where the technetium complexes fit into the scheme, these data were not obtained to avoid radioactive contamination of the apparatus.

The foregoing results show that the thermal decompositions are extremely complex. Although internal oxidation–reduction occurs, interpretations are complicated by the volatilization of intermediate products.

Conclusion

The reaction of transition metal hexafluorides with hydrazinium(+2) fluoride in anhydrous hydrogen fluoride can be represented by

$$3N_2H_6F_2 + 4MF_6 \longrightarrow 2N_2H_6(MF_6)_2 + N_2 + 6HF \quad (4)$$

This reaction is fast and is complete within a few minutes at room temperature. The hydrazinium(+2) bishexafluorometalates(V) formed are very soluble in hydrogen fluoride. In the presence of excess hydrazinium(+2) fluoride, the reduction proceeds further

$$3N_2H_6F_2 + 2N_2H_6(MF_6)_2 \longrightarrow 4N_2H_6MF_6 + N_2 + 6HF \quad (5)$$

The second reaction is, however, much slower. It is complete only after several days at room temperature. Hydrazinium(+2) hexafluorometalates(IV) are much less soluble in hydrogen fluoride than the corresponding pentavalent complexes. It is interesting that it is possible to oxidize the freshly formed tetravalent complex to the pentavalent one if the former is treated with an excess of metal hexafluoride in hydrogen fluoride.

The formation of hydrazinium(+2) bishexafluorometalates(V) requires an excess of hexafluoride over that required stoichiometrically by eq 4. If the reaction is carried out with exact stoichiometric amounts, invariably mixtures of the pentavalent and tetravalent complexes result.

The over-all reaction in the presence of excess reducing agent may be written

$$3N_2H_6F_2 + 2MF_6 \longrightarrow 2N_2H_6MF_6 + N_2 + 6HF \quad (6)$$

No evidence was obtained for the formation of hydrazinium(+2) heptafluorometalates(V) in this work, although a compound of that type was isolated with uranium hexafluoride.[4]

Although the crystallographic and infrared data observed are consistent with the expected compound hydrazinium(+2) hexafluoromolybdate(IV) for the final complex isolated in the molybdenum system, we were unable to isolate a pure product, even after repeated washing with hydrogen fluoride. No reliable magnetic data were possible.

In general, the results of this study confirm the trend in reactivities of the transition metal hexafluorides. In particular, the relative inertness of tungsten hexafluorides compared to other hexafluorides was amply demonstrated.

The properties of the hexafluorometalates isolated in this study appear to set this class of compounds apart from the previously known analogous alkali metal complexes. Presumably, the responsibility lies with the unique nature of the hydrazinium(+2) cation.

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The Hexafluoroiodine(VII) Cation, IF_6^+

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The 1:1 adduct between AsF_5 and IF_7 has been investigated. The X-ray powder diffraction pattern of the white, crystalline solid can be indexed in the face-centered cubic system with $a = 9.49$ A. Density measurements indicate four molecules per unit cell. A pressure–temperature curve gives a heat of reaction, 43.9 kcal mole^{-1}, for the dissociation process: complex (s) = $IF_7(g) + AsF_5(g)$. Infrared and Raman measurements show that $IF_7 \cdot AsF_5$ has the ionic structure, $IF_6^+AsF_6^-$, in the solid state. The IF_6^+ cation has an octahedral configuration (point group O_h). The force constants of IF_6^+ are calculated and compared with those of isoelectronic SbF_6^- and TeF_6. These calculations indicate that the bonding in IF_6^+ is best described by a mainly covalent sp^{3}d^2 hybridization model.

Introduction

Halogen mono-, tri-, penta-, and heptafluorides exist and their structures are relatively well established. Owing to their amphoteric nature these fluorides can form (by combining with strong Lewis acids and bases) cations and anions containing one F^- ion less or more than the parent molecule. However, the structure of and the bonding in these ions have not been investigated. This group of compounds offers a unique chance to study the influence of the number of free-electron pairs, of coordination number, and of a positive or negative charge at the central atom on the structure and bonding. Therefore, a systematic investigation of these halogen fluoride ions has been initiated.

The structure of and bonding in ClF_2^-,[1–3] ClF_2^+,[4,5] and ClF_4^- [6,7] have recently been reported. In this paper we present structural data on IF_6^+. The formation of a solid adduct between IF_7 and a strong Lewis acid, such as AsF_5, has first been reported by Seel and Detmer,[8,9] and later by Pavlath.[10] However, no data concerning the nature and structure of this adduct have been published.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a standard Pyrex-glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Iodine heptafluoride (Alfa Inorganics, Inc.) and AsF_5 (98%, Ozark-Mahoning Co.) were purified by several low-temperature vacuum distillations. Little etching could be observed in the vacuum line. The purity of the volatile compounds was determined by measurements of their vapor pressures, molecular weights, and infrared spectra. Owing to their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Preparation of $IF_6^+AsF_6^-$.—In a typical experiment, IF_7 (20 mmoles) was combined under vacuum with AsF_5 (35 mmoles) at −196°. The temperature of the mixture was slowly increased to 0° and kept at that temperature for 45 min. Unreacted IF_7 and excess AsF_5 were removed by distillation at 20°. *Anal.* Calcd for $IAsF_{12}$: As, 17.4; F, 53.0; I, 29.5. Found: As, 18.3; F, 52.2; I, 28.8.

Elemental Analysis.—Products were analyzed for fluorine, iodine, and arsenic. The sample was fused using the Parr bomb technique (Na_2O_2 and a trace of starch). Fluorine was determined either by titration with $Th(NO_3)_4$ using alizarine red as indicator or by gravimetric analysis as PbFCl, arsenic by the iodometric titration of As(V), and iodine by a reduction to iodide with hydrazine sulfate followed by potentiometric titration with $AgNO_3$.

Infrared Spectra.—The infrared spectrum of solid $IF_6^+AsF_6^-$ was recorded on Beckman Models IR-9 and IR-11 prism-grating spectrophotometers in the range 4000–400 and 800–33 cm^{-1}, respectively. Samples were dry powders between AgCl plates or polyethylene disks. The polyethylene disks were protected against interaction with $IF_6^+AsF_6^-$ by a very thin Teflon sheet. Compensation of bands due to the window material was achieved by placing an empty cell into the reference beam.

Raman Spectra.—The Raman spectrum of solid $IF_6^+AsF_6^-$ was recorded on a Cary Model 81 spectrophotometer, using the blue mercury line (4358 A) as the exciting line and a saturated KNO_2 solution as a filter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses were used.

X-Ray Powder Data.—Debye–Sherrer powder patterns were taken using a Phillips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (~0.3-mm o.d.).

Density Measurements.—The density of $IF_6^+AsF_6^-$ was found using the displacement method.[11] A perfluorinated amine (3M Co., FC-43) was used to fill the pycnometer.

Dissociation Pressure Measurements.—The complex was transferred to a Monel container (15-cm length and 0.5-in. o.d.) closed by a Monel bellows-seal valve (Hoke Inc., M482M). The container was connected to a precision-dial manometer (0–30 ± 0.02 in., Wallace and Tiernan, Inc., FA145). The Monel tube containing the sample was immersed into a constant-temperature oil bath (accuracy ±0.1°); the manometer and the connecting tubing not immersed into the oil bath were kept at 80° by external electrical heating. No corrections were necessary owing to the increased temperature of the manometer. Since the pressures did not approach a constant value, pressure readings were taken as a function of the time over periods of about 24 hr. A slow, continuous pressure increase was observed. Since it appeared to be linear and was probably due to some chemical side reaction, the dissociation pressures were extrapolated for time zero. The gas above the solid was pumped off after completion of the measurements taken at each temperature. A plot was made of log pressure (mm) *vs.* reciprocal temperature, and the "heat of dissociation," $\Delta H_d°$ [12] (estimated accuracy ±1.6 kcal $mole^{-1}$), of $IF_6^+AsF_6^-$ was found from its slope.

Results

Synthesis.—Iodine heptafluoride and AsF_5, when mixed at 0°, produced the 1:1 complex, $IF_6^+AsF_6^-$, a white, crystalline, hygroscopic solid. Elemental analysis of the solid complex and molecular weight and infrared measurements of the gas phase above the solid complex clearly indicate a 1:1 combining ratio, the latter measurements showing that the complex is completely dissociated in the gas phase at 25°.

Thermochemical Properties.—Based on observed data (temperature [°C], pressure [mm]: 25.2, 2.1; 33.3, 5.6; 36.1, 7.6; 41.5, 14.7), a plot of log P_{mm} *vs.* T^{-1} (in °K) for the heterogeneous equilibrium

$$IF_6^+AsF_6^-(s) = IF_7(g) + AsF_5(g)$$

is a straight line. The equation

$$\log P_{mm} = 16.418 - \frac{4800}{T}$$

represents these dissociation data in the temperature range 25.2–41.5°. By extrapolation, a dissociation pressure of 2.0 mm was obtained at 25°. From the slope of the log P_{mm} *vs.* T^{-1} curve $\Delta H_d° = 43.9$ kcal $mole^{-1}$ was found. From $\Delta F°_T = -RT \ln K_{p(atm)}$, a free energy change, $\Delta F°_{298} = 7.8$ kcal $mole^{-1}$, and from $\Delta S°_T = (\Delta H° - \Delta F°_T)T^{-1}$, an entropy change, $\Delta S°_{298} = 121.0$ cal deg^{-1} $mole^{-1}$, were found for the dissociation process at 25°. A heat of formation of IF_6^+-AsF_6^-(s), $\Delta H_f°_{298} = -538$ kcal $mole^{-1}$, was calculated based upon $\Delta H_f°_{298}[IF_7(g)]^{13} = -229.1$ kcal $mole^{-1}$ and the estimated $\Delta H_f°_{298}[AsF_5(g)]^{14} = -265$ kcal $mole^{-1}$.

X-Ray Powder Data.—Table I lists calculated and observed X-ray powder diffraction data (indexed in the face-centered cubic system) for $IF_6^+AsF_6^-$. From these data, the calculated unit cell dimension is a = 9.49 A. Density measurements using the perfluori-

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[1] K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 905 (1965).

[2] K. O. Christe and J. P. Guertin, *ibid.*, **4**, 1785 (1965).

[3] K. O. Christe, W. Sawodny, and J. P. Guertin, *ibid.*, **6**, 1159 (1967).

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

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

[6] K. O. Christe and J. P. Guertin, *ibid.*, **5**, 473 (1966).

[7] K. O. Christe and W. Sawodny, *Z. Anorg. Allgem. Chem.*, in press.

[8] F. Seel and O. Detmer, *Angew. Chem.*, **70**, 163 (1958).

[9] F. Seel and O. Detmer, *Z. Anorg. Allgem. Chem.*, **301**, 113 (1959).

[10] A. E. Pavlath, U. S. Patent 2,993,937 (1961).

[11] J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).

[12] It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, $\Delta H_d°$ will be used throughout the test to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.

[13] "JANAF Interim Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1961.

[14] A. Glassner, Argonne National Laboratory Report ANL-5750, U. S. Government Printing Office, Washington 25, D. C., 1957.

TABLE I

X-RAY POWDER DATA FOR $IF_6^+AsF_6^-$

d (obsd), A	*d* (calcd), A	Intensity	*h k l*	*d* (obsd), A	*d* (calcd), A	Intensity	*h k l*
5.43	5.49	vw	1 1 1	1.309	1.316	m	6 4 0
4.72	4.75	vs	2 0 0	1.288	1.291	vvw	7 2 1
3.32	3.35	s	2 2 0	1.262	1.268	s	6 4 2
2.83	2.86	vvw	3 1 1	1.230	1.235	vvw	5 5 3
2.72	2.74	m	2 2 2	1.202	1.205	vvw	6 5 1
2.52	2.53	vvw	3 2 1	1.185	1.186	vvw	8 0 0
2.35	2.37	vvw	4 0 0	1.150	1.151	m	6 4 4
2.21	2.23	vw	3 3 0				8 2 0
2.152	2.176	vvw	3 3 1	1.116	1.118	w	8 2 2
2.104	2.122	m	4 2 0				6 6 0
2.013	2.022	w	3 3 2	1.085	1.089	vw	6 6 2
1.924	1.937	ms	4 2 2	1.059	1.061	w	8 4 0
1.850	1.861	vw	4 3 1	1.034	1.035	w	8 4 2
1.816	1.826	vw	5 1 1	1.009	1.011	vvw	6 6 4
			3 3 3	0.949	0.949	vvw	10 0 0
1.666	1.678	m	4 4 0				8 6 0
1.596	1.604	vvw	5 3 1	0.931	0.930	w	10 2 0
1.573	1.581	s	6 0 0				8 6 2
			4 4 2	0.915	0.913	vvw	6 6 8
1.532	1.539	vvw	5 3 2	0.881	0.881	vw	10 4 0
1.492	1.500	m	6 2 0				8 6 4
1.423	1.430	m	6 2 2	0.867	0.866	vvw	10 4 2
1.365	1.369	w	4 4 4				

nated amine, FC-43, resulted in a density (d^{24}) of 3.28 g cm^{-3}. This density value indicates four "molecules" of $IF_6^+AsF_6^-$ per unit cell ($d_{calcd} = 3.33$ g cm^{-3}).

Vibrational Spectra.—Figure 1 shows the infrared spectrum of solid $IF_6^+AsF_6^-$. The band at 404 cm^{-1} does not actually have as high an intensity as indicated by the spectrum recorded using AgCl windows, since the AgCl windows begin to absorb in this range. Figure 2 shows the Raman spectrum of solid $IF_6^+AsF_6^-$. The observed frequencies of the infrared and Raman spectrum are listed in Table II.

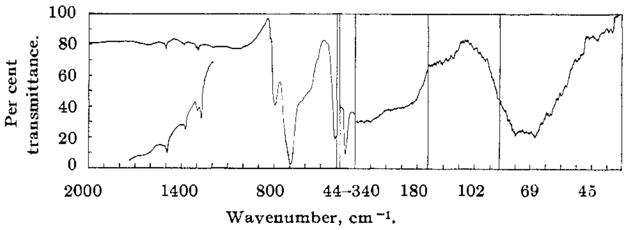

Figure 1.—Infrared spectrum of $IF_6^+AsF_6^-$.

Calculation of Force Constants.—For the calculation of the force constants the *G* and *F* matrices were set up according to the method of Wilson, Decius, and Cross,[15] assuming a valence force field. There is only one vibration for each species in A_{1g}, E_g, and F_{2g}. Therefore, the corresponding force constants can be evaluated unequivocally from the observed frequencies. However, in species F_{1u} two vibrations (one stretching and one deformational mode) occur. Hence, three force constants have to be calculated from two normal frequencies only, thus leaving the problem undetermined. If no additional data (such as isotopic data or rotation–vibration interaction constants) are available, simplifications have to be made concerning the force field or the method of solving the corresponding secular equation.[16] In our calculations a previously published method[17] was used overcoming this difficulty by the introduction of an additional minimizing condition, thus allowing the calculation of a complete set of force constants without additional data except for the normal frequencies. It has been shown[16] that this method yields values for the diagonal force constants comparable to those of the general valence force field if the symmetry species under consideration contains one stretching and one deformation mode. This is true for the F_{1u} species of octahedral XY_6. The symmetry force constants obtained for IF_6^+, isoelectronic TeF_6, and SbF_6^- [18] are shown in Table III.

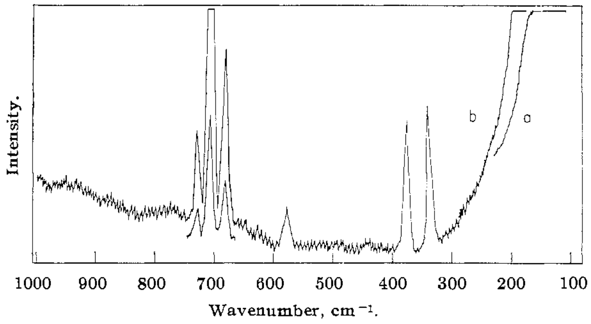

Figure 2.—Raman spectrum of $IF_6^+AsF_6^-$. a, Single slit; b, double slit.

TABLE II

VIBRATIONAL SPECTRA OF $IF_6^+AsF_6^-$(s) AND THEIR ASSIGNMENTS

Obsd freq, cm^{-1}		Assignment (point group)	
Infrared	Raman	IF_6^+ (O_h)	AsF_6^- (O_h)
1499 w		$\nu_1 + \nu_3$ (F_{1u})	
1386 w, br			$\nu_1 + \nu_3$ (F_{1u})
1307 1282 w			$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
828 w			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
797 790 ms		ν_{asym}, ν_3(F_{1u})	
	732 (2)	ν_{sym}, ν_2 (E_g)	
	708 (10)	ν_{sym}, ν_1 (A_{1g})	
695 vs			ν_{asym}, ν_3 (F_{1u})
	683 (5)		ν_{sym}, ν_1 (A_{1g})
616 w, sh			
580 w, sh	583 (1)		ν_{sym}, ν_2 (E_g)
521 w, sh			
404 m		δ_{asym}, ν_4 (F_{1u})	δ_{asym} ν_4 (F_{1u})
	377 (3)		δ_{sym}, ν_5 (F_{2g})
	340 (4)	δ_{sym}, ν_5 (F_{2g})	
[245][a]			δ_{sym}, ν_6 (F_{2u})
66		Lattice vibration	

[a] Calculated from $\nu_2 + \nu_6$.

Discussion

Synthesis and Properties.—Our synthesis of the IF_7–AsF_5 adduct was similar to that reported earlier.[9] However, it was found advantageous to use a considerable excess of AsF_5 which, owing to its higher volatility, can be removed from the solid complex more easily than excess IF_7. No tendency to form a product containing relatively stable $As_2F_{11}^-$ or higher polymeric anions was observed, as shown by elemental analysis.

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(15) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

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

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(18) W. Sawodny, unpublished results.

TABLE III

SYMMETRY FORCE CONSTANTS OF THE ISOELECTRONIC SERIES IF_6^+, TeF_6, AND SbF_6^-

Species	Force constant	IF_6^+	TeF_6	TeF_6[a]	SbF_6^- [18]
A_{1g}	$F_{11} = f_r + 4f_{rr} + f_{rr}'$	5.609	5.498	5.50	5.098
E_g	$F_{22} = f_r - 2f_{rr} + f_{rr}'$	5.995	5.083	5.08	3.803
F_{1u}	$F_{33} = f_r - f_{rr}'$	5.334	4.792	4.98	3.813
	$F_{34} = 2(f_{r\alpha} - f_{r\alpha}'')$	0.040	0.021	0.24	0.019
	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$	0.641	0.412	0.40	0.336
F_{2g}	$F_{55} = f_\alpha - 2f_{\alpha\alpha}' + f_{\alpha\alpha}'''$	0.323	0.274	0.27	0.221

[a] S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **44**, 3353 (1966).

This in agreement with the general finding that AsF_6^- has a much smaller tendency to add excess AsF_5 to form di- and polymeric anions, whereas for SbF_5 very often only complexes containing 2 or more moles of SbF_5[19] per mole of Lewis base are isolated. Thus, Seel and Detmer[9] have reported the preparation of two solids of the composition $IF_7 \cdot 2.4SbF_5$ and $IF_7 \cdot 3SbF_5$.

The observed dissociation pressure of 2.0 mm at 25° for the solid IF_7–AsF_5 adduct is in fair agreement with the value of about 2–3 mm at 20° reported earlier.[9] Unfortunately, only estimated values are available for the heat of formation of AsF_5. Therefore, the $\Delta H_f°_{298}$ value of $IF_6^+AsF_6^-$ contains the possible error inherent in the estimated value[14] of $\Delta H_f°_{298}$ of $AsF_5(g)$ used in our calculation.

Crystal Structure.—The crystal structure found for $IF_6^+AsF_6^-$ is face-centered cubic. The observed *d* spacings and density values agree well with those calculated. The high symmetry of the unit cell of IF_6^+-AsF_6^- (face-centered cubic) seems plausible since both IF_6^+ and AsF_6^- have octahedral symmetry (as shown later in the discussion) and, thus, are approximately spherical ions. No crystal structures of similar XF_6^+-YF_6^- salts are known. However, the cation to anion radius ratio in $IF_6^+AsF_6^-$ is roughly comparable to that in RbF or CsF, both having the cubic face-centered NaCl arrangement. In $IF_6^+AsF_6^-$ the iodine and arsenic atoms occupy the positions of the sodium and chlorine atoms in the NaCl lattice. Since both the arsenic and iodine atoms are considerably heavier than the fluorine atoms, they dominate the scattering. Consequently, the stronger lines are due to scattering from the face-centered cubic arsenic–iodine array. Additional lines of lower intensity not expected for a simple NaCl structure (having mixed, even and odd Miller indices) are obviously caused by scattering from the fluorine atoms grouped around the arsenic and iodine atoms. The reasonableness of the X-ray data found for the $IF_6^+AsF_6^-$ can be demonstrated further by calculating the average volume of each fluorine neglecting the volume of the highly charged central atoms since they occupy interstices in the fluoride packing. This method was originally suggested by Zachariasen[20,21] and recently applied by Penneman[22] to the X-ray data reported for $NF_4^+AsF_6^-$.[11,23] The average fluorine volume thus obtained for $IF_6^+AsF_6^-$ (17.8 A^3) is in fair agreement with that found for $NF_4^+AsF_6^-$ (17.0 A^3), the slight increase probably being due to the fact that contributions to the volume from the iodine central atom cannot completely be neglected.

Vibrational Spectra.—The simplicity of the vibrational spectra and the occurrence of all bands characteristic for AsF_6^- suggest that $IF_7 \cdot AsF_5$ is ionic and contains the AsF_6^- anion. Consequently, the IF_7 part of the adduct should be present in the form of IF_6^+. Table II shows the vibrational spectra of $IF_6^+AsF_6^-$ together with their assignment for point group O_h. An octahedral ion of the type XY_6, such as AsF_6^- and possibly IF_6^+, has O_h symmetry. The six normal modes of vibration are classified as $A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$. 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 spectrum. Accordingly, the normal modes associated with AsF_6^- can be assigned without difficulty. All five active modes were observed in agreement with the selection rules, and the frequencies and intensities were similar to those of other AsF_6^--containing complexes such as ClF_2^+-AsF_6^-,[5] $NF_4^+AsF_6^-$,[24] $AsCl_4^+AsF_6^-$,[25] and $K^+AsF_6^-$.[4,26] The only deviation from the selection rules is observed for ν_2 (E_g). This mode should be only Raman active but was also observed in the infrared spectrum as a weak shoulder. However, 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 $IF_6^+AsF_6^-$, according to the X-ray data reported in this paper, has four molecules per unit cell) can cause this mode to become infrared active. The same effect occurs in the infrared spectra of $ClF_2^+AsF_6^-$,[5] $NF_4^+AsF_6^-$,[24] and $AsCl_4^+$-AsF_6^-,[25] in which this mode occurs at 609, 581, and 587 cm^{-1}, respectively.

The remaining bands of the $IF_6^+AsF_6^-$ spectra, therefore, should be due to the IF_6^+ cation. Octahedral IF_6^+ (symmetry O_h) being isoelectronic with AsF_6^- should exhibit the same features as AsF_6^- except for slight frequency shifts of the modes. The higher mass of the central atom in IF_6^+ compared to AsF_6^- should cause a shift toward lower frequencies. This effect, however, is compensated to a certain extent by the positive charge on the central atom in IF_6^+ compared to the negative charge in AsF_6^-. Furthermore, the increase in the radius of the central atom in IF_6^+ should affect the bending modes more than the stretching modes. Keeping these effects in mind we would

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(21) F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).

(22) R. A. Penneman, *Inorg. Chem.*, **6**, 431 (1967).

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

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

expect the IF_6^+ modes to show a similar pattern as AsF_6^- and to have frequencies not too different from those observed for AsF_6^-, if IF_6^+ really has octahedral symmetry. Since O_h represents the highest possible symmetry for XY_6, any other structure would be of lower symmetry and should result in a much higher number of bands in the vibrational spectra. The observed frequencies, relative intensities, and number of bands agree only with an octahedral structure for IF_6^+. The assignment of the vibrational spectra is given in Table II. In the infrared spectrum only one band was observed in the range expected for ν_4 (F_{1u}). Therefore, coincidence of ν_4 (F_{1u}) of AsF_6^- and IF_6^+ is assumed. In the Raman spectrum three bands were observed for IF_6^+ as expected for symmetry O_h. It should be pointed out that ν_2 (E_g) occurs at a slightly higher frequency than ν_1 (A_{1g}). This feature is somewhat surprising and to our knowledge has not been observed for any other octahedral XY_6. However, the relative intensities of the Raman bands and force constant calculations (as discussed later) strongly support the given assignment. Unfortunately, no polarization measurement (which would distinguish easily between ν_1 and ν_2, since ν_1 (A_{1g}) should be the only polarized band) could be taken owing to the solid state of the $IF_6^+AsF_6^-$ sample. The given assignment is further supported by comparison with the spectra of the series: SF_6, SeF_6, and TeF_6. Within this series the frequency difference, $\nu_1 - \nu_2$, decreases markedly from 131 cm^{-1} for SF_6 to 27 cm^{-1} for TeF_6.[27] This progressive decrease is probably due to a decrease in the nonbonded fluorine atom interactions with increase in the size of the central atom.[28] On this basis the occurrence of ν_2 (E_g) of IF_6^+ at a frequency slightly higher than that of ν_1 (A_{1g}) does not seem to be unreasonable.

Comparison of the relative intensities between the IF_6^+ and the corresponding AsF_6^- modes shows that the IF_6^+ bands have a higher intensity in the Raman spectrum, whereas the AsF_6^- bands have a higher intensity in the infrared spectrum. This observation is in good agreement with theoretical expectations, since IF_6^+ should exhibit a higher polarizability than AsF_6^- owing to the larger size of its central atom. Correspondingly, the smaller size of AsF_6^- causes a greater change of the dipole moment, thus explaining the higher intensities of the AsF_6^- infrared bands.

In the infrared spectrum of $IF_6^+AsF_6^-$ there are eight bands yet unassigned, all of them being of very low intensity and/or occurring outside the range expected for fundamental vibrations. Thus, the band at 66 cm^{-1} is assigned to a lattice vibration. The bands at 1386, 1307–1282, and 828 cm^{-1} can be assigned to the combination vibrations $\nu_1 + \nu_3$ (F_{1u}), $\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$), and $\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$), respectively, of AsF_6^-. All three bands are expected to be infrared active according to the selection rules and were also observed in the spectra of other AsF_6^--containing salts such as $ClF_2^+AsF_6^-$.[5] In the spectrum of the latter, $\nu_2 + \nu_3$ occurred also as a doublet. From the frequency of $\nu_2 + \nu_6 = 828$ cm^{-1} and the knowledge of $\nu_2 = 583$ cm^{-1} from the Raman spectrum, a value of 245 cm^{-1} was calculated for ν_6 (F_{2u}) of AsF_6^-. The ν_6 (F_{2u}) mode itself is inactive in both the infrared and Raman spectrum. Of the remaining bands the one at 1499 cm^{-1} is assigned to $\nu_1 + \nu_3$ (F_{1u}) of IF_6^+. There are only two shoulders of low intensity at 616 and 521 cm^{-1}, respectively, left for which no satisfactory explanation can be given presently.

In summary, all five fundamental vibrations expected for both AsF_6^- and IF_6^+ in the case of symmetry O_h 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 deviations from theoretical expectations are ν_2 (E_g) of AsF_6^- becoming weakly infrared active owing to crystal field effects. Thus, the observed vibrational spectra are consistent with the predictions made for distinct IF_6^+ and AsF_6^- ions, both having essentially octahedral symmetry (point group O_h).

The ionic structures, $IF_6^+AsF_6^-$ for the IF_7–AsF_5 adduct and $IF_4^{3+}(SbF_6^-)_3$ for the IF_7–$3SbF_5$ adduct in the solid state, have been postulated previously,[8,9] but no supporting data were given by these authors. The present investigation shows that the ionic structure, $IF_6^+AsF_6^-$, is correct for $IF_7 \cdot AsF_5$. The adduct between IF_7 and SbF_5 has not been investigated by us; however, its interpretation as $IF_4^{3+}(SbF_6^-)_3$ seems to be very unlikely because (i) an adduct of the composition $IF_7 \cdot 2.4\,SbF_5$ has been reported also,[9] indicating that the found stoichiometry may be accidental and due to the failure to remove excess SbF_5 successfully, and (ii) it is well established that SbF_6^- can form with excess SbF_5 polymeric anions such as $Sb_2F_{11}^-$.[19,29] For example, the $N_2F_4 \cdot 2SbF_5$ adduct was shown to have the structure $N_2F_3^+Sb_2F_{11}^-$.[19] Therefore, it seems more likely to interpret the adduct between IF_7 and SbF_5 in terms of IF_6^+ and polymeric $SbF_6^- \cdot xSbF_5$ rather than in terms of $IF_4^{3+}(SbF_6^-)_3$.

Force Constants.—Table III lists the symmetry force constants obtained for IF_6^+, together with those of isoelectronic TeF_6 and SbF_6^-.[18] In all three cases the mass of the central atom is large compared to that of fluorine. Therefore, coupling between the two modes of species F_{1u} is very small, and the approximating method[17] used for our calculation of force constants yields results close to those of a modified valence force field neglecting the coupling between ν_3 and ν_4 completely. In such cases of weak coupling the interaction constant, F_{34}, influences the diagonal force constants[16] only very slightly. This effect is demonstrated in Table III by comparison of our results for TeF_6 with those of the general valence force field (GVFF), calculated by using Coriolis ζ constants as additional data.[30] Whereas the value of F_{34} is 9% of the GVFF

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[27] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 119.

[28] L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, **17**, 594 (1961).

[29] J. Weidlein and K. Dehnicke, *Z. Anorg. Allgem. Chem.*, **348**, 278 (1966).

[30] See ref *a* of Table III.

value, the differences for F_{33} and F_{44} are only about 4 and 3%, respectively. These differences decrease further to about 2% when the internal valence force constant, f_r, given in Table IV is considered. The same arguments should be applicable to the potential constants of IF_6^+ and SbF_6^-. Therefore, the values of the valence force constant, f_r (which will be discussed in the following paragraphs), are considered to be very close to those of the GVFF.

Table IV

Valence Force Constants of IF_6^+, TeF_6, and SbF_6^- (mdynes/A)

	IF_6^+	TeF_6	TeF_6[30]	SbF_6^- [18]
f_r	5.60	5.01	5.10	4.02
f_{rr}	−0.06	0.07	0.07	0.22
f_{rr}'	0.27	0.22	0.12	0.21

Table IV lists the valence force constant, f_r, and the coupling constants, f_{rr} and f_{rr}', between perpendicular and between opposite bonds, respectively, for IF_6^-, TeF_6, and SbF_6^-. The deformational constants cannot be given explicitly because of the redundancy condition in species A_{1g} and because of the unknown frequency of the inactive F_{2u} mode. Similar arguments apply to the coupling constant, $f_{r\alpha}$, which is quite different from the GVFF value in TeF_6 and, therefore, cannot be considered to be meaningful.

The increase of the value of the valence force constant, f_r, from SbF_6^- toward IF_6^+ corresponds to that reported by Woodward[31] for similar isoelectronic series. It can be explained by the increasing positive charge on the central atom.

The octahedral structure of IF_6^+ could be explained by two different bond models: (i) an sp^3d^2 hybridization of the valence electrons of iodine resulting in mainly covalent I–F bonds and (ii) a semiempirical molecular orbital model[32-36] involving mainly three delocalized p-electron pairs of the iodine atom for the formation of three semiionic three-center, four-electron p–p σ bonds. It has recently been shown[3,5,7,37] that the valence force constants are especially suited to distinguish between these two types of bonding. For model i the value of the valence force constant, f_r, should be comparable to that of a covalent IF single bond, whereas for model ii f_r should be roughly half that of a covalent single bond. Table V shows a comparison of the valence force constant, f_r, values obtained for different iodine fluorides. It is obvious that IF_6^+ has the highest f_r value yet obtained for any iodine fluoride (part of the increase is certainly due to the positive charge on the central atom[31]). Therefore, only bond model i can be correct. This finding agrees well with theoretical expectations.

Table V

Comparison of I–F Valence Force Constants (mdynes/A)

Compound	f_r[I–F (axial)]	f_r[I–F (equat)]
IF_5[a]	4.68	3.64
IOF_5[b]	4.60	4.42
IF_7[c,d]	(4.10)	(3.01)
IF_6^+	5.60	

[a] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42,** 2236 (1965). [b] D. F. Smith and G. M. Begun, *ibid.*, **43,** 2001 (1965). [c] R. K. Khanna, *J. Mol. Spectry.*, **8,** 134 (1962). [d] These values are likely to be incorrect: W. Saodwny, unpublished results.

It should be pointed out that the marked difference of f_r[I–F (equat)] between IF_5 and IOF_5 (as shown in Table V) is mainly due to the different type of bonding in these two molecules. The equatorial I–F bonds in IF_5 consist, in analogy to ClF_5,[7] mainly of two semiionic three-center, four-electron p–p σ bonds, thus resulting in a much lower value for the valence force constant, f_r, whereas IOF_5 (possessing no free-electron pair on the central atom) most likely contains, in analogy to IF_6^+, mainly covalent sp^3d^2 hybridization bonds. Thus, the assumption, made by Smith and Begun,[38] that the I–F (equat) bond length in IOF_5 is similar to that in IF_5 is not justified. Furthermore, their way of explaining the strengthening of the I–F (equat) bond in IOF_5 (compared to that of IF_5) by the increased positive charge or valence of the central iodine atom is not plausible, since it should affect the axial I–F bond to the same extent as the equatorial one. However, as Table V shows, this is not the case.

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(37) W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *J. Chem. Phys.*, **35**, 908 (1961).

(38) See ref *b* of Table V.