at 863 cm^{-1} which is highly polarized ($\rho = 0.09$), but is unobserved in the infrared, is clearly the O-O stretching vibration. Thus, the O-O stretching frequency in CF_3OOSO_2F lies between that of CF_3OOCF_3 at 886 cm^{-1} [2a] and FSO_2OOSO_2F at 801 cm^{-1}.[2b] The characteristic absorption band due to the SOO bending vibration is seen at 322 cm^{-1}.

The assignment of the COO bending and O-O torsional modes is difficult due to the unexpected number of bands below 250 cm^{-1}. The two strongest bands at 226 and 210 cm^{-1} are assigned to the torsion and COO bending modes, respectively. The weaker bands at 190 and 180 cm^{-1} may be due to impurities, but no certain explanation can be suggested.

Discussion

Fluoro fluorosulfuryl peroxide, $FOOSO_2F$, is formally derived from the symmetrical peroxides FOOF and FSO_2OOSO_2F. The O-O bond is FSO_2OOSO_2F is rather easily cleaved to form fluorosulfate radicals,[23-25] and the O-O stretching frequency is found at 801 cm^{-1}.[2b] In contrast, the O-O bond in O_2F_2 is much stronger as a result of [π*-p] σ bonding[26] and the O-O stretching frequency is observed at 1306 cm^{-1}. The reactions of O_2F_2 undoubtedly involve the breaking of O-F bonds,[27-29] as a result of the O-O bond energy being much greater than the OF bond energy ($\Delta H_{\text{diss}} = 103.5$ *vs.* 18 kcal/mol).[30]

The chemistry of $FOOSO_2F$ has not been well investigated. While esr studies show that $FSO_2\cdot$ and $\cdot OOF$ radicals are formed on photolysis of $FOOSO_2F$,[31] the mass spectrum indicates that the O-O bond, not the S-O bond, is more easily ruptured.[2a] The chemistry of CF_3OOSO_2F remains to be elucidated.

The O-O stretching frequencies for $FOOSO_2F$ and CF_3OOSO_2F fall in the region 850-900 cm^{-1} suggesting, coupling of the O-O stretch with other normal modes not withstanding, that the O-O bond energies are similar to that of hydrogen peroxide. While the O-O bonds are expected to be stronger than the O-O bond in FSO_2OOSO_2F, the O-O bond dissociation energies are probably much lower than that for O_2F_2. These conclusions are in agreement with the ^{19}F nmr chemical shifts reported for $FOOSO_2F$ and O_2F_2 at −292 ppm[7,27] and <−800 ppm,[32] respectively (relative to $CFCl_3$). The abnormally low O-O stretching frequencies observed for SF_5OOSF_5 and SF_5OOSO_2F are attributed to extensive vibrational coupling rather than the existence of weak O-O bonds.[6] Some O-O stretching frequencies as determined by Raman studies and given for comparison are: FOOF, 1306 cm^{-1};[33] HOOH, 880 cm^{-1};[34] DOOD, 880 cm^{-1};[34] CF_3OOCF_3, 886 cm^{-1};[2a] CF_3OOSO_2F, 863 cm^{-1}; $FOOSO_2F$, 890 cm^{-1}; FSO_2OOSO_2F, 801 cm^{-1};[2b] SF_5OOSF_5, 751 cm^{-1};[6] SF_5OOSO_2F, 740 cm^{-1}.[6]

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Registry No. $FOOSO_2F$, 13997-94-9; CF_3OOSO_2F, 13990-10-8.

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Synthesis and Characterization of Oxotetrafluorotellurate(IV) and Dioxodifluorotellurate(IV) Compounds

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The synthesis and characterization by X-ray powder photography and Raman and infrared spectroscopy of M_2TeOF_4 and $M_2TeO_2F_2$ compounds are described. The M_2TeOF_4 compounds are shown to be isomorphous with M_2SbF_5 compounds. The unit cells of M_2TeOF_4 compounds are shown to be nearly the same as those of the comparable M_2SbF_5 compounds indicating that the anion volumes are very similar. The vibrational spectra of the $M_2TeO_2F_2$ compounds show evidence of oxygen bridging. The infrared and Raman spectra are shown to be consistent with a C_{4v} $TeOF_4^{2-}$ ion and a C_{2v} $TeO_2F_2^{2-}$ ion with oxygens in equatorial positions. Attempted preparations of M_2TeF_6 and $MTeO_2F$ compounds are described.

Introduction

Tellurium normally exhibits a higher coordination number than sulfur and selenium and this is reflected in the compounds of these elements in their highest oxidation state. The six valent oxy acids of S and Se are four-coordinate while that of Te is six-coordinate. The hexafluorides of S and Se show poor acceptor properties while TeF_6 forms adducts which may contain the TeF_7^- and TeF_8^{2-} ions.[1] The stable oxyfluoro anions are SO_3F^-, SeO_3F^-,[2] and

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$TeOF_5^-$,[3] reflecting again the change in preferred coordination number.

This difference in maximum coordination number, on the other hand, is not evident in the four valent ions and molecules of the chalcogens with fluorine and oxygen ligands. All three elements form trioxo trigonal-pyramidal anions in aqueous solution[4,5] and pentafluoro anions are known in all cases.[6] In this connection it is interesting that the highest possible coordination number appears to be limited to 5 in the case of fluoro ligands, although I(V) and Xe(VI) attain six-coordination in IF_6^- and XeF_6 and Se(IV) and Te(IV) will accept six chloro ligands.[7] There are several reports in the literature of the successful preparation of hexafluorotellurites[8-10] but more recent work suggests that this complex anion is not stable.[11] Among the oxyfluoro anions, sulfur and selenium dioxides accept a single fluoride ion to form SO_2F^- [12] and SeO_2F^-,[13] and condensation of $SeOF_2$ with an ionic fluoride gives $SeOF_3^-$ compounds.[14] While fluorosulfinites are known to contain discrete SO_2F^- ions,[12] the fluoroselenites are reported to be polymeric.[13] However the oxytrifluoroselenites are regarded as being nonpolymeric.[14] In view of the crystal structure reported for the analogous $SeOCl_3^-$ compound,[15] which is polymeric with Cl bridging, a reconsideration of the vibrational spectra for $KSeOF_3$ would be of interest.

As far as we are aware, no studies have been reported on oxyfluoro species of Te(IV) apart from the early work of Prideaux and Millott[16] and that of Metzner.[17] A study was begun to broaden our knowledge in this area and to extend our understanding of the stereochemistry of species with a lone valence shell electron pair.[18]

Experimental Section

Materials and Apparatus. Tellurium dioxide, 99.9% (B.D.H.), and the alkali metal fluorides [cesium fluoride, 99% (Ozark-Mahoning); rubidium fluoride, 99.9% (K. & K.); and potassium fluoride, 98% (B.D.H.)] were used after drying for 12 hr under vacuum. Barium fluoride, 99% (Fisher), was used similarly.

The tetraalkylammonium fluorides were prepared by literature methods.[19,20] Tetramethylammonium fluoride (Me_4NF) was prepared by dehydration of the trihydrate (Eastman Chemicals)[19] and the tetraethylammonium fluoride pentahydrate was formed on neutralization of 10% tetraethylammonium hydroxide (Eastman Chemicals) by 10% hydrofluoric acid.[20] The products were verified by fluoride analysis.

Hydrofluoric acid, 50% (J. T. Baker), was used directly. Acetonitrile (Eastman, anhydrous) was dried by distillation from phosphorus pentoxide.

The pentafluorotellurites $MTeF_5$ ($M = Cs$, K, Et_4N, Me_4N) were prepared by standard methods[21] and analyzed for fluoride.

Infrared spectra were taken as mulls, using CsBr plates, on a Beckman IR 20 infrared spectrometer. Raman spectra were recorded on a Jarrell-Ash series 300 spectrometer. For some spectra a Spex Industries double monochromator was used. A Spectra Physics argon ion laser was used in both cases and detection was by a cooled photomultiplier tube. A spike filter was used to remove plasma lines except where spectra were of very low intensity. Samples were contained in 5-mm o.d. Pyrex tubes.

The X-ray powder photographs were taken in Lindemann tubes using Cu Kα irradiation. A Debye–Scherrer camera of 11.5-cm diameter was used. Film skrinkage and other errors were allowed for by referencing the sample reflexes to those of KF. An insufficient number of simple reflexes were observed to carry out Nelson–Riley plots.

Preparation of the Compounds. Cs_2TeOF_4 and K_2TeOF_4. Cs_2TeOF_4 was prepared by mixing TeO_2, $CsTeF_5$, and CsF in the proportions 1:1:3 in a platinum boat.

$$TeO_2 + CsTeF_5 + 3CsF = 2Cs_2TeOF_4$$

A typical reaction had 0.277 g of TeO_2 (0.00173 mol), 0.617 g of $CsTeF_5$ (0.00174 mol), and 0.791 g of CsF (0.00523 mol). All materials were handled in a drybox. The boat was transferred to a quartz tube and heated slowly in a stream of nitrogen to 500°, at which temperature a clear colorless melt was formed. Further heating to 900° had no effect upon the products. A white crystalline product was obtained on cooling. *Anal.* Calcd for Cs_2TeOF_4: F, 15.65. Found: F, 15.7. An X-ray powder photograph showed no CsF, $CsTeF_5$, or TeO_2 lines.

K_2TeOF_4 was prepared in an analogous manner with a melt forming at 550°.

$$TeO_2 + KTeF_5 + 3KF = 2K_2TeOF_4$$

The product was stable to higher temperatures. Again an X-ray powder photograph revealed absence of starting materials TeO_2, KF, and $KTeF_5$.

An attempted preparation of Cs_2TeOF_4 by refluxing the reactants in DMSO for 24 hr showed no evidence of change in the starting materials. Furthermore, aqueous solutions of TeO_2 and an alkali metal fluoride required a large excess of HF for dissolution and yielded only the pentafluorotellurites.

$Cs_2TeO_2F_2$ and $Rb_2TeO_2F_2$. $Cs_2TeO_2F_2$ was prepared by mixing TeO_2 and CsF in the ratio 1:2.

$$TeO_2 + 2CsF = Cs_2TeO_2F_2$$

The reactants were handled in a drybox and placed in a platinum boat. The boat was heated slowly, in a stream of dry nitrogen, to 800° at which temperature a clear colorless melt was formed. Further heating (900°) had no effect upon the reaction. A typical reaction had 1.60 g of TeO_2 (0.0100 mol) and 3.04 g of CsF (0.0200 mol). A white crystalline product was obtained on cooling. An X-ray powder photograph revealed the absence of the starting materials CsF and TeO_2, as well as possible products $CsTeF_5$ and Cs_2TeOF_4.

The $Rb_2TeO_2F_2$ was prepared in an exactly analogous manner.

$$TeO_2 + 2RbF = Rb_2TeO_2F_2$$

Attempted preparation of $BaTeO_2F_2$ according to the reaction

$$TeO_2 + BaF_2 = BaTeO_2F_2$$

failed due to the absence of solution even on heating to 900°. At this temperature the characteristic red color of a melt of pure TeO_2 was observed unlike the $M_2TeO_2F_2$ melts. The retention of TeO_2 in high temperature melts containing fluorides is in sharp contrast to the case of sublimation of SeO_2 (~300°) out of fluoride melts under similar conditions.

In addition, attempted preparation of $BaTeO_2F_2$ from aqueous solution failed due to the insolubility of barium fluoride in 50% HF. Finally, attempted preparation of $M^I_2TeO_2F_2$ from aqueous solutions ($M^I = Cs$, Rb, K, or Et_4N) failed, M^ITeF_5 compounds being formed instead.

M^ITeO_2F. Attempted preparation of the monofluorodioxotellurites from melts according to the reaction

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$M^IF + TeO_2 \rightarrow M^ITeO_2F$ (M = Cs, Rb)

yielded only a mixture of TeO_2 and $M_2{}^ITeO_2F_2$ as indicated by an infrared spectrum. This is in sharp contrast with the analogous monofluorodioxoselenites which are readily prepared.[13]

$M^I{}_2TeF_6$. Two of the literature methods claiming preparation of salts of the hexafluorotellurate anion were attempted. The procedure for the preparation of the pyridinium salt $(PyH)_2TeF_6$ [8] yielded only the pentafluorotellurite $PyHTeF_5$. *Anal.* Calcd: F, 31.39. Found: F, 31.9. Similarly, the literature method for the dithiouronium salt[9] yields only the familiar pentafluorotellurite. The product was identified by its infrared spectrum. Seel and Massat have reported the preparation of $(NO)_2TeF_6$.[10] This compound is certainly of interest and would bear further study. Preparations were also attempted from aqueous HF solutions using Et_4NF and Me_4NF but these too yielded the pentafluorotellurite. Seemingly, the HF itself is a better fluoride acceptor, forming $HF_2{}^-$ preferentially and resulting in the failure to increase the coordination of tellurium.

A 1:1 molar mixture of MF and $MTeF_5$ (M = Cs, Me_4N) was shaken in acetonitrile for several days but this failed to produced the M_2TeF_6 species. The use of the tetralkylammonium fluorides Et_4NF or Me_4NF was thought promising due to their solubility in acetonitrile. However, only Me_4NF can be prepared as an anhydrous salt. This is accomplished by heating under vacuum at 130°,[19] a procedure which fails for Et_4NF due to decomposition. Attempted preparation of anhydrous Et_4NF by the method of Hayami, *et al.*,[20] used by Downs and Adams[11] yielded only the monohydrate in our hands. *Anal.* Calcd for $Et_4NF \cdot H_2O$: F, 10.27. Found: F, 10.2. An infrared spectrum did not show a C≡N stretching frequency and this eliminates the possibility of a $Et_4NF \cdot CH_3CN$ adduct.

A melt of stoichiometric amounts of CsF and $CsTeF_5$ though providing solution at 400° did not yield the hexafluorotellurite. Similarly, a melt with a large excess of CsF proved fruitless.

Fluoride Analysis. Fluoride analyses were done by titration with La^{3+} using a fluoride sensitive electrode. Interferences due to complexing of the fluoride by Te(IV) were avoided by removal of tellurium from solution. This was accomplished by precipitation with H_2S. After removal of the precipitated tellurium, the solution was neutralized and reduced in volume by heating on a hot plate. The tetraalkylammonium fluorides were determined directly.

Results and Discussion

X-Ray Powder Photography. A visual comparison of the powder photographs of Cs_2SbF_5 and Cs_2TeOF_4 shows that they are isomorphous solids. This is also true for the potassium salts. This result is not unexpected since the $TeOF_4{}^{2-}$ ion is isoelectronic with the $SbF_5{}^{2-}$ ion, both having a square-pyramidal shape as predicted by VSEPR theory.[22] This shape has been observed for the $SbF_5{}^{2-}$ ion.[23,24] The virtual identity of the powder photographs and the conclusion of the assignment of vibrational spectra conform the prediction of VSEPR theory, that the oxygen is axial. Both the antimony[24] and tellurium salts belong to the orthorhombic crystal system. Unit cell dimensions, as determined from photographs taken in this laboratory, are given in Table I. All powder data have been deposited with the American Society for Testing and Materials.

Table I. Unit Cell Dimensions (Å)[a]

	a	*b*	*c*
K_2SbF_5	6.25	13.68	6.48
K_2TeOF_4	6.24	13.83	6.46
Cs_2SbF_5	6.66	14.43	7.07
Cs_2TeOF_4	6.65	14.53	7.04

[a] Standard deviation on these dimensions is ±0.05 Å.

Table II. Raman and Ir Spectra of K_2TeOF_4 and Cs_2TeOF_4

K_2TeOF_4		Cs_2TeOF_4		Assignment (C_{4v})
Ir	Raman	Ir	Raman	
1675 vw				$2\nu_1$ (A_1)
1160 vw		1155 vw		$\nu_1 + \nu_2$ (E)
847 s	850 vs	840 s	837 vs	ν_1 (A_1)
777 w		790 vvw, 770 w		$\nu_2 + \nu_7$ (E)
		700 vw, sh		$\nu_4 + \nu_7$ (E)
475 s, sh	470 m	480 s, sh	461 m	ν_2 (A_1)
			390 m	ν_4 (B_1)
305–340 vs, br	344 m	330–360 vs, br	335 m	ν_7 (E)
275 br		265		ν_3 (A_1)
			190 w	ν_6 (B_2)
			129 w	ν_9 (E)
				ν_5 (B_1)
[340]		[360]		ν_8 (E)

Except for the $XeOF_4$ molecule, all of the square-pyramidal molecules and ions studied thus far have a bond angle between apical and equatorial ligands of less than 90°.[23,25-28] In $XeOF_4$ the ∠(OXeF) is 91.8° and, in terms of VSEPR theory,[23] the XeO bonding electron pairs have a greater repulsive action than the lone electron pair on the XeF bond pairs, causing the ∠(OXeF) to be greater than 90°. Moving one group to the left in the periodic chart, the isoelectronic $IOF_4{}^-$ ion is reported to have an ∠(OIF) of 88.5°.[28] This angle is considerably larger than those of other square-pyramidal molecules which are near 80°. It will be of interest to determine the ∠(OTeF) in $TeOF_4{}^{2-}$, the isoelectronic species one group further to the left in the series. In this connection it is interesting that a visual inspection of the powder photographs shows that the unit cells of the tellurium salts are larger than those of the antimony compounds. This is reflected in the mean values of *b* (Table I) for the tellurium and antimony salts. Since TeO and TeF bond distances are expected to be shorter than SbF′(axial) and SbF(equatorial) bond distances, it is tempting to account for the anomaly by suggesting that the ∠(OTeF) is opened up considerably compared to the ∠(F′SbF) of the $SbF_5{}^{2-}$ ion.

It has not been possible to fit the reflexes of the $M_2TeO_2F_2$ to either the cubic, tetragonal, or orthorhombic crystal systems. In the absence of any isomorphous compounds of known structure, it is not possible to gain any information about the state of aggregation of the $TeO_2F_2{}^{2-}$ ion in these new compounds. Attempts to prepare $BaTeO_2F_2$, which may be isomorphous with KIO_2F_2, a salt of known structure,[29] failed. The powder photographs of the two compounds (M = Rb, Cs) show them to be isomorphous.

Vibrational Spectra. K_2TeOF_4 and Cs_2TeOF_4. The infrared and Raman spectra of K_2TeOF_4 and Cs_2TeOF_4 are given in Table II. Since the M_2TeOF_4 compounds are isomorphous with M_2SbF_5 salts which contain individual $SbF_5{}^{2-}$ ions, the $TeOF_4{}^{2-}$ ions must be present as individual ions with little or no fluorine bridging. The $TeOF_4{}^{2-}$ ion is isoelectronic with $XeOF_4$ which is known to have a square-pyramidal structure with the oxygen in the apical position.[25] The $TeOF_4{}^{2-}$ ion undoubtedly has this C_{4v} structure also.

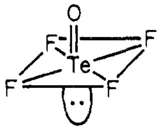

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Table III. Comparison of the Spectra of C_{4v} Species (XZY_4) Isoelectronic with $TeOF_4^{2-}$ [d]

Class	Mode no.	IF_5 [a] R	IF_5 [a] Ir	TeF_5^- [b] R	TeF_5^- [b] Ir	SbF_5^{2-} [c] R	SbF_5^{2-} [c] Ir	$XeOF_4$ [a] R	$XeOF_4$ [a] Ir	$TeOF_4^{2-}$ [d] R	$TeOF_4^{2-}$ [d] Ir	Approx description of mode (XZY_4)
A_1	ν_1	710 s, pol	710 vs	611 vs	618 ms	557 s	555 s	920 mw, pol	926 s	837 vs	840 s	$\nu(XZ)$
A_1	ν_2	614 vs, pol		504 s	(466 vs, br)	427 m		567 s, pol	576 m	461 m	480 m	$\nu_{sym}(XY_4)$-in phase
A_1	ν_3	318 m, pol	318 m	282 mw	283 m	278 w	260 m	285 w, pol	294 s		265 m	$\delta_{sym}(XY_4)$-umbrella
B_1	ν_4	602 sh		(472 s)		388 w		527 m		390 m		$\nu_{sym}(XY_4)$-out of phase
B_1	ν_5											$\delta_{asym}(XY_4)$-out of phase
B_2	ν_6	274 m		231 mw		220 w		233 mw		190 w		$\delta_{sym}(XY_4)$-in phase
E	ν_7	631 sh	635 br	(472 s)	(466 vs, br)	347–375 w	359–377 vs		608 vs	335 m	330–360 vs, br	$\nu_{asym}(XY_4)$
E	ν_8	370 w	372 m	338 mw	336 m	307 m	288 m	365 mw	361 s			$\delta(ZY_4)$ wag
E	ν_9	ca 200 w			164 mw	142	161	161 m		129 w		$\delta_{asym}(XY_4)$ in plane

[a] Reference 30. [b] Reference 6. [c] Reference 31. [d] Cs_2TeOF_4.

The infrared and Raman spectra are consistent with this.

In C_{4v} symmetry the normal modes belong to the representation

$$\Gamma = 3A_1 + 2B_1 + B_2 + 3E$$

Nine fundamentals are expected; all nine modes are Raman active whereas only six are infrared active ($3A_1 + 3E$). From the table it may be seen that seven fundamentals are observed. ν_5 in C_{4v} symmetry is very weak and is not even observed for TeF_5^-,[6] $XeOF_4$, and IF_5[30] which accounts for one of the absences. We assume that ν_8 is not observed due to a coincidence with ν_7. Four stretching modes are expected, $2A_1 + B_1 + E$. Judging from the spectra for SbF_5^{2-} [31] and TeF_5^- [6] the stretches should all lie above 300 cm^{-1}. Four fundamental stretching bands appear in the Raman spectrum of Cs_2TeOF_4 and the highest frequency peak at 837 cm^{-1} must be ν_1 (A_1), the TeO stretching mode. The peak at 390 cm^{-1} which is Raman active only must be ν_4 (B_1) and of the remaining two, that at 461 cm^{-1}, which is strongest in the Raman spectrum, must be the symmetric [TeF_4] stretch, ν_2 (A_1), while the peak which is most intense in the infrared must be ν_7 (E), the asymetric [TeF_4] stretch. The spectra of other related C_{4v} molecules are given in Table III for comparison and this assignment parallels that of Alexander and Beattie[31] for SbF_5^{2-} closely, both in the ordering and intensities of the bands. In $TeOF_4^{2-}$ and SbF_5^{2-} ν_7 lies at a lower frequency than ν_4, which is opposite to what is observed in other C_{4v} molecules. As one proceeds along the series IF_5, TeF_5^-, and SbF_5^{2-}, the positions of ν_7 and ν_4 approach each other to the point where they overlap in TeF_5^- [6] and finally in SbF_5^{2-},[31] ν_7 lies lower than ν_4. The same trend is therefore not surprising for the series $XeOF_4$, IOF_4^-, and $TeOF_4^{2-}$.

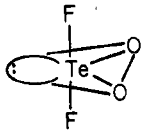
Assignment of the deformations is more difficult and comparison with these modes for other C_{4v} molecules is necessary. The lowest frequency mode in all of these species is ν_9 and the weak peak at 129 cm^{-1} in the Raman spectrum of $TeOF_4^{2-}$ is assigned to this mode. The remaining bands have been assigned to ν_3 and ν_6 on the basis of the assignments for other C_{4v} species and both position and intensity support this. Combination bands, which are observed in the infrared spectra of IF_5 and $XeOF_4$,[30] are also observed for M_2TeOF_4 compounds and their assignment (Table II) substantiates the assignments of the stretching vibrations of the $TeOF_4^{2-}$ ion.

Table IV. Raman and Ir Spectra of $Rb_2TeO_2F_2$ and $Cs_2TeO_2F_2$

$Rb_2TeO_2F_2$ Raman	$Rb_2TeO_2F_2$ Ir	$Cs_2TeO_2F_2$ Raman	$Cs_2TeO_2F_2$ Ir	Assignment (C_{2v})
	1070 vw, sh		1075 vvw	$\nu_1 + \nu_4$ (A_1)
795 vs, 780 vs, sh	805 vs	796 vs, 781 w	795 s, 777 s	ν_1 (A_1)
788 m, 767 m	765 vs	758 m	760 s, 755 vs	ν_6 (B_1)
	477 w, sh		480 w, sh	$\nu_5 + \nu_7$ (B_2)
411 w, 387 sh	400 ms, sh	404 mw, 385 w, sh	400 m, sh	ν_2 (A_1)
358 w		353 mw		ν_3 (A_1)
330 w		326 w	330 sh	ν_7 (B_1)
311 w	320 vs, br	315 sh	305 vs, br	ν_8 (B_2)
282 w	~270 m, sh	279 mw		ν_4 (A_1)
185 w		197 vw		ν_9 (B_2)

The $TeOF_4^{2-}$ ion is not present in solutions of TeO_2 in aqueous hydrofluoric acid. Raman spectra of solutions of varying Te(IV) and HF concentrations show the presence of the TeF_5^- ion and a second species which appears to be the $TeF_4(OH)^-$ ion.[32] Attempts to prepare M_2TeOF_4 salts from solution yield either TeO_2 or $MTeF_5$.

$Rb_2TeO_2F_2$ and $Cs_2TeO_2F_2$. The infrared and Raman spectra of $Rb_2TeO_2F_2$ and $Cs_2TeO_2F_2$ are given in Table IV and a comparison with isoelectronic species is given in Table V. XeO_2F_2[33] and $IO_2F_2^-$ in KIO_2F_2,[29] which are isoelectronic with the $TeO_2F_2^{2-}$ ion, exist as discrete nonpolymeric species although there is some anion bridging over oxygen in the latter case. To a first approximation $M_2TeO_2F_2$ compounds may be considered to consist of individual $TeO_2F_2^{2-}$ units. Valence-shell electron pair repulsion theory[22] would predict a C_{2v} structure with the lone electron pair and the oxygens in equatorial positions.



The normal modes for this symmetry belong to the representation $\Gamma = 4A_1 + A_2 + 2B_1 + 2B_2$. The Raman spec-

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Table V. Comparison of the Spectra of C_{2v} Species (XY_2Z_2) Isoelectronic with $TeO_2F_2{}^{2-}$

Class	No.	$SbF_4{}^-$ [a]		XeO_2F_2 [b]		$IO_2F_2{}^-$ [c]		$TeO_2F_2{}^{2-}$ [d]		Approx description (XY_2Z_2, Y eq, Z ax)
		Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	
A_1	ν_1	586 s	591 s	850 vs	848 ms	808 vs	816 vs, 805 vs	796 vs, 781 w	795 s, 777 s	$\nu_{sym}(XY_2)$
	ν_2	436 mw	436 w	537 vs		472 s	476 s	404 mw, 385 w, sh	400 m, sh	$\nu_{sym}(XZ_2)$
	ν_3	280 w	280 s	350 ms		363 ms	358 m, sh	353 mw		$\delta_{sym}(XY_2)$
	ν_4		163 w, sh	205 ms		319 s	322 m, sh	279 mw		$\delta_{sym}(XZ_2)$
A_2	ν_5	212 w, sh		224 w		190 m, sh	196 ms	[150] [e]		τ
B_1	ν_6	552 mw	552 s	882 s	905 s	830 w, sh	855–844 m	758 m	760 s, 755 vs	$\nu_{asym}(XY_2)$
	ν_7	258 w	249 s		324 s	345 m, sh	340 s, sh	326 w	330 sh	$\delta_{asym}(XY_2)$
B_2	ν_8	380 sh	381 s, br		585 vs		434 s	315 sh	305 vs, br	$\nu_{asym}(XZ_2)$
	ν_9		186 s	315 vs	317 ms		220 ms	197 vw		$\delta_{asym}(XZ_2)$

[a] Reference 11, Et_4NSbF_4. [b] Reference 33. [c] Reference 34. [d] $Cs_2TeO_2F_2$. [e] Calculated from $\nu_5 + \nu_7$ combination.

trum should consist of nine bands and the infrared eight. In all, ten bands are observed in the Raman spectrum and seven in the infrared spectrum (down to 250 cm^{-1}). Considering that ν_5 (or ν_9) is not observed in the Raman spectrum, the large number of fundamentals observed argues against individual C_{2v} anions. The doubling of some of the stretching modes indicates that there is coupling of modes between anions and anion bridging. The C_{2v} model may still be used for an approximate assignment assuming the doubled bands to belong to one mode. Two TeO stretching modes ν_1 and ν_6 are expected and the two highest bands are assigned to these. If the FTeF angle is close to 180°, the two TeF stretching vibrations should appear with one strong in the infrared and weak in the Raman and the other strong in the Raman and weak in the infrared. The band near 310 cm^{-1} which is very strong in the infrared and weak in the Raman spectrum is assigned to one of these modes, ν_8, and the band near 400 cm^{-1}, although equally intense in the Raman and infrared spectra, lies in the TeF stretching region and must be due to ν_2. It should be noted that ν_2, the symmetric IF stretching vibration in the $IO_2F_2{}^-$ ion, is also observed in both the infrared and Raman spectra.[34] The parallel in intensities of ν_2 and ν_8 for $IO_2F_2{}^-$ and $TeO_2F_2{}^{2-}$ indicates that the fluorines are in apical positions in $TeO_2F_2{}^{2-}$ also.

In the absence of polarization measurements, it is not possible to make an unequivocal assignment of the spectra and the band intensities do not permit as definite an assignment of the deformations as that for XeO_2F_2.[29] In the Raman spectrum of $Cs_2TeO_2F_2$, the two most intense of the remaining bands, at 353 and 279 cm^{-1}, may be assigned to the A_1 modes, ν_3 and ν_4, the symmetric TeO_2 and TeF_2 deformations, which are expected to be intense in the Raman effect. The band at 330 cm^{-1} in the infrared is assigned to the asymmetric TeO_2 deformation, ν_7, but in the absence of infrared spectra below 250 cm^{-1} it is not possible to assign ν_9 with certainty. The band at 197 cm^{-1} in the Raman spectrum may be due to this mode. The two very weak bands at 1075 and 480 cm^{-1} in the infrared spectrum probably arise from the same combination bands as observed in the spectrum of XeO_2F_2; 1075 cm^{-1} is $\nu_1 + \nu_4$ and, if the band at 480 cm^{-1} is due to the more intense combination of the two observed for XeO_2F_2, $\nu_5 + \nu_7$, then ν_5 may be assigned at 150 cm^{-1}. The order of the vibrations and their intensity fits quite well with those for isoelectronic C_{2v} species as shown in Table V.

The assignment of the asymmetric IO stretching vibration at a higher frequency than the symmetric is confirmed by polarization studies on aqueous $IO_2F_2{}^-$ solutions[31] and this assignment is in accord with that for XeO_2F_2, but the intensities of the bands show the order is reversed for $TeO_2F_2{}^{2-}$ This parallels the behavior of the C_{3v} species XeO_3, $IO_3{}^-$, and $TeO_3{}^{2-}$ where a similar inversion of the symmetric and asymmetric stretching vibrations occurs.[35]

Oxygen bridging between anions in KIO_2F_2 is indicated by IO distances of 2.82 and 2.85 Å, much shorter than the expected van der Waals distance of 3.5 Å, and this is reflected in the splitting of the IO stretching vibrations, ν_1 and ν_6. Bridging is expected in the case of $TeO_2F_2{}^{2-}$ also and this is reflected in the splitting of the TeO stretching bands.

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Registry No. TeO_2, 7446-07-3; $CsTeF_5$, 40895-24-7; CsF, 13400-13-0; Cs_2TeOF_4, 40892-02-2; $KTeF_5$, 13815-26-4; KF, 7789-23-3; K_2TeOF_4, 40982-03-3; $Cs_2TeO_2F_2$, 40892-04-4; RbF, 13446-74-7; $Rb_2TeO_2F_2$, 40902-53-2; K_2SbF_5, 40892-05-5; Cs_2SbF_5, 40902-54-3.

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