which the color changed from orange to green-brown. The solvent was removed by rotary evaporation and the residual oil was redissolved in 250 ml of distilled water. The aqueous solution was extracted with four 125-ml portions of benzene and then added to a solution of 5 g tetramethylammonium chloride in 25 ml of water. The cloudy solution was clarified by the addition of 50 ml of acetone and then rotary-evaporated to a volume of about 25 ml by which time the formation of black crystals had occurred. The crystals were filtered, washed with ethanol, and weighed; yield 0.21 g (0.71 mmol, 65%).

$Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$. A 0.30-g sample of orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ was degraded by potassium hydroxide in ethanol as described above for I. After the aqueous phase was extracted with benzene, it was added to a solution of 5 g of cesium chloride in 25 ml of water and rotary-evaporated to dryness. The solid was redissolved in 50 ml of water and 50 g of Dry Ice was added in order to convert the excess potassium hydroxide to potassium carbonate. The solution was again evaporated to dryness, redissolved in 25 ml of acetone, and filtered. A water solution of cesium chloride was added to ensure the complete precipitation of the complex and all of the solvent was again removed by rotary evaporation. The residue was redissolved in 25 ml of acetone and filtered. The addition of chloroform to the filtrate followed by cooling to 0° produced 0.20 g (0.57 mmol, 51%) of $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$. The product was recrystallized from acetone and chloroform to give 70 mg of very good crystals which were submitted for an X-ray diffraction study.

$[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}]$, II. A 0.31-g (1.1-mmol) sample of a mixture of the orange isomers of $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{11}(CH_3)\}$ was degraded by 5.0 g of potassium hydroxide in ethanol in exactly the same manner as described for I. The crystalline product isolated after the addition of tetramethylammonium chloride was a mixture of $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$ and $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}]$ in a ratio of about 1:5. The product was redissolved in 20 ml of absolute ethanol and filtered. The undissolved material was I while the filtrate consisted mainly of II and a small amount of I. The filtrate was passed through a 2 × 10 cm polyamide chromatography column and eluted with ethanol. If the extraction of the aqueous phase had been incomplete, a pale yellow-green band was first to be eluted. A dark green band was then eluted which, upon removal of the solvent, afforded 0.060 g (0.19 mmol, 36%) of black crystals of II.

$(\pi\text{-}C_5H_5)Co^{IV}(\pi\text{-}2\text{-}B_7CH_8)$, III. A 50-mg (0.17-mmol) sample of I was dissolved in 50 ml of dichloromethane. A 28-mg (0.17-mmol) amount of anhydrous, sublimed ferric chloride was added as a slurry in 25 ml of dichloromethane *via* an addition funnel. The solution was stirred under nitrogen for 0.5 hr during which time the color had become intensely green and a white precipitate had formed. The reaction mixture was transferred to a vacuum line where the solvent was removed. A dark green, nearly black, solid was sublimed at room temperature to a −80° cold finger. The sublimer was opened in a nitrogen-fillex drybox yielding approximately 25 mg (0.11 mmol, 65%) of III.

$(\pi\text{-}C_5H_5)Co^{IV}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}$, IV. A 52-mg (0.17-mmol) sample of II was oxidized by 28 mg (0.17 mmol) of ferric chloride as described immediately above. Approximately 25 mg (0.10 mmol, 60%) of IV was removed from the sublimer in the drybox.

Registry No. $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$, 37333-32-7; $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$, 38882-84-7; $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$, 38882-83-6; $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{11}\text{-}6\text{-}CH_3)$, 37333-33-8; $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{11}\text{-}7\text{-}CH_3)$, 37333-34-9; $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}]$, 38882-82-5; $(\pi\text{-}C_5H_5)Co^{IV}(\pi\text{-}2\text{-}B_7CH_8)$, 38882-81-4; $(\pi\text{-}C_5H_5)Co^{IV}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}$, 38882-80-3.

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Raman Spectra of Some Xenon(II) Compounds[1]

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The Raman spectra of the Xe(II) compounds $Xe_2F_3\cdot AsF_6$, $Xe_2F_3\cdot SbF_6$, $XeF\cdot AsF_6$, $XeF\cdot SbF_6$, $XeF\cdot Sb_2F_{11}$, $XeF\cdot Nb_2F_{11}$, $XeF\cdot Ta_2F_{11}$, $FXe(SO_3F)$, and $Xe(SO_3F)_2$ have been measured. Characteristic frequencies are assigned for the XeF^+ and $Xe_2F_3{}^+$ ions. In the spectra of $FXe\cdot MF_6$ and $FXe\cdot M_2F_{11}$ bands are observed in addition to those due to XeF^+ and the anion and these are assigned to the fluorine bridge Xe- - -F–M. The spectra of $FXe(SO_3F)$ and $Xe(SO_3F)_2$ are compared with those of other fluorosulfates.

Introduction

A variety of adducts of XeF_2 with pentafluorides such as SbF_5, AsF_5, TaF_5, NbF_5, PtF_5, RuF_5, IrF_5, and OsF_5 have been prepared. The majority have 2:1, 1:1, and 1:2 stoichiometries, *e.g.*, $2XeF_2\cdot SbF_5$, $XeF_2\cdot AsF_5$, and $XeF_2\cdot 2RuF_5$.[2-7] X-Ray crystallographic studies of $XeF_2\cdot 2SbF_5$, $XeF_2\cdot RuF_5$, and $2XeF_2\cdot AsF_5$ have shown that they may be formulated as $XeF^+\cdot Sb_2F_{11}{}^-$, $XeF^+\cdot RuF_6{}^-$, and $Xe_2F_3{}^+\cdot AsF_6{}^-$, respectively.[8-10] In $XeF\cdot Sb_2F_{11}$ the XeF^+ ion is bonded to the $Sb_2F_{11}{}^-$ ion by a relatively short fluorine bridge (2.35 Å) which Peacock, *et al.*, regarded as having considerable covalent character. In $Xe_2F_3\cdot AsF_6$ the $Xe_2F_3{}^+$ ion has the bent structure II. In $XeF^+\cdot RuF_6{}^-$ the bridging XeF bond length is 2.19 Å which is between the XeF bond lengths in $XeF\cdot Sb_2F_{11}$ and in $Xe_2F_3{}^+$.

From their spectroscopic studies Sladky, *et al.*,[7] concluded

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[1] Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

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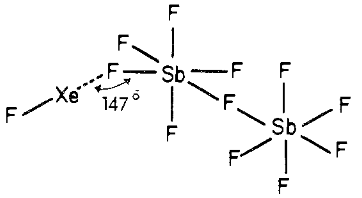
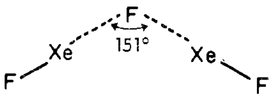
[10] F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).



I



II

that the 1:1 adducts of XeF_2 with RuF_5, PtF_5, and IrF_5 may be formulated as $XeF^+ \cdot MF_6^-$ salts. They also showed that the 2:1 adducts $2XeF_2 \cdot AsF_5$, $2XeF_2 \cdot RuF_5$, and $2XeF_2 \cdot OsF_5$ have Raman spectra consistent with the formulation $Xe_2F_3^+MF_6^-$ and that the 1:2 adducts $XeF_2 \cdot 2SbF_5$, $XeF_2 \cdot 2RuF_5$, and $XeF_2 \cdot 2IrF_5$ have Raman spectra consistent with the formulation $XeF^+M_2F_{11}$. For the $Xe_2F_3^+$ ion they observed an intense doublet at approximately 590 cm^{-1} which they attributed to the stretching of the shorter Xe–F bonds and a band at approximately 160 cm^{-1} which they attributed to a bending mode. For the $XeF \cdot MF_6$ and $XeF \cdot M_2F_{11}$ compounds these authors observed in addition to the anion frequencies a band at approximately 600 cm^{-1} which they assigned as the stretching frequency of $Xe-F^+$. They found the ν_2 and ν_5 modes of the MF_6^- ion to be split in some cases and for some compounds they observed the forbidden ν_3 mode; they attributed these observations to a lowering of the symmetry of the octahedral MF_6^- ion by fluorine bridging with the XeF^+ ion.

We have investigated the Raman spectra of a number of the adducts of XeF_2 including several that were studied by Sladky, *et al.*[7] Our results are generally in agreement with the earlier work but are more extensive and we have obtained direct spectroscopic evidence for the fluorine bridge. For comparison we have also investigated the Raman spectra of $FXeOSO_2F$ and $Xe(OSO_2F)_2$ of which the former has been shown by X-ray crystallography to have a predominantly covalent structure with collinear F–Xe–O bonds.[11]

Results and Discussion

$Xe_2F_3 \cdot AsF_6$ and $Xe_2F_3 \cdot SbF_6$. The solid-state spectra of these two compounds are given in Table I and Figure 1. In addition to the strong doublet at approximately 590 cm^{-1} and the relatively strong peak at approximately 160 cm^{-1}, which were observed previously by Sladky, *et al.*, in the compound $Xe_2F_3 \cdot AsF_6$ and which are attributed to the Xe–F stretching mode and an F–Xe- - -F bending mode, we also observed several other peaks which we assign to $Xe_2F_3^+$ for which a total of nine modes, all active in the Raman spectrum, are expected. The very weak doublet at 401–417 cm^{-1} in the $Xe_2F_3 \cdot AsF_6$ spectrum and the very weak peak at 420 cm^{-1} in the $Xe_2F_3 \cdot SbF_6$ spectrum are assigned to the stretching mode of the weak Xe- - -F bonds. The observed doublet splitting of the Xe–F stretch, and in one case of the Xe- - -F stretch, may reasonably be attributed to the expected in-phase and out-of-phase vibrations of the two bonds. At low frequencies several bands were observed in addition to the previously observed relatively intense peak at approximately 160 cm^{-1}. It seems reasonable to attribute these to other bending and torsional modes of $Xe_2F_3^+$ but a more definite assignment is not possible at present. Thus, we have observed seven of the expected nine lines of $Xe_2F_3^+$ in the spectrum of $Xe_2F_3 \cdot AsF_6$ and six of the lines in the spectrum of $Xe_2F_3 \cdot AsF_6$. For both compounds the expected ν_1, ν_2, and ν_5 vibrations of the octahedral anions are observed. It is not surprising that the Xe- - -F bonds in Xe_2F_3 have a lower stretching frequency and are longer and weaker than the terminal Xe–F bonds as the central fluorine has a formal positive charge in the covalent structure IIIa. This results in the central XeF bonds being considerably more polar than the terminal XeF bonds and, therefore, longer and weaker. The structure of $Xe_2F_3^+$ can be conveniently described in terms of resonance between the following valence-bond structures

Table I. Raman Spectra of $Xe_2F_3 \cdot MF_6$ Compounds

$Xe_2F_3 \cdot AsF_6$				$Xe_2F_3 \cdot SbF_6$		
Freq, cm^{-1}	Intens	Freq,[a] cm^{-1}	Assignment	Freq, cm^{-1}	Intens	Assignment
163	37	164	δ(F–Xe- - -F)			
255	5 (br)			161	21	δ(F–Xe- - -F)
				171	15	
367	7	369	$\nu_5(AsF_6^-)$	179	6	
401	<1		ν(Xe- - -F)	255	<1	
417				282	12	$\nu_5(SbF_6^-)$
580 sh		575 sh	$\nu_2(AsF_6^-)$	293	2	
588	100	588	ν(Xe–F)	296	2	
598	95	600		420	<1	ν(Xe- - -F)
681	20	683	$\nu_1(AsF_6^-)$			
				582	100	ν(Xe–F)
				591	66	
				645	24	$\nu_1(SbF_6^-)$

[a] Reference 7.

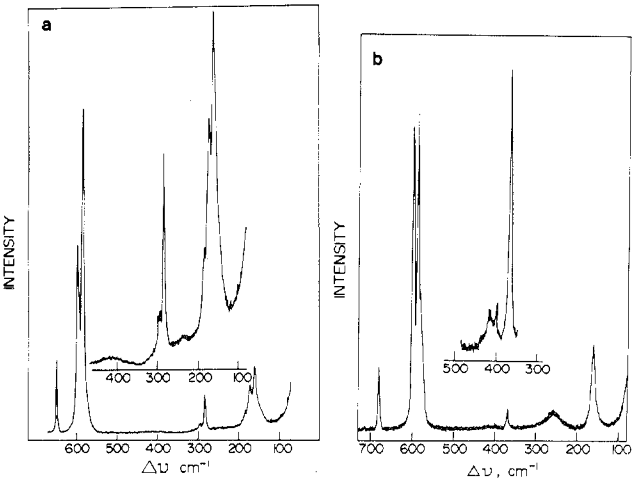
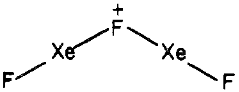
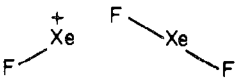


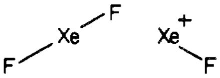
Figure 1. Raman spectra of (a) $Xe_2F_3 \cdot SbF_6$ and (b) $Xe_2F_3 \cdot AsF_6$.



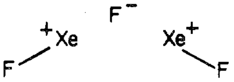
IIIa



IIIb



IIIc



IIId

$XeF \cdot AsF_6$ and $XeF \cdot SbF_6$. The spectra of these two compounds are given in Figure 2 and Table II. The Xe–F stretching frequency is assigned at approximately 610 cm^{-1} and the Xe- - -F bridging stretch at 340–380 cm^{-1}. This latter frequency is lower than that for the Xe- - -F stretch in

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Table II. Raman Spectra of $XeF \cdot MF_6$ Compounds

$XeF \cdot AsF_6$			$XeF \cdot SbF_6$		
Freq, cm^{-1}	Intens	Assignment	Freq, cm^{-1}	Intens	Assignment
99	1	δ(F–Xe- - -F)	141	23	δ(F–Xe- - -F)
146 sh	8		180	4	
155	15		267	11	$\nu_4(SbF_6^-)$
180	2		290	11	$\nu_5(SbF_6^-)$
339	21	ν(Xe- - -F)	337	6	ν(Xe- - -F)
387	6	$\nu_5(AsF_6^-)$	388	4	
417	5	$\nu_4(AsF_6^-)$?	447	15	ν(Sb- - -F)
443	3	ν(As- - -F)	467	13	
586	10	$\nu_2(AsF_6^-)$	586	6	$\nu_2(SbF_6^-)$
609	100	ν(Xe–F)	615	100	ν(Xe–F)
667	4	$\nu_1(AsF_6^-)$	645	15	$\nu_1(SbF_6^-)$
678	20		666	43	
724	5	$\nu_3(AsF_6^-)$	685	6	$\nu_3(SbF_6^-)$
731	5				

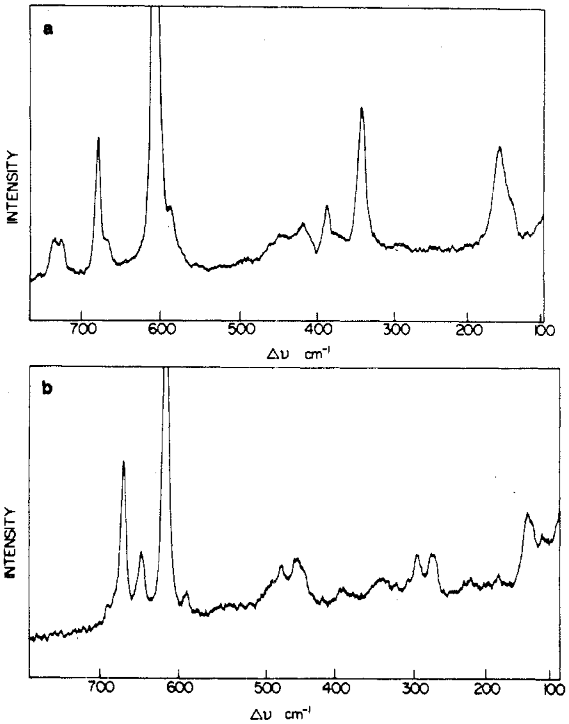

Figure 2. Raman spectra of (a) $XeF \cdot AsF_6$ and (b) $XeF \cdot SbF_6$.

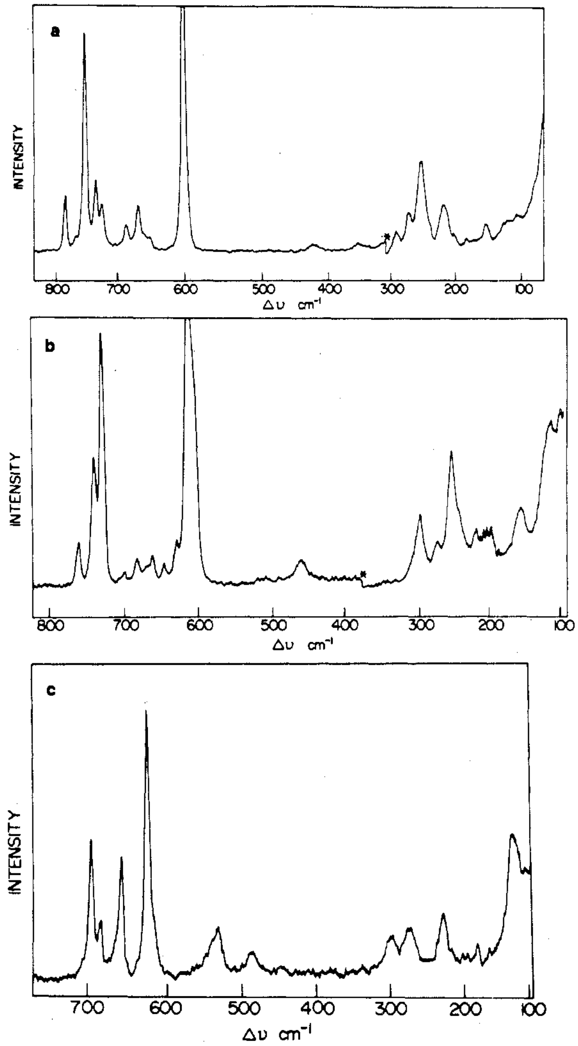

Figure 3. Raman spectra of (a) $XeF \cdot Nb_2F_{11}$, (b) $XeF \cdot Ta_2F_{11}$, and (c) $XeF \cdot Sb_2F_{11}$. Asterisk indicates base-line adjustment.

$Xe_2F_3^+$ but higher than that in $XeF \cdot Sb_2F_{11}$ (269 cm^{-1}, see next section). This is consistent with the expectation that the Xe- - -F bridge will be weaker than in $Xe_2F_3^+$ but stronger than in $XeF \cdot Sb_2F_{11}$ where the existence of a fluorine bridge has already been established by X-ray crystallography. In $XeF \cdot RuF_6$, which is the one compound of the type $XeF \cdot MF_6$ which has had its structure determined, the bridging bond length is 2.19 Å which is intermediate between that in $Xe_2F_3^+$ and $XeF \cdot Sb_2F_{11}$. In addition to the ν_1, ν_2, and ν_5 bands, of the SbF_6^- and AsF_6^- ions, the forbidden ν_3 mode also appears in both cases and for SbF_6^- the ν_5 mode is also split. This is very similar to the splitting of the AsF_6^- and SbF_6^- frequencies in their compounds with SeF_3^+ and other fluoro cations which has been attributed to reduction of the O_h symmetry of the anion to C_{4v} or C_{2v} by formation of strong fluorine bridges to the cation.[12] We conclude, therefore, that the similar splitting of the anion frequencies observed here may be attributed to fluorine bridging to the XeF^+ ion. We may note that Beattie, *et al.*,[13,14] have shown that the Bi- - -F bridging fluorine stretching mode is observed at 450 cm^{-1} in the infrared spectrum of α-BiF_5 which consists of infinite chains of trans-bridged BiF_6 octahedra. The Sn- - -F bridging fluorine stretching mode has been observed at 472 cm^{-1} in SnF_4.[14] In $SbCl_4F$, which also contains a bridging fluorine, a very weak band attributed to the bridging fluorine was observed at 446 cm^{-1} both in the infrared and in the Raman spectra.[13] In solid NbF_5, which has a cis-bridged structure, Beattie, *et al.*,[13] observed the bridging fluorine frequency at 479 cm^{-1} in the infrared. In the infrared spectrum of liquid SbF_5, which has a cis-bridged structure, a weak broad peak is observed at 450 cm^{-1}. This has been assigned as the Sb- - -F stretching frequency.[13]

Sladky, *et al.*,[7] previously reported the splitting of the anion frequencies ν_2 and ν_5 and the observation of the forbidden ν_3 mode in $XeF \cdot PtF_6$, $XeF \cdot RuF_6$, and $XeF \cdot IrF_6$ although they did not observe the Xe- - -F bridging stretch or the bending modes associated with the fluorine bridge. They concluded that the interaction between the anion and the cation is weak compared to the bonding interactions in XeF^+ or XeF_2 and that it is of a primarily ionic nature. Our observation of the Xe- - -F bridging stretching and bending

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(13) I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc. A*, 1910 (1971).

(14) I. R. Beattie, N. Cheetham, T. R. Gilson, K. M. S. Livingston, and D. J. Reynolds, *J. Chem. Soc. A*, 1910 (1971).

Table III. Raman Spectra of $XeF \cdot M_2F_{11}$ Compounds

$XeF \cdot Sb_2F_{11}$			$CsSb_2F_{11}$[a]		$XeF \cdot Nb_2F_{11}$			$CsNb_2F_{11}$		$XeF \cdot Ta_2F_{11}$			$CsTa_2F_{11}$	
Freq, cm^{-1}	Intens	Assignment	Freq, cm^{-1}	Intens	Freq, cm^{-1}	Intens	Assignment	Freq, cm^{-1}	Intens	Freq, cm^{-1}	Intens	Assignment	Freq, cm^{-1}	Intens
127	37	δ(F–Xe- - -F)			105	2	δ(F–Xe- - -F)			100	2	δ(F–Xe- - -F)		
180	4				121	2				112	7			
212	5	$Sb_2F_{11}^-$			151	4				154	10			
226	12		232	?	195	2				182	2			
269	11	ν(Xe–F)	291	39	200	3	$Nb_2F_{11}^-$			198-207	7	$Ta_2F_{11}^-$	202	9
293	8	$Sb_2F_{11}^-$	300		220	10		211	36	217	7			
484	7	ν(Sb- - -F)	332	4	263	19		251	48	239	10		236	20
528	16	$Sb_2F_{11}^-$	521	1	270	7		289	37	252	33		247	
603	<1		597	15	312	2	ν(Xe- - -F)			272	3			
619	100	ν(Xe–F)	603		345	2				295	23	ν(Xe- - -F)	291	14
651	39	$Sb_2F_{11}^-$	654	100	410	2	ν(Ta- - -F)			459	8	ν(Ta- - -F)	487	9
669	9				596	100	ν(Xe–F)	588	12	610	100	ν(Xe–F)	498	3
678	8				648	3	$Nb_2F_{11}^-$			626	10	$Ta_2F_{11}^-$		
688	48		685	93	661	11		666	44	643	3		640	3
			692		670	6		685	31	658	7		661	5
					715	11	NbF_5?			667	5			
					724	18	$Nb_2F_{11}^-$	726	100	679	7		682	3
					738	56				700	3		696	100
					752	3	NbF_5?			725	82		724	12
					765	13				734	40			

[a] P. A. W. Dean and R. J. Gillespie, unpublished results.

modes indicates that, although the Xe- - -F bond is weaker than in $Xe_2F_3^+$, it must be regarded as having a definite covalent character. A simple ionic formulation $XeF^+ MF_6^-$ is not entirely satisfactory for these compounds and a description in terms of the following resonance structures is more appropriate

$F–Xe–F–SbF_5$ $\quad$ $F–Xe^+ \ F–SbF_5^-$ $\quad$ $F–Xe–F \ SbF_5$

IVa $\quad$ IVb $\quad$ IVc

$XeF \cdot Sb_2F_{11}$, $XeF \cdot Nb_2F_{11}$, and $XeF \cdot Ta_2F_{11}$. The spectra are given in Figure 3 and in Table III and the assignments of the observed frequencies are also given in Table III. A complete assignment of the "anion" frequencies is not possible for these compounds but there is generally good agreement with the frequencies observed for other compounds containing these anions.

In $XeF \cdot Sb_2F_{11}$, the Xe–F stretching frequency is the highest observed for any of these compounds and the Xe- - -F stretching frequency is the lowest. This implies that the fluorine bridge is more unsymmetrical in this case than in any of the other compounds that have been studied. Nevertheless, Peacock, *et al.*,[8] have concluded from the length of this weak part of the bridge that it has an appreciable covalent character and this is in accord with our observation of the stretching frequency of this bond and some of the bending modes of the fluorine bridge.

The observed vibrational frequencies associated with the F–Xe- - -F group are summarized in Table IV. Although the available data are limited, there appears to be a reasonably good correlation between the Xe–F bond length and the X–F stretching frequency and a continuous variation is obtained from the strong Xe–F bond in $XeF \cdot Sb_2F_{11}$ to the weak Xe- - -F bond in this same compound (Figure 4).

The spectra of solutions of XeF_2 in SbF_5 contain, in addition to the lines previously observed for SbF_5,[12,13] a line at 619 cm^{-1} due to the Xe–F stretch and lines at 108 and 121 cm^{-1} due to F–Xe- - -F bending modes. Our Raman spectrum of SbF_5 is in good agreement with that reported by Beattie, *et al.*,[13] and with that reported by Commeyras and Olah[15] except that neither Beattier, *et al.*, nor we observed the rather weak, broad peak at 489 cm^{-1} which was reported by Commeyras and Olah. Although the very weak F- - -Xe stretch at ~450 cm^{-1} was not observed, the observation of the two low-frequency bending modes leads one to conclude that even in solution in liquid SbF_5 the $Xe–F^+$ ion is not "free" but is still bonded by a fluorine bridge to an $Sb_nF_{5n+1}^-$ polyanion.

Table IV. Vibrational Frequencies Associated with F–Xe- - -F

	Str modes, cm^{-1}		Bending modes, cm^{-1}	$r_{Xe–F}$, Å	$r_{Xe- - -F}$, Å
	ν(Xe–F)	ν(Xe---F)			
XeF_2	557	495	213	2.01	2.01
$Xe_2F_3 \cdot AsF_6$	588 598	401 417	163, 255	1.90	2.14
$Xe_2F_3 \cdot SbF_6$	582 592	420	161, 171, 179, 255		
$XeF \cdot RuF_6$	604 599			1.88	2.19
$XeF \cdot AsF_6$	609	339	99, 146, 155, 180		
$XeF \cdot SbF_6$	615	337 388	141, 180		
$XeF \cdot Nb_2F_{11}$	596	312 345	105, 121, 151, 195		
$XeF \cdot Ta_2F_{11}$	610	295	100, 112, 154, 182		
$XeF \cdot Sb_2F_{11}$	619	269	127, 180	1.84	2.35
XeF_2 in excess SbF_5	619		108, 121		

$FXeOSO_2F$ and $Xe(OSO_2F)_2$. The X-ray crystallographic data show that the molecule $FXeOSO_2F$ has C_s symmetry,[11] and therefore a total of 15 normal vibrational modes are expected, ten a′ and five a″ modes, all of which are expected to be active in the Raman spectrum.

The 15 vibrations of $FXeOSO_2F$ can be conveniently described in the same manner as the 12 vibrations of the covalent fluorosulfates $FOSO_2F$, $ClOSO_2F$, and $BrOSO_2F$ with the addition of three modes due to the Xe–F group: the Xe–F stretch (a′) and the O–Xe–F (a′) and the Xe–F wag (a″). Assignments are given for all 15 modes in Table V.

Since XeF_2 and $FXeOSO_2F$ have two collinear bonds at Xe, it is expected that $Xe(OSO_2F)_2$ will have two linear O–Xe–O bonds and it will also presumably have C_s symmetry like $FXeOSO_2F$ and the halogen fluorosulfates $FOSO_2F$, $ClOSO_2F$, $BrOSO_2F$, and $Br(OSO_2F)_2^-$. If there is some

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(15) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, 91, 2929 (1969).

Table V. Raman Spectrum of $FXeOSO_2F$, $Xe(OSO_2F)_2$, and Some Related Molecules

$FOSO_2F$[a]	$ClOSO_2F$[a]	$HOSO_2F$[a]	$BrOSO_2F$[b]	SO_3F^-[c]	$FXeOSO_2F$	$Xe(OSO_2F)_2$	$Br(OSO_2F)_2^-$[a]	Assignment
1502 (<1)	1478 (<1)	1445	1438 (2)	1285	1386 (1) 1371 (1)	1420 (1) 1416 (1) 1388 (<1)	1378 (15)	SO_2 asym str (a″)
1250 (8)	1225 (5)	1230	1306 (4)	1084 vs	1193 (1)	1238 (1) 1214 (2)	1223 (3)	SO_2 sym str (a′)
788 (7)	856 (1.5)	961	884 (2.5)		1009 (1) 969 (1)	954 940 (4)	1020 (1)	S-OX str (a′)
857 (3)	830 (1.5)	851	832 (1)	741 m	801 (1) 794 (1)	818 (<1)	780 (1)	SF str (a′)
880 (10)	706 (10)	3000	464 (4)		434 (2)	436 (5)	437 (4)	O-X str (a′)
577 (<1)	573 (<1)	560	659 (6)	586 m	614 (5) 582 (2)	610 (7) 599 (<1)	618 (10)	SO_2 bend (a′)
530 (<1)	534 (1)	552	570 (1)	570 m	553 (2)	570-584 (<1)	574 (1)	SO_2 rock (a″)
					539 (20) 532 (18) 527 (15)			Xe-F str (a′)
					521 (100)			
500 (1.5)	486 (4.5)	490	537 (1)	405 s		539 (<1)	557 (1)	S-F wag (a′)
390 (1)	389 (<1)	393	390 (1)		392 (2)	385 (1)	398 (1)	SO_2 twist (a″)
395 (4)	363 (8)	405	317 (10)		253 (10)	256 (9) 253 (10)	261 (4)	S-OX bend (a′)
					239 (4)			O-Xe-F bend and/or lattice modes (a″)
242 (3)	212 (2.5)	1179	175 (4)		179 (3)			X-O-S bend (a′)
137 (1)		686?		107 (6)		116 (3)		S-OX torsion (a″)

[a] A. M. Qureshi, L. E. Levchuk, and F. Aubke, *Can. J. Chem.*, **49**, 2544 (1971). [b] A. M. Qureshi and F. Aubke, *Inorg. Chem.*, **10**, 1116 (1971). [c] J. Goubeau and J. B. Milne, *Can. J. Chem.*, **45**, 2321 (1967).

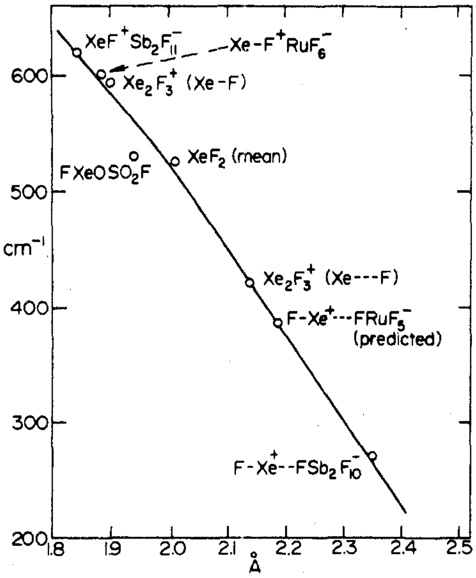

Figure 4. Bond lengths and stretching frequencies for Xe-F bonds.

restricted rotation around the S-OXe bond, then three configurations are possible for the molecule: cis,cis, cis,trans, trans,trans. Twenty-seven normal modes are expected for the $Xe(OSO_2F)_2$ molecule with C_s symmetry. However, as coupling between the two fluorosulfate groups is expected to be small, it is very probable that only one frequency for the various modes of the fluorosulfate group will be observed instead of the in-phase and out-of-phase modes that would, in principle, be expected for each vibration of a single fluorosulfate group. An approximate analysis of the spectrum may be given in terms of the modes of a single SO_3F group as found in the halogen fluorosulfates and $FXeOSO_2F$ and the modes of the linear OXeO group, of which only the symmetric stretch would be expected to be active in the Raman spectrum (Table V). Strictly speaking, if $Xe(OSO_2F)_2$ has C_s symmetry, the OXeO antisymmetric stretch is, in principle, Raman active but it is likely to be very weak. A reasonable assignment of the observed bands for $FXeOSO_2F$ and $Xe(OSO_2F)_2$ can be made by comparison with the spectra of the related molecules (Table V). In particular, we found that the spectrum of $Xe(OSO_2F)_2$ is very similar to that of the isostructural molecule $Br(OSO_2F)_2^-$.[16] The bands at frequencies of 700 cm^{-1} and above can be assigned without ambiguity but at lower frequencies there are some difficulties in making precise assignments which have not been solved completely satisfactorily. It is noteworthy that the SO_2 and SF stretching frequencies fall between those of a typical covalent fluorosulfate such as $ClOSO_2F$ and the ionic fluorosulfate anion SO_3F^-. This is in accord with the conclusions from the X-ray crystal investigation of $FXeOSO_2F$ which showed[11] that, although the Xe-F bond has a normal length between that of XeF_2 and XeF^+, the Xe-O bond is abnormally long and this was interpreted as indicating that there is a major contribution from the ionic structure $F\text{-}Xe^+OSO_2F^-$. For the bis(fluorosulfate), we find that the SO and SF stretching frequencies are somewhat higher than in the mono(fluorosulfate) and close to those of the covalent fluorosulfates. Consequently, we conclude that the bis(fluorosulfate) is not as ionic as the mono(fluorosulfate); *i.e.*, there is a smaller contribution from structures such as $FSO_2OXe^+\text{-}OSO_2F^-$. The assignment of the remaining frequencies is more difficult. It seems obvious, however, that the very strong band at 521 cm^{-1} should be assigned as the Xe-F stretch of $FXeOSO_2F$ as this is close to the Xe-F frequencies observed for XeF_2 and, like all the Xe-F bands we have observed in other compounds, is relatively very strong. As may be seen in Figure 4 the frequency also correlates well with the Xe-F bond length. The origin of the strong triplet just above this XeF band is, however, not so obvious. It seems most probable that it is also associated with the Xe-F stretch and perhaps it arises from a solid-state (factor group) splitting. If we assume that the correlation we have given earlier between the Xe-F stretching frequency and the bond length also applies approximately to Xe-O bonds, we would expect a frequency in the region of 400 cm^{-1} for the Xe-O stretch. On this basis, the 434-cm^{-1} peak in the spectrum of

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$FXeOSO_2F$ could be attributed to the Xe-O stretch and the relatively strong 436-cm^{-1} peak in the spectrum of the bis(fluorosulfate) may be assigned in the same way. This is in agreement with the assignment of a band at 457 cm^{-1} to the Xe-O stretching mode in the spectrum of $FXeOTeF_5$[17] and at 434 cm^{-1} in $Xe(OTeF_5)_2$[18] and 477 cm^{-1} in $XeOTeF_5^+AsF_6^-$.[19] The assignment of the other low-frequency modes also cannot be made with complete certainty, but possible assignments are given in Table V. See Figure 5 for the Raman spectra of $FXeOSO_2F$ and $Xe(OSO_2F)_2$.

Experimental Section

Xenon Difluoride. XeF_2 was prepared by mixing equimolar quantities of xenon and fluorine in a Pyrex vessel, followed by exposure to uv irradiation, according to the method described by Streng and by Holloway.[20,21] The XeF_2 obtained was checked for purity by ^{19}F nmr (in HF solution) and by Raman spectroscopy on the solid.

Antimony Pentafluoride. SbF_5 was obtained from Ozark Mahoning Co. and was purified by double distillation at atmospheric pressure in an all-glass apparatus.

Arsenic Pentafluoride. AsF_5 was obtained from Ozark Mahoning Co. No other ^{19}F nmr peaks, other than that due to AsF_5, were found at −80°, so it was used directly.

Hydrogen Fluoride. Anhydrous HF was obtained from Harshaw Chemical Co. and was purified as described previously.[22]

Raman Spectra. Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with an electronic amplifier and recorder. Exciting radiation was the green 5145-Å line of a Spectra Physics Model 140 argon ion laser or the 6328-Å line of a Spectra Physics 125 He-Ne laser. The Raman shifts were estimated to be accurate to 2 cm^{-1}. Samples were sealed in Kel-F tubes (3.18-mm i.d., 3.90-mm o.d.) or glass capillaries, 1.6–1.8 mm o.d., which were mounted at 90° to the laser beam. For low-temperature spectra, the sample tube was mounted in a quartz tube with an evacuated jacket, silvered except at the center. Nitrogen was boiled off from a dewar and passed through the tube and the temperature was measured with a thermocouple. All glass capillary samples were placed in glass in a drybox, wax sealed, and immediately flame sealed after withdrawing them from the drybox.

Vacuum Line. All manipulations were carried out in vacuum systems constructed from Monel metal, Kel-F, and Teflon equipped with Whitey valves with Kel-F tips and Kel-F traps attached with Swagelok fittings. All reactions were carried out in $^3/_4$-in. o.d. Kel-F reaction vessels equipped with Teflon valves.

Preparation of $2XeF_2 \cdot SbF_5$, $XeF_2 \cdot SbF_5$, and $XeF_2 \cdot 2SbF_5$. Approximately 0.01 mol of SbF_5 was transferred to a Kel-F reaction vessel in a drybox. The required amount of XeF_2 was transferred in a glove bag to another Kel-F reaction vessel and about 10–12 ml of HF was distilled on it. The mixture was warmed to room temperature to dissolve all the XeF_2. The XeF_2-HF solution was transferred *via* an evacuated Kel-F T piece onto the SbF_5 that was cooled to −78° (Dry Ice–trichloroethylene bath) and the HF was removed under vacuum until complete dryness. [Sometimes to ensure complete removal of HF, the solids or the concentrated solutions were warmed to −64° (chloroform–liquid N_2 slush bath) and pumped.]

Preparation of $2XeF_2 \cdot AsF_5$ and $XeF_2 \cdot AsF_5$. A weighed amount of AsF_5 was distilled onto an XeF_2-HF mixture kept at −196° (~0.01 mol of XeF_2 in 10 ml of HF). The procedure was then exactly the same as for the preparation of the XeF_2–SbF_5 compounds. The yield was essentially quantitative.

Preparation of $XeF_2 \cdot 2TaF_5$ and $XeF_2 \cdot 2NbF_5$. In a typical experiment, 2.32 mmol of XeF_2 was mixed with 4.82 mmol of TaF_5 in a Kel-F trap in a drybox. The components were then fused together at 100° for 10 min and reaction was then quenched with liquid N_2. It was pumped to constant weight at room temperature yielding a yellow product.

In a typical experiment, 1.26 mmol of XeF_2 was added to 2.89 mmol of NbF_5 in a Kel-F trap in a drybox. The components were then heated together for 10 min at 100° to give a yellow melt. The reaction was quenched with liquid N_2, then allowed to warm to room temperature, and pumped to constant weight to yield 1.34 mmol (0.7295 g) of a yellow product.

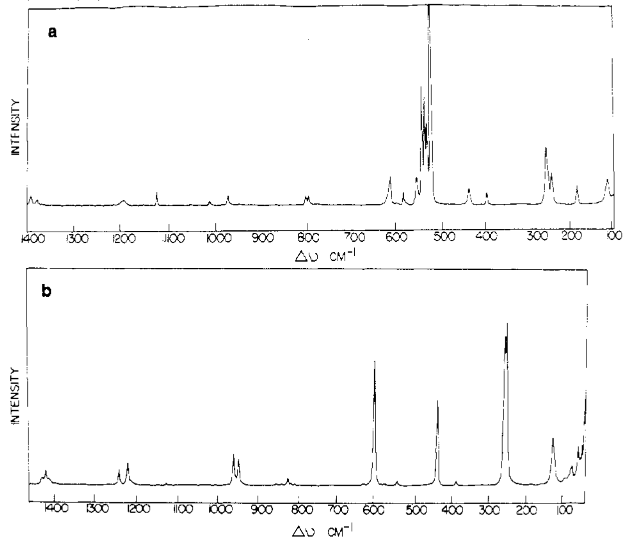

Figure 5. Raman spectra of (a) $FXeOSO_2F$ and (b) $Xe(OSO_2F)$.

Preparation of $FXeOSO_2F$. A slight excess of XeF_2 dissolved in HF was added to the appropriate quantity of HSO_3F at −196°. Excess HF was removed at approximately −24° and excess XeF_2 was removed under vacuum at room temperature. The product was a white solid which had a Raman spectrum identical with that of another sample prepared using Bartlett's original method,[11] which did not involve the use of solvent HF. The product was stored under nitrogen at −78°.

Preparation of $Xe(OSO_2F)_2$. The required quantity of XeF_2 dissolved in HF was added to the appropriate quantity of HSO_3F at −196°. Excess HF was removed at −78°. The product was a pale yellow solid which had a Raman spectrum identical with that of a sample prepared by Bartlett's method. It was stored under nitrogen at −78°.

Preparation of $CsTa_2F_{11}$. Approximately 15 g of anhydrous HF was condensed onto 4.22 mmol of cesium fluoride in a Kel-F trap at −196°. The CsF was then dissolved at room temperature and the solution added *via* a Kel-F T piece to a Kel-F trap containing 8.26 mmol of tantalum pentafluoride at −196°. The mixture was warmed to room temperature, the components were dissolved, and the HF was removed under vacuum at −60°. The white solid obtained was then pumped until it had constant weight at room temperature (2.90 g).

Preparation of $CsTaF_6$. Approximately 15 g of HF was condensed onto 2.98 mmol of CsF in a Kel-F trap at −196°. After warming and dissolving at room temperature the solution was transferred *via* a Kel-F T piece onto 2.94 mmol of tantalum pentafluoride in a Kel-F trap at −196°. After warming and dissolving at room temperature, the HF was removed at −60°. The white solid was then pumped until it had constant weight (2.99 mmol).

Preparation of $CsNbF_6$. The same procedure was followed as for the $CsTaF_6$ preparation.

Registry No. XeF_2, 13709-36-9; SbF_5, 7783-70-2; AsF_5, 7784-36-3; TaF_5, 7783-71-3; NbF_5, 7783-68-8; HSO_3F, 7789-21-1; CsF, 13400-13-0; $Xe_2F_3 \cdot AsF_6$, 21308-45-2; $Xe_2F_3 \cdot SbF_6$, 38682-18-7; $XeF \cdot RuF_6$, 26500-06-1; $FXeFRuF_5$, 38723-85-2; $XeF \cdot AsF_6$, 26024-71-5; $FXeFAsF_5$, 38682-20-1; $XeF \cdot SbF_6$, 30864-32-5; $FXeFSbF_5$, 38682-21-2; $XeF \cdot Nb_2F_{11}$, 38682-22-3; $FXeFNb_2F_{10}$, 38682-23-4; $XeF \cdot Ta_2F_{11}$, 38682-24-5; $FXeFTa_2F_{10}$, 38682-25-6; $XeF \cdot Sb_2F_{11}$, 38682-26-7; $FXeFSb_2F_{10}$, 38682-27-8; $CsSb_2F_{11}$, 23751-61-3; $CsNb_2F_{11}$, 38682-30-3; $CsTa_2F_{11}$, 38682-29-0; $CsTaF_6$, 16923-68-5; $CsNbF_6$, 12062-12-3; $FXeOSO_2F$, 25519-01-1; $Xe(OSO_2F)_2$, 25523-77-7.

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Absorption Spectra of $K_3Na(SO_4)_2$-Na_2CrO_4 and $LiKSO_4$-K_2CrO_4 Single Crystals[1]

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Absorption spectra of two mixed-crystal systems of chromate ion are reported. In one of these systems, $K_3Na(SO_4)_2$-Na_2CrO_4, the CrO_4^{2-} ion occupies a site of C_{3v} symmetry whereas in the other, $LiKSO_4$-K_2CrO_4, it occupies a C_3 site. Four absorption band systems are observed and are assigned, on the basis of polarization data, as follows: 4000 Å, $^1T_1 \leftarrow {}^1A_1$; 3600 Å, $^1T_2 \leftarrow {}^1A_1$; 2700 Å, $^1T_2 \leftarrow {}^1A_1$; 2400 Å, $^1T_1 \leftarrow {}^1A_1$.

Introduction

Many theoretical calculations have been carried out on the electronic structure of the T_d transition metal oxyanions.[2-7] Most of the experimental work has dealt with permanganate[8-15] with little information available for related systems.[16-18] The present investigation is concerned with the electronic spectrum of the chromate ion at helium temperatures. The systems chosen were $K_3Na(SO_4)_2$-Na_2CrO_4 and $LiKSO_4$-K_2CrO_4 mixed crystals.

These crystal systems were chosen for the following reasons. (i) The CrO_4^{2-} ion occupies a position of C_{3v} symmetry in the $K_3Na(SO_4)_2$ crystal and C_3 in the $LiKSO_4$ crystal.[19] These symmetry reductions ($T_d \rightarrow C_{3v}$ for the potassium-sodium salt and $T_d \rightarrow C_3$ for the lithium-potassium salt) should produce state splittings and allowedness-forbiddeness characteristics which might permit unique identifications for the states of the hypothetical parent tetrahedral molecule ion.

(ii) Both mixed-crystal systems are hexagonal. Consequently, polarization studies parallel ($\vec{E} \parallel \vec{C}$) and perpendicular ($\vec{E} \perp \vec{C}$) to the crystal c axis should refer to A ← A and E ← A transitions, respectively.

(iii) Both crystals are easily grown in virtually any desired host-guest concentration ratio.

Experimental Section

All chemicals were reagent grade. The sodium and potassium sulfates were obtained from J. T. Baker. The lithium sulfate was obtained from Fisher and the potassium chromate from Allied Chemical and Dye Corp. The sodium:potassium ratio chosen[20] in preparing the $K_3Na(SO_4)_2$ was 1.58. The lithium:potassium ratio chosen[20] in preparing the $LiKSO_4$ was 2.07. The crystals were grown from aqueous solutions. The chromate concentration in the sodium-potassium salt was 0.20 mol % and in the lithium-potassium salt was 3.5 mol %.

Spectroscopic measurements were made using a Cary 14 spectrophotometer in conjunction with both immersion and contact liquid-helium dewars. No appreciable differences were noted in the spectra obtained using either type of dewar. However, although the crystal temperature was found to be higher (*i.e.*, ~15°K) in the contact dewar, the inherent resolution was actually better because only two layers of quartz (instead of eight) intruded on the light path and allowed the use of smaller slit widths.

The nominal spectral bandwidths, based on slit width and instrumental dispersion factors, were as follows: 30 cm^{-1} at 25,000 cm^{-1}; 50 cm^{-1} at 30,000 cm^{-1}; 70 cm^{-1} at 35,000 cm^{-1}; 90 cm^{-1} at 40,000 cm^{-1}; 150 cm^{-1} at 45,000 cm^{-1}. The band maxima of sharp peaks were locatable with an uncertainty not larger than ±15 cm^{-1}.

Results

The absorption spectra obtained are shown in Figures 1 and 2. We describe here three absorption regions in detail (~ 3600, 2700, 2400 Å) and one other (~4000 Å) very briefly. In all cases, the $LiKSO_4$-K_2CrO_4 crystal cracked during the cooling from 77 to 4.2°K. This cracking, presumably caused by a phase change, greatly increased light-scattering effects. Therefore, all observations on $LiKSO_4$-K_2CrO_4 were restricted to 77°K.

Absorption Band Centered at 4000 Å. The vibrational analysis of the unpolarized spectrum is given in Table I. This lowest energy band has an apparent origin in the region of 21,500 cm^{-1}. It exhibits four weak but distinct vibrational peaks spaced by 807 cm^{-1}. The ~800-cm^{-1} vibrational interval common to this and all other resolved bands is the totally symmetric breathing frequency ν_1 (a_1) of the various excited states. The totally symmetric vibration has an average frequency of 847 cm^{-1} in the $^1A_1$ ground state.[21]

As is evident from Figure 2, this weak absorption band appears more intense in the ⊥-polarization spectrum for the C_{3v} system whereas it appears equally intense in both the ⊥- and ∥-polarization spectra of the C_3 system. Assuming these observations to reflect site effects, this lowest energy band must be assigned as an electric dipole forbidden $^1T_1 \leftarrow {}^1A_1$ transition of the parent tetrahedral ion. This assignment accords with the solidly based designation of the analogous "far-red" bands of permanganate ion.[14,15]

Absorption Band Centered at 3600 Å. The absorption spectra are shown in Figures 1 and 2. This absorption band appears comparably intense in both polarization directions regardless of whether the CrO_4^{2-} ion occupies a substitutional site of either C_{3v} or C_3 symmetry. In both cases, the spectra obtained in the ∥- and ⊥-polarization directions clearly represent electric dipole allowed transitions. The only electronic

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