in the hydroxyl bridge.[9] The bands at 520 and 1048 cm^{-1}, respectively, have been assigned to these vibrations. The band at 450 cm^{-1} is in the region of the vanadium-oxygen single-bond stretch in vanadium complexes.[10] The band at approximately 1500 cm^{-1} in vanadium(III) squarate trihydrate and all other trivalent metal squarate trihydrates is assigned to be a mixture of the C-C and C-O stretch vibrations.[2,8,11] The spectrum contained a very broad band at approximately 3200 cm^{-1} which was assigned to the O-H stretch in water and the hydroxyl radical where there is considerable hydrogen bonding.

The vanadium(III) ion is a d^2 configuration with a $^3T_{1g}$ (F) ground state in an octahedral crystal field. The band in the electronic spectrum of $V^{III}(OH)(C_4O_4)\cdot 3H_2O$ at 17,900 cm^{-1} can be assigned to the d-d transition of $^3T_{2g}$ (F) ← $^3T_{1g}$ (F). The $^3T_{2g}$ (F) ← $^3T_{1g}$ (F) transition in a $V(H_2O)_6{}^{3+}$ solution appears at 17,200 cm^{-1}.[12] The band in the electronic spectrum at 26,000 cm^{-1} can be assigned to the d-d transition of $^3T_{1g}$ (F) ← $^3T_{1g}$ (F). This band in a $V(H_2O)_6{}^{3+}$ solution appears at 25,000 cm^{-1}.[12] By using these assignments for d-d transitions, it was possible to estimate the crystal field splitting parameter $10Dq = 18{,}900$ cm^{-1} and the Racah parameter $B = 611$ cm^{-1}. These values compare favorably to the values of $10Dq = 18{,}600$ cm^{-1} and $B = 665$ cm^{-1} for $V(H_2O)_6{}^{3+}$ [12] and suggest that the vanadium ion could be in a slightly distorted octahedral field.

In conclusion, it appears that the data reported here best fit the dimeric structure first proposed by Niu[8] for the iron(III) squarate complex. The infrared spectrum appears to contain bands characteristic of hydroxyl bridges. The infrared spectrum also contains those bands associated with uncoordinated oxygen atoms on the squarate anion. The electronic spectra suggest that the vanadium atoms are in a slightly distorted octahedral field. All of these data agree well with the dimeric structure.

Registry No. Vanadium(III) squarate trihydrate dimer, 35918-74-2.

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The Tetrafluoroiodate(III) Anion, IF_4^-

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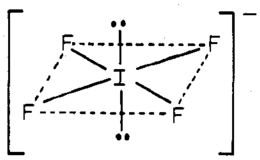
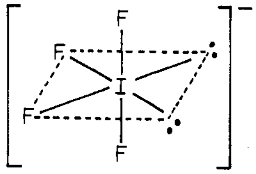
The salts $CsIF_4$ and Cs_3IF_6 were prepared and characterized by infrared and Raman spectroscopy. The vibrational spectra observed for IF_4^- are consistent with a square-planar structure of symmetry D_{4h}. The Raman spectrum previously reported for IF_4^- and interpreted in terms of a nonplanar structure of symmetry C_{2v} can be attributed to IF_6^-. Force constants were computed for IF_4^- and are compared to those of BrF_4^-, ClF_4^-, and XeF_4.

Introduction

The existence of salts containing the IF_4^- anion was first reported[1] in 1960 by Hargreaves and Peacock. When studying the reaction between CsI and IF_5, they obtained depending upon the reaction conditions different products. At elevated temperature the solid product was reported[1] to be $CsIF_6$ whereas at ambient temperature it was believed to be $CsIF_4$. In 1961, Asprey, Margrave, and Silverthorn reported[2] the syntheses of IF_4^- salts by direct fluorination of iodides. In 1969, Shamir and Yaroslavsky published[3] the Raman spectrum of "$CsIF_4$" prepared by the method[1] of Hargreaves. They observed nine bands and concluded[3] that IF_4^- is not square planar (I) but possesses structure II. These results were quite unexpected since the related ClF_4^- and BrF_4^- anions and the isoelectronic XeF_4 molecule are all square planar.[4-7] Recently, Christe pointed out[8] that the Raman spectrum, attributed[3] by Shamir and Yaroslawsky to IF_4^-, closely resembles that of IF_6^-. Hence, it appeared interesting to study the vibrational spectrum of a sample of $CsIF_4$ which had been prepared from IF_3 and CsF by the method[9] of Schmeisser, *et al.*



D_{4h}, I



C_{2v}, II

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Table I. Vibrational Spectrum of $CsIF_4$ and Its Assignment Compared to Those of Isoelectronic XeF_4, BrF_4^-, and ClF_4^- and Those of the Approximately Square-Planar Part of IF_5

Obsd freq, cm^{-1} (intens[a])										Assignment in point group D_{4h}	Approx description of vibration
$CsIF_4$		$CsBrF_4$[b]		$CsClF_4$[c]		XeF_4[d]		IF_5[e]			
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman		
	522 (10)		523 (10)		505 (10)		543 (10)		616 vs	ν_1 (A_{1g})	$\nu_s(XF_4)$ in phase
271 ms		317 s		425 s		291 ms		318 m	318 m	ν_2 (A_{2u})	$\delta_s(XF_4)$ out of plane
	195 (0+)		246 (0.7)		288 (1)		235 (0+)		276 w	ν_3 (B_{1g})	$\delta_s(XF_4)$ in plane
	455 (7.2)		449 (7.9)		417 (9)		502 (8.2)		604 m	ν_4 (B_{2g})	$\nu_s(XF_4)$ out of phase
448 vs		478 vs		590 vs		586 vs		640 vs		ν_6 (E_u)	$\nu_{as}(XF_4)$
			[183][f]						200 vw	ν_7 (E_u)	$\delta_{as}(XF_4)$ in plane

[a] Uncorrected Raman intensities. [b] Reference 6. [c] Reference 4. [d] Reference 11. [e] References 12, 13. [f] Frequency taken from the $NO^+BrF_4^-$ spectrum.

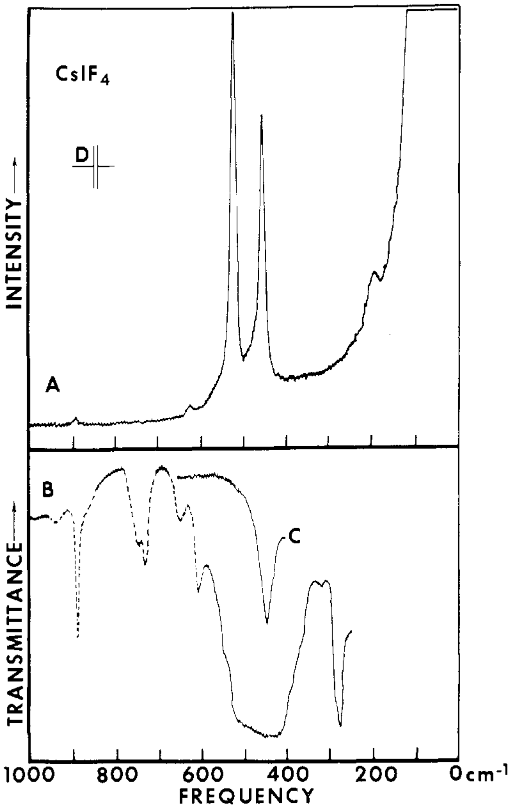

Figure 1. Vibrational spectrum of $CsIF_4$. Traces A, B, and C represent the Raman spectrum of the solid, the infrared spectrum of the solid, and the infrared spectrum of a CH_3CN solution, respectively. D indicates the spectral slit width.

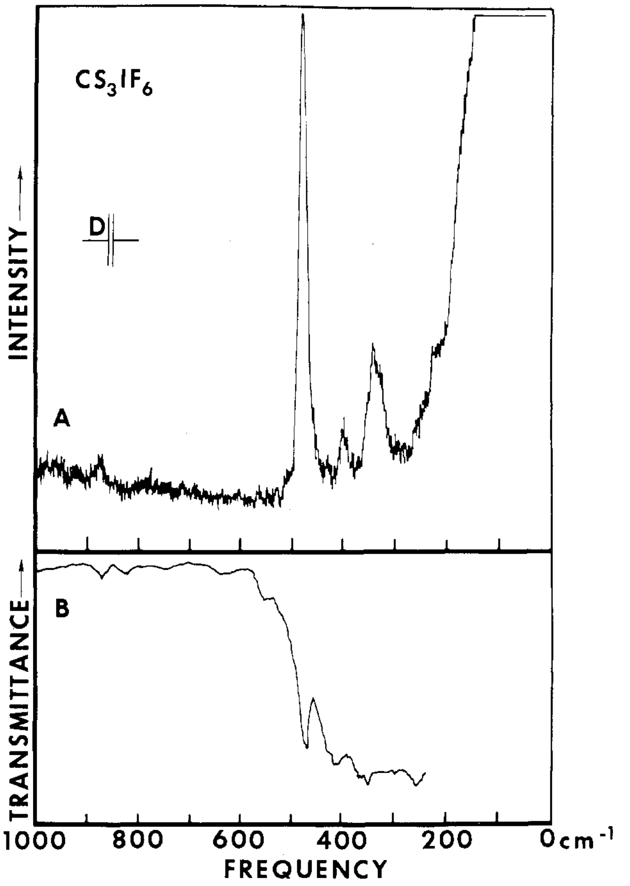

Figure 2. Raman (trace A) and infrared (trace B) spectra of solid Cs_3IF_6.

Experimental Section

The preparation and characterization of $CsIF_4$ and Cs_3IF_6 has previously been described.[9,10] Owing to their hygroscopic nature the compounds were handled outside of the vacuum line in the dry nitrogen atmosphere of a glove box.

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Spectra were obtained of dry powders as AgBr or AgCl pellets and of CH_3CN solutions in a Wilks minicell between AgCl plates. Raman spectra were recorded on a Cary 83 spectrophotometer using the 4880-A exciting line of an Ar ion laser. Glass melting point capillaries were used as sample containers in the transverse viewing-transverse excitation technique.

Debye-Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries of 0.5-mm o.d.

Results and Discussion

Vibrational Spectra. Figures 1 and 2 show the vibrational spectra of $CsIF_4$ and Cs_3IF_6. As can be seen, the spectra of $CsIF_4$ and Cs_3IF_6 are quite distinct. This indicates that for Cs_3IF_6 a formulation as $CsIF_4 \cdot 2CsF$ is unlikely. The observed frequencies are listed in Table I. The X-ray powder diffraction patterns of $CsIF_4$ and Cs_3IF_6 (Table II) also differ strongly from each other and from those of the $CsIF_6$ and the $CsF \cdot 3IF_5$ adducts[8] and consequently are very useful for distinguishing between the different adducts.

The vibrational spectrum observed in this study for $CsIF_4$ is very different from that[3] previously reported. It is simpler (only three Raman bands) and strongly resembles those of square-planar XeF_4,[11] BrF_4^-,[6] and ClF_4^-.[4] In addition to the three Raman bands two infrared bands were observed following the rule of mutual exclusion. These observations are entirely consistent with a centrosym-

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Table II. X-Ray Powder Data for $CsIF_4$ and Cs_3IF_6

$CsIF_4$				Cs_3IF_6			
d, Å	Intens	*d*, Å	Intens	*d*, Å	Intens	*d*, Å	Intens
4.41	vw	1.854	vw	3.48	ms	1.801	mw
4.16	w	1.814	w	3.41	m	1.776	vw
3.82	m	1.688	w	3.35	w	1.759	vw
3.75	vs	1.567	vw	3.27	vs	1.735	vw
3.66	vw	1.538	s	3.03	mw	1.710	m
3.57	m	1.509	ms	2.96	mw	1.653	w
3.41	m	1.478	vs	2.87	w	1.607	w
3.35	ms	1.455	w	2.65	w	1.555	mw
3.27	vw	1.432	w	2.60	ms	1.496	w
3.12	vw	1.399	mw	2.39	ms	1.460	w
3.05	mw	1.356	m	2.32	vw	1.416	m
2.91	w	1.294	ms	2.25	vw	1.370	w
2.56	vw	1.257	mw	2.20	vw	1.336	mw
2.51	vw	1.193	mw	2.106	mw	1.310	mw
2.38	ms	1.138	m	2.030	m	1.281	vw
2.27	s	1.127	vw	1.990	m	1.265	w
2.23	w	1.112	m	1.959	mw	1.223	w
2.207	w	1.079	m	1.892	w	1.153	w
2.088	w	1.067	m				
2.013	vs	1.009	m				
1.986	w	0.945	m				
1.947	vw	0.879	mw				
1.901	vw	0.867	mw				
1.881	s						

metric square-planar structure of symmetry D_{4h} (model I). They also indicate that the Raman spectrum previously assigned[3] to IF_4^- was not due to IF_4^- but to IF_6^-.[8]

Assignments for the IF_4^- anion in point group D_{4h} are given in Table I and were made based upon the following considerations. For IF_4^- of symmetry D_{4h}, the seven normal modes are classified as $A_{1g} + A_{2u} + B_{1g} + B_{2g} + B_{1u} + 2\,E_u$. Of these, only the A_{1g}, B_{1g}, and B_{2g} modes will be Raman active, whereas the A_{2u} and the two E_u modes will be infrared active. The B_{1u} mode is inactive in both the infrared and Raman spectra. Comparison with the modes belonging to the square-planar part of IF_5 [12,13] (see Table I) shows that the E_u deformation vibration of IF_4^- should occur below 250 cm^{-1}, the lower limit of our spectrometer. The assignment of the observed bands to the individual modes (see Table I) was done in complete analogy with XeF_4 [11], BrF_4^-, [6] and ClF_4^- [4] and, hence, needs no further discussion. Since the E_u stretching mode is very broad for all solid tetrafluorohalogenate(III) salts, we have also recorded the infrared spectra of $CsIF_4$ and $CsBrF_4$ in CH_3CN solution. For each salt a single sharp band centered at 448 and 478 cm^{-1}, respectively, was observed. This permits the accurate determination of the band centers and also eliminates the possibility[6] of symmetry D_{2h} for which the doubly degenerate E_u mode of D_{4h} should split into its components. Several less intense bands were observed for $CsIF_4$ above 600 cm^{-1}. These were of varying relative intensity and, hence, are attributed to impurities or hydrolysis products.

The vibrational spectrum of Cs_3IF_6 shows bands at about 480, 405, 345, 255, and 225 cm^{-1} in both the Raman and infrared spectra. Their number and activity rule out an octahedral structure for IF_6^{3-} as one might also expect from the fact that IF_6^- is not octahedral.[8] Unfortunately, the observed spectrum does not allow a reliable determination of the symmetry of IF_6^{3-}. However, the pronounced difference in the vibrational spectra of IF_4^- and IF_6^{3-} should be useful for distinguishing the two ions.

Table III. Symmetry and Internal Force Constants (mdyn/Å) of ClF_4^-, BrF_4^-, IF_4^-, and XeF_4 Computed for Different Modified Valence Force Fields Using the Frequency Values of Table I

Computing method	ClF_4^-				BrF_4^-			IF_4^-						XeF_4		
	$F_{67} \equiv 0$		$F_{77} \equiv \min$		$F_{67} \equiv 0$	$F_{77} \equiv \min$	$F_{67} \equiv {}^1/_2\lvert F_{67}(\max) - F_{67}(\min)\rvert$	$F_{67} \equiv 0$		$F_{77} \equiv \min$		$F_{67} \equiv {}^1/_2\lvert F_{67}(\max) - F_{67}(\min)\rvert$		$F_{67} \equiv 0$	$F_{77} \equiv \min$	$F_{67} \equiv {}^1/_2\lvert F_{67}(\max) - F_{67}(\min)\rvert$
ν_7	150	250	150	250	183			100	200	100	200	100	200	200		
$F_{11} = f_r + 2f_{rr} + f_{rr'}$	2.853				3.060			3.052						3.302		
$F_{22} = f_\gamma$	0.630				0.577			0.514						0.597		
$F_{33} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$	0.232				0.169			0.106						0.155		
$F_{44} = f_r - 2f_{rr} + f_{rr'}$	1.946				2.258			2.319						2.822		
$F_{66} = f_r - f_{rr'}$	1.832	1.711	1.925	2.004	1.69	1.764	1.890	1.724	1.705	1.734	1.748	1.802	1.806	2.962	3.001	3.137
$F_{67} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'})$	0	0	0.061	0.166	0	0.065	0.253	0	0	0.015	0.059	0.156	0.178	0	0.063	0.302
$F_{77} = f_\alpha - f_{\alpha\alpha'}$	0.085	0.253	0.083	0.231	0.145	0.142	0.164	0.046	0.184	0.046	0.182	0.057	0.192	0.183	0.193	0.231
f_r	2.116	2.055	2.162	2.202	2.18	2.212	2.274	2.205	2.196	2.210	2.217	2.244	2.246	3.012	3.032	3.099
f_{rr}	0.227				0.20			0.183						0.120		
$f_{rr'}$	0.284	0.344	0.237	0.198	0.48	0.448	0.385	0.481	0.491	0.476	0.469	0.442	0.440	0.050	0.031	−0.037
Probable values of																
f_r	2.13 ± 0.07				2.227 ± 0.047			2.221 ± 0.025						3.055 ± 0.044		
f_{rr}	0.23				0.20			0.183						0.120		
$f_{rr'}$	0.27 ± 0.07				0.433 ± 0.047			0.466 ± 0.025						0.007 ± 0.044		

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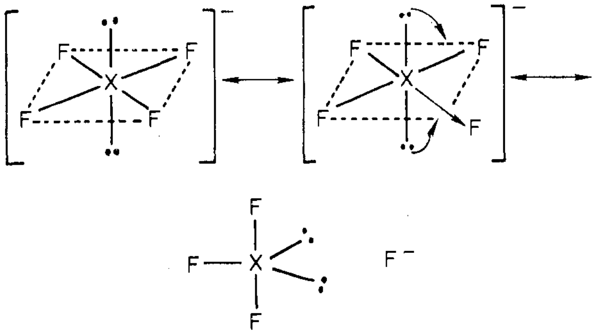
Force Constants. Table III shows the symmetry and some of the internal force constants of IF_4^-. For comparison the force constants obtained for XeF_4 and BrF_4^- and ClF_4^- are also listed. Except for the E_u block all the symmetry force constants are unique. The E_u block is underdetermined since only two frequency values are available for the determination of three force constants. It has recently been shown[14-16] that in similar underdetermined systems consisting of one stretching and one deformation mode, mathematical constraints such as minimizing or maximizing the value of one of the symmetry force constants can be used to narrow down the range of the possible solutions. In particular, one might expect[14,16] that in strongly coupled systems the values of the general valence force field (GVFF) will fall within the range given by $F_{67} = 0$ as the lower and by F_{77} = minimum as the upper limit. These ranges were computed for IF_4^-, BrF_4^-, ClF_4^-, and XeF_4 and are listed in Table III. It can be seen that for the very weakly coupled (heavy central atom) IF_4^- and XeF_4 the resulting valence force constant range becomes so narrow that it might not include any more the GVFF values. The condition $F_{67} = {}^1/_2\,|F_{67}(\max) - F_{67}(\min)|$ has been suggested[17] by Sawodny as a conservative empirical upper limit for weakly coupled systems and was used to determine the uncertainties in the valence force constants of BrF_4^-, IF_4^-, and XeF_4 listed in Table III. These relatively small uncertainties suggest that the given values are good approximations of the GVFF.

For most of the square-planar species of Table III, including IF_4^-, ν_7 has not been observed. Consequently, force fields were also computed assuming minimum and maximum values covering the most likely range for ν_7. The results shown in Table III demonstrate that the values of f_r, f_{rr}, and $f_{rr'}$ are very little influenced by changing the value of ν_7. Comparison of the uncertainty limits of IF_4^- with those of BrF_4^- and ClF_4^- show that these increase, as expected, with increasing coupling, *i.e.*, decreasing mass of the central atom.

Analysis of the results given in Table III allows the following conclusions. (i) The series ClF_4^-, BrF_4^-, IF_4^- shows the expected smooth trends. Whereas, the value of the stretching force constant, f_r, remains almost constant, the deformation force constants markedly decrease with increasing size of the central atom. (ii) The relatively low values of f_r in all three ions indicate strong ionic contributions to the halogen–fluorine bonds. The values are about half of those obtained for mainly covalent single bonds and may be interpreted in terms of semiionic three-center four-electron p-σ bonds.[4,6] (iii) The value of the stretch-stretch interaction constant, f_{rr}, decreases from ClF_4^- to IF_4^-. It reflects decreasing repulsion between the right angular fluorine ligands with increasing radius of the central atom. (iv) The surprisingly large positive values of the collinear F–X–F stretch-stretch interaction constant, $f_{rr'}$, can be explained by the following orbital-following model. Stretching of one X–F bond will tend to make the remaining XF_3 part to partially adopt the structure of the XF_3 molecule which is known to have one short equatorial and two long axial X–F bonds. Hence, the stretching of one X–F bond should cause a bond shortening of the collinear X–F bond as depicted by the mesomeric structures



The increase in the $f_{rr'}$ value from ClF_4^- to IF_4^- can be explained by the increasing ease with which the two free valence electron pairs of the central halogen atom can follow the stretching of the X–F bond. The fact that XeF_4 has a considerably smaller $f_{rr'}$ value than IF_4^- might be due to the lower polarity of the X–F bond in XeF_4 as is also indicated by its higher f_r value (3.02 mdyn/Å).

In summary, the observed vibrational spectrum and force constant analysis strongly support a square-planar structure of symmetry D_{4h} for IF_4^-. These results confirm the suggestion[8] that the previously reported[3] Raman spectrum was not due to IF_4^- but due to IF_6^-.

Registry No. $CsIF_4$, 36245-63-3; Cs_3IF_6, 28223-33-8.

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