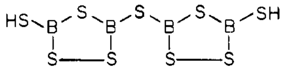
$(HBS_2)_3(s)$ is $(HBS_2)_3(g)$, whereas the latter is not present in the vapor of $H_2S{\cdot}xBS_2$. Appearance of high molecular weight ions at temperatures above 150 °C indicates that the activity of $H_2S$ has decreased due to loss of $H_2S(g)$ and $H_2B_2S_5(g)$ and that $H_2B_4S_9$ and $(BS_2)_n$ have become the important vapor species. The fact that $B_nS_{2n}^+$ high molecular weight ions were observed in this work from samples with compositions close to $BS_2(s)$ supports the proposal that the ions result from molecules of $(BS_2)_n(g)$.

The metastable decomposition of $H_2B_2S_5^+$ into $HBS_3^+$ relates the intense 108 and 107 peaks in the mass spectrum of $H_2B_2S_5$ to fragmentation of $H_2B_2S_5^+$. A relationship between $H_2B_2S_5^+$ and $HBS_3^+$ at 155 °C was reported by EWG,[10] and an unsuccessful special search for the metastable decomposition of $H_2B_2S_5^+$ into $HBS_3^+$ was reported.[11] Edwards et al.[12] previously reported the metastable decomposition of $B_8S_{16}^+$ into $B_8S_{14}^+$.

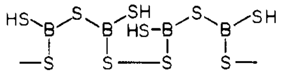
The high melting point, the insoluble nature, and the diffuse lines of the x-ray powder pattern indicate that $H_2S{\cdot}xBS_2$ is polymeric in the solid state. If it were a molecular solid with molecules, e.g., of $H_2B_4S_9$ with a structure based on that of $I_2B_2S_3$[15,17]



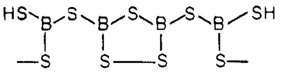
then its melting point should be lower than 400 °C; metathioboric acid, which has been shown to be a molecular solid, melts incongruently at 139 °C.[13] Melting samples III or IV and heating them above their melting points produce the same color changes one observes as sulfur is melted and heated to its boiling point; this property indicates that polymeric sulfur–sulfur bonds are present in the melt. Finally, polymerization is indicated by the fact that $H_2B_2S_5$, soluble in the benzene in which it is prepared, becomes insoluble after removal of the solvent.

The Raman emission at 440 cm$^{-1}$ in Table VI was assigned to the S–S stretch by comparison with the S–S stretching frequencies assigned by others.[18-20] The fact that it was a very strong peak indicates that S–S bonds are important in solid $H_2S{\cdot}xBS_2$. The infrared absorptions in the region from 850 to 1055 cm$^{-1}$ were assigned to B–S stretches by comparing spectra of I with natural boron and with 92% $^{10}B$. The infrared absorptions of product IV in Table V at 2542 cm$^{-1}$ for the Nujol mull and at 2552 cm$^{-1}$ for the $CS_2$ solution and the Raman emission of product III in Table VI at 2553 cm$^{-1}$ were assigned to the S–H stretch. Nujol mulls of product III did not show an absorption between 2500 and 2600 cm$^{-1}$. These observations support the conclusion that product IV contained relatively more $H_2S$ than did product III and thus was nearer in composition to $H_2B_2S_5$. Probably the $CS_2$ solution contained $H_2B_2S_5$ molecules.

Two interactions between molecules of $H_2B_2S_5$ could cause them to polymerize and to lose $H_2S$ to approach the composition $(BS_2)_n$: (1) a tendency to form intermolecular S–S bonds



and (2) loss of $H_2S$ because of steric interaction of SH groups



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**Registry No.** I/II, 13703-97-4; III, 63148-36-7; IV, 61349-21-1; $I_2B_2S_3$, 13845-20-0.

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# Synthesis and Characterization of the Difluorotris(fluorosulfate) of Uranium(V): $UF_2(SO_3F)_3$[1]

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A new U(V) compound, $UF_2(SO_3F)_3$, has been synthesized by the reaction of $UF_6$ and $SO_3$ in both the gaseous phase and $CFCl_3$ solution. This leads to a blue-green solid, the x-ray powder diffraction pattern of which has been recorded. Its oxidation state has been deduced from chemical analysis, the electronic absorption spectrum, and magnetic measurements. The environment around uranium is discussed from Raman and infrared spectra recorded at ambient and liquid nitrogen temperatures.

## Introduction

As part of a continuing investigation of uranium fluorides in the highest oxidation state, the possibility of obtaining new derivatives was examined in which one or several fluorine atoms would be replaced by another univalent ligand. In this connection, the well-known ability of the fluorosulfate ion, $SO_3F^-$, to take the place of a fluoride ion[2,3] in many compounds prompted the search for the existence of any uranium fluorosulfate or mixed uranium–fluoride–fluorosulfate.

Several methods of preparing such compounds were considered for this study. One possible route was the replacement of a labile halide in compounds of the type $UX_n$ ($n$ = 4–6) with $S_2O_6F_2$[4] or with the reactive halogen fluorosulfates $XOSO_2F$ (X = Br, Cl, F).[5] In fact, efforts along this line are in progress, but the results of this work will be reported at a later time. Another method included the insertion of $SO_3$ into a U–F bond, which will presently be described. This route has been successfully employed in the production of many fluorosulfates from ionic[6,7] to covalent[8] to bridging[9] species. The results of this study have shown that the reaction of $UF_6$ and $SO_3$ leads to a perfectly well defined compound, $UF_2(SO_3F)_3$, the preparations and physical properties of which are now to be given.

## Experimental Section

**Materials.** The compound $UF_6$, purchased from Comurhex, was purified from HF by pumping at dry ice temperature. $SO_3$ was kindly supplied by Ugine Kuhlmann Co. and was purified by distillation. $CFCl_3$ was purchased from Dehon (Paris) and was dried by storage over $P_2O_5$.

**Apparatus.** The volatile materials were transferred in a vacuum line made for the most part of Monel metal tubing equipped with valves purchased from F.W. Co and with differential gauges from Etudes et Constructions Aêronautiques. The qualitative and quantitative analysis of various volatile products was accomplished by a standardized microsublimation unit[10] constructed of Monel metal tubing (2-mm i.d.) attached directly to the vacuum line. For reactors, depending upon their experimental requirements, 300-mL Erlenmeyer flasks, Kel-F tubes, or Monel cylinders were used, these vessels being attached to the vacuum line through Kel-F or Monel valves. The nonvolatile solid samples were handled under nitrogen in a drybox containing $P_2O_5$ as a desiccant. Thermal decomposition of the solid samples was studied using a Arion M.C.B. microcalorimeter.

**Spectra.** Infrared spectra were recorded with a Beckman Model IR 9 and a Perkin-Elmer Model 457 spectrometer in the ranges 4000–400 and 4000–250 $cm^{-1}$, respectively. For these spectra, the powdered samples were pressed between thin plates of AgCl. Due to the reactivity of the U(V) compound with both KBr and AgBr, no spectrum could be recorded below 400 $cm^{-1}$. Low-temperature spectra at about −190 °C were obtained with a homemade glass cryostat cooled with liquid nitrogen. The gaseous by-products were studied in the infrared region with a 10 cm long Monel-body gas cell equipped with AgCl windows. The Raman spectra at room temperature were recorded with a Coderg Model T 800 spectrophotometer using the 514.5-nm line of a Spectra Physics Model 165 laser filtered with a Coderg premonochromator. Low-temperature spectra were obtained with the same exciting line of a similar laser on another T 800 spectrometer equipped with interferential filters that were unable to cut out the plasma and ghost lines below 150 $cm^{-1}$. In addition, at 80 K, owing to the sample low Raman scattering, a very slow scanning rate was required to obtain reproducible results; thus, a complete spectrum could not be recorded all in one run. For the room-temperature Raman spectra, the neat powders were contained in glass capillaries (~2-mm o.d.). Below room temperature, the spectra were obtained with an Air Liquide cryostat in which the solids were contained in a 30 cm long, ~2-mm o.d. glass tube. The frequency accuracy was estimated to be approximately ±3 $cm^{-1}$ for the infrared spectra and ±1 $cm^{-1}$ for the Raman spectra. The visible and near-infrared spectra were recorded on a Cary 14 instrument. The powdered samples were ground with prefluorinated fluorocarbon oil in the drybox, and the resulting mulls were pressed between two $CaF_2$ plates separated by a 1 mm thick Teflon spacer which also served to protect the mull from the outside atmosphere. The $^{19}F$ NMR spectra used for identification of the reaction by-products were obtained on a Varian NV 14 spectrometer operating at 56.4 MHz. For these spectra, the solutions were contained in a 6-mm o.d. Kel-F tube hot-pinched and placed into a 8-mm o.d. calibrated NMR tube. The $CFCl_3$ solvent effectively served as an internal reference for the calibration of these spectra.

**X-Ray Diffraction Patterns.** The Debye–Scherrer powder patterns were taken using a 114.6 mm diameter Philips Camera with copper K$\alpha$ radiation. The samples were contained in Lindemann glass capillaries ($\phi$ 0.5 mm) and studies in the temperature range +40 to −120 °C were made possible by use of a Meric cryostat and a homemade 114.6-mm camera for the latter study.

**Magnetic Measurements.** Magnetic measurements were obtained via the Faraday method using a Setaram (2 mV $mg^{-1}$) microbalance or a homemade Weiss balance (50 mV $mg^{-1}$) and a Drush (9000 Oe) or a Transfos-Standard (4200 Oe) magnet with homemade cryostats in the 300–130 or 150–5 K range, respectively. Attempts to obtain EPR spectra were made with a Varian V 4502-15 (up to 13.5 kG) spectrometer, with a 3-cm cavity.

**Analyses.** Elemental analyses for U, S, and F were performed by Alfred Bernhard Microanalytical Laboratory, Elbach, West Germany.

**Reactions.** The reaction of $UF_6$ with $SO_3$ was achieved both in the gaseous phase and in $CFCl_3$ solution.

For the reaction between the two gases, a reactor consisting of two glass bulbs separated by a glass–Teflon high-vacuum stopcock was used. First 2.67 mmol of $UF_6$ (43 torr at 22 °C) was expanded into the 1141 mL volume of bulb A; next, 2.62 mmol of $SO_3$ (160 Torr at 22 °C) was added into the 301 mL volume of bulb B. Upon opening the separation stopcock, the $SO_3$ entered bulb A reacting vigorously and exothermically with the $UF_6$ and forming a finely transient beige species which finally deposited as a blue-green film within the interior of bulb A. After 1 h was allowed for the reaction to become complete, a total pressure of 18.8 Torr was registered in a volume of 2303 mL at 22 °C. An infrared spectrum of these gaseous products showed only excess $UF_6$ and $S_2O_6F_2$ to be present with the notable absence of $SO_3$, thus signifying the total consumption of the $SO_3$. This was also confirmed by the microsublimation experiment which further gave the result that 88 and 12 mol % of the volatiles were $UF_6$ and $S_2O_6F_2$, respectively. The former implied that 2.06 mmol of $UF_6$ remained unreacted or that 0.606 mmol of $UF_6$ did react, and the latter showed that 0.292 mmol of $S_2O_6F_2$ was produced. This gives a ratio of ~2 for the $UF_6$ reacted over $S_2O_6F_2$ produced and a ratio of ~4 for the $SO_3$ reacted over $UF_6$ reacted. An x-ray powder pattern diagram verified the solid blue-green product to be identical with that obtained as described below.

For the reaction between $UF_6$ and $SO_3$ in $CFCl_3$, a 300 mL glass Erlenmeyer flask equipped with a glass-encased stirring magnet was employed. Initially, $4.359_6$ g ($5.44 \times 10^{-2}$ mol) of $SO_3$ was condensed into the reactor followed by 158.910 g (~107 mL) of $CFCl_3$, in which the $SO_3$ did not dissolve. Next, $6.377_5$ g ($1.81 \times 10^{-2}$ mol) of $UF_6$ was sublimed into the reactor, and the mixture subsequently warmed up to −50 °C. At this temperature a rust-colored intermediate species became apparent in the $CFCl_3$ solution; but upon gradual warming of the mixture to room temperature with constant stirring overnight, the reaction yielded a blue-green, finely divided product insoluble in $CFCl_3$. As expected a Raman spectrum of the volatile products showed only unreacted $UF_6$ and $S_2O_6F_2$, in the $CFCl_3$. Furthermore, an $^{19}F$ NMR spectrum of this solution showed only two resonances at −764 and −43 ppm with respect to internal $CFCl_3$, corresponding to $UF_6$ and $S_2O_6F_2$, respectively. A rough estimation of the unreacted $UF_6$ over produced $S_2O_6F_2$ ratio from this spectrum gave a value of 0.95 as compared to an expected value of 0.66. After isolation, $7.639_9$ g of solid blue-green products was found compared to a theoretical mass of $7.803_2$ g for $UF_2(SO_3F)_3$ based upon the total consumption of $SO_3$.

Anal. Calcd for $UF_2(SO_3F)_3$: U, 41.53; F, 16.57; S, 16.78; O, 25.12. Found: U, 41.68; F, 16.51; S, 16.57; O (by difference), 25.24.

## Results and Discussion

**Synthesis.** Even though the formation of a uranium fluorosulfate containing compound was not unexpected from the reaction

$$2UF_6 + 8SO_3 \rightarrow 2UF_2(SO_3F)_3 + S_2O_6F_2$$

the production of $S_2O_6F_2$ was a little surprising at first. Initially a U(VI) compound was expected, but the blue-green color indicated a lower valence for uranium. This was consistent with the observation of $S_2O_6F_2$. Since $UF_6$ has been shown to be an effective fluorinating agent in the past,[11,12] it may be concluded that $SO_3$ was effectively fluorinated in this reaction. Such a process has already been described in reactions of $XeF_6$[13] and $CrF_5$[14] with $SO_3$ which involve a reduced form of the elemental fluoride and the production of $S_2O_6F_2$.

The reaction as observed in both the gas and solution phases of $UF_6$ with $SO_3$ indicates a more complicated pathway than a simple fluorination of $SO_3$. The formation of a rust brown

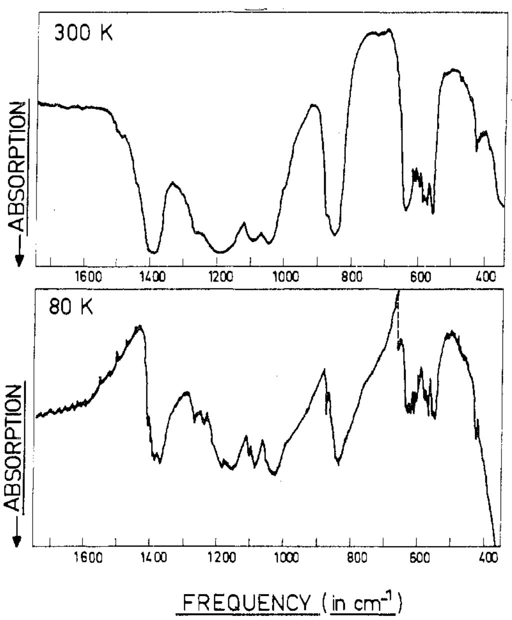

**Figure 1.** Infrared spectra at 300 and 80 K.

solution in the $CFCl_3$ en route to the insoluble blue-green product at room temperature signifies a stepwise reaction. Several modes may be considered: (i) the formation of an unstable U(VI) mixed fluoride–fluorosulfate which eventually liberates $S_2O_6F_2$ and generates the U(V) compound; (ii) the formation of a $UF_6{\cdot}nSO_3$ adduct at low temperature which finally rearranges to yield $S_2O_6F_2$ and $UF_2(SO_3F)_3$; or (iii) the actual fluorination of $SO_3$ by the $UF_6$ giving $S_2O_6F_2$ and $UF_5$, the latter of which undergoes insertion by $SO_3$ to form the $UF_2(SO_3F)_3$. Microcalorimetry has shown that $UF_2(SO_3F)_3$ is stable up to ~120 °C. Further studies are being conducted to establish the exact nature of the aforementioned intermediate and the course of reaction and decomposition. In any case, no doubt exists as to the overall reaction at room temperature to yield $UF_2(SO_3F)_3$. What needed to be clarified, though, was the nature of this new compound.

**X-Ray Data.** The lines found for the x-ray diffraction pattern of $UF_2(SO_3F)_3$ are listed in Table I. All attempts to index the diagram with an automatic method[15] from the film data at room temperature failed with symmetries higher than monoclinic. A low-temperature x-ray diffraction pattern at ~150 K showed the same lines as at ambient temperature except for a contraction along each of the three axes. A comparison of the lines with those from several fluorine, oxygen, and/or sulfur-containing uranium compounds failed to turn up any similar pattern which might be useful in determining its crystal structure.

**Table I.** X-Ray Diffraction Pattern of $UF_2(SO_3F)_3$ at Ambient Temperature

| *d*, Å | Intens | *d*, Å | Intens |
|---|---|---|---|
| 8.66 | <5 | 2.986 | 15 |
| 7.53 | 65 | 2.873 | 15 br |
| 5.73 | 100 | 2.769 | <5 |
| 5.41 | 45 | 2.691 | <5 |
| 5.15 | 25 | 2.597 | 15 br |
| 4.77 | 5 | 2.509 | 5 |
| 4.33 | 40 | 2.390 | 5 |
| 4.17 | <5 | 2.330 | <5 |
| 3.91 | 20 | 2.252 | <5 |
| 3.75 | 35 | 2.217 | 5 |
| 3.52 | 20 | 2.144 | 5 br |
| 3.36 | 60 | 2.097 | 5 br |
| 3.26 | 30 | 2.056 | 5 |
| 3.20 | <5 | 2.023 | 5 |
| 3.09 | 5 | | |

**Vibrational Data.** The infrared (Figure 1) and Raman (Figure 2) spectra of $UF_2(SO_3F)_3$ were recorded at both ambient and liquid nitrogen temperatures in an effort to resolve somewhat the structure of this compound. In the case of the $SO_3F$ group, several bonding types have been documented in structural as well as spectroscopic terms: (a) ionic,[16,17] (b) ionic perturbed,[18,19] (c) covalent monodentate,[20,21] (d) bidentate bridging,[22,23] (e) tridentate bridging,[24] and even (f) tetradentate bridging.[25] In cases (a), (b), (e), and (f), the vibrations have generally been interpreted in terms of $C_{3v}$ symmetry, with 6 modes (3 A′ and 3 E) including three stretching vibrations, i.e., two S–O and one S–F, at frequencies higher than 650 cm$^{-1}$. In cases (c) and (d), the symmetry is reduced to $C_s$ with the E modes becoming nondegenerate. This results in a total of 9 modes (6 A′ and 3 A″) including four stretching vibrations, i.e. three S-O and one S-F, observed at higher frequencies.

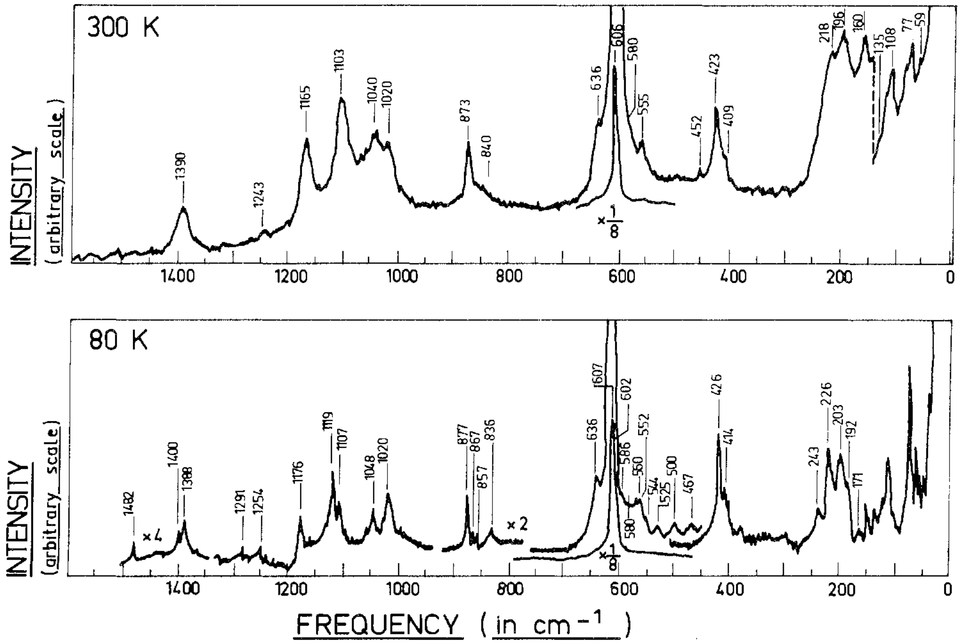

**Figure 2.** Raman spectra at 300 and 80 K; intensity factors are indicative.

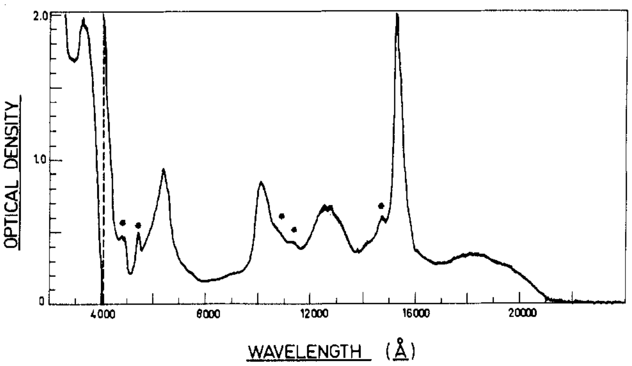

**Figure 3.** Visible and near-infrared spectrum (* spurious bands). (Intensities were corrected from the scattering effect dependent background.)

An inspection of Figures 1 and 2 shows that in the S-O stretching modes region there are clearly too many vibrations to be interpreted in terms of only one type of $SO_3F$ groups. The average value of the two highest strong bands (1380 and 1180 $cm^{-1}$, IR) (see Table II) lies around 1280 $cm^{-1}$, which is near the usually found value of 1270 $cm^{-1}$ for bidentate bridging groups, as shown in $X_2Sn(SO_3F)_2$ compounds, for which a structural determination has verified bridging $SO_3F$ groups[23] when X = $CH_3$[26] and when X = $F^3$ or $Cl^{22}$ in which cases a similar structure has been deduced from $^{119}Sn$ Mössbauer and vibrational spectroscopy.

The number of vibrations in the S–F region (800–900 $cm^{-1}$) shows that there are probably two types of $SO_3F$ groups, as found for $SbF_3(SO_3F)_2$.[27] No evidence can be found from the spectra about the second type of $SO_3F$ group. The intensities of the bands assigned to bridging bidentate groups suggest that at least two of the three fluorosulfate groups are bridging bidentate ones. Assuming there are two nonbridged F ligands (vide infra), a third tridentate group should yield a ninefold coordinated species, which should exhibit some steric hindrance.[28] A third nonbridged bidentate or a covalent monodentate group should yield an eight-fold coordinated species, as recently shown for $\beta$-$UF_5$,[29] or a seven-coordination, as shown for several $M_2UF_7$ salts (M = K, Rb, Cs, $NH_4$),[28,30] respectively, which appears therefore more reasonable for U(V) compounds.

The two U–F stretching modes have been found at 636 and 606 $cm^{-1}$ for the asymmetrical and symmetrical modes, respectively, in good agreement with others found at 626 $cm^{-1}$ for $ClO_2UF_6$[31] and 618 $cm^{-1}$ for $NOUF_6$,[32] both containing U(V) but with or nearly with $O_h$ symmetry of the $UF_6^-$ group.

One trend that appears to hold in $UF_2(SO_3F)_3$, as well as in $SnF_2(SO_3F)_2$[3] and $SbF_3(SO_3F)_2$,[27] is the preference of $SO_3F$ groups to be involved in bridging with the central atoms when a competition could involve it with the F atom. This is further supported by the absence of an infrared band at around 380 $cm^{-1}$ as noted in both $\alpha$- and $\beta$-$UF_5$,[33] as well as in $UOF_4$,[34] which removes the possibility of F bridging for $UF_2(SO_3F)_3$; this region has been shown to be quite specific for such bridging, if it occurs.[35] In the present case, though, the relative infrared and Raman exclusion of the two U–F modes at 636 and 606 $cm^{-1}$ (see Table II) indicates a linear or weakly bent F–U–F grouping.

**Visible and Near-Infrared Spectra.** The electronic absorption spectrum of $UF_2(SO_3F)_3$ was observed (Figure 3) and gave further proof of the +5 oxidation state of uranium. Such a spectrum may be assigned to the crystal field splitting and vibronic coupling effects on the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ [Rn] $5f^1$ system. These transitions have mainly been studied with an octahedral crystal field;[36-39] only a few studies have been reported for the eightfold cubic coordination.[40,41] Since the actual symmetry around uranium in $UF_2(SO_3F)_3$ was not known, comparisons were made with both categories of spectra. As a result of the relative intensities and location of bands, the spectrum of $UF_2(SO_3F)_3$ was found to be closer to the octahedral than cubic type spectra. Therefore, it was not unreasonable to approximate the crystal field symmetry around U to that of a distorted octahedron. The effects of a particular distortion on the energy level splittings for a species with $O_h$ symmetry have been studied by Selbin[42] and Karraker[37] on both theoretical and experimental bases. The spectrum of $UF_2(SO_3F)_3$ was thus tentatively assigned as in Table III by comparison with previous assignments and found to agree very well with the conclusions that have been drawn concerning the effect of the lower crystal field symmetry on the energy level splittings. First of all, the transition $\Gamma_7 \rightarrow \Gamma'_7$ (in $O_h$ notation) which was found at 6489 $cm^{-1}$ for $UF_2(SO_3F)_3$ is in the range reported for numerous U(V) complexes[43] and is consistent with the statement by Selbin et al. that the $\Gamma'_7$ level is nearly unaltered by the lower symmetry field.[42] Second, the $\Gamma_8$ and $\Gamma'_8$ quadruplet levels are significantly split by 2276 and 1988 $cm^{-1}$, respectively, due to the present expectedly high departure from octahedral symmetry. This large splitting observed for $\Gamma'_8$ for instance is a reciprocal proof of the statement by Selbin et al.[44] that the magnitude of the $\Gamma'_8$ splitting measures the magnitude of the distortion. The large $\Gamma_8$ splitting, associated with vibronic interactions,[37] leads to a very broad and low-lying band in the infrared region as observed at ~3200 $cm^{-1}$ in the present study. Finally, the $\Gamma_6$ level which is supposed to increase with the distortion[42,43] is found here at the relatively high value of 15 528 $cm^{-1}$ above the ground level.

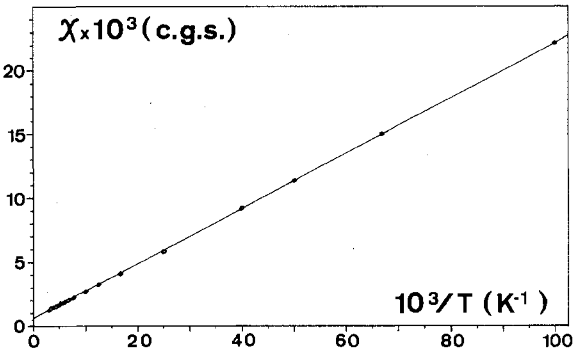

**Figure 4.** Magnetic susceptibility dependence with temperature.

**Magnetochemistry.** The magnetic measurements were achieved in order to further confirm the oxidation state of uranium. The compound has been found to be paramagnetic in the observed temperature range (5–300 K). The relationship between the magnetic susceptibility $\chi$ and the reciprocal temperature $T^{-1}$, as shown in Figure 4, is quite linear and is indicative of a Curie law $\chi = CT^{-1} + N\alpha$, where $C$ is the Curie constant ($C = 0.21 \pm 0.01$ cgsu) and $N\alpha$ is a second-order Zeeman term ($N\alpha = (0.65 \pm 0.05) \times 10^{-3}$ cgsu). The effective magnetic moment $\mu_e$ was determined from the Curie constant $\mu_e = 2.828C^{1/2} = 1.30\ \mu_B$ (Bohr magneton). This value is in agreement with results for other U(V) compounds.[36,45,46] From spectroscopic data the multiplet width was shown to be higher than 3200 $cm^{-1}$ which is large compared to $kT$ (~200 $cm^{-1}$ at 300 K). This results[47] in $\mu_e = g[J(J+1)]^{1/2}$ and a $g$ value of ~0.5 which is comparable with the measured $g$ values from $UF_6^-$ compounds.[48]

The $g$ value may also be evaluated from spectroscopic results. It has been shown[42] that Lande factors for distorted and regular $O_h$ ligand fields do not vary significantly. As a rough approximation, the $g$ octahedral formula[49] may be used where $g = 2\cos^2\theta - 8(K/3)^{1/2}\sin\theta\cos\theta - (2/3)(1-K)\sin^2\theta$ and $\sin 2\theta = 2(3K)^{1/2}\zeta/(E_{\Gamma'_7} - E_{\Gamma_7})$; $K$ is the orbital reduction factor and has been shown to vary from 0.77 for $O_h$ distorted $Cs^+UF_6^{-}$[49] to 0.80 for U(V) in lanthanide oxide

**Table II.** Vibrational Frequencies (cm$^{-1}$) for $UF_2(SO_3F)_3$ and Related Molecules[a]

| $UF_2(SO_3F)_3$ | | | | | | | | | SO$_3$F group freq | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IR | | | | Raman | | | | | | | | |
| 300 K | | 80 K | | 300 K | | 80 K | | | | | | |
| Freq | Intens | Freq | Intens | Freq | Intens[f] | Freq | Intens | Approx assignment | $ClOSO_2F$[b] (IR) | $[Br(OSO_2F)_2]_2$[c] $[Sn(OSO_2F)_6]$ (Raman) | $(CH_3)_2$[d] $Sn(SO_3F)_2$ (IR) | $F_2Sn(SO_3F)_2$[e] (IR) |
| | | | | | | | | | | 1500 } * | | |
| | | | | | | | | | | 1487 } | | |
| 1485 | w, sh | n.o. | | n.o. | | 1482 | vw | | 1453 | 1420 } + | | |
| | | | | | | | | | | 1387 } | | |
| 1390 | vs | 1380 | vs | 1390 | 18.0 | 1400 | mw | | | | 1350 | 1412 |
| 1370 | vs | 1370 | vs | | | 1388 | mw | | | 1248* | | |
| 1265 | s, sh | 1265 | mw | 1243 | 3.0 | 1291 | vw | | 1231 | 1197 } + | | |
| | | 1235 | mw | | | 1254 | vw | | | 1145 } | | |
| 1185 | vs, br | 1180 | vs, br | 1165 | 27.5 | 1176 | m | $\nu(SO_3)$ | | | 1180 | 1109 |
| | | 1150 | vs, br | | | | | | | | | |
| 1100 | s | 1100 | ms | 1103 | 32.0 | 1119 | m | | | | 1076 | 1070 |
| 1080 | s | 1085 | s | | | 1107 | m | | | 985* | | |
| 1040 | s | 1050 | vs, br | 1040 | 9.0 | 1048 | m | | 860 | 1002+ | | |
| | | 1030 | vs, br | 1020 | 6.0 | 1020 | m | | | | | |
| 870 | s, sh | 870 | mw | 873 | 25.5 | 877 | m | | | | 827 | 855 |
| | | | | | | 867 | vw | | | 865* | | |
| 845 | vs | 840 | vs, br | 840 | 9.0 | 857 | vw | $\nu(SF)$ | 830 | 850 } + | | |
| | | | | | | 836 | w | | | 830 } | | |
| 635 | s | 633 | m | 636 | 32.0 | 636 | w | $\nu_{asym}(UF_2)$ | | | 620 | 628 |
| 605 | mw | 605 | mw | 606 | 5 × 100.0 | 607 | vvs | $\nu_{sym}(UF_2)$ | | | | |
| | | 597 | sh | | | 602 | sh | | | 596* | | |
| 592 | mw | 585[g] | mw | | | 586 | w | | 573 | 582+ | | |
| 580 | ms, sh | 580[g] | mw | 580 | 30.0 | 580 | w | | | | 590 | 590 |
| 570 | ms | 570[g] | m | | | 560 | w | | 530 | 558* | | |
| | | | | | | | | | | 560+ | | |
| 555 | s | 555[g] | m | 555 | 20.0 | 552 | w | | | | | |
| | | 550[g] | m | | | 544 | w | | | | 554 | 548 |
| | | 520[g] | vw | | | 525 | vw | | | | | |
| | | 505[g] | vw | | | 500 | vw | | | 430* | | |
| ~460 | vw, sh | ~460 | vw, sh | 452 | 2.5 | 467 | vw | | 485 | 435+ | | |
| 420 | m | 425 | m, sh | 423 | 32.5 | 426 | ms | | | | | |
| | | | | 409 | 14.5 | 414 | sh | Def and lattice modes | | | 417 | 430 |
| | | | | | | | | | | 414* | | |
| | | | | 218 | 13.5 | {243 | w | | 394 | 416+ | 304 | 280 |
| | | | | | | {226 | m | | | | | |
| | | | | 196 | 17.5 | {203 | m | | n.o. | 264* | | |
| | | | | | | {192 | sh | | | 266+ | | |
| | | | | 160 | 13.5 | 171 | w | | | | | |
| | | | | 135 | 2.5 | | | | | | | |
| | | | | 108 | 32.0 | | | | | | | |
| | | | | 75 | 22.0 | | | | | | | |
| | | | | 59 | 6.5 | | | | | | | |

[a] Key for this and other tables: s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very; asym, asymmetric; sym, symmetric; *, cation modes; +, anion modes. [b] References 20 and 21. [c] Reference 27. [d] Reference 26. [e] Reference 3. [f] Uncorrected relative intensities. [g] Values taken from spectra recorded on a Beckman IR9 instrument.

Table III. Visible and Near-Infrared Absorption Data

| Frequency, wavenumbers | | | Intens, optical density units | Tentative assignment ($D_4$ symmetry)[a] |
|---|---|---|---|---|
| Electronic transitions | Vibronic transitions | Frequency shift (+) | | |
| ~3200[b] | | | w, br | $\Gamma_6(\Gamma_8) \leftarrow \Gamma_7$ |
| 5476 | | | 0.34 | $\Gamma_7(\Gamma_8) \leftarrow \Gamma_7$ |
| 6489 | | | 2.00 | $\Gamma_7(\Gamma'_7) \leftarrow \Gamma_7$ |
| | ~7052 | ~563 | w, sh | U-F str |
| 7825 | | | 0.67 | $\Gamma_6(\Gamma'_8) \leftarrow \Gamma_7$ |
| 7975 | | | 0.67 | |
| 9813 | | | 0.85 | $\Gamma_7(\Gamma'_8) \leftarrow \Gamma_7$ |
| 15528 | | | 0.92 | $\Gamma_6(\Gamma_6) \leftarrow \Gamma_7$ |
| | ~16130 | ~600 | w, sh | U-F str |
| 29410 | | | 3.96 | Charge transfer |

[a] Symbols in parentheses are related to $O_h$ symmetry. [b] Observed in infrared spectra as a very weak and broad (~500 cm$^{-1}$ wide) line.

matrix.[50] In the case of $UF_2(SO_3F)_3$, $K$ was roughly assumed to be equal to 0.8. The spin–orbit coupling constant $\zeta$ may be obtained by interpolation between the values for Pa(IV) and Np(VI) which resulted in the value[49] of $\zeta = 1947$ cm$^{-1}$. The $(E_{\Gamma'_7} - E_{\Gamma_7})$ value is taken from Table III and is equal to 6489 cm$^{-1}$. It yields a mean $g$ value of around −0.6, which is in agreement with the previous calculation. The definition of $\theta$ from $\tan 2\theta = 2(3K)^{1/2}/(V/\zeta - K/2)$[49] allowed the evaluation of $V \approx 3170$ cm$^{-1}$, where $V$ is the $(\Gamma_2 - \Gamma_5)$ $O_h$ ligand field splitting without spin–orbit coupling.

When compared with the Curie constants $C$ and splitting $V$ values for several six- and eightfold coordinated oxides and fluorohydrates of U(V),[41] the $UF_2(SO_3F)_3$ $C$ value (0.21 cgsu) appears to be intermediate between $C = 0.1$ for six- (octahedral environment) and $C = 0.4$ for eight-coordination (cubic environment) which hold at $V \approx 3000$ cm$^{-1}$. This further shows that our crude assumption of a distorted octahedral environment was not unreasonable.

The above calculated $V$ splitting results[49] in a high value for the **g**-tensor anisotropy. This anisotropy and a significant increase of the relaxation rate due to the closeness of the $\Gamma_6$ and $\Gamma_7$ levels[50] may account for the absence of EPR signals up to 13.5 kG at 77 K on the powdered sample.

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**Registry No.** $UF_2(SO_3F)_3$, 63284-60-6; $UF_6$, 7783-81-5; $SO_3$, 7446-11-9.

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