Table V. Values of the Experimentally Obtained Excess Entropies of Mixing ΔS^E_{exptl} and the Calculated Entropies ΔS^E_{calcd} at 0.5 Mole Fraction

System	δ_{12}, A^{-1}	ΔS^E_{exptl}, cal mol^{-1} deg^{-1}	ΔS^E_{calcd}, cal mol^{-1} deg^{-1}
AgBr–LiBr	0.0473	−0.27	−0.24
AgBr–NaBr	0.0000	−0.08	0.00
AgBr–KBr	−0.0399	−0.22	−0.12
AgBr–RbBr	−0.0533	−0.30	−0.23
AgBr–CsBr	−0.0701	−0.31	−0.40

to indicate the correctness of the functional form[2] of eq 8 predicted from conformal solution theory, and the $\Delta G^E =$

ΔH^M assumption made in previous published work is shown to be invalid.

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Adducts of Chlorine Oxide Trifluoride with Group V Element Pentafluorides. Structural Study of the Hexafluoro Anions

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The adduct formation of $ClOF_3$ with PF_5, AsF_5, VF_5, SbF_5, TaF_5, NbF_5, and BiF_5 was studied. With each of these pentafluorides a one-to-one complex is formed and characterized by X-ray powder diffraction patterns and vibrational spectra. The latter strongly support ionic structures. Both orbital valence and Urey-Bradley force fields were computed and evaluated for PF_6^-, AsF_6^-, VF_6^-, SbF_6^-, TaF_6^-, NbF_6^-, and BiF_6^-.

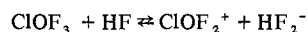## Introduction

Chlorine oxide trifluoride exhibits amphoteric properties. It forms adducts with Lewis bases or acids[1-6] according to

$$ClOF_3 + AF_n \rightleftharpoons ClOF_2^+ + AF_{n+1}^-$$

$$ClOF_3 + BF_m \rightleftharpoons ClOF_4^- + BF_{m-1}^+$$
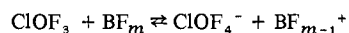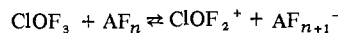
where AF_n and BF_m stand for acid and basic molecules, respectively.

We have previously shown[1] that $ClOF_3$ is ionized in anhydrous HF according to

$$ClOF_3 + HF \rightleftharpoons ClOF_2^+ + HF_2^-$$

Likewise Christe, *et al.*,[2-4] described examples of adducts derived from both acids and bases. In this paper we wish to report the basic property of $ClOF_3$ toward group V element pentafluorides.

Adducts of $ClOF_3$ with AsF_5 and SbF_5 have already been reported elsewhere.[1,2,4,5] In this paper we report the results of a systematic study involving a large number of pentafluorides.

Experimental Section

Materials. Chlorine oxide trifluoride has been prepared either according to a photolytic process[1] or, with a much better yield, according to the chemical process described by Pilipovich, *et al.*[7] $ClOF_3$ was stored as a complex with KF to prevent any decomposi-

tion during storage. Impurities not forming a stable KF adduct are pumped off at 25° while pure $ClOF_3$ is obtained by vacuum pyrolysis at 60-80°.

SbF_5 was purchased from the Societe des Usines Chimiques de Pierrelatte and the other pentafluorides were prepared[8] by reaction between fluorine and the corresponding elements (purchased from Prolabo). Prior to use, the volatile pentafluorides were purified by fractional condensation and checked for purity by Raman and infrared spectroscopy, powder X-ray diffraction pattern, and microsublimation whenever the physical state of the sample allowed these methods to be used.

Apparatus. The "fluorine line" used in this work is for the most part made of Monel metal tubing equipped with valves purchased from F.W. Co. and Etudes et Constructions Aeronautiques Co. (ECA) differential gauges for the ranges 0-10 and 0-100 mm and with Bourdon gauges for the ranges 0-100 and 0-5000 mm. Occasionally we have also used an Atlas MCT manometer for the very low pressure measurements. For observation, part of the apparatus was equipped with Kel-F tubes and Kel-F valves purchased from Viennot Co.

Before use the vacuum line was passivated with ClF_3 and the compound to be handled. We noticed this procedure to be specially useful whenever $ClOF_3$ is handled; otherwise slight amounts of ClO_2F were produced.

Spectra. Infrared spectra were recorded with a Beckman Model IR 9 and a Perkin-Elmer Model 457 in the ranges 4000-400 and 4000-250 cm^{-1}, respectively, while an FS 720 spectrophotometer was used in the 400-40-cm^{-1} range.

Spectra of gases were recorded using a 10 cm long Monel-body gas cell equipped with AgCl windows sealed with Teflon gaskets. Powders were pressed between two thin plates of AgCl 12 mm in diameter. In order to prevent loss of energy due to the IR 9 beam height which is larger than the pellet diameter we used a beam condenser with this apparatus.

Rather good spectra in the lower frequency range could be obtained by using two silicon plates (29 mm in diameter and 1 mm in thickness, Silicon Z F chemical polish type, 30-50 ohm/cm, purchased from Silec Co). The powders were put between these plates probably due to their highly polished surface, the attack was slow

(1) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **273**, 415 (1971).
(2) K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 2205 (1972).
(3) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2209 (1972).
(4) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, **11**, 2212 (1972).
(5) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **271**, 1366 (1970).
(6) K. Zuchner and O. Glemser, *Angew. Chem.*, **84**, 1147 (1972).
(7) D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

(8) A. D. Beveridge and H. C. Clark, *Halogen Chem.*, **3**, 91 (1967); F. Fairbrother, *ibid.*, **3**, 123 (1967); L. Kolditz, *ibid*, **2**, 116 (1967).

enough to allow scanning of a spectrum (about 30 min).

Raman spectra were recorded with a Coderg PHO spectrophotometer, using as exciting light a 125 A or 165 Spectra Physics laser, the wavelengths used being 632.8 and 488 nm or 514.5 nm, respectively.

The samples were handled in 4-mm o.d. Kel-F or FEP Teflon tubing (from Viennot Co and Penntube Plastics, respectively) attached to a Kel F valve.

The polarization measurements have been achieved with a half-wave plate, two analyzers, and a λ/4 plate. As sample containers both a 4-ml Kel-F body cell equipped with 17-mm diameter sapphire windows and FEP tubes as described by Brownstein and Shamir[9] were used. The proper adjustments were checked with liquid CCl_4 through measurements of its depolarization ratios.

X-Ray Diffraction Patterns. The Debye-Scherrer powder patterns were taken using a 114-mm diameter Philips instrument with copper Kα radiation (1.5418 A). The samples were loaded in the dry nitrogen atmosphere of a glove box into quartz capillaries (~0.5 mm). Attempts were made to obtain single crystals by slow sublimation into quartz capillaries. So far we have only been able to get partial results.

General Synthetic Procedures. All reactions between $ClOF_3$ and pentafluorides were carried out in tubes similar to those described for Raman spectroscopy. The entire operation was conducted with two tubes, called A and B. Depending on their vapor pressure, the pentafluorides were either condensed or put in a dry glove box into A. An excess of ClF_3O was condensed into B. The exact amounts of starting materials were determined by weighing. An excess of $ClOF_3$ was taken from B and condensed into A at −196°. The mixture in A after being left at room temperature for about 15 min was cooled to about −15° in a Dry Ice-acetone mixture. Unreacted $ClOF_3$ was slowly transferred from A to B which was cooled to −196°. Finally A was allowed to reach room temperature and the operation was stopped when no more $ClOF_3$ was released from A. Both tubes were weighed again, thus permitting a cross check of the material balance.

It is worth saying that this technique has also been used with HF as solvent. This was done to avoid any polyanion formation. For instance with SbF_5 we could have obtained some $Sb_2F_{11}^-$.[2] To give an example of the accuracy of this method, 1.413 mmol of $ClOF_3$ reacted with 1.414 mmol of SbF_5.

Results

Characterization and General Properties of the Adducts. $ClOF_3$ combines with the group V element pentafluorides PF_5, AsF_5, SbF_5, BiF_5, VF_5, NbF_5, and TaF_5 to give 1:1 adducts. These adducts are white, crystalline solids at room temperature and are very reactive toward moisture and organic materials.

The adducts are stable at room temperature except for those involving PF_5 and VF_5 which exhibit a dissociation pressure of about 3.5 and 2.5 mm, respectively. However, all the complexes are soluble in anhydrous HF, the bismuth-derived adduct being the least soluble.

X-Ray powder data of the adducts are listed in Table I.[10] Isomorphism of the whole group is apparent from these results and the preliminary data obtained with a VF_5 adduct single crystal were not incompatible with an orthorhombic unit cell as proposed by Christe, *et al.*, for $ClOF_2^+PtF_6^-$ and $ClOF_2^+AsF_6^-$.[2,11] However, some further studies on single crystals are necessary to give conclusive results.

Figure 1 gives the infrared spectra for the solids in the range 4000-400 cm^{-1} while Figure 2 is representative of the 400-40-cm^{-1} range.

Frequencies around 400 cm^{-1}, the lower and upper limit for Beckman IR 9 and FS 720 instruments, respectively, were checked with a Perkin-Elmer 457 whose spectral range covers 4000-250 cm^{-1}.
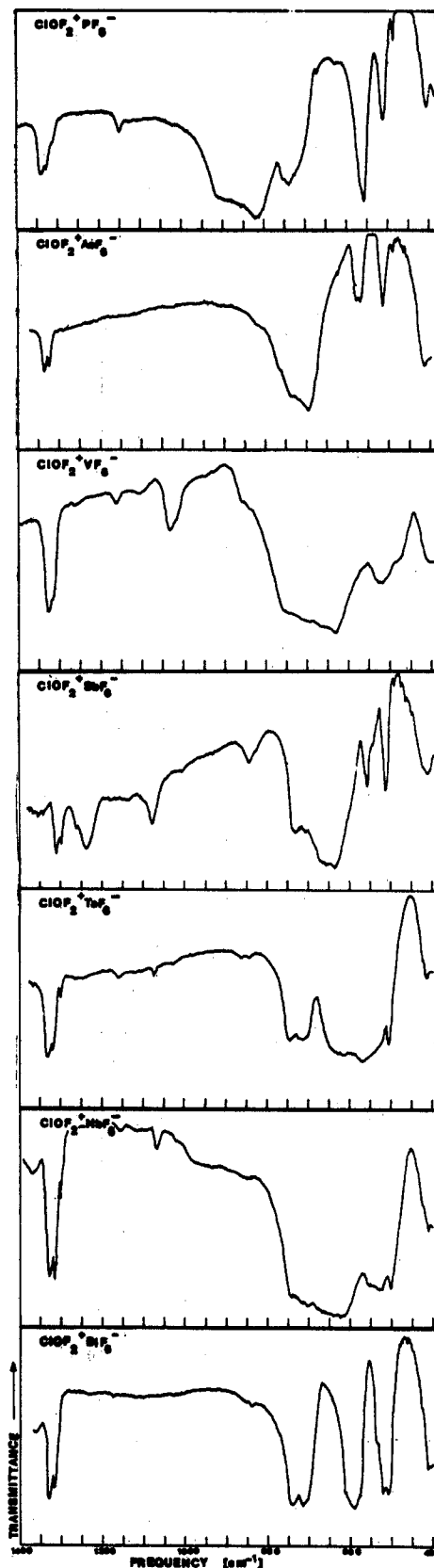
(9) M. Brownstein and J. Shamir, *Appl. Spectrosc.*, **26**, 77 (1972).

(10) See paragraph at end of paper regarding supplementary material.

(11) C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, **11**, 2201 (1972).

Figure 1. Infrared spectra of solid $ClOF_3$ adducts in the range 400-4000 cm^{-1}. (No band was observed above 1400 cm^{-1}.)

Figure 3 and 4 give the Raman spectra for the solids and HF solutions, respectively.

Tables II-VIII[10] give the observed frequencies together with the proposed assignments. Assignments for the anions
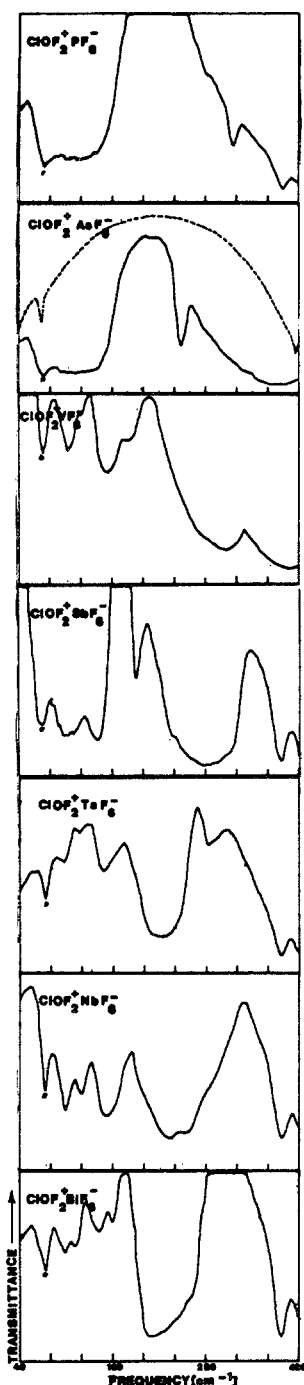
Figure 2. Infrared spectra of solid $ClOF_3$ adducts in the range 40–400 cm^{-1}. The curve of transmission recorded without the sample is shown with the $ClOF_2^+AsF_6^-$ spectrum. The band marked with an asterisk is due to the polyethylene lens of the spectrometer.

were made by analogy with those previously reported in the literature.[9,12-23]

(12) J. A. Evans and D. A. Long, *J. Chem. Soc. A*, 1688 (1968).
(13) R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1969).
(14) N. A. Matwiyoff, L. B. Asprey, and W. E. Wageman, *Inorg. Chem.*, **9**, 2014 (1970).
(15) O. L. Keller, Jr., *Inorg. Chem.*, **2**, 783 (1963).
(16) J. Shamir, J. Binenboym, and H. H. Claasen, *J. Amer. Chem. Soc.*, **90**, 6223 (1968).
(17) R. D. Peacock and I. L. Wilson, *J. Chem. Soc. A*, 2030 (1969).
(18) J. Shamir and D. Yellin, *Isr. J. Chem. 7*, 421 (1969).
(19) A. M. Qureshi and F. Aubke, *Can. J. Chem.*, **48**, 3117 (1970).
(20) M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, **47**, 4159 (1969).
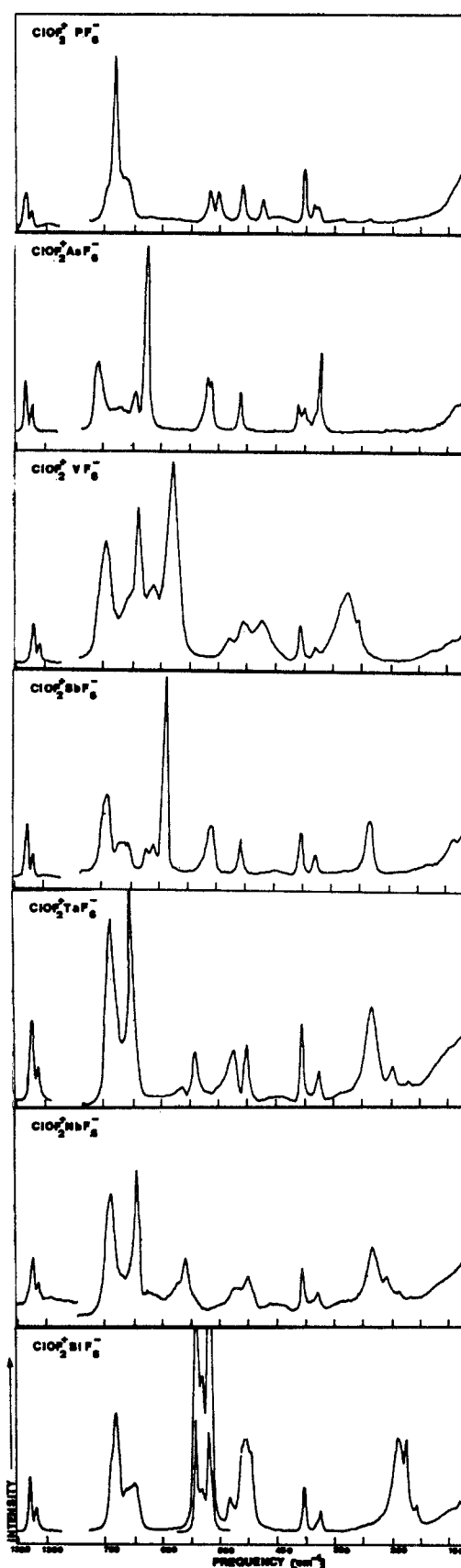

Figure 3. Raman spectra for solid $ClOF_3$ adducts (spectral slit width 4 cm^{-1}).

(21) W. B. Fox, C. A. Wamser, R. Eibeck, D. K. Huggins, J. S. MacKenzie, and R. Juurik, *Inorg. Chem.*, **8**, 1247 (1969).
(22) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967).
(23) H. A. Carter, W. M. Johnson, and F. Aubke, *Can J. Chem.*, **47**, 4619 (1969).
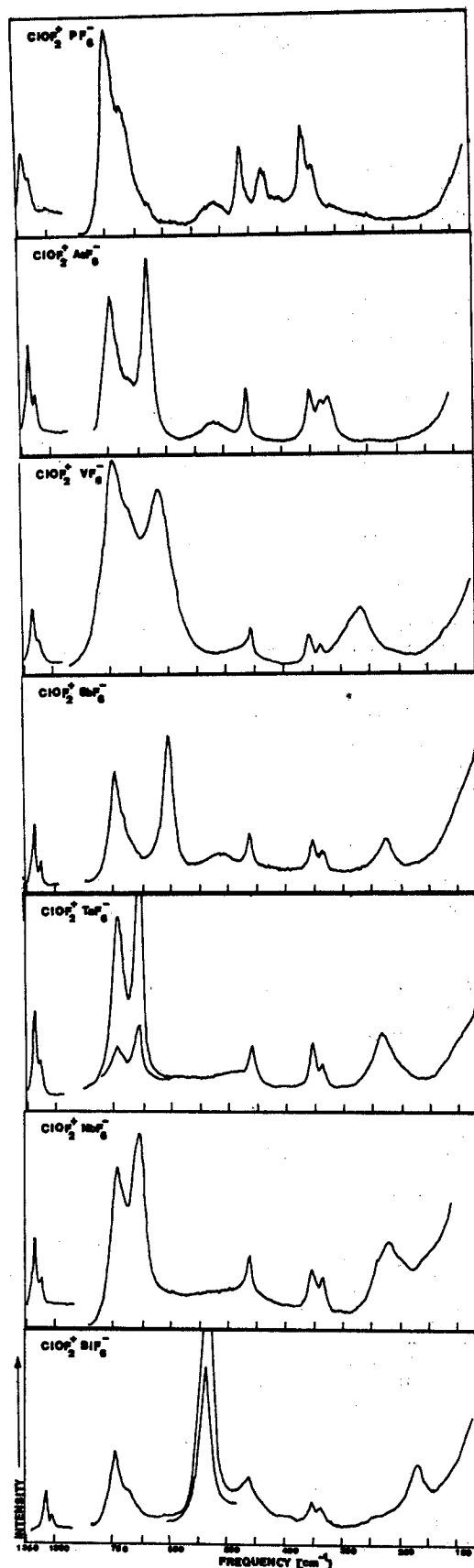
Figure 4. Raman spectra for HF solutions of $ClOF_3$ adducts (spectral slit width 4 cm^{-1}).

The ionic structure $ClOF_2{}^+MF_6{}^-$ (M = P, V, As, Nb, Sb, Ta, Bi) is obvious from the vibrational spectra, although

some departure from the O_h group symmetry selection rules is found for the anion in the solid state

As reported in Tables II–VIII[10] the presence of small quantities of $ClO_2{}^+$ ion accounts for some weak infrared bands[24] observed in the solid. $ClO_2{}^+$ may be produced by reaction of the complex with traces of moisture. The ν_1 band of $ClO_2{}^+$ sometimes appears also in Raman spectra of HF solutions but complete exclusion of moisture during handling prevents this partial hydrolysis.

Vibrational Assignment. The assignments for $ClOF_2{}^+$ in point group C_s have previously been reported.[4,25] However, there is a possible inversion in the assignment of $\nu_4(a')$ and $\nu_6(a'')$. To clear up this point we have carefully examined the depolarization ratios. The two bands are relatively close together (around 400 and 380 cm^{-1}, respectively) and it was necessary graphically to substract their mutual contribution from each other.

The depolarization ratios were measured six times in a $ClOF_3$–HF solution. It was found that within 95% accuracy the higher frequency gives a significantly lower depolarization ratio than the lower one, *i.e.*, 0.725 ± 0.015 vs. 0.805 ± 0.055, respectively. Therefore unlike the assignment given by Pace and Samuelson[26] for the isoelectronic molecule SOF_2, the higher frequency was assigned to $\nu_4(a')$ and the lower one to $\nu_6(a'')$. Christe, *et al.*,[4] have reported force field calculations for both assignments.

As all group V hexafluoro anions were studied in this work, it was interesting to compute and compare their force constants. Whereas the spectra of the HF solutions agree with those expected for octahedral anions, those of the solids show deviations. For example, selection rules are not strictly followed and minor band splittings are observed. However, these effects are relatively well understood and in the absence of precise structural data these anions can be treated as being octahedral.

The following frequency values were used for the force field computations. For $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(f_{2g})$ the Raman frequencies of the HF solution and for $\nu_3(f_{1u})$, $\nu_4(f_{1u})$, and $\nu_6(f_{2u})$ the infrared frequencies of the solid were adopted. This procedure was supported by the fact that the anion bands or, in the case of splittings, their averaged frequencies did not deviate very much from solid to solution.

The F-matrix definitions for the Urey–Bradley force field (UBFF) and orbital valence force field (OVFF)[27] were taken from ref 28.

The force constants were computed by a weighted least-squares method using the program FOND of Tournarie[29] written for the IBM 360-91 computer. This program through a proper strategic adjustment (*"methode du simplexe"*) is able to find the minimum of a several-variable function in a bounded space.

Tables IX and X list the observed and calculated frequencies and force constants for both UBFF and OVFF force fields. In addition, calculations have been made using only five fundamental vibrations, in order to check the observed ν_6 value which could have been confused with lattice vibrations.

(24) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

(25) R. Bougon, *C. R. Acad. Sci., Ser. C*, **274**, 696 (1972).

(26) E. L. Pace and H. V. Samuelson, *J. Chem. Phys.*, **44**, 3682 (1966).

(27) D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 873, 878, 884 (1948); **45**, 264 (1949).

(28) H. Kim, P. A. Souder, and H. H. Claasen, *J. Mol. Spectrosc.*, **26**, 46 (1968).

(29) M. Tournarie, private communication.

Table IX. Observed and Calculated Frequencies and Force Constants for Subgroup Va Element Hexafluoro Anions

| | Freq, cm⁻¹ | | | | | | Force constants,[b] mdyn/Å | | | | Av % dev | |
	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_3(f_{1u})$	$\nu_4(f_{1u})$	$\nu_5(f_{2g})$	$\nu_6(f_{2u})$	K	F	F'	H or D	$\nu_1-\nu_3$	$\nu_4-\nu_6$
						PF₆⁻						
Obsd	746	561	817	557	475	316						
UBFF(5)[a]	760.6	541.6	831.6	540.1	484.5	309.6	2.700	0.944	-0.120	0.125		
UBFF	759.1	543.4	830.6	539.3	487.4	314.8	2.697	0.938	-0.110	0.140	2.2	2.1
OVFF	764.9	541.2	829.9	549.7	469.4	319.2	2.659	0.973	-0.118	0.285	2.5	1.2
						AsF₆⁻						
Obsd	682	568	696	379	369	248						
UBFF(5)[a]	682.5	555.9	708.2	376.7	370.7	228.5	3.243	0.492	-0.092	0.092		
UBFF	679.3	559.5	706.8	372.2	379	245.1	3.213	0.488	-0.066	0.125	1.1	1.9
OVFF	693.2	555.2	702.9	379.7	364	249.1	3.100	0.570	-0.073	0.197	1.6	0.6
						SbF₆⁻						
Obsd	653	561	667	280	273	190						
UBFF(5)[a]	653	561.2	666.7	280	272.9	144.5	3.476	0.324	-0.091	0.0005		
UBFF	642.9	568.2	666.2	269.2	289.3	183.8	3.456	0.293	-0.045	0.065	1.0	4.4
OVFF	643.7	567.3	666.3	279.4	274.9	189.6	3.455	0.296	-0.050	0.156	0.9	0.4
						BiF₆⁻						
Obsd	592	519	582	216	218	150						
UBFF(5)[a]	591.5	517.6	584	215.9	218	106	2.975	0.235	-0.070	0.020		
UBFF	578.9	525.5	585	206	232.4	144.8	3.006	0.186	-0.034	0.041	1.3	4.8
OVFF	577.8	525.6	585.3	215.3	219.9	149.7	3.027	0.178	-0.038	0.111	1.4	0.4

[a] Frequencies and force constants calculated without the observed value of ν_6. [b] K is stretching along a bond; H is angle deformation; F and F' are interactions between nonbonded fluorine atoms adjacent and opposite to each other, respectively; D is the Heath and Linnett[27] angle deformation from overlapping.

Table X. Observed and Calculated Frequencies and Force Constants for Subgroup Vb Element Hexafluoro Anions

| | Freq, cm⁻¹ | | | | | | Force constants,[b] mdyn/Å | | | | Av % dev | |
	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_3(f_{1u})$	$\nu_4(f_{1u})$	$\nu_5(f_{2g})$	$\nu_6(f_{2u})$	K	F	F'	H or D	$\nu_1-\nu_3$	$\nu_4-\nu_6$
						VF₆⁻						
Obsd	663	520	690	304	314	156						
UBFF(5)[a]	663.2	521.6	687.5	304.2	313.8	206.2	2.57	0.588	-0.037	-0.037		
UBFF	687.5	509	684.6	311.3	292.1	159	2.493	0.699	-0.097	-0.159	2.2	3.7
OVFF	666.1	516.8	692.3	304	313.1	156.1	2.660	0.576	-0.083	-0.220	0.5	0.1
						NbF₆⁻						
Obsd	704	540	610	244	271	154						
UBFF(5)[a]	682.2	510.6	638.7	243.5	271.6	151.2	2.468	0.685	-0.078	-0.175		
UBFF	680	511.5	638.7	243.2	272.3	153.8	2.478	0.676	-0.075	-0.168	4.8	0.3
OVFF	640	524.8	640	241.8	278.1	153.5	2.784	0.451	-0.050	-0.136	5.6	1.3
						TaF₆⁻						
Obsd	707	534	600	224	278	148						
UBFF(5)[a]	687.8	518.4	621.9	224	277.9	156.7	2.561	0.683	-0.079	-0.165		
UBFF	693	515.2	622.2	224.7	275.7	148.5	2.526	0.712	-0.089	-0.188	1.7	0.6
OVFF	655.2	534.5	619.9	223.0	283.6	147.5	2.904	0.475	-0.060	-0.171	3.6	0.9

[a] Frequencies and force constants calculated without the observed value of ν_6. [b] See Table IX.

The average percentage deviations of the calculated values from the observed values are given for the three stretching vibrations $\nu_1(a_{1g})$, $\nu_2(e_g)$, $\nu_3(f_{1u})$ and for the three bending vibrations $\nu_4(f_{1u})$, $\nu_5(f_{2g})$, $\nu_6(f_{2u})$.

In addition data for the isoelectronic molecules[30] are given in Table XI for comparison.

In order to check the validity of the findings concerning the trends in force constants, calculations were performed using general valence force field and five force constants. For comparable force constants, *i.e.*, stretching and bending, the trends were found the same as those observed with UBFF and OVFF (see Table XII[10]).

Discussion

The calculated force constant values are in good agreement with the experimental frequencies for both UBFF and OVFF, and as expected,[28] the agreement is significantly

(30) P. Labonville, J. R. Ferraro, M. C. Wall, S. M. C. Basile, and L. J. Basile, *Coord. Chem. Rev.*, **7**, 257 (1972).

Table XI. Force Constants (OVFF) Compared between Hexafluoro Anions and Isoelectronic Molecules

| Isoelectronic species | Force constants,[a] mdyn/Å | | | |
	K	F	F'	D
PF₆⁻, SF₆	2.66, 3.59	0.97, 0.95	-0.12, -0.16	0.28, 0.60
AsF₆⁻, SeF₆	3.10, 4.25	0.57, 0.47	-0.07, -0.14	0.20, 0.45
SbF₆⁻, TeF₆	3.45, 4.62	0.30, 0.32	-0.05, -0.09	0.16, 0.20
BiF₆⁻, PoF₆[b]	3.03	0.18	-0.04	0.11
VF₆⁻, CrF₆	2.66, ...	0.38, ...	-0.08, ...	-0.22, ...
NbF₆⁻, MoF₆	2.78, 3.97	0.45, 0.61	-0.05, -0.10	-0.14, -0.34
TaF₆⁻, WF₆	2.90, 4.32	0.47, 0.61	-0.06, -0.11	-0.17, -0.32

[a] Force constants for hexafluoride molecules are taken from ref 30. [b] No experimental frequency values are available for PoF₆.

better with OVFF than with UBFF for the bending vibrations.

When calculations are made without using the experimental ν_6 value, the relative shift found is not too large except in the case of SbF₆⁻, BiF₆⁻, and VF₆⁻. This does not necessarily imply that in these cases experimental ν_6 values are

wrong. More likely the force field chosen using only five frequencies may be incorrect.

Concerning the trends in force constant sets there is a clear distinction between subgroups Va and Vb. Data are almost constant in Vb while variations are more pronounced in Va. On account of an increase in bonding strength with atomic number, the stretching force constant K increases from P to Sb in Va, but its value is lower for Bi than for Sb, which may be due to a longer central atom–fluorine distance, giving a stronger ionic contribution.

The angular deformation constants H or D, again almost constant and negative in Vb, decrease from P to Bi in Va and possess a positive value. This suggests that the fluorine atom arrangement around the central atom gives a stiffer configuration in Va than in Vb and that in Va this stiffness is decreasing from P to Bi.

The value of the repulsive force constant F is approximately constant in Vb and decreases in Va from P to Bi in agreement with the increase in bond length and with the above remarks concerning the stiffness.

Table XI listing OVFF force constants for both the hexafluoro anions and the isoelectronic molecules shows that the trends are the same for both species, and as expected, values are of the same magnitude. The decrease in stiffness from comparison of D or H values is less pronounced for Va hexafluoro anions than for the corresponding isoelectronic molecules. To sum up, the strong basic property of $ClOF_3$ makes possible the preparation of stable one-to-one adducts with group V element pentafluorides. The new crystalline

phases have been defined by their X-ray powder patterns, while their ionic structure has been characterized by vibrational spectroscopy. The investigations performed on the entire group of possible XF_6^- anions allow a discussion of the OVFF and UBFF force field trends in this group. These force fields give good agreement between observed and calculated frequencies.

Contribution from the Department de Chimie-Physique, IRCHA, Vert-Le-Petit, France, and the Department de Chimie, Universite de Bretagne Occidentale, Brest-Cedex, France

X-Ray Photoelectron Spectroscopy Study of Some Metal(II) Halide and Pseudohalide Complexes

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In order to examine the value of ESCA spectroscopy in the field of metal coordination complexes, we have investigated a number of compounds of general formula $C^I_2(MX_4)$, where M is a divalent metal (Co, Zn, and in some cases Mn, Ni, and Cu), X = Cl, Br, NCO, NCS, or NCSe, and C^I is a monovalent tetraalkylammonium cation (alkyl = methyl, ethyl, and in some cases *n*-butyl). For comparison, some related octahedral complexes, $C^I_4(MX_6)$, and salts containing the same cations and anions were also considered. The *fine structure* observed in *metal* $2p_{3/2}$ spectra when the metal atom has unpaired d electrons varies with the ligand X along the spectroscopic series and with the metal. This behavior qualitatively agrees with a *multiplet splitting* mechanism. In addition, changes in *binding energies* of all the elements, with changing cation, ligand, or metal, also appear to correlate with a multiplet splitting mechanism.

I. Introduction

Recent photoelectron spectroscopic studies on coordination complexes[2] using the ESCA technique of Siegbahn and coworkers[3] have shown the usefulness of this new tool. We have applied it to an investigation of a series of complexes of general formula $C^I_2(MX_4)$, where M is a metal of oxida-

tion number 2 (Mn, Co, Ni, Cu, and Zn), X = Cl, Br, NCO, NCS, or NCSe, and C^I is a (monovalent) tetraalkylammonium cation (R = methyl, ethyl, or *n*-butyl).[4] In such complexes the coordination geometry around the metal atom in solids is generally a distorted tetrahedron. For the sake of comparison, some related octahedral complexes, $C^I_4(MX_6)$, have been considered.

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(2) (a) J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, 9, 2374 (1970); (b) C. D. Cook, K.-Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 93, 1904 (1971); (c) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 8, 2642 (1969); (d) D. Leibfritz and W. Bremser, *Chem.-Ztg.*, 94, 882 (1970); (e) G. J. Leigh, J. N. Murrell, W. Bremser, and W. G. Proctor, *J. Chem. Soc. D*, 1661 (1970); (f) M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, 74, 1116 (1970).

(3) (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967; (b) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werne, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

(4) R. Kergoat, J. E. Guerchais, and F. Genet, *Bull. Soc. Fr. Mineral. Cristallogr.*, 93, 166 (1970).