ of 123 MHz obtained from an SCF type calculation on the excited $3P$ state of $Al^+(3P)$. The reasonableness of this SCF $A_{iso}$ calculation for $Al^+$ can be gauged by using an established procedure for correcting neutral atomic values of $A_{iso}$ for nuclear charge effects. The charge correction method described by Gordy utilizing experimentally based correction factors for nuclear quadrupole results yields an $A_{iso}$ value for $Al^+$ of 141 MHz which agrees within 16% to the ab initio SCF calculation. This larger $A_{iso}$ value for $Al^+$ yields a % $3p$ character of 26% for $Al^+$. Hence the sum of the individual orbital occupancies in $AlF^-$ is reduced from 124% to 95% or 99% depending upon which $Al^+$ $A_{iso}$ parameter is chosen (the SCF value or the charged corrected neutral value). Therefore the FACM results utilizing charge corrected atomic values do produce a reasonable sum for the spin density based on the four independent experimental parameters of $A_{iso}$ and $A_{dp}$ for both Al and F.

The negative charge correction to the $19F$ neutral value of $A_{iso}$ used in the above FACM analysis causes only a small increase in 2P, character from 7% to 9%. Even this small amount of apparent open shell 2P character on fluorine cannot be accounted for by spin polarization effects alone. Therefore a small deviation from a full -1 charge on fluorine is indicated to account for the small degree of open shell 2P character reflected in the $19F$ hfs. Throughout these discussions $A_{iso}$ and $A_{dp}$ are defined in the following manner

$$A_{iso} = \frac{1}{2} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \frac{3(\cos^2 \theta - 1)}{r^2}$$

where all symbols have their standard definitions and the average is over the spin density.

**Theoretical Calculations for $AlF^+$.** Using an MCSCF wave function with a 6-orbital active space we obtained essentially the same equilibrium bond length (1.590 Å) as the PNO-Cl/CEPA study of Klein and Rossini. The basis set consisted of the Dunning-Hay double-$\zeta$ basis [11s,7p,2d/9s,5p,1d] contracted to [6s,4p,2d/4s,2p,1d] augmented with several sets of d functions. All possible excitations were allowed within the 6s, 7s, 7p, 2s, 3p, and 3$\pi_3$ orbitals. Although an experimental determination of the $Al^+$ bond length has not been reported, Huber and Herzberg report the bond lengths of several Rydberg excited states of $AlF$ in the 1.596-1.598 Å range. The MCSCF geometry optimization was performed with GAMESS. A comparison of the $AlF^+$ HF and MCSCF wave functions revealed no significant differences such as were evident in the corresponding wave functions for AIO and SiO$^+$. Presumably this is due to the much larger electronegativity of the fluorine cation than the oxygen atom, to use AIO as a comparison. Both

**Table III. Orbital Occupancy of the Reference Configurations for $AlF^+$**

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$\pi_x$</th>
<th>$\pi_y$</th>
<th>$\pi_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table IV. Total Energies and Selected One-Electron Properties for $AlF^+$ with use of the (18s,12p,3d/12s,6p,2d) $\rightarrow$ (12s,8p,3d/8s,4p,2d) Basis**

<table>
<thead>
<tr>
<th>properties</th>
<th>SCF$^a$</th>
<th>MRSD-Cl$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{iso}$</td>
<td>2298</td>
<td>2572</td>
</tr>
<tr>
<td>$A_{dp}$</td>
<td>197</td>
<td>203</td>
</tr>
<tr>
<td>isotropic hyperfine$^c$</td>
<td>(2343)$^f$</td>
<td>(2622)</td>
</tr>
<tr>
<td>anisotropic hyperfine$^c$</td>
<td>63</td>
<td>73</td>
</tr>
<tr>
<td>electric field gradient$^d$</td>
<td>-1.33</td>
<td>-1.29</td>
</tr>
<tr>
<td>nuclear quad. coupling$^e$</td>
<td>-46.9</td>
<td>-45.5</td>
</tr>
<tr>
<td>Mulliken spin pop.</td>
<td>(3s) 0.77</td>
<td>0.74</td>
</tr>
<tr>
<td>(3p) 0.17</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>(2p) 0.01</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

$A_{iso}$ dipole moment = 2.35 D (origin = Al, F along the $z$ direction)

The SCF energy with this basis is -341.1643 hartrees. The CI energy was -341.5947 hartrees. There were 27 383 spin-adapted configurations selected from 7276 230 generated. Hyperfine parameters are given in units of MHz. The conversion factors used for converting $\sigma$ in atomic units to $\sigma$ (iso) are the following: 139.1 ($^2Al$), 179.2 ($^2PF$). Table V contains the results for converting $\sigma$ (iso) to $\sigma$ (aniso) and the following: 139.1 ($^2Al$), 502.2 ($^2PF$). Note: the theoretical anisotropic results listed in this table correspond to $A_{iso}$, where $A_{iso}$ is defined in the text discussion of the experimental ESR results. The isotropic values in parentheses have been scaled by the ratio (HF density at the nucleus-exact)/(HF density at the nucleus—this basis) in order to approximately account for the basis set deficiencies. The electric field gradient is given in atomic units. The nuclear quadrupole coupling constants are given in MHz and are defined as $eq^2/h$.

at the HF and MCSCF levels of theory the fluorine gross atomic population is substantially greater than 9, indicating that the electron vacancy resides mostly on Al. A larger (18s,12p,3d/12s,6p,2d) even-tempered primitive basis contracted to (12s,8p,3d/8s,4p,2d) was chosen for evaluating the hyperfine properties. The d exponents (0.40, 0.39, and 0.11 on Al; 0.97 and 0.74 on F) were partially optimized at the SCF level. At the optimal geometry of the cation (1.599 Å) this basis yielded a neutral SCF energy of -341.4778 hartrees compared to a near HF limit value of -341.4832 hartrees at the optimal neutral geometry (1.654 Å).

Because an MCSCF calculation involving 86 basis functions and thousands of configurations is prohibitively large for the programs currently at our disposal, the CI property evaluations were performed with an alternative set of virtual orbitals, known as $K$ orbitals, which have been shown to closely mimic the frozen natural orbitals in cases where the HF configuration dominates the wave function. This, in turn, results in a more rapidly convergent CI expansion.

Properties were computed by using a CI wave function which consisted of all single and approximately 27 000 selected double excitations generated from the 10 space orbital products (25 spin-adapted configurations) listed in Table III. The selection of double excitations on the basis of their second-order energy
contributions was necessary due to the fact that in excess 3.8 million are possible. An estimated 91% of the MR SD–CI correlation energy was variationally recovered. Total energies and selected one-electron properties for AIF+ are listed in Table IV. The CI calculated $A_{\text{iso}}$ and $A_{\text{dip}}$ values for Al of 36.5 and 2572 MHz, respectively, show excellent agreement with the observed values of $A_{\text{iso}} = 37 (5)$ MHz and $A_{\text{dip}} = 2819 (6)$ MHz. (See Table II.) The CI value of $A_{\text{iso}} = 2622$ MHz which has been scaled to correct for basis set deficiencies shows even closer agreement with experiment. (See Table IV.) The CI calculated values of $A_{\text{iso}} = 197$ MHz and $A_{dip} = 94$ MHz for $^{19}$F hfs also show reasonable agreement with neon matrix experimental results of $A_{\text{iso}} = 218 (5)$ MHz and $A_{\text{dip}} = 128 (3)$ MHz for the AIF+ radical.

The Mulliken population analysis of the AIF+ wave functions was conducted in the manner described in the SiO+ report. Since the populations for the various valence orbitals of AIF+ were obtained from ab initio wave functions which yield nuclear hyperfine parameters in excellent agreement with experiment, it is especially interesting to compare these theoretical populations with experimental populations obtained from the commonly applied free atom comparison method (FACM) discussed in the previous section. The FACM results utilizing the charge corrected neutral atomic values of $A_{\text{iso}}$ and $A_{\text{dip}}$ compare with the theoretical populations in the following manner (theoretical CI populations are underlined):

\[
\begin{align*}
\text{Al}^{3s} & : 73\% \text{ vs. } 61\%; \text{Al}^{3p}\,^{3p} & : 18\% \text{ vs. } 26\%
\end{align*}
\]

F$^{2s}\,^{2s}$ = 0\% vs. 0.4\%; F$^{2p}\,^{2p}$ = 3\% vs. 9\%.

The reasonable agreement between these two very different methods of obtaining orbital occupancies for AIF+ should be contrasted with a similar comparison for the 3s and 3p, orbitals of Si in SiO+. The ESR FACM results for SiO+ of 17% “s” and 56% “p,” (based on neutral atomic Si parameters) differ substantially from the theoretical populations of 30% “s” and 27% “p,” which were also obtained from a CI wave function yielding $A_{\text{iso}}$ and $A_{\text{dip}}$ values for $^{28}\text{Si}$ within 10% of the neon matrix experimental results. The source of the different results for the two methods in the SiO+ case has been analyzed in detail and found to result from core–other valence overlap effects. This type of inner-shell effect is not the result of spin polarization. For these types of diatoms the largest contributor to the core–other valence overlap effect comes from the overlap of the $p_z$ orbital on the nonmetal atom. In AIF+, the $2p_z$ spin density on F is approximately 10 times less than the $2p_z$ spin density on O in SiO+. This major difference in the electronic structure of these two isoelectronic $^2\Sigma$ radicals accounts for the approximate agreement of experimental (FACM) and theoretical populations for AIF+ and the large disagreement for SiO+. The information gained in these studies should aid in distinguishing between those radicals that can be analyzed by the simple FACM approach and those that require more extensive theoretical analysis.

**Electronic Ground State and g Tensor.** AIF+ has not been previously observed by any spectroscopic method. However, the observed g tensor and the theoretical calculations discussed above clearly indicate that the electronic ground state is $^2\Sigma$.

Since the observed values of $g_{\text{iso}}$ and $\Delta g_{\text{g}}$ ($\Delta g_{\text{g}} = g_{\text{g}} - g_{\text{e}}$) for AIF+ are so small, only qualitative information can be obtained. The magnetic parameters for the $^2\Sigma$ isoelectronic series AIF+, MgF, AlO, and SiO+ presented in Table II reveal very similar g values. The values for $\Delta g_{\text{g}}$ probably reflect only small neon matrix shifts since theory indicates that $g_{\text{e}}$ would be zero in a first-order analysis. The small negative value of $g_{\text{iso}}$ for AIF+ indicates that spin-orbit coupling between the ground $^2\Sigma$ state and a regular $^2\pi$ excited state is dominant. This $^2\pi$, state is probably best described as an Al 3p, orbital. Hence a small amount of spin–orbit coupling between Al 3p, in the ground electronic state and Al 3p, in an excited $^2\pi$, would readily account for the observed $g_{\text{iso}}$ value of 2.0000 (5). An accurate prediction of the location of this excited $^2\pi$, state based on g tensor data alone cannot be made for AIF+ given the small value of $\Delta g_{\text{g}}$.

**Conclusion.** The AIF+ radical cation has been studied experimentally for the first time and found to have a $^2\Sigma$ ground state. Both laser sputtering and high-temperature vaporization methods were used for generating AIF(g) which was photoionized during neon matrix deposition experiments at 4 K. The ion mass spectrometry technique developed for this AIF+ study should have widespread applications for other matrix investigations of reactive intermediates.

The magnetic parameters of AIF+ in a neon matrix were determined by ESR and showed excellent agreement with those calculated by ab initio theoretical methods. The electronic structure of AIF+ was compared with the isoelectronic $^2\Sigma$ radicals AlO, MgF, and SiO+. Orbital populations for the unpaired electron were obtained from the commonly applied free atom comparison method (FACM) and from a Mulliken type population analysis of a CI wave function which yielded $A_{\text{iso}}$ and $A_{\text{dip}}$ values in close agreement with experiment. Population results from these two independent methods showed reasonable agreement in the case of AIF+ but not for SiO+. This difference was attributed to a large “core–other valence overlap effect” in SiO+ that was not significant in the AIF+ case since the spin density on the F 2p, was approximately 10% that of the spin density on the O 2p, in SiO+. These findings should help predict those radical types which are inappropriate for the simple FACM analysis of ESR data.

**Acknowledgment.** Support from the National Science Foundation (CHE-8508085) and the Camille and Henry Dreyfus Foundation is gratefully acknowledged (L.B.K.). Part of the theoretical analysis was supported by a grant from the National Science Foundation (E.R.D.). A Dana Foundation undergraduate research scholarship is also gratefully acknowledged.