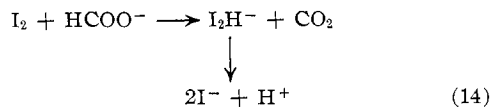


The kinetic isotope data, which thus eliminate hypoiodite formation and proton transfer as possible pathways, are consistent with transfer of a hydride ion from carbon to iodine



Such a process involves carbon-hydrogen bond cleavage, the importance of which would depend on the water content of the solvent because of hydrogen bonding to the oxygen atoms of formate. Simultaneous interaction of iodine with one of the oxygen atoms may also be involved. This is suggested by the fact that

$k_{\text{H}}/k_{\text{D}} = 3.4$ for the thallium(III) oxidation of formate,¹⁸ a process which undoubtedly occurs *via* interaction of Tl^{3+} on the oxygen of formate. Our values of $k_{\text{H}}/k_{\text{D}}$ in the range of 2.2 to 3.8 agree fairly closely with the thallium(III) value, but are considerably lower than $k_{\text{H}}/k_{\text{D}} = 7$, observed in the permanganate-formate reaction which is assumed to proceed *via* simple hydride transfer.^{4,5}

Acknowledgment.—This work was supported by the National Science Foundation under Grant No. GP-2968. We are grateful to Professor E. A. Halevi for helpful discussions concerning the isotope results.

(18) J. Halpern and S. M. Taylor, *Discussions Faraday Soc.*, **29**, 174 (1960).

CONTRIBUTION FROM THE WESTERN RESEARCH CENTER, STAUFFER CHEMICAL COMPANY, RICHMOND, CALIFORNIA

Complex Fluoro Cations. III.¹ Tetrafluoronitrogen(V) Cation, NF_4^+ . Vibrational and Fluorine-19 Nuclear Magnetic Resonance Spectra of $\text{NF}_4^+\text{AsF}_6^-$

BY KARL O. CHRISTE, JACQUES P. GUERTIN, ATTILA E. PAVLATH, AND WOLFGANG SAWODNY²

Received August 25, 1966

Fluorine-19 nuclear magnetic resonance and infrared and Raman spectroscopy confirm the postulated ionic structure, $\text{NF}_4^+\text{AsF}_6^-$, for the $\text{NF}_3\text{-F}_2\text{-AsF}_5$ adduct in the solid state and in HF solution. The NF_4^+ cation, with four equivalent fluorine atoms, has a tetrahedral configuration (point group T_d). The force constants of NF_4^+ are calculated and compared with those of NF_3 and isoelectronic species, BF_4^- and CF_4 .

Introduction

The existence of an $\text{NF}_3\text{-F}_2\text{-AsF}_5$ adduct has recently been reported.^{3,4} In a subsequent paper¹ we have described the synthesis and properties of this complex. On the basis of X-ray data, the high thermal stability, and theoretical considerations, the ionic structure, $\text{NF}_4^+\text{AsF}_6^-$, was proposed.¹ The object of this paper is to support further the proposed ionic nature and structure of this compound (in the solid state and in HF solution) by spectroscopic data. In addition, it is interesting to compare the bond strength (based on valence force constants) in NF_4^+ with that in NF_3 and isoelectronic BF_4^- and CF_4 .

Experimental Section

The preparation of $\text{NF}_4^+\text{AsF}_6^-$ by the glow discharge of a 1:1 mole mixture of NF_3 and AsF_5 in the presence of excess fluorine has been described earlier.¹ In the sample used for the spectroscopic investigations, except for small amounts of CuF_2 , none of the possible impurities, such as $\text{NO}^+\text{AsF}_6^-$ or complex copper salts, could be detected. The combined results of X-ray, infrared, mass spectral, and elemental analyses indicated that the

sample contained at least 95% $\text{NF}_4^+\text{AsF}_6^-$ (the remainder was CuF_2). Manipulations outside the vacuum line were done in the dry nitrogen atmosphere of a glove box.

Infrared Spectra.—Infrared spectra were recorded on a Beckman Model IR-9 prism-grating spectrophotometer in the range 4000–400 cm^{-1} . Samples of NF_4^+ -containing salts, as dry powders, were placed between AgCl windows held in place by a screw-cap metal cell equipped with neoprene O rings.

Raman Spectra.—The Raman spectra were recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 Å) as the exciting line and saturated KNO_3 solution as the filter. For the solid complex, a Pyrex tube (7-mm o.d.) having an inner hollow glass cone for variable sample thickness or a glass-plunger type of reflection cell was used. Owing to the very fine particle size of the sample, the better spectra were obtained using the latter technique. The Raman spectrum of the complex in HF solution was taken using a technique described in the literature.⁵

¹⁹F Nuclear Magnetic Resonance Spectra.—A Varian Associates Model HA-100 spectrometer operating at 94.6 Mcps was used to record the ¹⁹F nuclear magnetic resonance spectra. Solid $\text{NF}_4^+\text{AsF}_6^-$ (0.15 g) was placed into a Teflon FEP tube equipped with a Monel bellows-seal valve (Hoke, M482M). The tube was connected to a vacuum line having only Monel and Teflon FEP construction. Purified liquid HF (~0.5 ml) was condensed into the tube. After allowing 1 hr for complete mixing at 25°, the clear solution above some undissolved material was transferred mechanically (decanted) into a Teflon FEP nmr tube (~4-mm o.d.). The nmr tube was "heat sealed" under vacuum

(1) Part II of this series: J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).

(2) Visiting Scientist from the Institut für Anorganische Chemie, Technische Hochschule, Stuttgart, Germany.

(3) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Letters*, **2**, 83 (1966).

(4) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *ibid.*, **2**, 79 (1966).

(5) H. H. Hyman and L. A. Quarterman, "Noble Gas Compounds." The University of Chicago Press, Chicago, Ill., 1963, p 275.

and inserted into a standard 5-mm o.d. glass nmr tube to facilitate spinning of the sample. Fluorocarbon-11 (CFCl_3) was used as an external standard ($\delta = 0.0$ ppm). Chemical shifts and coupling constants, J_{NF} and J_{AsF} , were obtained using the side-band technique

Results

^{19}F Nuclear Magnetic Resonance Spectrum.—The ^{19}F nuclear magnetic resonance spectrum of a solution of $\text{NF}_4^+\text{AsF}_6^-$ in liquid HF is shown in Figure 1. The relatively low intensity observed for the resonance lines of NF_4^+ is most probably due to the insufficient solubility of the complex in liquid HF resulting in a substantial quantity of $\text{NF}_4^+\text{AsF}_6^-$ remaining undissolved. The following chemical shifts relative to CFCl_3 were obtained: (i) a strong singlet at $\delta = +196.1$ ppm (HF solvent), (ii) a quadruplet at $\delta = +69.5$ ppm (AsF_6^-) having a coupling constant $J_{\text{AsF}} \sim 870$ cps, and (iii) a triplet at $\delta = -213.5$ ppm (NF_4^+) having a coupling constant $J_{\text{NF}} = 234$ cps. For comparison, F_2 in liquid HF and NF_3 have chemical shifts $\delta = -428.7$ and -146.9 ppm,⁶ respectively, and $\text{NO}^+\text{AsF}_6^-$ in liquid HF shows a quadruplet at $\delta = +69.5$ ppm having a coupling constant $J_{\text{AsF}} \sim 870$ cps.⁷ The latter value is comparable to that of $\text{Ag}^+\text{AsF}_6^-$ ($J_{\text{AsF}} = 930$ cps) in aqueous solution.⁸ A tenfold scale expansion of the ^{14}N - ^{19}F triplet shows that the half-band width is no larger than 10 cps (probably somewhat less). Under these conditions, the pen width itself is ~ 10 cps. However, at this scale expansion, the lines of the triplet begin to show a slight broadening near the base line, indicating that the actual half-band width is not much smaller than 10 cps.

Vibrational Spectra.—Figure 2 shows the infrared spectrum of $\text{NF}_4^+\text{AsF}_6^-$. The band at 406 cm^{-1} does not actually have as high an intensity as shown in the figure, since the AgCl windows begin to absorb in this range. The broad band of medium intensity at about 520 cm^{-1} and the two weak bands at 828 and 915 cm^{-1} do not show a constant relative intensity ratio when compared to the rest of the spectrum. These bands are due to the CuF_2 impurity. However, the 828-cm^{-1} band contains some contribution from $\text{NF}_4^+\text{AsF}_6^-$. The infrared spectrum of CuF_2 reported by Sadtler⁹ does not seem reliable, disagreeing with the spectrum of anhydrous CuF_2 (from Alfa Inorganics Inc.) that we had recorded as a dry powder between AgCl plates. The bands due to CuF_2 are noted in Figure 2 by an asterisk. The Raman spectra of the solid and its HF solution were rather weak in intensity and could be obtained only under very extreme conditions. The spectrum of the solid shows bands at $813, 687, 625, 520, 488,$ and 378 cm^{-1} . Again, the band at $\sim 520\text{ cm}^{-1}$ is due to the CuF_2 impurity. The spectrum of the HF solution of the complex had a lower intensity; however, it did show a band at 815

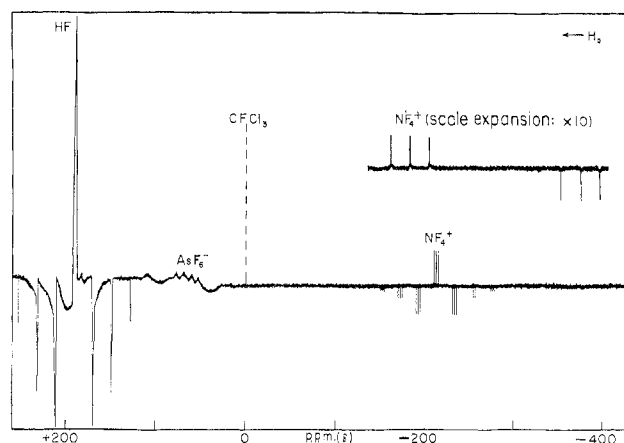


Figure 1.— ^{19}F nuclear magnetic resonance (94.6 Mcps) spectrum of a solution of $\text{NF}_4^+\text{AsF}_6^-$ in liquid HF at 25° . The dotted line is the resonance line of the external standard, fluorotrichloromethane (CFCl_3). The triplet assigned to NF_4^+ is shown with a tenfold scale expansion.

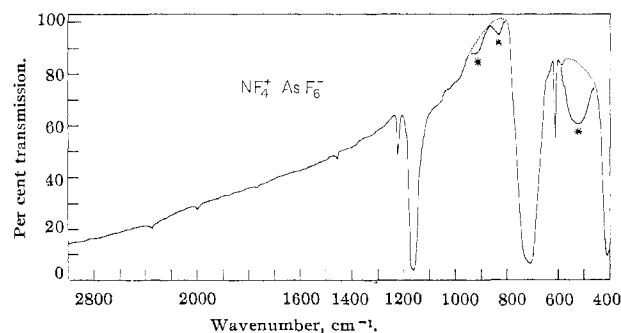


Figure 2.—The infrared spectrum of solid $\text{NF}_4^+\text{AsF}_6^-$ taken as a powder between AgCl windows. Asterisks indicate bands due to CuF_2 .

cm^{-1} , corresponding to the strongest of the bands (813 cm^{-1}) observed in the spectrum of the solid.

Table I lists the observed frequencies (and their assignments) of the infrared and Raman spectra of $\text{NF}_4^+\text{AsF}_6^-$.

Calculation of Force Constants.—The force constants of NF_4^+ were calculated by a recently published method.¹⁰ Using this method, the normal vibrations are sufficient data to allow the calculation of a complete set of constants. Table II compares the valence force constants obtained by this method with the valence force constants of the general valence force field (GVFF). A good approximation of the GVFF values is expected especially for the fluorides of the first-row elements of the periodic system.¹¹ The symmetry force constants of NF_4^+ (Table III) were calculated using the set of normal vibrations obtained from Table I. Hence, the valence force constant (f_r) and coupling force constant (f_{rr}) are 6.061 and 0.445 mdyne/A, respectively. Because of the redundancy condition in A_1 , it is not possible to give explicit data for the deformation constants.

(6) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962).

(7) K. O. Christe, J. P. Guertin, and A. E. Pavlath, unpublished results.

(8) E. L. Muettterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

(9) "High Resolution Spectra of Inorganics and Related Compounds," Y404S, Sadtler Research Laboratories, Inc., Philadelphia, Pa.

(10) W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, **21**, 995 (1965).

(11) J. Goubeau, *Angew. Chem. Intern. Ed. Engl.*, **5**, 567 (1966).

TABLE I
 VIBRATIONAL SPECTRA OF $\text{NF}_4^+\text{AsF}_6^-$ AND THEIR ASSIGNMENT

| Infrared Solid | Observed frequencies, cm^{-1} | | Assignment (point group) | |
|--------------------|--|----------------------|---|--|
| | Solid | Raman HF solution | NF_4^+ (T_d) | AsF_6^- (O_h) |
| 2330 vw | | | $2\nu_3$ ($A_1 + E + F_2$) | |
| 1995 vw | | | $\nu_1 + \nu_3$ (F_2) | |
| 1768 vvw | | | $\nu_3 + \nu_4$ ($A_1 + E + F_1 + F_2$) | |
| 1455 vw | | | $\nu_1 + \nu_4$ (F_2) | |
| 1223 w | | | $2\nu_4$ ($A_1 + E + F_2$) | |
| 1159 s | | | ν_{asym}, ν_3 (F_2) | |
| 828 vw | | | | $\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$) |
| [835] ^a | 813 m | 815 vw | ν_{sym}, ν_1 (A_1) | |
| 709 vs | | | | ν_{asym}, ν_4 (F_{1u}) |
| | 687 w | | | ν_{sym}, ν_1 (A_{1g}) |
| 611 m | 625 w | | $\delta_{\text{asym}}, \nu_4$ (F_2) | |
| 581 vw | | | | ν_{sym}, ν_2 (E_g) |
| | 488 w | | $\delta_{\text{sym}}, \nu_2$ (E) (?) | |
| 406 m | | | | $\delta_{\text{asym}}, \nu_3$ (F_{1u}) |
| | 378 w | | | $\delta_{\text{sym}}, \nu_5$ (F_{2g}) |
| [147] ^b | | | | $\delta_{\text{sym}}, \nu_6$ (F_{2u}) |

^a Value calculated from $(\nu_1 + \nu_3)$ and $(\nu_1 + \nu_4)$. ^b Value calculated from $(\nu_2 + \nu_6)$.

 TABLE II
 COMPARISON OF VALENCE FORCE CONSTANTS (MDYNES/A)

| | GVFF ^a | Our method |
|---------------|-------------------|-------------------|
| NF_3 | 4.36 ^b | 4.39 ^c |
| CF_4 | 6.07 ^d | 6.88 ^c |
| BF_3 | 7.25 ^e | 7.29 ^f |

^a In cases such as the highly symmetric molecules listed in Table II, where frequency data alone are insufficient to specify a unique force field for certain symmetry species and isotopic data are not available or cannot be successfully applied, additional data such as Coriolis ζ constants are required (see J. L. Duncan, *J. Mol. Spectry.*, **13**, 338 (1964), and I. W. Levin and S. Abramowitz, *J. Chem. Phys.*, **43**, 4213 (1965); **44**, 2562 (1966)). Therefore, it should be noted that our method and others using only frequency data are in such cases an approximation, since numerous different solutions for the force field can exist, all satisfying the given frequency data. There are considerable discrepancies in comparing the values reported by Levin and Abramowitz for the valence force constants of BF_3 and NF_3 with those given in Table II. However, determination of reliable Coriolis ζ constants is difficult for BF_3 (see N. Dreska, K. N. Rao, and L. H. Jones, *J. Mol. Spectry.*, **18**, 404 (1965)) and we believe that the constants of species A_1 as given by Levin and Abramowitz for NF_3 are not correct (see W. Sawodny, comment on Levin and Abramowitz's paper, to be published in *J. Chem. Phys.*). Consequently, the data of footnotes *b* and *e* are given in Table II. ^b P. M. Schatz, *J. Chem. Phys.*, **29**, 481 (1958). ^c W. Sawodny, unpublished. ^d J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 1089 (1964). ^e D. C. McKean, *ibid.*, **22**, 269 (1966). ^f See ref 10.

 TABLE III
 SYMMETRY FORCE CONSTANTS OF NF_4^+ (MDYNES/A)

| | | | |
|-------|------------------|----------------|----------------|
| A_1 | F_{11} 7.396 | | |
| E | $(F_{22}$ 0.888) | | |
| F_2 | F_{33} 5.616 | F_{34} 0.770 | F_{44} 0.975 |

Discussion

Few structural possibilities exist for a 1:1:1 adduct formed from NF_3 , F_2 , and AsF_5 . If we exclude very unlikely structures requiring either more than eight valence electrons for the nitrogen atom or extremely unusual oxidation and coordination numbers for the arsenic atom, such as a hypothetical AsF_8^- , the only remaining plausible structure is $\text{NF}_4^+\text{AsF}_6^-$. This structure satisfies the octet rule for the nitrogen atom and

results in two highly symmetrical and saturated (based on coordination number) ions of high stability. Since the octet rule is strictly applicable to the first-row elements of the periodic system, it is expected that NF_4^+ is an ideal sp^3 hybrid (tetrahedron), analogous to isoelectronic BF_4^- and CF_4 .

¹⁹F Nuclear Magnetic Resonance Spectrum.—An ideal tetrahedral species, XF_4^+ , in which X has no nuclear spin ($I = 0$), should exhibit only a single ¹⁹F nuclear magnetic resonance line, since the four fluorine atoms are equivalent. However, when X is ¹⁴N, having a nuclear spin of $I = 1$, the fluorine resonance would split into three peaks ($2I + 1$). These three lines should be of equal intensity since ¹⁴N has three equally probable spin states, and the splitting equals the ¹⁴N-¹⁹F coupling constant. Indeed, the spectrum of NF_4^+ did show three resonance lines of equal intensity. Comparison with the coupling constants of NF_3^6 and $\text{N}_2\text{F}^+^{12}$ ($J_{\text{NF}} = 155$ and 328 cps, respectively) reveals that the observed coupling constant of NF_4^+ ($J_{\text{NF}} = 234$ cps) is within the expected range. Although comparison of the integrated areas for the fluorine atoms attached to the nitrogen atom with those attached to the arsenic atom would be very desirable in order to determine the stoichiometry of this compound, it was not possible to do this within the accuracy required (owing to the vast difference in heights and half-band widths between these two groups of peaks).

The nuclear quadrupole moment of ¹⁴N offers a method of relaxation of the nitrogen atom. If the ¹⁴N nucleus is in a spherically asymmetric electric field, this nuclear quadrupole relaxation will broaden the lines of the triplet considerably. For example, the half-band width of the peaks of the N_2F^+ triplet is ~ 105 cps.¹² Since the observed resonance lines of the ¹⁴N-¹⁹F triplet of NF_4^+ are exceedingly narrow (see the tenfold expanded scale insert of Figure 1) and their half-band width is no larger than 10 cps (probably somewhat less), the ¹⁴N nucleus likely exists in a spherically sym-

metric electric field in which quadrupole-induced relaxation is not effective. This effect indicates a tetrahedral arrangement of the fluorine atoms around the nitrogen atom of NF_4^+ . Other theoretically possible cations such as NF^+ , NF_2^+ , NF_3^+ , N_2F_3^+ , etc., would likely result in much stronger nuclear quadrupole relaxation and, consequently, much greater line broadening. Therefore, such species can be ruled out and only NF_4^+ agrees with the observed ^{19}F nmr spectrum.

Similarly, an ideal octahedral species, XF_6^- , in which X is ^{75}As having a nuclear spin of $I = 3/2$ should exhibit a quadruplet having lines of equal intensity.¹³ The relatively small deviation in J_{AsF} of $\text{NO}^+\text{AsF}_6^{-7}$ or $\text{NF}_4^+\text{AsF}_6^-$ in HF solution and $\text{Ag}^+\text{AsF}_6^{-8}$ in H_2O can be attributed to the different solvent. The nuclear quadrupole moment of ^{75}As offers a method of relaxation of the arsenic atom, causing considerable broadening of the quadruplet lines.¹³

Vibrational Spectra.—Table I shows the vibrational spectra of $\text{NF}_4^+\text{AsF}_6^-$. The following section discusses the assignment of the observed frequencies. An octahedral anion of the type XY_6^- , such as AsF_6^- , has O_h symmetry. The six normal modes of vibration are classified as $\text{A}_{1g} + \text{E}_g + 2\text{F}_{1u} + \text{F}_{2g} + \text{F}_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g} , E_g , and F_{2g} modes will be Raman active, assuming that the selection rules are valid and that the octahedron is not distorted. The remaining F_{2u} mode is inactive in both the infrared and Raman spectra. Accordingly, the normal modes associated with AsF_6^- can be assigned without difficulty. All five active modes were observed. The ν_2 (E_g) mode was not observed in the Raman spectrum owing to the mode's relatively low intensity^{14,15} and the difficulty in obtaining a spectrum of higher total intensity. However, this mode was observed in the infrared spectrum as a very weak band at 581 cm^{-1} . It should not be infrared active, but it is known that slight distortion of the AsF_6^- octahedron or crystal field effects (e.g., in-phase and out-of-phase motions of the AsF_6^- groups are possible, since $\text{NF}_4^+\text{AsF}_6^-$, according to X-ray data,¹ has two molecules per unit cell) can cause this mode to become infrared active. The same effect occurs in the infrared spectra of $\text{ClF}_2^+\text{AsF}_6^-$,¹⁴ $\text{AsCl}_4^+\text{AsF}_6^-$,¹⁵ and $\text{IF}_6^+\text{AsF}_6^-$,¹⁶ in which this mode occurs at 609, 587, and 581 cm^{-1} , respectively. Therefore, the observed vibrations in the infrared and Raman spectra of $\text{NF}_4^+\text{AsF}_6^-$ agree well with those expected for AsF_6^- , the frequencies and intensities being similar to those of other AsF_6^- -containing complexes such as $\text{ClF}_2^+\text{AsF}_6^-$,¹⁴ $\text{AsCl}_4^+\text{AsF}_6^-$,¹⁵ $\text{IF}_6^+\text{AsF}_6^-$,¹⁶ and K^+AsF_6^- .^{17,18}

The remaining bands of the $\text{NF}_4^+\text{AsF}_6^-$ spectra, therefore, should be due to the NF_4^+ cation. A tetrahedral cation of the type XY_4^+ , such as perhaps NF_4^+ ,

(13) K. J. Packer and E. L. Muetterties, *Proc. Chem. Soc.*, 147 (1964).

(14) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(15) J. Weidlein and K. Dehnicke, *Z. Anorg. Allgem. Chem.*, **337**, 113 (1965).

(16) K. O. Christe and W. Sawodny, to be published.

(17) K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).

(18) K. Bühler, Dissertation, Technical University, Stuttgart, Germany, 1959.

has T_d symmetry. The four normal modes of vibration are classified as $\text{A}_1 + \text{E} + 2\text{F}_2$. While all four modes are Raman active, only the two F_2 modes are infrared active. Consequently, the two infrared bands at 1159 and 611 cm^{-1} are assigned to the triply degenerate antisymmetric stretching and the triply degenerate antisymmetric deformation vibrations, ν_3 (F_2) and ν_4 (F_2), respectively, of NF_4^+ . Of the remaining Raman bands, the one with the highest intensity at 813 cm^{-1} is assigned to the symmetric stretching vibration of NF_4^+ . The Raman spectrum of a solution of $\text{NF}_4^+\text{AsF}_6^-$ in HF further affirmed the position of this band. Owing to the small amounts of sample available, the solution was rather dilute. Therefore, the intensity of this Raman spectrum was quite low. However, a band at $\sim 815\text{ cm}^{-1}$ was definitely observed. Additional support for the assignment of this band is obtained from the two combination vibrations $\nu_1 + \nu_3$ and $\nu_1 + \nu_4$ observed in the infrared spectrum. The weak Raman line at 625 cm^{-1} corresponds to the 611 cm^{-1} band observed in the infrared and, therefore, is assigned to ν_4 (F_2). The remaining Raman line at 488 cm^{-1} , having no counterpart in the infrared, can be assigned to the symmetric deformation vibration ν_2 (E) of NF_4^+ .

The infrared spectrum shows five additional bands of low intensity. Their frequencies are too high and their intensities too low for fundamental vibrations. All five bands can be assigned to overtones or combination bands of NF_4^+ . Their frequencies and relative intensities are in good agreement with those of the known spectra of isostructural CF_4 .¹⁹ Consequently, the above given assignment for the fundamentals of NF_4^+ is strongly supported.

In summary, all five fundamental vibrations expected for AsF_6^- were observed with proper frequencies and intensities. In addition, they follow the principle of mutual exclusion as expected for a group having a symmetry center. The only deviation from theoretical expectations was ν_2 (E_g) becoming infrared active owing to crystal field effects. However, this effect also occurs in the case of other AsF_6^- -containing complexes.¹⁴⁻¹⁶ For NF_4^+ , T_d symmetry was confirmed by observing the correct number of infrared-active vibrations (two). Out of the four expected Raman-active modes only the three having the highest intensities were observed owing to the low over-all intensity of the spectrum. However, ν_3 (F_2), not observed in the Raman spectrum, is known from the infrared spectrum since the rule of mutual exclusion is not followed, as predicted for T_d symmetry. Thus, the observed vibrational spectra are consistent with the predictions made for an NF_4^+ cation and an AsF_6^- anion, and all frequencies needed for the evaluation of the valence force constant of NF_4^+ are established with certainty.

Force Constants.—Table III lists the symmetry force constants of NF_4^+ . All values, except F_{22} , are considered reliable, since they are based on the certain

(19) J. Goubeau, W. Bues, and F. W. Kumpmann, *Z. Anorg. Allgem. Chem.*, **283**, 123 (1956).

frequencies, ν_1 , ν_3 , and ν_4 . However, only F_{22} depends on ν_2 , the assignment of which is somewhat uncertain. This possible variation in F_{22} , however, would not influence any of the other constants since F_{22} is the only symmetry force constant in the species E. Furthermore, F_{22} does not influence the valence force constant of NF_4^+ , the constant of greatest interest. This is a basis for the following considerations.

The NF_4^+ cation is isoelectronic with CF_4 and BF_4^- . Woodward²⁰ compared force constants of species within similar isoelectronic series and suggested that the force constant increases as the magnitude of the positive charge of the central atom increases assuming only single bonds are involved. This theory should also apply to the isoelectronic series: BF_4^- , CF_4 , NF_4^+ . In this series, bonding orbitals of the central atom have the same hybridization (sp^3). Also, partial double-bond character is not possible owing to the strict validity of the octet rule for the first-row elements of the periodic system. However, Table IV indicates that Woodward's suggestion does not apply to the series BF_4^- , CF_4 , NF_4^+ . The valence force constant does increase from BF_4^- to CF_4 , but it decreases from CF_4 to NF_4^+ . All three f_r values for the series were calculated by the same method¹⁰ and therefore should be comparable. Since this method uses only frequency data, it does not result in a unique force field.²¹ However, in the case of this isoelectronic series (tetrahedral XF_4), the results should be relatively close to a unique force field since only five constants have to be determined from four frequencies. Furthermore, only the valence force constants with values similar to those of the GVFF (see Results section and ref 11) are compared. Even if there is some deviation, its magnitude should be similar within this isoelectronic series. Table IV also shows the bond orders ($n = f_r/f_1$) calculated according to the rules of Siebert²² and Goubeau.²³ Except for the bond order of NF_4^+ , the values of n are slightly greater than 1 (these small deviations may be due to the inaccuracy inherent in the determination of the single bond values, f_1). Although the valence force constant of NF_4^+ is larger than that of NF_3 , owing to the difference in the number of free electron pairs on the bonding atoms,²³ it is not as large as it should be according to Siebert's single-bond value²² or Woodward's predictions.²⁰ This de-

TABLE IV
FORCE CONSTANTS OF THE ISOELECTRONIC SPECIES
 BF_4^- , CF_4 , AND NF_4^+ ; ALSO THOSE OF NF_3 (MDYNES/Å)

| | BF_4^- | CF_4 | NF_4^+ | NF_3 |
|-------|-------------------|-------------------|-----------------|-------------------|
| f_r | 5.28 ^a | 6.88 ^a | 6.06 | 4.39 ^a |
| f_1 | 5.06 | 6.08 | 7.09 | 4.25 |
| n | 1.04 | 1.13 | 0.85 | 1.03 |

^a W. Sawodny, unpublished.

crease in the bond order of NF_4^+ may be due to considerable polarization of the N-F bond in NF_4^+ (caused by the positive charge on the nitrogen atom bonded to highly electronegative fluorine atoms).

A comparison of the bond orders of isoelectronic NF_4^+ and ONF_3 indicates an even greater polarization for the N-F bonds of ONF_3 than for those of NF_4^+ . Based on recently published frequency data,²⁴ the following bond orders were calculated for ONF_3 : $n_{\text{NF}} = 0.52$ and $n_{\text{NO}} = 1.63$. It should be noted, however, that NF_4^+ and ONF_3 may have opposite-direction polarizations of the N-F bonds. The polarization of the bonds in ONF_3 can be described as a contribution from the following resonance structure, $\text{O}=\text{NF}_2^+ \text{F}^-$. The same polarizing direction for the bonds in NF_4^+ would result in the structure, $\text{F}=\text{NF}_2^{2+} \text{F}^-$, energetically less favorable than the structure NF_3F^+ . In spite of this reversed polarizing direction of the N-F bonds of NF_4^+ and ONF_3 , the total amount of covalent bonding (expressed by the sum of the bond orders of all the bonds) is about the same in both species (3.32 and 3.19, respectively).

Acknowledgments.—We thank Dr. H. H. Hyman and co-workers of Argonne National Laboratories, Argonne, Ill., and Dr. A. C. Jones of Shell Development Co., Emeryville, Calif., for their help in obtaining the Raman spectra, and Dr. W. E. Tolberg and co-workers of Stanford Research Institute, Menlo Park, Calif., who prepared the HF solution of our $\text{NF}_4^+\text{AsF}_6^-$ sample and recorded its ^{19}F nuclear magnetic resonance spectrum. We are also indebted to Dr. C. Sederholm of IBM, Palo Alto, Calif., for his help in interpreting the ^{19}F nmr spectrum. This work was supported by the Advanced Research Projects Agency and administered by the Office of Naval Research.

(20) L. A. Woodward, *Trans. Faraday Soc.*, **54**, 1271 (1958).

(21) See footnote a of Table II.

(22) H. Siebert, *Z. Anorg. Allgem. Chem.*, **273**, 170 (1953).

(23) J. Goubeau, *Angew. Chem.*, **69**, 77 (1957).

(24) W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, *J. Am. Chem. Soc.*, **88**, 2604 (1966).