

Contribution from the Department of Chemistry,
University of Washington, Seattle, Washington 98195**Vibration Spectra and Structure of Lanthanide Fluorosulfate Compounds**

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Vibration spectra of a series of lanthanide(III) fluorosulfate compounds are reported and assigned. The spectra suggest mixed coordination types of the anion. Fluorescence emission of the Eu compound along with the vibration spectra indicate octacoordination and tri- and bidentate fluorosulfate groups.

Introduction

Vibration spectra of a wide variety of fluorosulfate compounds are known.¹⁸ These measurements are generally employed to deduce evidence regarding structure and bonding from the number and energies of observed anion vibrations. In an attempt to characterize further the recently prepared, moisture-sensitive lanthanide fluorosulfates we have measured their vibrational spectra and in some cases their visible fluorescence emissions and/or uv-visible absorption spectra.

Fluorescence investigations of lanthanide complexes have been prompted largely by interest in their potential application as laser materials. They are also ideal systems for the study of energy-transfer processes and vibronic interactions in crystals,² especially as various energies are available for excitation. The present measurements are of interest in the latter regard.

In this paper we report and discuss the results of spectroscopic measurements of scandium, yttrium, and the lanthanide(III) fluorosulfates.

Experimental Section

The details of preparation and analysis of the lanthanide fluorosulfate compounds are given in a separate paper.¹

Infrared spectra of Nujol mulls held between silver chloride disks were measured on a Perkin-Elmer 225 infrared spectrometer. The mulls were prepared under anhydrous conditions and spectra from 1400 to 400 cm^{-1} recorded immediately. Spectra between 400 and 200 cm^{-1} were likewise recorded using silicon disks to support the mull.

Samples for Raman spectra were contained in sealed melting point capillaries. Measurements were obtained using an instrument centered around a Spex 1401 double monochromator. Spectra of each of the samples were measured using for excitation the emissions among 4579, 4880, 5145, 5682, and 6471 Å of a Coherent Radiation 52MG Ar⁺-Kr⁺ mixed-gas laser with which useful measurements could be obtained. Fluorescence emissions were recorded along with the Raman spectra or instead of the Raman spectra for many of the sample-excitation energy combinations. Low-temperature measurements were accomplished by passing cold dry nitrogen over the sample in a vacuum-jacketed cell or attaching the capillary to a cold finger from a Dewar enclosed in a vacuum jacket with a quartz entrance window and a lens system for collection of the scattered radiation. The estimated maximum error for all these measurements is $\pm 3 \text{ cm}^{-1}$.

The uv-visible measurements were taken on a Cary 14 spectrometer using Nujol mulls on filter paper as the sampling medium. Any hydrolysis of the samples in Nujol mulls was not apparent since no changes were observed in repeated measurements of the same sample within about 1 h after the first.

Results and Discussion

The ir and Raman spectra of all the lanthanide(III) fluorosulfates are similar. Typical examples of the vibration spectra are shown in Figure 1 and Table I. The spectra are more complex than those of any of the individual fluorosulfate types (vide infra). They can, however, be explained in terms of more than one manner of association to the nuclear atom. Two types of fluorosulfate groups are suggested, for example, to explain the complex spectra of $\text{Sr}(\text{SO}_3\text{F})_2$ ¹⁸ and $\text{Sn}(\text{SO}_3\text{F})_4$.^{10a}

Having two types of fluorosulfate groups rules out nine- and six-coordination for the known 1:3 metal to ligand stoi-

Table I. Typical Vibration Spectra of Lanthanide Fluorosulfate Compounds and Suggested Assignments^a

Raman, cm^{-1}	Ir, cm^{-1}	Suggested assignment
70		} Lattice vibrations
120		
135		
198		
218		
345	360	
426	430	
444		Trident ν_6 (E) O-S-F def
561	568	} Bident ν_3 (A') SO_3 def, trident ν_3 (A ₁) SO_3 def, trident ν_3 (E) SO_3 def,
578		
595	592	
609	607	} bident ν_4, ν_8 (A', A'') SO_3 def
827	825	
845	848	} Trident ν_2 (A ₁) SF str
881		
897	893	} Bident ν_3 (A') SF str
	918	
	1108	} Bident ν_2 (A') SO_2 str
1120	1125	
1151		Trident ν_1 (A ₁) SO_3 str
1242		Trident ν_4 (E) SO_3 str
1270	1282	} Bident ν_1, ν_7 (A', A'') S-O str
1307	1311	

^a Values listed are for $\text{Ho}(\text{SO}_3\text{F})_3$ spectra shown in Figure 1. ν_n designations are for bidentate and tridentate SO_3F^- ions independently.

chiometry. The only practically feasible coordination numbers remaining are 7 and 8, considering coordination only to oxygen and coordination numbers less than 6 unlikely. A satisfactory structural model depends upon making a definitive choice between coordination numbers 7 and 8.

The lanthanide spectra are matched very well by a superposition of the band positions reported for tridentate and bidentate fluorosulfate groups.^{17,18} Furthermore, the six-band portion of the lanthanide fluorosulfate Raman spectra which is attributable to tridentate groups is generally more than twice as intense as the corresponding group of bands assignable to a bidentate ligand. The suggestion is that of the three fluorosulfate groups per each metal atom two are tridentate and one bidentate giving the metal a coordination number of 8. Eight-coordination is common for the lanthanides. Europium, for example, seems to prefer eight-coordination with ligands which bind through oxygen.^{21,23} Further independent experimental evidence for the coordination number is given by visible emission measurements.

An indication of the nearest-neighbor symmetry about the metal is given by the relatively sharp visible emission spectra due to inner f-f electron transitions on the lanthanide ions. Useful fluorescent emissions from many of the lanthanide fluorosulfate compounds are excited by one or more of the Ar⁺ or Kr⁺ laser frequencies used to obtain the Raman spectra. These energies must be absorbed directly into the f-f electronic energy states of the metal to give the resulting fluorescence. The character of the observed fluorescence is related to the site symmetry of the metal ion by the governing crystal field selection rules.⁹

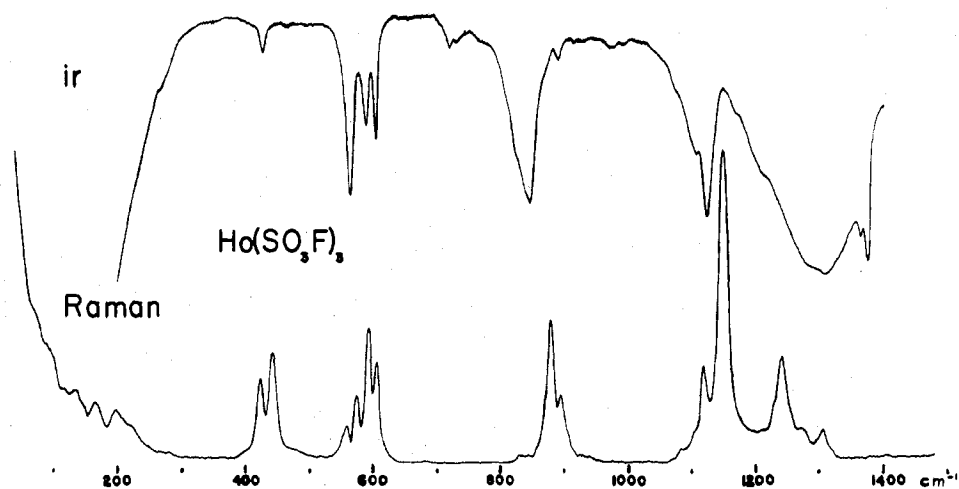


Figure 1. Typical vibration spectra of lanthanide(III) fluorosulfate compounds. Intensity scale is arbitrary. Ir spectrum is from compound in Nujol on CsBr plates. Ir bands at 720–730 and 1360–1380 cm^{-1} are due to Nujol.

The dependence of lanthanide fluorescent emissions upon the symmetry of the crystal or ligand field surrounding the metal is well studied, especially for europium.^{21–24} Along with the Raman spectrum of europium fluorosulfate, which is typical of the Raman spectra of lanthanide fluorosulfates, several relatively sharp bands attributable to fluorescence emissions of the Eu^{3+} ion are observed. The popularly studied Eu^{3+} fluorescence is favored for study to obtain the nearest-neighbor symmetry in lanthanide fluorosulfates for several further reasons: (1) several useful emissions in the conveniently measured visible region can be excited by at least four Kr^+-Ar^+ ion laser frequencies; (2) the luminescence bands observed for europium fluorosulfate are fewer and sharper at room temperature than those observed for any other of the fluorosulfates; (3) spectral identification is simplified since pertinent quantum numbers and energy levels of Eu^{3+} are well-known.²⁵

The fluorescence observed for europium fluorosulfate at room temperature and at -150°C is reproduced in Figure 2. The same spectrum is obtained using 5682-, 5145-, or 4880-Å radiation for excitation.

Several observations are useful to the interpretation of these spectra. (1) The intensity of the fluorescence is only 1–2 orders of magnitude greater than that of the Raman bands. This is a relatively weak fluorescence. (2) Transitions from the $^5\text{D}_1$ states are not observed. It is, however, likely that the $^5\text{D}_1$ level is populated directly by 4880-Å radiation being absorbed, for example, into the $^5\text{D}_1-^7\text{F}_2$ transition. The absence of emissions from $^5\text{D}_1$ may be explained by efficient radiationless degradation to the $^5\text{D}_0$ level^{21,22} and/or by the crystal field selection rule which allows no electric dipole transitions in cubic symmetry. The former process must be highly operative since the emissions allowed by magnetic dipole selection rules, $^5\text{D}_1-^7\text{F}_{0,2}$, are also not observed. Further support for this conjecture is given in the observation of an identical spectrum when 5682-Å radiation is used for excitation. This energy is likely to be absorbed directly into the vibronic levels of $^5\text{D}_0$ instead of into $^5\text{D}_1$ from electronic levels high above the ground state. No Raman spectrum is observed with 5682-Å excitation suggesting a different, more efficient absorption–emission process for this energy. Transitions from $^5\text{D}_1$ to $^7\text{F}_{0-6}$ are expected to be weak,²⁶ although may reportedly be as much as 25% of transition intensities from $^5\text{D}_0$.²⁷ In the present case, it is clear that intensity from $^5\text{D}_1-^7\text{F}_{0-6}$ emissions is essentially nonexistent. Thus, interpretation of the observed measurements is simplified since luminescence from $^5\text{D}_1$ or $^5\text{D}_2$ levels does not complicate the spectra. The spectra can be confidently assigned to the $^5\text{D}_0-^7\text{F}_{1,2,4}$ transitions. (3) The

Table II. Fluorescence Emissions of Europium and Holmium Fluorosulfates at Various Temperatures^a

	$\text{Eu}(\text{SO}_3\text{F})_3$		$\text{Ho}(\text{SO}_3\text{F})_3$	
	Room temp	-150°C	Room temp	-130°C
$^5\text{D}_0-^7\text{F}_1$	16 906	16 916	Probably	18 643
	16 854	16 850	$^5\text{I}_8-^5\text{F}_4$	18 596
$^5\text{D}_0-^7\text{F}_2$	(16 330)	16 312	and	18 505
	16 240	16 235	$^5\text{I}_8-^5\text{S}_2$	18 500
	(16 164)	16 162	(18 442)	18 440
	(16 103)	16 112	18 360	18 347
			18 302	18 300
$^5\text{D}_0-^7\text{F}_4$	14 480		18 243	18 242
	14 378			(18 230)
	(14 313)		$^5\text{I}_8-^5\text{F}_5$	15 540
				15 460
				15 418
				15 357
				15 282
			$^5\text{I}_8-^5\text{I}_4$	13 448
				13 412
				13 362
				13 352
				13 328
				13 330
				13 320
				13 320
				13 300
				13 300

^a ν values are in cm^{-1} ; parentheses indicate weak shoulders flanking major bands.

fluorescence spectrum of europium fluorosulfate at room temperature is grossly altered when the sample is near the temperature of liquid nitrogen (Figure 2). The former is consistent with D_4 symmetry if the bands which are almost 2 orders of magnitude less intense and flanking the major features are ignored. Then the single intense band at 16240 cm^{-1} is the $^5\text{D}_0-^7\text{F}_2$ transition and the bands at 16906 and 16854 cm^{-1} are the $^5\text{D}_0-^7\text{F}_1$ emission. The latter agrees with C_{2v} symmetry,^{21,22,24} which is expected to give four and three bands in the $^5\text{D}_0-^7\text{F}_2$ and $^5\text{D}_0-^7\text{F}_1$ groups, respectively. The wavenumbers are listed in Table II along with visible fluorescence emissions observed for $\text{Ho}(\text{SO}_3\text{F})_3$.

The emissions measured at room temperature are about 2 orders of magnitude more intense than those measured near liquid nitrogen temperature. Explanation of this temperature dependence in terms of a phase change is ruled out since the low-temperature fluorescence shows lower symmetry and decreased intensity, whereas decreasing symmetry is expected to increase the fluorescence intensity, and because no change is observed in the Raman spectrum at the lower temperature.

The Ho fluorescence is also simpler at the lower temperature while the Raman spectrum does not change, Figure 3.

All of the observations however can be readily explained if the room-temperature spectrum is due to emissions from molecules in which an excited low-energy vibration has removed the D_{4h} or D_{4d} symmetry of a square or square-antiprismatic arrangement of the fluorosulfate oxygens thus lowering the effective symmetry to D_4 . At the lower temperature the vibration is relaxed to the ground state and the remaining weak Eu emission, which was underlying the phonon-assisted fluorescence, reflects the C_{2v} symmetry given by the oxygens and sulfur bridges.

The differences in the relative positions of some of the bands in the high- and low-temperature emission spectra, Table II, offer further support for the interpretation that the electronic transitions at the two temperatures involve different vibronic states of the system. The temperature dependence of the holmium fluorosulfate luminescence shown in Figure 3 is also in agreement with the above explanation.

Moreover, the frequency and intensity patterns of the $^5D_0-^7F_1$ and $^5D_0-^7F_2$ emissions are considered to be indicative of the crystal field symmetry of europium(III). The present low-temperature measurements are much like those previously observed for some eight-coordinate chelate complexes of europium(III).^{23,24} Our emission measurements easily favor the choice of eight-coordination over that of seven-coordination.

Only very sparse weak absorption measurements could be obtained in keeping with the white appearance and proposed cubic metal-oxygen symmetry of the compounds. The few weakly observed transitions have energies near those of free-ion measurements. No detailed analytical use was made of these data.

Assignment of Vibration Spectra

Vibration spectra have been measured of compounds containing fluorosulfate ions,³⁻⁵ covalent monodentate fluorosulfate,⁶⁻¹⁰ bidentate and bridging fluorosulfate,⁹⁻¹⁷ and tridentate groups.¹⁷⁻¹⁹ Each of these variously bound fluorosulfate groups gives characteristic correlatable ir and Raman spectra which are useful for distinguishing the different types and indicating the strength of anion-cation association.

The vibration spectra of the lanthanide(III) fluorosulfates can be readily assigned based upon previously measured spectra of bidentate and tridentate fluorosulfate groups.^{17,18} Nine ir and Raman bands are expected from bidentate (C_s symmetry) fluorosulfate and six are given by the tridentate (C_{3v} symmetry) groups. Most of these 15 features are clearly observed above 300 cm^{-1} in spectra of all except the Sc compound (Figure 1 and Table III). Scandium shows only bands assignable to bidentate ligands.

While the lanthanide fluorosulfate vibration frequencies are generally in the range of known energies of tri- and bidentate fluorosulfate groups, the differences between the S-O stretching wavenumbers in a given spectrum are less than those previously observed and the S-F stretching frequency is higher than usual.

The deviations from previous observations correspond to the noted frequency changes accompanying increased anion-metal interaction with no symmetry change.^{15,18} Considering C_{3v} symmetry and CsSO_3F vs. divalent tridentate fluorosulfates of, e.g., Fe, Co, and Ni, the general result is pronounced increase in the S-F stretching frequency ν_2 , $100-150\text{ cm}^{-1}$, smaller increase in the ν_1 S-O stretching, ν_3 S-O deformation, and ν_5 S-O deformation wavenumbers, $10-50\text{ cm}^{-1}$, and decrease of the ν_4 S-O stretching frequency, $20-70\text{ cm}^{-1}$. The position of the ν_6 S-F deformation is not significantly changed. Similar changes are expected for bidentate groups which, of course, have the E modes split. This splitting is expected to increase with increased anion-cation interaction.

Identification of the bi- and tridentate lanthanide(III) fluorosulfate frequencies is facilitated in light of the changes dependent upon increased anion-cation interaction; however, explanation of the differences from d-block transition metal compounds on this basis is unacceptable.

It is more probable that eight fluorosulfate oxygens arranged around the metal ion require the O-S-O angle of bi- and tridentate ligands to be smaller than for six-coordinate geometry. Vibrational interaction between the S-O bonds is decreased as the O-S-O angles move closer to 90° and consequently the S-O stretching wavenumbers move closer together. On the other hand, the O-S-F angle is nearer to 180° leading to increased S-O to S-F coupling and higher S-F stretching frequencies.

Variations based on this simple change in geometry are manifest in spectra of the lanthanide(III) compounds by the continuously decreased separation of the bands assigned to symmetric (ν_1) and asymmetric (ν_4) stretching of the tridentate $-\text{SO}_3$ groups with decreased cation size from 107 cm^{-1} for La to 84 cm^{-1} for Lu (Table III). No concurrent similar trends in any of the individual S-O stretching frequencies, which would signal dependence upon increased anion-cation interaction, are observed.

Moreover, generally increased separation of the upper and lower frequencies assigned to S-O stretching of the bidentate ligand is observed from the Ln through the Lu compounds. This suggests increased coupling between the S-O and SO₂ bonds and consequent frequency separation. The S-F stretching wavenumbers also generally increase through the series of compounds from La to Lu, Table III. However, trends in frequency differences are likely more reliable indicators of structural variations than absolute frequencies since the latter will be more dependent upon environmental changes, especially for the polar S-F and S-O bonds which are on the outside of the complex.

Compounds of the smaller lanthanide ions have a feature at about 1400 cm^{-1} in the Raman spectra and increased relative intensity of other bands near those seen in the spectrum of $\text{Sc}(\text{SO}_3\text{F})_3$ which are assignable to bidentate ligands (Table III). Some shifting to seven-coordination in the Tm, Yb, and Lu compounds could explain these variations.

The position of the S-F stretching vibration has been suggested as a measure of the strength of cation-anion interaction and covalent character of the anion in fluorosulfate compounds.¹⁷⁻¹⁹ Higher values between 710 and 890 cm^{-1} indicate greater interaction. Trends to higher values are observed with increased polarizing power of the cation in alkali and alkaline earth metal compounds. This trend was not observed in spectra of some metal bis(fluorosulfate) compounds.¹⁸ It was thus concluded that an S-F stretching frequency above 800 cm^{-1} is evidence only that cation-anion interactions are stronger than those present in ionic fluorosulfates.

Considering the high S-F stretching wavenumbers observed for the lanthanide(III) compounds, it appears that molecular geometry and crystal structure must be included in arguments relating S-F stretching frequency to strength of anion-cation interaction. The various dependencies will be better resolved when more x-ray crystal structures of fluorosulfate compounds are known. The S-F stretching wavenumber is also likely complicated by Fermi resonance interaction with the overtone of the $400-450\text{ cm}^{-1}$ O-S-F angle deformation vibration. The number of bands in the S-F stretching region of spectra of some of the lanthanide fluorosulfates as well as the relative ir and Raman intensities might be explained by such interaction.

Contrary to the suggestion given by the S-F stretching frequency, the low value of the S-O stretching frequency is

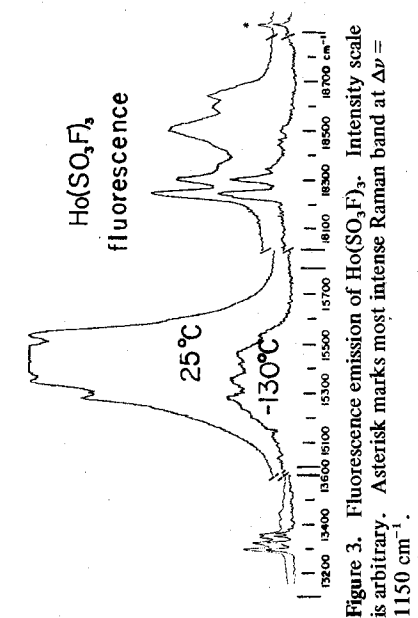


Figure 3. Fluorescence emission of $\text{Ho}(\text{SO}_3\text{F})_3$. Intensity scale is arbitrary. Asterisk marks most intense Raman band at $\Delta\nu = 1150 \text{ cm}^{-1}$.

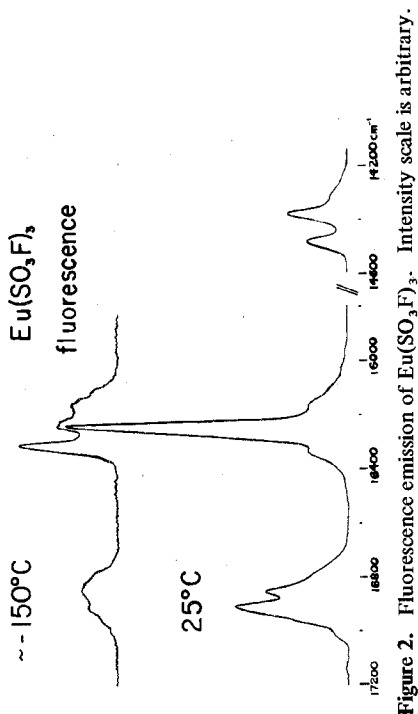


Figure 2. Fluorescence emission of $\text{Eu}(\text{SO}_3\text{F})_3$. Intensity scale is arbitrary.

Table III. Raman Spectra of Scandium, Yttrium, and the Lanthanide Fluorosulfate Compounds^a

$\text{Sc}(\text{SO}_3\text{F})_3$	$\text{Y}(\text{SO}_3\text{F})_3$	$\text{La}(\text{SO}_3\text{F})_3$	$\text{Nd}(\text{SO}_3\text{F})_3$	$\text{Sm}(\text{SO}_3\text{F})_3$	$\text{Eu}(\text{SO}_3\text{F})_3$	$\text{Gd}(\text{SO}_3\text{F})_3$	$\text{Tb}(\text{SO}_3\text{F})_3$	$\text{Dy}(\text{SO}_3\text{F})_3$	$\text{Er}(\text{SO}_3\text{F})_3$	$\text{Tm}(\text{SO}_3\text{F})_3$	$\text{Yb}(\text{SO}_3\text{F})_3$	$\text{Lu}(\text{SO}_3\text{F})_3$	Rel intens	Approx assignment
105	71	75	88	115	116	120	124	124	68	66	66	66	w, b	Lattice modes
119	92	106	111	124	116	120	124	115	114	112	112	112	w, sh	
130	122	128	130	135	138	135	135	138	132	134	134	134	w, b	Bi- and trident O-S-F def
170	173	182	188	169	200	198	169	200	194	199	199	199	w, b	
212	191	206	205	190	218	218	190	218	218	221	221	221	w, sh	Bi- and trident O-S-O def
225	214	221	240	289	337	345	289	337	338	334	334	334	w, b	
422	426	418	422	422	422	426	422	422	430	429	429	429	m, sp	Bi- and trident O-S-F def
570	445	430	437	440	446	444	440	446	448	448	448	448	m, sp	
590	564	562	567	567	567	561	575	560	565	565	565	565	w, sp	Bi- and trident O-S-O def
622	578	576	576	576	578	578	575	593	581	581	581	581	m, sp	
	597	594	596	594	596	595	593	593	599	598	598	598	s, sp	Bi- and trident O-S-O def
	613	607	609	608	609	609	607	612	612	612	612	612	m, sp	
	788	781	802	826	826	827	835	826	827	820	810	810	w, b	Bi- and trident O-S-F def
	840	834	837	840	840	845	832	840	841	841	833	834	w, b	
	872	875	880	879	882	881	882	882	886	886	880	874	s, sp	Bident SO_2 sym str
	885	889	892	896	896	897	898	900	902	900	928	874	w, sh	
1106	1125	1111	1116	1118	1120	1120	1120	1122	1126	1125	1116	1118	m, sp	Trident SO_3 sym str
	1149	1141	1145	1148	1147	1151	1150	1148	1156	1156	1150	1148	vs, sp	
	1248	1248	1244	1248	1245	1242	1246	1241	1248	1244	1236	1236	m, b	Bident S-O and SO_2 str
	1274	1260	1268	1269	1269	1270	1270	1272	1283	1283	1276	1275	w, sh	
1400	1315	1288	1295	1299	1302	1309	1305	1303	1316	1316	1308	1325	w, b	Mono- or bident SO_3 str?
	1405	1396	1375	1375	1375	1375	1375	1375	1375	1375	1375	1375	w, sp	

^a Key: b, broad; m, medium; s, strong; sp, sharp; sh, shoulder; w, weak; vs, very strong. Relative intensities are generally the same for all except the Sc compound. Values are in cm^{-1} .

in keeping with weak lanthanide(III)-metal interaction; however, this energy may be lowered by weaker intra- or intermolecular associations. The low wavenumber of the corresponding assignment for $\text{Cu}(\text{SO}_3\text{F})_2$ (1306 cm^{-1}) is accounted for by weaker axial associations of the $\text{S}=\text{O}$ group.^{17,18}

Upon the above discussion, full assignment of typical spectra is given in Table I. The assignments are in agreement with observed ir and Raman intensities. The A_1 features are strong in the Raman spectra and the E vibrations are most intense in the ir.

Many of the observed Raman wavenumbers listed in Table I are $\sim 10\text{ cm}^{-1}$ different from the ir counterparts, especially the stretching frequencies, and some of the intense Raman bands are very weak or not apparent in the ir. These observations can be accounted for in terms of coupling between equivalent anions in the crystal lattice.

The Raman bands below 300 cm^{-1} are probably due to lattice modes. The lattice, cation-anion stretching vibrations of some fluorosulfate compounds have been assigned, e.g., 138 cm^{-1} for Na- and KSO_3F , 250 cm^{-1} for $\text{Ca}(\text{SO}_3\text{F})_2$, 261 cm^{-1} for $\text{Zn}(\text{SO}_3\text{F})_2$, and 262 cm^{-1} for $\text{Cu}(\text{SO}_2\text{F})_2$.^{17,18} The Raman features around 200 cm^{-1} in the lanthanide(III) spectra are assigned to analogous vibrations.

In summary, we have given good evidence for octa-coordination and tri- and bidentate fluorosulfate groups in a new series of lanthanide complexes and have assigned their vibration spectra on this basis.

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Registry No. $\text{Sc}(\text{SO}_3\text{F})_3$, 58438-33-8; $\text{Y}(\text{SO}_3\text{F})_3$, 58438-34-9; $\text{La}(\text{SO}_3\text{F})_3$, 58438-35-0; $\text{Nd}(\text{SO}_3\text{F})_3$, 58438-37-2; $\text{Sm}(\text{SO}_3\text{F})_3$, 58438-38-3; $\text{Eu}(\text{SO}_3\text{F})_3$, 58438-39-4; $\text{Gd}(\text{SO}_3\text{F})_3$, 58438-40-7; $\text{Tb}(\text{SO}_3\text{F})_3$, 58438-41-8; $\text{Dy}(\text{SO}_3\text{F})_3$, 58438-42-9; $\text{Ho}(\text{SO}_3\text{F})_3$,

58438-43-0; $\text{Er}(\text{SO}_3\text{F})_3$, 58438-44-1; $\text{Tm}(\text{SO}_3\text{F})_3$, 58438-45-2; $\text{Yb}(\text{SO}_3\text{F})_3$, 58438-46-3; $\text{Lu}(\text{SO}_3\text{F})_3$, 58438-47-4.

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