tion potentials[32,61,62] for some chlorides are as follows (eV): Cl, 12.97; BCl_3, 11.7; CCl_4, 11.7; $SiCl_4$, 12.0; $GeCl_4$, 12.1; $SnCl_4$, 12.1.

To pursue the matter further, we plot as small circles in Figure 3 all these photoelectron data plus those for BX_3 (X = F, Cl, Br).[62,65] To these data are added the inherently less accurate electron-impact ionization potentials for POX_3,[3] MOF_3[3] (M = P, V, Nb, Ta), ReO_3Cl, and OsO_4.[31] Sulfuryl fluoride, SO_2F_2[3], is not shown but lies at 13.3 eV. The small open cricles are for CX_4, and the barred circles are for POX_3,[3] which seem to lie systematically lower than the other points. The dioxodihalide data (Table VII) are shown as the large circles. The positions along the horizontal axis are the energies to remove the outermost p electron from the free halogen atoms or from O; to anticipate our conclusions, the oxofluorides and OsO_4 are at the O position. The 45° line represents the IP's of the free atoms. Figure 3 shows, for this group of tetrahedral molecules (plus BX_3) with a relatively electronegative central atom (the lowest electronegativity is that of Ti at 1.5 eV), that the spread of IP's is less than 1 V for the bromides, chlorides, and oxides and that the shift from the free halogen (or O) IP is less than 1.5 eV. For the fluorides, this spread should be larger. The IP's of TiF_4 and ZrF_4 are reported as 13.0 ± 1 and 14.5 eV (taken equal to $AP(ZrF_3^+)$); that for TiF_4 seems low. To the extent that the electron-impact data are correct, we can predict IP's. Those of SO_2Cl_2, $NbOCl_3$, $TaOCl_3$, and WO_2Cl_2, for instance, ought to be ~12.0 eV; and those of H_2SO_4, H_2WO_4, etc., and of ReO_3F should be about 13.0 eV. The expected uncertainty in each of these, relative to our base data, is ±0.5 eV.

The interpretation of these observations is that for the oxobromides and oxochlorides the electron is removed from a nonbonding MO of predominantly halogen p_π character. For the oxofluorides and for OsO_4 (obviously) the electron is removed from an MO of predominantly O character. For MoO_2BrCl it should then come from a Br atom, consistent with an IP (11.1 ± 0.5 eV) that lies closer to the 10.9 ± 0.5 eV value for MoO_2Br_2 than to the 12.2 ± 0.5 eV value for MoO_2Cl_2. Furthermore, there are implications about the photoelectron spectra of the three-dimensional arrays of molecules $TiX_4 \cdots MoO_2X_2 \cdots OsO_4$ or $SiX_4 \cdots SO_2X_2$. The centers of gravity of the nonbonding orbitals formed from the p AO's should remain fairly constant irrespective of the central atom and should move in a predictable manner with changes of the other ligand groups. Thus in the sequences of MO_2X_2, there should be a set of bands due to the oxygens at 13+ eV while the halogen bands move from about 14–16 eV (F) to 12+ to 11+ eV for the chlorides and bromides.

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[65] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc. A*, 1551 (1971).

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On Alkali Metal Fluoride–Iodine Pentafluoride Adducts

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Received August 30, 1971

The syntheses and properties of novel 1:3 adducts between alkali metal fluorides and IF_5 are described. Infrared and Raman spectra are reported for $CsF \cdot 3IF_5$, $CsIF_6$, $RbIF_6$, KIF_6, and a mixture of $RbIF_6$ with $RbF \cdot 3IF_5$. The previously reported discrepancies in the vibrational spectra of IF_6^- salts can be rationalized by assuming mixtures of 1:1 and 1:3 adducts. Powder diffraction X-ray data are given for KIF_6, $RbIF_6$, and $CsIF_6$. Partial pyrolysis, vibrational spectroscopy, and differential thermal analyses show no evidence for the existence of distinct 1:2 adducts as intermediate products from the decomposition of the 1:3 adducts. The previous conclusions are confirmed that IF_6^- is not octahedral and does not have a symmetry higher than C_{2v}. The FNO–IF_5 and FNO–BrF_5 systems were briefly studied. Whereas BrF_5 does not form an FNO adduct, IF_5 combines with FNO to form a white, crystalline 1:1 adduct having a dissociation pressure of about 30 mm at 21°.

Introduction

The vibrational spectra of the alkali metal fluoride–iodine pentafluoride adducts were previously studied by at least four different research groups.[1-4] All four groups reached the same conclusion that the IF_6^- anion is not octahedral. This conclusion was also supported by the results of a recent Mössbauer study.[5] However, the vibrational spectra reported by the four groups for IF_6^- differed strongly and no plausible explanation could be offered for these discrepancies. Recently, Klamm and Meinert reported[6] the formation of IF_4Cl by treating CsCl with IF_5. Their failure to isolate and characterize this novel, yellow, volatile compound was attributed[6] to rapid reaction with the glass container. Our attempts to duplicate Klamm and Meinert's observations[6] in an inert metal–Teflon reaction system were unsuccessful. The most volatile yellow reaction product was, as expected, Cl_2. However, from the material balance, it became obvious that the solid residue was not the expected $Cs^+IF_6^-$ but the novel $CsF \cdot 3IF_5$ adduct. Furthermore, the vibrational spectra of $CsF \cdot 3IF_5$ showed bands previously attributed[1,2] to

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[1] K. O. Christe, J. P. Guertin, and W. Sawodny, *Inorg. Chem.*, **7**, 626 (1968).

[2] S. P. Beaton, D. W. A. Sharp, A. J. Perkins, I. Sheft, H. H. Hyman, and K. O. Christe, *ibid.*, **7**, 2174 (1968).

[3] H. Klamm, N. Meinert, P. Reich, and K. Witke, *Z. Chem.*, **8**, 393 (1968).

[4] H. Klamm, H. Meinert, P. Reich, and K. Witke, *ibid.*, **8**, 469 (1968).

[5] S. Bukshpan, J. Soriano, and J. Shamir, *Chem. Phys. Lett.*, **4**, 241 (1969).

[6] H. Klamm and H. Meinert, *Z. Chem.*, **10**, 270 (1970).

$CsIF_6$, indicating that most of the discrepancies in the previously reported data may have been due to varying mixtures of $Cs^+IF_6^-$ and $CsF \cdot 3IF_5$. Consequently, a systematic study of the alkali metal fluoride–iodine pentafluoride system was carried out, the results of which are reported in this paper. The existence of the $CsF \cdot 3IF_5$ adduct has also been discovered in an independent study by Hyde[7] but has not been published.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrosyl fluoride was prepared from NO and F_2 at −196°. Iodine pentafluoride (Allied Chemical) and BrF_5 (Matheson) were treated with F_2 until colorless. All materials were purified prior to use by fractional condensation. The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ∼−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with hollow inside glass cones for variable sample thicknesses or Pyrex or clear Kel-F capillaries were used as sample containers. For the capillaries, the transverse viewing–transverse excitation technique and for the conical tubes, the axial viewing–transverse excitation technique were used.

X-Ray powder diffraction patterns were taken using a Phillips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (∼0.5-mm o.d.). The densities were measured by the displacement method using a perfluorinated amine (FC 43, 3M Co.) to fill the pycnometer.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used to obtain the dta data. The samples were sealed in aluminum pans, and heating rates of 10°/min in N_2 were used.

Preparation of the Adducts.—Dry CsF (19.02 mmol) was placed into a 30-ml prepassivated 316 stainless steel cylinder and purified IF_5 (80.08 mmol) was added at −196°. The cylinder was placed on a shaker at 60° for 2 days. Unreacted IF_5 was removed at 25° by pumping for 3 hr. The cylinder contained 15.370 g of a stable, white, crystalline solid (weight calculated for $CsF \cdot 3IF_5$ 15.551 g). Therefore, CsF (19.02 mmol) had reacted with IF_5 (56.24 mmol) in a mole ratio of 1:2.96 producing the adduct $CsF \cdot 3IF_5$.

Finely powdered $CsF \cdot 3IF_5$ (10.81 mmol) when heated *in vacuo* to 90° for 12 hr lost IF_5 (21.63 mmol) forming the salt $Cs^+IF_6^-$.

Similarly, RbF (21.06 mmol) was combined with IF_5 (161.34 mmol) in a 150-ml prepassivated Monel cylinder and shaken at 60° for 144 hr. Unreacted IF_5 (114.59 mmol) was removed at 20° by pumping for 5 hr. Therefore, RbF (21.06 mmol) had reacted with IF_5 (46.75 mmole) in a mole ratio of 1:2.22 corresponding to a 73.98% conversion of RbF to $RbF \cdot 3IF_5$. More IF_5 (11.47 mmol) was slowly removed by an additional 15 hr of pumping at 25°. At this point the $RbF:IF_5$ ratio corresponded to 1:1.73.

Finely powdered $RbF \cdot 1.73\ IF_5$ (5.775 g) when heated *in vacuo* to 95° for 14 hr lost IF_5 (2.630 g, 11.85 mmol). A white, crystalline, stable solid resulted which according to the material balance had the composition $RbF \cdot 0.73IF_5$ or 27 mol % RbF + 73 mol % $RbIF_6$.

Potassium fluoride (37.87 mmol) was combined with IF_5 (101.21 mmol) in a 30-ml stainless stell cylinder. The cylinder was shaken for 50 hr at 60°. Unreacted IF_5 (17.61 mmol) was removed at 20° by pumping for 3 hr. Therefore, KF (37.87 mmol) had reacted with IF_5 (83.60 mmol) in a mole ratio of 1:2.21. Upon continued pumping at 25°, the solid kept losing additional amounts of IF_5. Pyrolysis at 60° *in vacuo* for 14 hr resulted in a white, stable, crystalline product having the composition $KF \cdot 0.95IF_5$.

Sodium fluoride, when heated to 60° for 50 hr on a shaker in the presence of a large excess of IF_5, did not combine with the latter to form a stable adduct.

Gaseous FNO was added in increments at 25° to liquid IF_5 (15.96 mmol) contained in a Teflon FEP U trap. Upon FNO addition, the mixture turned yellow and a slightly exothermic reaction occurred. After addition of 5.32 mmol of FNO (corresponding to $FNO \cdot 3IF_5$), the mixture was still liquid. The addition of an additional 5.32 mmol of FNO resulted in partial solidification. A total of 18.98 mmol of FNO was added and the temperature of the mixture was cycled several times between −196 and +25°. Unreacted FNO (2.89 mmol) was removed *in vacuo* at −24°. Hence, FNO (16.09 mmol) had reacted with IF_5 (15.96 mmol) in a mole ratio of 1:0.99 to form a white, crystalline solid. This solid had a dissociation pressure of about 30 mm at 21°. The vapor phase above the solid was shown by infrared spectroscopy to consist of equimolar amounts of FNO and IF_5.

Bromine pentafluoride (4.20 mmol) and FNO (8.40 mmol) were combined at −196° in a Teflon FEP U trap. Upon warm-up, the mixture melted forming a yellowish liquid. The mixture remained liquid at −64° and could be completely removed *in vacuo* at this temperature, not yielding a solid at any time. Hence, no stable solid adduct is formed at temperatures as low as −64°.

Results and Discussion

Syntheses and Properties.—The formation of distinct 1:3 and 1:1 adducts for the alkali metal fluoride–iodine pentafluoride systems was established by syntheses. Thus, KF, RbF, and CsF, can combine with more than an equimolar amount of IF_5. For CsF an almost theoretical conversion to a stable 1:3 adduct was achieved. This 1:3 adduct can be pyrolyzed under vacuum at 90° to form the known 1:1 adduct. When $CsF \cdot 3IF_5$ was slowly heated in a sealed glass capillary under 1 atm of N_2, the material became pasty at 105–110° and partial melting started at about 123°. At 140–150°, IF_5 started to distil off the solid, and the glass container was attacked. A sample of $CsIF_6$ started to attack the glass container at ∼160°, the temperature at which partial melting began. The dta data are in fair agreement with these observations. Thus, $CsF.3IF_5$ showed a gradual, continuous endotherm starting at about 153° indicating the loss of IF_5. The slight temperature difference might be due to the faster heating rate used for the dta study. No evidence for a stepwise decomposition, *i.e.*, for the formation of a distinct, intermediate 1:2 adduct was obtained. The dta curve of $CsIF_6$ showed an endotherm from 223 to 227°.

The isolation of clearly defined $RbF \cdot 3IF_5$ and $KF \cdot 3IF_5$ adducts is more difficult owing to their marginal stability at 25° and the relatively low volatility of IF_5 which must be used in excess for their syntheses. Furthermore, the conversion of RbF to an IF_5 adduct was found to be slow. After 2 days the conversion to $RbF \cdot 3IF_5$ was only 45% and after 6 days only 74%. It is unlikely that at this point the product consisted mainly of $RbIF_6$ and some $RbF \cdot 3IF_5$ since a mixture of

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[7] Hyde, G. A. Olin Corp., private communication.

TABLE I

X-RAY POWDER DATA FOR KIF_6, $RbIF_6$, AND $CsIF_6$

KIF_6			
d, Å			
Obsd	Calcd	Intens	*hkl*
7.82	7.86	mw	110
6.94	6.80	m	200
6.36	6.39	m	111
4.53	4.53	vs	300
3.92	3.93	vs	220
3.77	3.78	w	310
3.68	3.68	m	003 221
3.50	3.50	w	302
3.41	3.40	m	400
3.21	3.20	w	222
3.09	3.11	m	312
2.92	2.89	m	402
2.77	2.75	m	004
2.71	2.71	w	500 322 104
2.58	2.58	vw	114 420
2.55	2.55	vw	331 204
2.35	2.35	w	304
2.16	2.17	w	105
2.14	2.14	w	521
2.02	2.02	m	414
1.947	1.945	w	530
1.901	1.901	m	315 334
1.861	1.861	w	621
1.835	1.835	m	006
1.796	1.799	m	325
1.745	1.743	w	540
1.707	1.709	w	524
1.574	1.570	w	007
1.481	1.477	w	732
1.461	1.461	mw	902 227 813

$RbIF_6$			
d, Å			
Obsd	Calcd	Intens	*hkl*
7.10	6.91	w	200
6.57	6.57	w	111
4.63	4.61	w	300
3.99	3.99	vs	220
3.76	3.78	mw	221
3.50	3.49	m	113 400
3.27	3.29	w	222
3.13	3.11	m	213
2.97	2.97	m	402 303
2.83	2.84	m	104
2.77	2.77	w	500
2.49	2.49	w	510 502
2.41	2.42	mw	332
2.21	2.21	m, b	205 520
2.06	2.07	m, b	522
1.994	1.996	mw, b	440
1.937	1.937	m	006
1.897	1.893	mw	621
1.870	1.870	mw	702
1.838	1.838	m	415
1.784	1.784	w	306
1.746	1.746	w	712
1.605	1.603	w	811 525
1.535	1.535	w	900 227
1.493	1.493	mw	813 634
1.467	1.469	w	643
1.442	1.443	mw	108 733

$CsIF_6$			
d, Å			
Obsd	Calcd	Intens	*hkl*
7.39	7.23	w	200
6.80	6.78	w	111
4.13	4.13	vs	220
3.90	3.90	m	221
3.61	3.58	s	400
3.39	3.39	mw	222
3.26	3.28	m	320
3.07	3.07	m	402
2.92	2.91	m	104
2.85	2.86	w	500
2.57	2.57	w	502
2.47	2.46	m	422
2.26	2.26	m	205 521
2.12	2.13	m	305
2.05	2.05	w	612 603
1.992	1.992	mw	424 620
1.955	1.955	mw	621
1.932	1.932	mw	702 116
1.886	1.886	mw	415 622
1.833	1.833	w	540 443
1.787	1.787	w	800 226
1.657	1.658	mw	811

73% $RbIF_6$ and 27% RbF was obtained upon pyrolysis of the product at a temperature at which $RbIF_6$ is stable. To obtain mainly the 3:1 adducts of IF_5 with either RbF or KF, removal of unreacted IF_5 must be stopped as soon as the IF_5 removal rate decreases sharply. Otherwise, the products will contain larger amounts of $RbIF_6$ and KIF_6, respectively. A mixture of RbF (27%), $RbIF_6$ (23%), and $RbF \cdot 3IF_5$ (50%), having the empirical composition $RbF \cdot 1.73IF_5$ when heated in a sealed glass capillary, did not show a sharp melting point but started to become cloudy at 130–140° and to decompose slowly with IF_5 evolution. A sample of RbF (27%) and $RbIF_6$ (73%) started to become cloudy at ~170° with attack of the glass container. The dta curve for the RbF–$RbIF_6$–$RbF \cdot 3IF_5$ sample showed the onset of an endotherm at 137° which reached its maximum at 162°. The RbF–$RbIF_6$ sample showed only a large exotherm starting at 249° which is ascribed to attack on the aluminum container. A sample of KIF_6 containing ~5 mol % KF when heated in a sealed glass tube started to give off some IF_5 at ~130°. Its dta curve showed the onset of a large endotherm at ~180° followed by a second endotherm centered at about 240°. Sodium fluoride did not form any adduct with IF_5 under reaction conditions similar to those used for the remaining alkali metal fluoride adducts.

The fact that CsF and RbF form well-defined 1:3 adducts with IF_5 and are not just $CsIF_6$ or $RbIF_6$ containing varying amounts of loosely attached IF_5 is supported by the following arguments. A well-defined, stable 1:3 adduct was isolated for CsF. This $CsF \cdot 3IF_5$ adduct shows a distinct vibrational spectrum and X-ray powder diffraction pattern (see below). The partially pyrolyzed $RbF \cdot 3IF_5$ adduct of the empirical composition $RbF \cdot 1.73IF_5$ showed only the bands characteristic of the 1:1 and the 1:3 adducts.

Nitrosyl fluoride does not form a solid 1:3 adduct with IF_5. However, it forms a solid 1:1 adduct which has a dissociation pressure of about 30 mm at 21°. This is in contrast to previous reports by Seel and coworkers,[8,9] who reported $FNO \cdot IF_5$ to be a liquid com-

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(8) F. Seel and N. Massat, *Z. Anorg. Allg. Chem.*, **280**, 186 (1955).

(9) F. Seel and W. Birnkraut, *Angew. Chem.*, **73**, 531 (1961).

plex. No adduct formation was observed between BrF_5 and FNO at temperatures as low as −64°.

X-Ray Powder Data.—Table I lists calculated and observed X-ray powder diffraction data for KIF_6, $RbIF_6$, and $CsIF_6$ indexed in the hexagonal system. From these data the following unit cell dimensions were calculated: KIF_6, $a = 15.72$, $c = 11.00$ Å; $RbIF_6$, $a = 15.97$, $c = 11.61$ Å; $CsIF_6$, $a = 16.52$, $c = 11.89$ Å. Density measurements resulted in the following densities: KIF_6, $d^{24} = 3.55$ g cm^{-3}; $CsIF_6$, $d^{24} = 4.05$ g cm^{-3}. These density values indicate 18 "molecules" of $MeIF_6$ per unit cell (KIF_6, $d_{\text{calcd}} = 3.55$ g cm^{-3}; $CsIF_6$, $d_{\text{calcd}} = 3.98$ g cm^{-3}). Bougon, Charpin, and Soriano recently reported[10] rhombohedral unit cells for the related adducts, $KBrF_6$, $RbBrF_6$, and $CsBrF_6$. Since these rhombohedral unit cells can be referred to hexagonal ones,[10] the possibility of indexing the $MeIF_6$ patterns in the rhombohedral system was examined. However, some of the observed reflections do not belong to one of the following two categories: $-h + k + l = 3n$ and $h - k + l = 3n$. Hence, the possibility of rhombohedral unit cells must be ruled out for the IF_6^- salts. The fact that the $MeIF_6$ unit cells contain 6 times as many molecules as the $MeBrF_6$ ones agrees well with the lower symmetry suggested for IF_6^- on the basis of the observed vibrational spectra.[1–4,10,11] The powder pattern of $CsF \cdot 3IF_5$ was distinct from that of $CsIF_6$ but could not be indexed. The density of $CsF \cdot 3IF_5$ was measured and found to be $d^{24} = 3.42$ g cm^{-3}.

Vibrational Spectra.—Figure 1 shows the infrared spectra of KIF_6, $RbIF_6$, $CsIF_6$, $CsF \cdot 3IF_5$, and $RbF \cdot 1.7IF_5$. Figures 2 and 3 show the corresponding Raman spectra. The observed frequencies are listed in Table II. As can be seen, the spectra of the 1:1 and 1:3 adducts show a marked difference. Furthermore, the spectrum of partially pyrolyzed $RbF \cdot 3IF_5$ shows only bands due to $RbIF_6$ and $RbF \cdot 3IF_5$. This is evidence for the nonexistence of a distinct 1:2 adduct as an intermediate decomposition product.

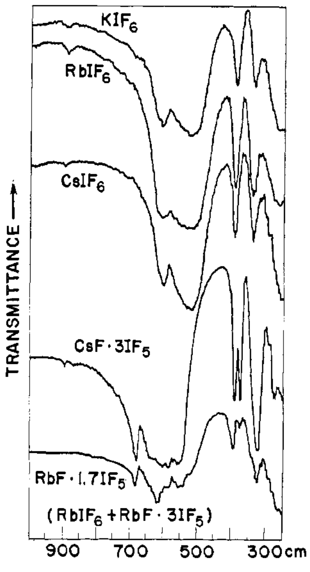

Figure 1.—Infrared spectra of the IF_5 adducts as dry powders in AgBr disks.

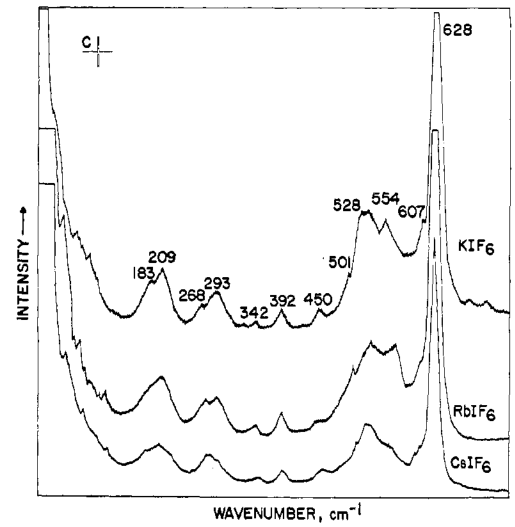

Figure 2.—Raman spectra of KIF_6, $RbIF_6$, and $CsIF_6$. C indicates spectral slit width.

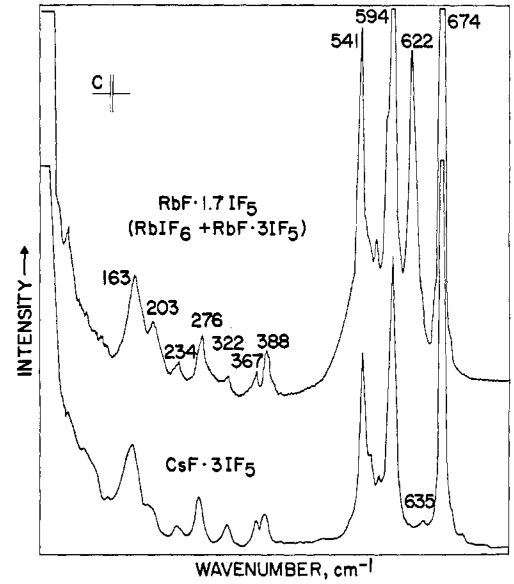

Figure 3.—Raman spectra of $CsF \cdot 3IF_5$ and $RbF \cdot 1.73IF_5$.

The large number of bands observed for $MeIF_6$ (at least 12 or 13) rules out symmetries higher than C_{2v} for IF_6^-. Distinction between eclipsed or staggered models (differing by one infrared-active stretching mode[4]) cannot be made due to the unresolved band shape of the 520-cm^{-1} infrared band. In addition, the large number of "molecules" (18) per unit cell can be expected to cause the spectra to deviate somewhat from that of the free ion. Hence, conclusions based on such subtle spectral differences would be purely speculative.

Similarly, it is difficult to interpret the vibrational spectrum of $CsF \cdot 3IF_5$. The spectrum is not a simple composite of those of $CsIF_6$ and free IF_5 as one might expect for an ideal molecular adduct. An example of such an ideal molecular adduct of IF_5 was found[12] by Sladky and Bartlett for $XeF_2 \cdot IF_5$. However, some of the bands of $CsF \cdot 3IF_5$ have frequencies somewhat sim-

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[10] R. Bougon, P. Charpin, and J. Soriano, *C. R. Acad. Sci., Ser. C*, **272**, 565 (1971).

[11] J. Shamir and I. Yaroslavsky, *Isr. J. Chem.*, **7**, 495 (1969).

[12] F. O. Sladky and N. Bartlett, *J. Chem. Soc. A*, 2188 (1969).

TABLE II

VIBRATIONAL SPECTRA OF KIF_6, $RbIF_6$, $CsIF_6$, $CsF \cdot 3IF_5$, AND $RbF \cdot 1.7KF_6$

[OBSERVED FREQUENCY (cm^{-1}), INTENSITY]

KIF_6		$RbIF_6$		$CsIF_6$		$CsF \cdot 3IF_5$		$RbF \cdot 1.7KF_6$	
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman
						677 s	674 (10)	677 s	674 (10)
						635 sh }	635 (0+)		
625 sh	628 (10)	620 sh	622 (10)	620 sh	620 (10)				622 (3)
609 s	607 sh	599 s	598 sh	599 s	599 sh			610 vs	
							593 (5.3)		594 (5)
						584 } vs	585 sh	584 ms	585 sh
						569	568 (0+)		565 (0.4)
	{ 554 (2)		{ 562 (2)		{ 554 sh	552	557 (0+)	550 s	557 sh
570–500		570–500		570–500		545 sh }	543 (3.0)		541 (3)
vs, b	{ 528 (2.4)	vs, b	{ 528 (2)	vs, b	{ 527 (2)				530 sh
	{ 501 (0+)		{ 501 (0+)		{ 502 sh				
	450 (0.3)		447 (0+)		451 (0.3)				
393 ms	392 (0.6)	391 ms	391 (0.5)	390 ms	391 (0.5)			391 s	388 (0.5)
						385 m	382 (0.5)		
						369 m	367 (0.3)	370 mw	367 (0.2)
	342 (0+)		348 (0+)		347 (0+)				
341 ms		337 ms		335 ms				335 sh	
						320 s	319 (0.4)	318 s	322 (0.1)
290 w	293 (1.0)	288 sh	292 (0.7)					285 sh	292 sh
268 ms	268 sh	260 ms	270 sh	260 ms	275 (0.8)	271 m	271 (0.9)	260 s	276 (0.5)
							231 (0.2)		234 (0.2)
	209 (1.5)		208 (1.1)		199 (1.1)				203 } (0.6)
	183 sh						186 (0.2)		186 }
							157 (1.5)		163 (1)

ilar to those[13,14] of IF_5. Hence, the possibility of a nonideal molecular adduct cannot be ruled out. The increased deviation of the spectrum from that of free IF_5 might be explained by the ionic lattice (Cs^+ and IF_6^- ions) polarizing the soft IF_5 molecule and thereby distorting it. We have observed that single crystals of $CsF \cdot 3IF_5$ can be obtained from IF_5 solutions, and, therefore, the exact structure of this interesting adduct could be studied by X-ray diffraction.

Comparison of the results of this study with those reported earlier[1-4] resolves the previously unexplainable discrepancies. The two sets of Raman data reported[2] by Christe were due to the 1:1 and 1:3 adducts, respectively. The data reported[2] by the Argonne group were due to the 1:3 adduct, whereas the Glasgow group worked with a 1:1 adduct showing several additional unexplainable bands. Klamm, *et al.*, reported[3] the best set of data for KIF_6 and $CsIF_6$. They are in good agreement with those found in the present study for the 1:1 adducts. The fact that a number of experienced investigators mistook the 1:3 adducts for 1:1 adducts demonstrates that quantitative syntheses and elemental analyses may in some rare instances be insufficient for characterizing new adducts. For the $MeF + IF_5$ reaction, incomplete conversion of MeF to $MeF \cdot 3IF_5$ resulted in material balances and elemental analyses closely corresponding to those expected for pure $MeIF_6$.

The BrF_6^- and IF_6^- anions present a very interesting structural problem. Vibrational spectra indicate that IF_6^- is of low symmetry, whereas BrF_6^- appears to be of higher symmetry and possibly to have a symmetry center.[10] This dissimilarity might be due to the different size of the central atom resulting for BrF_6^- in a maximum coordination number of 6 and, consequently, a sterically inactive free electron pair. For the larger iodine atom, the maximum coordination number is 7 and the free electron pair should become sterically active. Hence, a determination of the exact structure of both ions, which are isoelectronic with XeF_6, is very desirable. Since the size of the central atom in XeF_6 should be intermediate between those of Br and I in BrF_6^- and IF_6^-, respectively, one might expect the structure of XeF_6 to contain contributions from both the BrF_6^- and IF_6^- structures, possibly giving rise to a dynamic pseudo Jahn–Teller effect.[15,16] Consequently, the existence of a stable 1:1 adduct between FNO and IF_5 was examined. In the case of a stable adduct, single crystals could be grown by sublimation and studied by X-ray diffraction techniques. However, the appreciable dissociation pressure of $FNO \cdot IF_5$ and the relatively low volatility of IF_5 prevented the successful growth of suitable single crystals. In this context, the possibility of synthesizing $NO^+BrF_6^-$ was also examined.

The vibrational spectrum of IF_4^-, recently reported[11] by Shamir and Yaroslavsky, strongly resembles those of the IF_6^- salts. The following facts cast some doubt on the conclusions reached by Shamir and Yaroslavsky for IF_4^-: (i) their IF_4^- salt was prepared from CsI and IF_5 which under slightly different reaction conditions yield $CsIF_6$;[17] (ii) $CsCl + IF_5$ yield $CsIF_6$; (iii) the spectrum resembles that of IF_6^-; (iv) a C_{2v} structure is completely unexpected for IF_4^-.

Acknowledgment.—The author wishes to express his gratitude to Drs. D. Pilipovich and C. J. Schack for helpful discussions, to Dr. W. V. Johnston for recording the dta curves, and to Dr. J. Cape of the Science Center of North American Rockwell for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.

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