organotin hydrides increases with increasing numbers of organic groups attached to the tin atom.[15] The halostannanes SnH_3X, X = Cl, Br, or I, however, are much less stable than SnH_4 and decompose upon sublimation at -35 °C.[16] Therefore, it was of some interest to attempt the preparation of CF_3SnH_3 as the trifluoromethyl group can be likened to an organic group since the linkage is through carbon, yet the ligand is very electronegative (more electronegative than Cl[17]). The experimental evidence indicates that a volatile tin compound is formed, a compound that decomposes faster than SnH_4 and has a chemical shift more deshielded than that of $ClSnH_3$ ($\delta(SnH_3Cl)$ 6.93[16]). Taken with the mass spectral data, which indicate $CF_3SnH_n^+$, $SnFH_n^+$, and SnH_n^+, these results argue strongly for the formation of CF_3SnH_3, but the compound is clearly less stable than stannane. Presumably the fact that the (trifluoromethyl)germanium hydrides are easily synthesized and stable for weeks at ambient temperatures[10,18] while the tin-containing analogues are not is a reflection of the relative electronegativities of the two central elements.

In summary the sealed-tube reactions between $SnBr_4$ and $(CF_3)_2Hg$ are a very convenient method of preparing the (trifluoromethyl)tin bromides CF_3SnBr_3 and $(CF_3)_2SnBr_2$ if the appropriate times and temperatures are used. However, outside of the relatively narrow temperature ranges established here the yields drop dramatically. Further substitution of trifluoromethyl groups is also indicated, but the trisubstituted compound decomposes almost immediately. The reaction of the bromides with stoichiometric amounts of CH_3Li or $(CH_3)_2Cd$ converts these compounds to the mixed methyl(trifluoromethyl)tin compounds virtually quantitatively. On the basis of the yields and availability of the reagents, the present preparation of the alkyl(perfluoromethyl)tin compounds is the most convenient synthesis known. (Trifluoromethyl)stannane appears to be much less stable than SnH_4, as are the stannyl halides.

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Registry No. CF_3SnBr_3, 65094-19-1; $(CF_3)_2SnBr_2$, 65094-20-4; $CF_3Sn(CH_3)_3$, 754-25-6; $(CF_3)_2Sn(CH_3)_2$, 65059-36-1; $Sn(CH_3)_4$, 594-27-4; $CF_3SnBr(CH_3)_2$, 72244-71-4; $CF_3SnBr_2CH_3$, 72251-81-1; $(CF_3)_2H_9$, 371-76-6; $SnBr_4$, 7789-67-5; $(CH_3)_2Cd$, 506-82-1; CH_3Li, 917-54-4; CF_3SnH_3, 72244-72-5; SnH_4, 2406-52-2.

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Synthesis and Properties of Chlorine(I) and Bromine(I) Trifluoromethanesulfonates and Raman Spectra of CF_3SO_2X (X = F, OH, OCl)

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The synthesis and characterization of the new hypohalites CF_3SO_3Cl and CF_3SO_3Br are described. Both compounds are thermally unstable at 22 °C, decomposing to CF_3Cl and SO_3 for the hypochlorite and $CF_3SO_3CF_3$, $CF_3SO_2OSO_2OCF_3$, SO_3 and Br_2 for the hypobromite. The hypochlorite is prepared by reaction of CF_3SO_3H with ClF and the hypobromite by reaction of CF_3SO_3Cl with bromine. The low-temperature Raman spectrum of CF_3SO_3Cl suggests C_1 symmetry and assignments of 20 of the expected 21 fundamentals are given. These assignments were aided by an analysis of the Raman spectra of CF_3SO_2F and CF_3SO_2OH, which are reported for the first time.

Introduction

Halogen derivatives of strong oxyacids contain the halogen in a formal positive oxidation state.[3,4] These +1 compounds are then very useful sources of the electrophiles Cl^+, Br^+, and I^+. The potential of such compounds is apparent by considering one of the better characterized examples, $BrOSO_2F$. This reactive compound undergoes electrophilic addition to olefins, substitutive electrophilic dehalogenation reactions with various chlorides and bromides, and one-electron oxidation by Br^+ with metals and serves as a source of Br^+ in the formation of polyhalogen cations.[3]

$$BrOSO_2F + CH_2CF_2 \rightarrow BrCH_2CF_2OSO_2F$$

$$2BrOSO_2F + FCCl_3 \rightarrow 2BrCl + FCCl(OSO_2F)_2$$

$$3BrOSO_2F + Au \rightarrow Au(SO_3F)_3 + \tfrac{1}{2}Br_2$$

$$BrOSO_2F + Cl_2 \xrightarrow{SbF_5} BrCl_2^+ + FSO_3^-$$

Clearly any new compound with properties similar to those of $BrOSO_2F$ would be immediately useful in synthesis.

Halogen(I) derivatives of several strong monoprotic acids have been prepared. These include $HOSO_2F$ (Cl,[5] Br,[6] I[7]), $HOClO_3$ (Cl,[8] Br[9]), $HOSeF_5$ (Cl, Br, I[10]), $HOTeF_5$ (Cl, Br, I)[11] and $HONO_2$ (Cl,[12] Br[13]). Not all of these compounds have good thermal stability and none have been investigated to the same extent as $BrOSO_2F$. One very strong acid, for which only the iodine compound is known, is CF_3SO_2OH.[14] This acid and its organic derivatives (triflates) have been extensively investigated since its discovery in 1954.[15,16]

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However, due to the lack of a suitable strong, synthetically useful oxidizing agent containing the CF_3SO_3 group, the synthesis of many desired compounds is difficult or impossible at the present time. We therefore undertook the synthesis of $BrOSO_2CF_3$ and $ClOSO_2CF_3$.[17]

This paper reports the synthesis and characterization of $XOSO_2CF_3$ (X = Cl and Br) and an analysis of the Raman spectrum of the hypochlorite. No previous assignments for a simple covalent CF_3SO_3 derivative were available, and the related compounds CF_3SO_2F and CF_3SO_2OH were also examined. Previous attempts to obtain the Raman spectrum of CF_3SO_3H were unsuccessful due to very strong fluorescence. This problem was avoided in our work by careful elimination of organic impurities.

Experimental Section

General Procedure. All work was carried out in Pyrex and stainless steel vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Temperatures were measured by using a digital copper–constantan thermocouple. Quantities of reactants and products were measured either by direct weighing or by *PVT* measurements with the assumption of ideal gas behavior.

Routine IR spectra were taken on a Perkin-Elmer 337 spectrometer at 5–100 torr. A 10-cm Pyrex glass cell fitted with AgCl windows was employed. IR spectra for assignment were taken on a Perkin-Elmer 180 spectrometer at 5–15 torr. Raman spectra were taken with a Spex 14018 double monochromator with photon-counting detection. Excitation was via the 515.4-nm line of an Ar^+ ion laser using 150–350 mW of power. Depolarization ratios were determined by method IV as described by Claassen et al.[18] A low-temperature glass cell similar to that described by Brown et al. was used to record the low-temperature spectra.[19] The cell was cleaned thoroughly with $Na_2Cr_2O_7/H_2SO_4$ before use with CF_3SO_3H. No hydrocarbon materials were allowed to contact the sample area.

Unless otherwise noted, NMR spectra were recorded on a Varian XL-100-15 spectrometer using 20–15 mol % solutions in $CFCl_3$. Spectra were at 94.1 MHz for F with $CFCl_3$ as an internal reference.

Molecular weights were determined by vapor density measurements using a calibrated Pyrex bulb fitted with a glass–Teflon valve. Determinations were made on successive fractions of each sample.

Melting points were taken in a Pyrex tube fitted with a glass–Teflon valve. The compound was pumped under vacuum onto the wall of the tube cooled by liquid N_2 forming a crystalline ring. The tube was placed in an ethanol bath, which was cooled to −112 °C prior to the measurement and then warmed slowly with proper agitation.

Vapor pressures and boiling points of the products were measured by a static method. Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purifications, the reaction products were separated via GLC on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 2 ft × $^3/_8$ in. column packed with 40% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P was used in most cases.

Reagents. CF_3SO_3H was obtained from Aldrich Chemical Co. and was purified by distillation. Bromine was dried over P_4O_{10} and distilled before using. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 at 250 °C in a Monel bomb and was taken out of the bomb at −111 °C to prevent contamination by ClF_3 and unreacted Cl_2. Fluorine was obtained from Air Products and was passed through a NaF scrubber before use.

Preparation of CF_3SO_2OCl. The compound was prepared many times in varying amounts. A typical procedure is described. CF_3SO_3H was vacuum transferred through a short glass connection into a ~15 mL Kel-F reactor cooled to −196 °C and fitted with a 304 stainless steel valve. The exact amount of acid was determined by weighing the container before and after transfer. The reactor containing 10.0 mmol of acid was then warmed to 22 °C so that the acid liquefied. It was then cooled to −196 °C and ClF (11.0 mmol) was added from an all stainless steel vacuum line. The mixture was then warmed slowly from −111 to −78 °C (~6 h) and held at −78 °C until all the solid acid was gone and the contents consisted of two liquid layers (~8 h). The lower layer, canary yellow in color, is CF_3SO_2OCl and the upper colorless layer is HF. The contents were then pumped on at −78 °C into a Kel-F trap at −196 °C. When essentially no further volatile material was collected, the remaining pale yellow liquid was essentially pure CF_3SO_2OCl. Measurement of the HF removed by weight, after removing other volatiles at −111 °C, indicated the reaction was quantitative within experimental error.

CF_3SO_2OCl: pale yellow to colorless crystals, mp −84.0 to −83.0 °C; ^{19}F NMR (−40 °C neat) 73.5 (s) (external $CFCl_3$); Raman at ca. −78 °C, see Results and Discussion.

The decomposition of CF_3SO_3Cl was carried out by attaching a Kel-F reactor to a glass vacuum system of 1250 mL volume. The CF_3SO_2OCl (2.23 mmol) was allowed to stand for 2 days, during which time the pressure increased to 48 torr. The contents of the line and reactor were then pumped into a trap at −196 °C and separated through traps at −111 and −196 °C. The −111 °C trap contained a white solid presumed to be SO_3 on the basis of its appearance and considerable experience in handling SO_3, and the −196 °C trap contained 2.20 mmol of CF_3Cl (mol wt 105.1, calcd 104.5) with an IR spectrum indistinguishable from that of a pure, known sample of CF_3Cl.

Preparation of CF_3SO_2OBr. This compound was prepared many times and a typical procedure is described. Onto CF_3SO_2OCl (5.0 mmol) at −196 °C in a ~15-mL Kel-F reactor was condensed Br_2 (2.5 mmol) by vacuum transfer. The reactor was placed in a −60 °C bath and shaken by hand. Immediate evolution of Cl_2 was apparent and the liquid phase turned from yellow to a dark red-brown. The latter became more viscous with time and solidified after ~2 h. The reaction was then warmed to −20 °C with shaking. The liquid phase became wine red and the evolution of additional Cl_2 was evident. After 2 h, the reactor was cooled to −78 °C and pumped on through a trap at −196 °C. After a few minutes, the reactor was closed again, warmed to −20 °C for a few minutes, and recooled to −78 °C and pumping was continued for ~30 min. This resulted in a yellow crystalline solid at −78 °C and Cl_2 (2.5 mmol) in the trap. The latter was measured by reaction with a weighed amount of Hg.

CF_3SO_2OBr: yellow crystalline solid, wine red liquid, mp −27.0 to −26.0 °C; ^{19}F NMR (−20 °C neat) 73.3 (s) (external $CFCl_3$); no Raman or IR spectra were successfully recorded.

Decomposition of CF_3SO_2OBr (3.52 mmol) was carried out in the same way as CF_3SO_2OCl. After 20 h, no further pressure increase was noted (initial pressure increase was rapid). The contents of the line and reactor was then pumped into a trap at −196 °C. The total volatile material corresponded to 3.53 mmol. Some nonvolatile white solid (SO_3) remained in the −196 °C trap. The volatiles were condensed onto Hg, and 1.76 mmol of Br_2 was removed. The remaining 1.77 mmol was separated by passing through traps at −80 and −196 °C. The −80 °C trap contained 0.18 mmol of a new compound identified as $CF_3SO_3SO_2OCF_3$. The −196 °C trap contained 1.56 mmol of $CF_3SO_2OCF_3$ and a trace of CF_3Br.

$CF_3SO_2OCF_3$: bp 19.9 °C; mp −106.0 to −105.0 °C; mol wt found 218.7, calcd 218.0; IR 1465 (s), 1280 (sh, s), 1260 (vs), 1230 (vs), 1148 (sh, s), 1135 (vs), 955 (s), 790 (m), 760 (w), 607 (w), 540 (vw), 505 (vw) cm^{-1}; ^{19}F NMR ϕ^* 74.3 (q, CF_3S), ϕ^* 53.6 (q, OCF_3) (J_{FF} = 3.5 Hz); ΔH_{vap} = 6.99 kcal/mol; ΔS_{vap} = 23.9 eu; $\log P\,(\text{torr}) = 8.0958 - 1528.1/T$. These data are in substantial agreement with that reported by Noftle and Cady (bp 21.1 °C, mp ~−108.2 °C).[20]

$CF_3SO_2OSO_2OCF_3$: mol wt found 297.9, calcd 298.0; IR 1485 (s), 1464 (s), 1290 (s), 1270 (vs), 1250 (vs), 1151 (vs), 1143 (sh, s), 974 (s), 810 (m), 790 (vs), 770 (s), 750 (sh, m), 615 (m), 595 (m), 561 (w), 539 (vw), 510 (m) cm^{-1}; ^{19}F NMR ϕ^* 72.9 (s, CF_3S), ϕ^* 56.1 (s, OCF_3).

Results and Discussion

Synthesis and Properties of CF_3SO_2OX (X = Cl, Br).

The new hypohalites CF_3SO_2OCl and CF_3SO_2OBr are prepared

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in high yield by the following low temperature reactions.

$$CF_3SO_3H + ClF \xrightarrow{-78\ °C} CF_3SO_2OCl + HF$$

$$2CF_3SO_2OCl + Br_2 \xrightarrow{-60,\ -20\ °C} 2CF_3SO_2OBr + Cl_2$$

Both are thermally unstable at 22 °C with $CF_3SO_2OBr \ll CF_3SO_2OCl$. The thermal decomposition is straightforward for the hypochlorite, yielding CF_3Cl and SO_3 as the only products.

$$CF_3SO_2OCl \xrightarrow{22\ °C} CF_3Cl + SO_3$$

The decomposition is mildly exothermic as is evident when a pure liquid sample of CF_3SO_2OCl is warmed to 22 °C in a Kel-F container. After a short time, the nearly colorless liquid begins to reflux.

The decomposition of CF_3SO_2OBr is more complex. Essentially no CF_3Br is detected and the products are SO_3, $CF_3SO_2OCF_3$, $CF_3SO_2OSO_2OCF_3$, and Br_2.

$$CF_3SO_2OBr \xrightarrow{22\ °C} CF_3SO_2OCF_3\ (90\%),\ CF_3SO_2OSO_2OCF_3\ (10\%),\ SO_3,\ Br_2\ (100\%)$$

This decomposition may initially form CF_3Br and SO_3, which are utilized in subsequent reactions to form the observed products.

$$CF_3SO_2OBr \rightarrow CF_3Br + SO_3$$

$$CF_3Br + CF_3SO_2OBr \rightarrow Br_2 + CF_3SO_2OCF_3 \xrightarrow{SO_3} CF_3SO_2OSO_2OCF_3$$

The formation of $CF_3SO_2OCF_3$ in this way has been demonstrated independently.[21] On the other hand, CF_3Cl has been shown not to react with CF_3SO_2OCl.[21] Thus the two decompositions are probably analogous, but for CF_3SO_2OBr the primary decomposition products may undergo secondary reactions.

The three halogen(I) derivatives of CF_3SO_3H form an interesting series. The iodine compound is a relatively high melting solid (mp 122 °C) and is said to be thermally stable to 170 °C[14]. Clearly this stability, when compared to CF_3SO_2OCl and CF_3SO_2OBr, is high and must be due to stabilization via polymerization as suggested by Dalziel and Aubke from their IR spectra.[14] The ultimate thermal decomposition of CF_3SO_2OI is similar to that of CF_3SO_2OBr.

$$2CF_3SO_2OI \xrightarrow{170\ °C} I_2 + SO_3 + CF_3SO_2OCF_3$$

This polymerization in the case of the iodine compound renders the compound less useful for synthetic purposes.

The reactivity of CF_3SO_2OX (X = Cl, Br) is high. They add to a variety of olefins by a stereospecific cis addition[22] and undergo substitutive electrophilic dehalogenation reactions like FSO_2OBr with a variety of organic[21] and inorganic substrates.[23] As was anticipated, many new trifluoromethanesulfonates can be prepared and the ultimate scope of this reaction is under active investigation. In all respects, the reactivity of CF_3SO_2OX (X = Cl, Br) appears to parallel that of FSO_2OBr. In the first synthesis of FSO_2OBr from $S_2O_6F_2$ and Br_2, the compound was described as a red-black liquid. This was subsequently found to be due to a bromine impurity and probably formation of the unstable Br_3OSO_2F.[6,24] Bromine(I) trifluoromethanesulfonate is similar. When free of Br_2, it is a clear wine red liquid. When contaminated with small amounts of Br_2, it is a dark red-brown liquid. In all probability, $CF_3SO_2OBr_3$ is formed and is responsible for the striking color change.

Chlorine(I) trifluoromethanesulfonate is remarkably electrophilic. It is considerably more reactive than FSO_2OCl, undergoing reactions with many alkyl halides at low temperature whereas FSO_2OCl must be heated in some cases. With CF_2Cl_2, CF_3SO_2OCl reacts above −50 °C, whereas FSO_2OCl required heating at 80 °C.[4,25] Chlorine(I) trifluoromethanesulfonate even adds to SF_4,[23] whereas FSO_2OCl was unreactive.[26] This greater reactivity may be due to a more pronounced Cl^+ character in the trifluoromethanesulfonate but no direct evidence can be presented for this at the present time.

The spectroscopic characterization of CF_3SO_2OBr is limited at the present to its ^{19}F NMR spectrum. Attempts to record the low-temperature Raman spectrum were unsuccessful due to the strong absorption of laser light by the colored compound. Wavelengths up to 620 nm were ineffective in surmounting this problem. Its infrared spectrum could not be recorded due to its instability and reactivity with window materials (KCl or AgCl). For CF_3SO_2OCl the low-temperature Raman spectrum was readily obtained and is discussed in the following section. The IR spectrum of CF_3SO_2OCl was obtained at 22 °C, but decomposition and rapid attack of the window materials (KCl or AgCl) made the observed frequencies uncertain. This did not prove to be a problem, since 20 of 21 fundamentals were observed in the Raman spectrum.

Analysis of the Raman Spectra of CF_3SO_2X (X = F, OH, OCl). In order to assign the Raman spectrum of CF_3SO_2OCl, it was desirable to have available a related series of compounds. The only compounds for which any detailed studies had been attempted were various ionic salts of $CF_3SO_3^-$ and several compounds such as $I(OSO_2CF_3)_3$ and $Rb[I(OSO_2CF_3)_4]$.[14] The complexity of the observed spectra of the latter precluded comparison with the simple, covalent CF_3SO_2OCl, and large differences might be expected in going from a covalent CF_3SO_2O- to $CF_3SO_3^-$. We therefore undertook an investigation of the Raman spectra of CF_3SO_2F and CF_3SO_2OH to aid in the assignment of CF_3SO_2OCl. In addition to aiding in the assignment of CF_3SO_2OCl, CF_3SO_2F and CF_3SO_2OH suggested a resolution for conflicting assignments for the $CF_3SO_3^-$ ion.

CF_3SO_2F and CF_3SO_2OH. CF_3SO_2F and CF_3SO_2OH, a pseudoisoelectronic pair differing in mass by only two units, have, as liquids, very similar Raman spectra from 0 to 1500 cm^{-1} (Figure 1). Frequency, relative intensity, and polarization data are presented in Table I along with the proposed assignment based on C_s symmetry overall but local C_{3v} symmetry for the CF_3 group. CF_3SO_2OH would have an SO(H) stretch replacing the SF stretch of CF_3SO_2F and the additional stretching, bending and torsional modes of the OH group. However, the OH stretch would be outside the 0–1500-cm^{-1} range and the OH torsion would probably be too weak and broad to observe. The OH bend might be expected in the 1000–1200-cm^{-1} region by analogy to H_2SO_4, CH_3SO_2OH, FSO_2OH, and $ClSO_2OH$[27] and SF_5OH.[28]

The only band present in CF_3SO_2OH with no counterpart for CF_3SO_2F, a polarized band at 1122 cm^{-1}, is assigned to the SOH bend. The symmetric and antisymmetric SO_2

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Table I. Infrared and Raman[a,b] Data and Assignment of Fundamentals for CF_3SO_2F, CF_3SO_2OH, and CF_3SO_2OCl

CF_3SO_2F[c] Raman			CF_3SO_2OH[c,d] IR[d]	CF_3SO_2OH[c,d] Raman			CF_3SO_2-OD IR[d]	CF_3SO_2OCl[c] Raman			FSO_2OCl[e] IR	FSO_2OCl[e] Raman			description[f] and symmetry[g] C_s	C_1
			3050	~3000	w	p ?	2320								ν(OH)	
			2390	~2300	w	?	1810								ν(OH)	
1467	1	~1.0	1420	1400	4	0.82	1420	1435	6	0.78	1453 vs	1478	5	1.0	$\nu_{as}(SO_2)A''$	
1270	25	0.11	1256	1244	19	0.22	1256	1241	35	0.21	1231 vs	1225	45	0.10	$\nu_s(SO_2)A'$	
~1235 sh	0.5	~1.0	1220	~1232	~3	?		~1226	?	dp ?					$\nu_d(CF_3)E$	$\nu_{as}(CF_3)A''$
								~1139	?	p						$\nu_{as}(CF_3)A'$
1140	5	0.29	1156	~1152 sh	~4		1156	1125	23	0.14					$\nu_s(CF_3)A_1$	$\nu_s(CF_3)A'$
				1122	13	0.12									δ(SOH)A'	
			930	930	13	0.09	930	821	29	0.53	860 vs	856	15	0.40	ν(SO(X))A'	
829	3	0.18									827 vs	830	15	0.60	ν(SF)A'	
771	100	<0.04	778	775	100	<0.06	778	771	40	0.45					$\delta_s(CF_3)A_1$	
								685	100	0.29	710 s	706	100	0.15	ν(OCl)A'	
611	2	0.23	622	620	4	0.31	622	594	10	0.21	579 and 570 s	573	7	p	$\delta(SO_2$ bend)A'	
564	7.5	0.92	572	570	23	0.91	572	569	13	0.92					$\delta_d(CF_3)E$	$\delta_{as}(CF_3)A''$
								556	12	0.55						$\delta_{as}(CF_3)A'$
			500	499	4	0.82	500								δ(SO(H) wag)A'	
488	2.5	0.83									485 m	486	45	0.65	δ(SF wag)A'	
463	2	0.92		478 sh	~2	0.89		499	4	0.79	538 and 531 s	534	7	1.0	$\delta(SO_2$ rock)A''	
								411	57	0.53	369 m	363	80	0.37	δ(SO(Cl) wag)A'	
333	≤19.5	≤0.71[c]		340	≤26	≤0.82[c]		336	≤30	≤0.62[c]					$\delta(SCF_3$ wag)A'	
not obsd or 333	?	dp[c]		not obsd or 340	?	dp[c]		not obsd or 336	?	?	349 w	389	6	1.0	$\delta(SO_2$ twist)A''	
								321	48	0.70						$\rho(CF_3)A'$
301	37	0.29		312	79	<0.33		302	52	0.45					ν(CS)A'	
								211	20	0.38		212	25	0.50	δ(SOCl)A'	
196	2	~1.0		201	2	~1.0		198	?	?					$\rho(CF_3)E$	$\rho(CF_3)A''$
								184	9	0.48						2τ(OCl)
								~90	~2	~1.0?						τ(OCl)

[a] All observed frequencies are in cm^{-1}. Abbreviations used are as follows: w, weak, m, medium; s, strong; vw, very weak; vs, very strong; sh, shoulder; p, polarized; dp, depolarized. [b] Raman data are listed in the order frequency in cm^{-1}, relative intensity on a scale where the most intense band is 100, and depolarization ratio or designation as polarized or depolarized. Depolarization ratio measurements were made by method IV of Claassen, Selig, and Shamir (*Appl. Spectrosc.* **1969**, *23*, 8) for CF_3SO_2F, CF_3SO_2OH, and CF_3SO_2OCl. The numbers reported are really R rather than ρ_s in the notation of Table I of Claassen, Selig, and Shamir since f has not been measured for the Spex 14018 double monochromator used in this work. [c] Raman data from this work for CF_3SO_2F, CF_3SO_2OH, and CF_3SO_2OCl as pure liquids near −78, −20, and −78 °C, respectively. In each case a single band near 335 cm^{-1} is assigned to $\delta(SCF_3$ wag)A'. The data are as follows: CF_3SO_2F, 333 cm^{-1}, 19.5, 0.71; CF_3SO_2OH, 340 cm^{-1}, 26, 0.82; and CF_3SO_2OCl, 336 cm^{-1}, 30, 0.62. The $\delta(SO_2$ twist) mode either is too weak to observe or is degenerate with $\delta(SCF_3$ wag). If $\delta(SO_2$ twist) and $\delta(SCF_3$ wag) are degenerate, then $\delta(SF_3$ wag)A' may be expected to contribute most of the intensity and to be weakly polarized so that its depolarization ratio is less than the observed value. For CF_3SO_2F and CF_3SO_2-OH $\delta(SO_2$ twist)A'' is expected to be depolarized and for CF_3SO_2OCl $\delta(SO_2$ twist)A'' need not be depolarized but may be expected to be less polarized than $\delta(SCF_3$ wag)A'. [d] IR data of Balicheva, Ligus, and Fialkov[30] for pure liquid at room temperature. [e] IR and Raman data of Qureshi, Levchuk, and Abuke[42] and Abuke and DesMarteau.[3] [f] Some discussion of the descriptions of some of the modes has been given elsewhere.[35,38,43,48–51] [g] CF_3SO_2F and CF_3SO_2OH are assumed to possess C_s symmetry overall but local C_{3v} symmetry for the CF_3 group. CF_3SO_2OCl is assumed to possess only C_1 symmetry overall but local C_s symmetry for the CF_3 group.

Table II. Summary of Observed Frequencies (cm^{-1}) below 1500 cm^{-1} for CF_3SO_2F and CF_3SO_2OH[a] Fundamentals

CF_3SO_2F Raman[d]	CF_3SO_2OH		CF_3-SO_2OD IR	description[b] and symmetry[c] C_s
	IR	Raman[d]		
1467 dp	1420	1400 dp	1400	$\nu_{as}(SO_2)A''$
1270 p	1256	1244 p	1256	$\nu_s(SO_2)A'$
~1235 dp	1220	~1232 ?	1220	$\nu_d(CF_3)E$
1140 p	1156	~1152 ?	1156	$\nu_s(CF_3)A_1$
		1122 p		$\delta(SOH)A'$
829 p	930	930 p	930	$\nu(SF)/\nu(SO(H))A'$
771 p	778	775 p	778	$\delta_s(CF_3)A_1$
611 p	622	620 p	622	$\delta(SO_2\ \text{bend})A'$
564 dp	572	570 dp	572	$\delta_d(CF_3)E$
488 wp	500	499 wp	500	$\delta(SF\ \text{wag})/\delta(SO(H)\ \text{wag})A'$
463 dp		478 sh, dp		$\delta(SO_2\ \text{rock})A''$
333 wp		340 wp		$\delta(SCF_3\ \text{wag})A'$
not obsd or 333 dp		not obsd or 340 dp		$\}\ \delta(SO_2\ \text{twist})A''$
301 p		312 p		$\nu(CS)A'$
196 d		201 dp		$\rho(CF_3)E$

[a] For detailed information see Table I including its footnotes. [b] Some discussion of the descriptions of some of the modes has been given elsewhere.[35,38,43,48–51] [c] CF_3SO_2F and CF_3SO_2OH are assumed to possess C_s symmetry overall, but local C_{3v} symmetry for the CF_3 group. [d] Abbreviations are as follows: p, polarized; dp, depolarized; wp, weakly polarized.

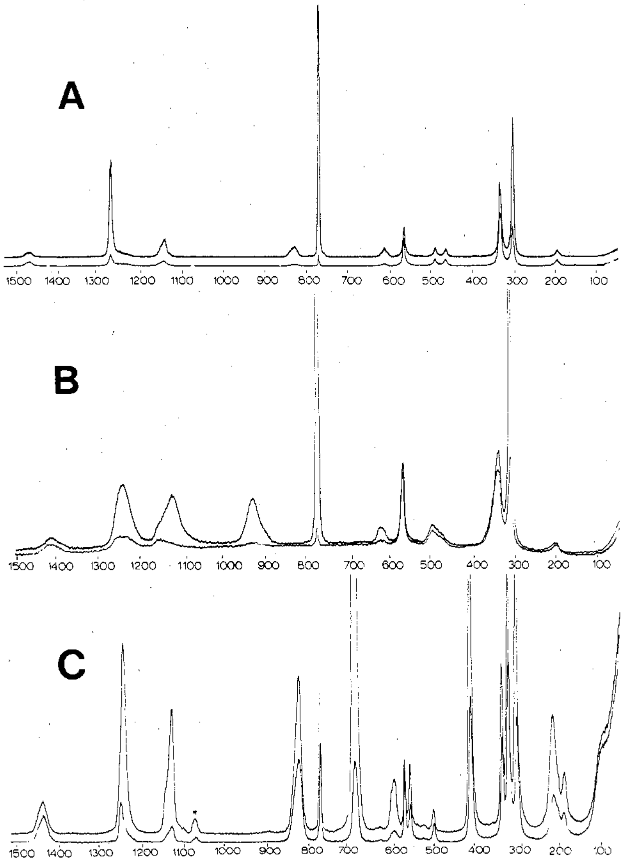

Figure 1. Raman spectra of the liquid CF_3SO_2F at −78 °C (A), CF_3SO_2OH at −20 °C (B), and CF_3SO_2OCl at −78 °C (C). The band near 1070 cm^{-1} (C) marked with an asterisk is due to SO_3 impurity.

stretches assigned at 1467 and 1270 cm^{-1}, respectively, for CF_3SO_2F are higher than those for CF_3SO_2OH at 1400 and 1244 cm^{-1}, respectively, due to the higher electronegativity of F over OH.[29] The CF_3 group, which should provide the remaining bands above 1000 cm^{-1}, is assumed to follow C_{3v} selection rules due to free rotation along the CS bond. The symmetric CF_3 stretch is assigned to the polarized band at 1140 cm^{-1} in CF_3SO_2F and to the shoulder at ~1152 cm^{-1} on the SOH bend at 1122 cm^{-1} in CF_3SO_2OH. The very weak depolarized shoulder at ~1235 cm^{-1}, on the symmetric SO_2 stretch at 1270 cm^{-1}, in CF_3SO_2F is assigned to the degenerate CF_3 stretch. Analogously, the degenerate CF_3 stretch is assigned to the weak band suggested to be present at ~1232 cm^{-1}, on the side of the symmetric SO_2 stretch at 1244 cm^{-1}, in a perpendicular polarization scan of CF_3SO_2OH.

The infrared data of Balicheva, Ligus, and Fialkov[30] for liquid CF_3SO_2OH and liquid CF_3SO_2OD near room temperature became consistent with our assignment by reversal of their CF stretch and symmetric SO_2 stretch assignments. Our assignment for the 1000–1500-cm^{-1} region is summarized in Table II.[31]

The region 700–1000 cm^{-1} is expected to contain only two modes. Several compounds with CF_3S groups have a strong polarized Raman band near 750 cm^{-1}.[32–34] Although this band is usually labeled as a symmetric CF_3 deformation, normal-coordinate analyses of the $CF_3SO_3^-$ ion by both Miles, Doyle, Cooney, and Tobias[33] (MDCT) and Burger, Burczyk, and Blaschette[34] (BBB) show more CF_3 and CS stretching character in this mode than CF_3 deformation character. For both CF_3SO_2F and CF_3SO_2OH, the most intense and highly polarized bands in the Raman spectra at 771 and 775 cm^{-1}, respectively, are labeled as the symmetric CF_3 deformation. However, in spite of the fact that we follow the usual practice of labeling a band as the symmetric CF_3 deformation, we believe that the mode responsible for the strong polarized Raman band near 775 cm^{-1} is a far more complex motion than a symmetric CF_3 (umbrella) deformation.[35] For CF_3SO_2OH

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(29) Fox, W. B.; Franz, G. *Inorg. Chem.* **1968**, *5*, 946.

(30) Balicheva, T. G.; Ligus, V. I.; Fialkov, Y. Y. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1973**, *18*, 1701.

(31) The absence of an IR band at ~1120 cm^{-1} due to the SOH bend in CF_3SO_2OH is most probably due to a different extent of hydrogen bonding and consequent different SOH bend frequency between room temperature where the IR data were recorded and near −20 °C where the Raman spectra were recorded. If the local C_{3v} symmetry of the CF_3 group were broken to the extent that the degenerate CF_3 stretch were split, then an additional polarized Raman band would be expected in the 1100–1300-cm^{-1} region. One might assign the 1122-cm^{-1} polarized Raman band in CF_3SO_2OH as an asymmetric CF_3 stretch of A′ symmetry under C_s symmetry rather than the SOH bend. But then it is difficult to understand why such a band is not observed for CF_3SO_2F if the cause of the band is the removal of the C_{3v} local symmetry of the CF_3 group. It is, of course, possible that the local C_{3v} symmetry of the CF_3 group is broken but the band is too weak to observe or is so weakly polarized and so slightly shifted that it is not distinguishable from the bands at ~1232 and ~1235 cm^{-1} for CF_3SO_2OH and CF_3SO_2F, respectively. However, we base our analysis on the assumption that the CF_3 group retains its local C_{3v} symmetry in both compounds.

(32) (a) Griffiths, J. E. *Spectrochim. Acta, Part A* **1967**, *23*, 2145 (CF_3SF_5). (b) Carter, H. A.; Wang, C. S.; Shreeve, J. M. *Spectrochim. Acta* **1973**, *29*, 1479 (CF_3SCF_3, $CF_3S(O)CF_3$, CF_3SSCF_3). (c) Borrajo, J.; Varetti, E. L.; Aymonino, P. J. *J. Mol. Struct.* **1975**, *29*, 163 (CF_3SH). (d) Kirschmerer, R. L.; Shreeve, J. M. *Inorg. Chem.* **1975**, *14*, 2431 ($CF_3S(O)F$, $CF_3S(O)Cl$). (e) Burger, H.; Pawelke, G.; Haas, A.; Willner, H.; Downs, A. J. *Spectrochim. Acta, Part A* **1978**, *34*, 287 ($(SCF_3)_3N$). (f) Holmes-Smith, R. D.; Stobart, S. R. *Inorg. Chem.* **1979**, *18*, 538 (SCF_3GeH_3, $(SCF_3)_2GeH_2$, $SCF_3GeH_2GeH_3$).

(33) Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta, Part A* **1969**, *25*, 1515 ($Na[CF_3SO_3]$, $Ba[CF_3SO_3]_2$).

(34) Burger, H.; Burczyk, K.; Blaschette, A. *Monatsh. Chem.* **1970**, *101*, 102 ($Ag[CF_3SO_3]$).

(35) It is reasonable that the symmetric CF_3 stretching, symmetric CF_3 (umbrella) deformation, and CS stretching symmetry coordinates for a CF_3S group of local C_{3v} symmetry may couple strongly in these compounds to form a normal coordinate similar to the result of BBB[34] for $CF_3SO_3^-$. It may well be that no CF_3S containing compound has any normal mode that is a symmetric CF_3 (umbrella) deformation group frequency in the sense of having 66% or more contribution to the calculated frequency from one diagonal force constant.[36]

(36) Fuhrer, H.; Kartha, V. B.; Kidd, K. G.; Kruger, P. J.; Mantsch, H. H. *NRC Bull.* **1976**, *No. 15*, 189–92.

the polarized Raman band at 930 cm^{-1} is assigned to the SO(H) stretching mode as are the IR bands in CF_3SO_2OH and CF_3SO_2OD at 930 cm^{-1}. For CF_3SO_2F, the analogous mode to SO(H) stretching in CF_3SO_2OH is SF stretching which is assigned to the polarized Raman band at 829 cm^{-1}.

For a CF_3 group of local C_{3v} symmetry, the degenerate CF_3 deformation and CF_3 rocking modes remain. The regions expected for these weak depolarized bands are 515–560 and 215–310 cm^{-1}, respectively.[32a,c,37] The depolarized bands at 564 and 570 cm^{-1} in CF_3SO_2F and CF_3SO_2OH, respectively, are assigned to the degenerate CF_3 deformation. The only weak depolarized Raman bands near the expected range of 215–310 cm^{-1}, at 196 and 201 cm^{-1} in CF_3SO_2F and CF_3SO_2OH, respectively, are assigned to the degenerate CF_3 rock.

Although the CS stretching mode has been assigned from 450 to 500 cm^{-1} in several molecules containing CF_3S groups,[32b–e] a medium to strong polarized Raman band near 325 cm^{-1} has been assigned to ν(CS) in CF_3SF_5[32a] and the $CF_3SO_3^-$ ion.[33,34] The normal-coordinate analyses of the $CF_3SO_3^-$ ion by MDCT[33] and BBB[34] both show this mode to have significant CF_3 and SO_3 deformation contributions. The second most intense bands, both polarized, in the Raman spectra at 301 and 312 cm^{-1} for CF_3SO_2F and CF_3SO_2OH, respectively, are labeled as the CS stretching mode. However, in spite of the fact that we label a band as CS stretching, we believe that the mode responsible for the strong polarized Raman bands near 310 cm^{-1} is a more complex motion.[38]

The four bands remaining unassigned for each compound must be due to five remaining modes of an XSO_2Y system. These may be classified as follows under C_s symmetry:[39] XSY deformation (A′), SO_2 bend (A′), SO_2 twist (A″), SO_2 rock (A″), and SO_2 wag (A′). An alternative description,[40] which we will adopt, is to use SX wag (A′) and SY wag (A′) rather than XSY deformation (A′) and SO_2 wag (A′). In either description under C_s symmetry, there will be three polarized (A′) modes and two depolarized (A″) modes. The fact that three of the four observed bands appear to be depolarized is an anomaly. However, the data for CF_3SO_2F suggest an explanation. The four frequencies and their depolarization ratios are: 611 cm^{-1} and 0.23, 488 cm^{-1} and 0.83, 463 cm^{-1} and 0.92, and 333 cm^{-1} and 0.71. Taking the apparently depolarized band with the lowest depolarization ratio as being an overlap of a weakly polarized and a depolarized pair of bands gives a fifth frequency. An alternative possibility is that the band corresponding to one of the depolarized modes is too weak to observe. In either case, the observed band with the next lowest depolarization ratio is taken as weakly polarized. For CF_3SO_2F the following list results: 611 cm^{-1} (p), 488 cm^{-1} (wp), 463 cm^{-1} (dp), 333 cm^{-1} (wp). The fifth frequency is either not observed or is 333 cm^{-1} (dp).

Assignments for these five frequencies are made to be consistent with the following XSO_2Y cases: FSO_2F,[39,41] FSO_2OH,[27] $HOSO_2OH$,[27a] $DOSO_2OD$,[27a] FSO_2Cl,[39,40] $HOSO_2Cl$,[27] FSO_2Br,[41] $ClSO_2Cl$,[39,41] FSO_2OF,[3,42] FSO_2OCl,[3,42] FSO_2OBr,[3] and FSO_2OI.[3] For the two depolarized modes, the SO_2 rock has been assigned to a higher frequency than the SO_2 twist in all cases. Consequently, we assign 463 cm^{-1} as the SO_2 rock, and the SO_2 twist either is not observed or is 333 cm^{-1}. For FSO_2Y compounds with Y = OH,[27a,b,42] Cl,[39,40] Br,[41] OF,[3,42] OCl,[3,42] OBr,[3] and OI,[3] the SF wag has been assigned in the range 308–500 cm^{-1} with all but two in the range 385–500 cm^{-1}. Consequently, we assign 488 cm^{-1} as the SF wag. For these same FSO_2Y cases, the SO_2 bend has always been assigned as the highest of the five XSO_2Y system frequencies and in the range 555–627 cm^{-1}. Consequently, we assign the SO_2 bend to the polarized band at 611 cm^{-1}. The remaining weakly polarized band at 333 cm^{-1} is assigned to the SCF_3 wag consistent with the SCF_3 wag in CF_3SF_5 being assigned at 320 cm^{-1}.[32a] If these assignments are extended to the analogous bands for CF_3SO_2OH with the SF wag in CF_3SO_2F becoming an SO(H) wag in CF_3SO_2OH, the summary shown in Table II can be made for all the bands below 1500 cm^{-1}.[43] No bands assignable to the CF_3 torsion were observed.

Our data and assignments for CF_3SO_2OH are of particular interest due to the discrepancy between the results of Miles, Doyle, Cooney, and Tobias[33] (MDCT) for $Na[CF_3SO_3]$ and $Ba[CF_3SO_3]_2$ and Burger, Burczyk, and Blaschette[34] (BBB) for $Ag[CF_3SO_3]$. Although both groups report strong IR bands in the 630–650-cm^{-1} range for the three solid salts, BBB observe a strong polarized Raman band at 635 cm^{-1} in aqueous $Ag[CF_3SO_3]$ but MDCT do not report any Raman bands between 600 and 700 cm^{-1} for aqueous $Na[CF_3SO_3]$ and $Ba[CF_3SO_3]_2$. Consequently, BBB and MDCT are led to make different assignments for the CF_3 and SO_3 deformations. Both groups support their results by adopting analogous conflicting assignments for $CCl_3SO_3^-$ salts.

On the basis of our CF_3SO_2OH assignments, the BBB assignments for the SO_3 and CF_3 deformations of the $CF_3SO_3^-$ ion are strongly favored.[45] Table III presents our assignments for CF_3SO_2OH and the $CF_3SO_3^-$ and $CCl_3SO_6^-$ and $CCl_3SO_3^-$ salt data of BBB and MDCT. For $CF_3SO_3^-$ and $CCl_3SO_3^-$ salts we retain the assignments of BBB except for a reversal of $\nu_d(SO_3)$ and $\nu_d(CF_3)$ for $CF_3SO_3^-$.[46] The changes in as-

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(37) (a) Burger, H.; Cichon, J.; Demuth, R.; Grobe, J. *Spectrochim. Acta, Part A* **1973**, *29*, 943 (CF_3SH, CF_3SD, CF_3SeH, CF_3SeD). (b) Burger, H.; Eujen, R. *Ibid.* **1975**, *31*, 1645 (CF_3GeX_3, X = F, Cl, Br, I). (c) Wahi, P. K.; Patel, N. D. *Can. J. Spectrosc.* **1977**, *22*, 88 (CF_3SeH, CF_3SeD).

(38) It is reasonable that the mode responsible for these bands involves CS stretching, CF_3 deformation, and possibly some kind of SO_2X deformation motion in analogy to the result of BBB[34] for $CF_3SO_3^-$. It is probably true that there is no normal mode in these compounds that is a CS stretching group frequency in the sense of having 66% or more contribution to the calculated frequency from one diagonal force constant.[36]

(39) Toyuki, H.; Shimizu, K. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2364.

(40) Gillespie, R. J.; Robinson, E. A. *Spectrochim. Acta* **1962**, *18*, 1473.

(41) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1961**, *39*, 2171.

(42) Qureshi, A. M.; Levchuk, L. E.; Aubke, F. *Can. J. Chem.* **1971**, *49*, 2544.

(43) Alternate notation for some of the modes is possible. Our $\delta(SO_2$ bend) would be called $\delta(SO_2$ scissors) by some authors. Our $\delta(SO_2)$ rock is a motion in the SO_2 plane using the convention of Morino and Shimanouchi.[44] Some authors would call this mode $\delta(SO_2$ in-plane). In addition coupling effects may be present which would make other descriptions more appropriate for some modes. For the two bands between 300 and 350 cm^{-1} a description suggested by a referee is $\delta(CF_3$–S in-plane) and $\delta(CF_3$–S out-of-plane). In the absence of additional information, we have chosen to retain our description of $\delta(SCF_3$ wag) and ν(CS) with proper qualification of the latter.[38] However, the nature of the modes responsible for the bands between 300 and 350 cm^{-1} must remain uncertain.

(44) Morino, Y.; Shimanouchi, T. *Pure Appl. Chem.* **1978**, *50*, 1707.

(45) Lowering the C_{3v} symmetry of the SO_3 segment of the $CF_3SO_3^-$ ion to the C_s symmetry of CF_3SO_2OH as an XSO_2Y structure changes the single A_1 mode $[\delta_s(SO_3)]$ and two E modes $[\delta_d(SO_3)$ and $\rho(SO_3)]$ into three A′ modes [SO_2 bend, SO(H) wag, and SCF_3 wag] and two A″ modes [SO_2 rock and SO_2 twist]. Reference to Table III shows the following association between the $CF_3SO_3^-$ ion assignments of BBB and ours for CF_3SO_2OH: $\delta_s(SO_3)$ at 635 cm^{-1} with $\delta(SO_2$ bend) at 620 cm^{-1}, $\delta_d(SO_3)$ at 521 cm^{-1} with a small splitting (incompletely resolved, see Figure 1B) into δ(SO(H) wag) at 499 cm^{-1} and $\delta(SO_2$ rock) at 478 cm^{-1}, $\rho(SO_3)$ at 359 cm^{-1} with $\delta(SCF_3$ wag) (and possibly $\delta(SO_2$ twist)) at 340 cm^{-1}. Also 570 cm^{-1} as $\delta_d(CF_3)$ in CF_3SO_2OH, with local C_{3v} symmetry for the CF_3 group, agrees well with 582 cm^{-1} in the $CF_3SO_3^-$ ion.

Table III. Infrared and Raman[a,b] Data and Assignment of Fundamentals for CF_3SO_2OH and Several $CX_3SO_3^-$ Salts

CF_3SO_2OH[c]				$Ag[CF_3SO_3]$[d]		$Na[CF_3SO_3]$[e]				$Ba[CF_3SO_3]_2$[e] IR	$Ba[CCl_3SO_3]_2$[f] IR	$Na[CCl_3SO_3]$[e]				description[i] and symmetry[j]	
IR	Raman			IR	Raman	IR	Raman					IR	Raman			C_{3v}	C_s
1420	1400	4	0.82	1270 vsb		1280 vs, vbd	1285	22	0.79	1290	1253 vs	1260 s, bd	1250	35	0.95	$\nu_d(SO_3)E$	$\nu_{as}(SO_2)A''$
1256	1244	19	0.22							vs, vbd		1232 s, bd					$\nu_s(SO_2)A'$
1220	1232	~3	?	1167 s		1168 s	1188	16	1.31	1180	802 vs	812 s[h]	814	66	0.94[h]	$\nu_d(CX_3)E$	
1156	1152	~4	?	1237 s	1237 s	1232 m	1230	29	0.60		420 w	410 s, bd	413	100	0.24	$\nu_s(CX_3)A_1$	
	1122	13	0.12														$\delta(SOH)A'$
930	930	13	0.09	1038 vs	1039 sp	1036 s	1038	100	0.10	1036 s	1078 vs	1066 s	1060	65	0.27	$\nu_s(SO_3)A_1$	$\nu(SO(H))A'$
778	775	100	<0.06	767 m	772 sp		766	41	0.08	771 m	255 m		247	97	0.83[h]	$\delta_s(CX_3)A_1$	$\delta_s(CX_3)A'$
622	620	4	0.31	646 vs	635 sp	630 s				637 s	629 vs	616 s	621	9	0.50	$\delta_s(SO_3)A_1$	$\delta(SO_2\ bend)A'$
572	570	23	0.91	582 m	582 w	591 s	580	36	0.88	592 s	272 vw		261	97	0.83[h]	$\delta_d(CX_3)E$	
500	499	4	0.82	521 s		531 s 515 s	520	4	dp	530 s 513 s	548 s	544 s	548	16	1.08	$\delta_d(SO_3)E$	$\delta(SO(H)wag)A'$
	478 sh	~2	0.89														$\delta(SO_2\ rock)A''$
	340	≤26	≤0.82[c]														
	not obsd or			356 s	359 m	351 m	353	61	0.81	358 m	352 m	333 m	339	53	0.96	$\rho(SO_3)E$	$\delta(SCF_3wag)A'$
	340	?	dp[c]														$\delta(SO_2\ twist)A''$
	312	79	<0.33	323 m	326 mp	319 m	321	73	0.50	327 m	834 m	812 s[h]	829	66	0.94[h]	$\nu(CS)A_1$	
	201	2	~1.0	227 w			208	5	dp		135 s[g]		177	43	dp	$\rho(CX_3)E$	

[a] All observed frequencies are in cm^{-1}. Abbreviations used are as follows: w, weak; m, medium; s, strong; vw, very weak; vs, very strong; sh, shoulder; bd, broad; vbd, very broad; p, polarized; dp, depolarized. [b] Raman data are listed in the order frequency in cm^{-1}, relative intensity on a scale where the most intense band is 100, and depolarization ratio or designation as polarized or depolarized. [c] IR data from ref 30, Raman data from this work (pure liquid near −20 °C) where the band at 340 cm^{-1} with relative intensity 26 and depolarization ratio 0.82 is assigned to $\delta(SF_3\ wag)A'$. The $\delta(SO_2\ twist)$ mode is either too weak to observe or is degenerate with $\delta(SCF_3\ wag)$. If $\delta(SO_2\ twist)$ and $\delta(SCF_3\ wag)$ are degenerate, then $\delta(SCF_3\ wag)$ would be expected to contribute most of the intensity and have a depolarization ratio <0.82 and $\delta(SC_2\ twist)A''$ would be expected to make a small contribution to the intensity and be depolarized. [d] IR and Raman data of BBB.[34] Raman data from aqueous solution and IR data from Nujol mull below 1100 cm^{-1} and CsI pellet above 1100 cm^{-1}. [e] IR and Raman data of MDCT.[33] Raman data from aqueous solution and IR data from mulls. [f] IR data of BBB.[34] A combination of Nujol mull data below 500 cm^{-1} and from 800 to 1000 cm^{-1} and CsI pellet data from 500 to 700 cm^{-1} and above 1000 cm^{-1}. [g] The IR data of BBB[34] for $Ba[CCl_3SO_3]_2$ in a Nujol mull show four bands below 200 cm^{-1}, ~190 (w), 182 (s), 135 (s), and 114 (s) cm^{-1}, while in a CsI pellet only one band, 187 (s) cm^{-1}, is observed. The best agreement with the Raman data of MDCT[33] for $Na[CCl_3SO_3]$ with a depolarized band at 177 cm^{-1} would be with 182 and 187 cm^{-1} for $Ba[CCl_3SO_3]_2$ in a Nujol mull and CsI pellet, respectively. However, the normal coordinate analysis of BBB suggests 135 cm^{-1} for $\rho(CX_3)E$, a result that seems more reasonable than $\rho(CCl_3)$ near 180 cm^{-1} since $\rho(CF_3)E$ is not far above 200 cm^{-1} in $Ag[CF_3SO_3]$ and $Na[CF_3SO_3]$. [h] The IR data show a single band at 812 cm^{-1} which we assign to both $\nu_d(CCl_3)E$ and $\nu(CS)A_1$. The Raman data show overlapping bands at 829 and 814 cm^{-1} where the total band system has relative intensity 66 and depolarization ratio 0.94. Using the suggestion of the normal coordinate analysis of BBB,[34] we assigned 829 cm^{-1} as $\nu(CS)A_1$ and 814 cm^{-1} as $\nu_d(CCl_3)$ with the expectation that $\nu(CS)A_1$ is the larger contributor to the intensity and is weakly polarized while $\nu_d(CCl_3)$ is depolarized. The Raman band system of 247 and 261 cm^{-1} has a total relative intensity of 97 and depolarization ratio of 0.83 with the 247-cm^{-1} component polarized and the 261-cm^{-1} component depolarized. [i] Some discussion of the description of the modes for CF_3SO_2OH has been given elsewhere.[35,38,43,48-51] [j] The $CX_3SO_3^-$ salts are assumed to possess C_{3v} symmetry while CF_3SO_2OH is assumed to possess C_s symmetry overall but local C_{3v} symmetry for the CF_3 group.

signment for the data of MDCT do avoid some of the disturbingly high depolarization ratios for overlapping A_1 and E modes in the original assignments of MDCT.[47] We offer Table III as the most reasonable and consistent accounting of the data presently available for CF_3SO_2OH and the $CF_3SO_3^-$ and $CCl_3SO_3^-$ salts.

CF_3SO_2OCl. The Raman spectrum of liquid CF_3SO_2OCl is far more complex than that of CF_3SO_2F or CF_3SO_2OH (Figure 1). The number of bands which are definitely polarized rules out all but C_1 symmetry overall. The complexity of the spectrum of CF_3SO_2OCl compared to CF_3SO_2OH is due to reducing the local C_{3v} symmetry of the CF_3 group to either C_s or C_1 in addition to the OCl stretch falling within the 0–1500-cm^{-1} region and the OCl torsion possibly being observable. Frequency, relative intensity, and polarization data are presented in Table I along with the proposed assignment based on C_1 symmetry overall but local C_s symmetry for the CF_3 group. These assignments were made by analogy to CF_3SO_2OH and CF_3SO_2F for many of the modes and FSO_2OCl[3,42] for the modes involving the SOCl fragment.

The frequency region 725–1500 cm^{-1} should contain three CF stretching modes, two SO_2 stretches, the SO(Cl) stretch, and the symmetric CF_3 deformation.[48] The antisymmetric and symmetric SO_2 stretches and symmetric CF_3 deformation are assigned at 1435 and 1241 cm^{-1} and 771 cm^{-1}, respectively, by analogy to CF_3SO_2OH. The symmetric CF_3 stretch is assigned to the band at 1125 cm^{-1} by analogy to CF_3SO_2OH (and CF_3SO_2F) and on the basis of the relatively high intensity. The two asymmetric CF_3 stretches are assigned to weak shoulders at ~1226 cm^{-1} on the symmetric SO_2 stretch at 1241 cm^{-1} and ~1139 cm^{-1} on the symmetric CF_3 stretch at 1125 cm^{-1}. The degenerate antisymmetric CF_3 stretch in C_{3v} local symmetry, from which these two modes are split in C_s symmetry, had been assigned to a weak band at ~1232 cm^{-1} on the side of the symmetric SO_2 stretch at 1244 cm^{-1} in CF_3SO_2OH. The remaining band at 821 cm^{-1} must be assigned to the SO(Cl) stretch. In CF_3SO_2OH the analogous SO(H) stretch is much higher at 930 cm^{-1}, but in FSO_2OCl the SO(Cl) stretch is at 856 cm^{-1} in satisfactory agreement with 821 cm^{-1} and of comparable relative intensity and polarization.[49]

The frequency region 400–725 cm^{-1} by analogy to CF_3SO_2OH and FSO_2OCl would contain the OCl stretch, the SO_2 bend and rock, and two CF_3 deformations. The most intense band in the Raman spectrum of CF_3SO_2OCl at 685 cm^{-1} is assigned to the OCl stretch in good agreement with 706 cm^{-1} for that mode in FSO_2OCl.[49] The band at 594 cm^{-1} for CF_3SO_2OCl is assigned to the SO_2 bend. The SO_2 bends in CF_3SO_2F and CF_3SO_2OH are at 611 and 620 cm^{-1}, respectively, and all three bands have similar band shapes. The SO_2 bend in FSO_2OCl is at 573 cm^{-1} with comparable relative intensity to the 594-cm^{-1} band of CF_3SO_2OCl.

The two CF_3 deformations, of A″ and A′ symmetry in C_s, are assigned at 569 and 556 cm^{-1}. These two bands have shapes similar to that of the 570-cm^{-1} band in CF_3SO_2OH assigned to the degenerate CF_3 deformation in C_{3v} local symmetry which would split under C_s symmetry. The fact that the 569-cm^{-1} band appears to be depolarized supports retention of local C_s symmetry by the CF_3 group. The SO_2 rock is assigned to the band at 499 cm^{-1} in CF_3SO_2OCl. The corresponding bands in CF_3SO_2F, CF_3SO_2OH, and FSO_2OCl are at 463, 478, and 534 cm^{-1}, respectively. The 499-cm^{-1} band of CF_3SO_2OCl and the 534-cm^{-1} band of FSO_2OCl have comparable relative intensities.

The band for CF_3SO_2OCl at 411 cm^{-1} is the second most intense band in the Raman spectrum and the most intense band below 500 cm^{-1}. The 411-cm^{-1} band of CF_3SO_2OCl is assigned to the SO(Cl) wag by analogy to FSO_2Cl where the second most intense band in the Raman spectrum and the most intense band below 500 cm^{-1} at 363 cm^{-1} is assigned as the SO(Cl) wag.[50]

Seven bands in the region 0–400 cm^{-1} complete the Raman spectrum of liquid CF_3SO_2OCl. The modes remaining to be assigned are the SCF_3 wag, the SO_2 twist, two CF_3 rocks, the CS stretch, the SOCl bend, and the OCl torsion. Reduction of the local symmetry of the CF_3 group from C_{3v} to C_s splits the degeneracy of the CF_3 rock and may dramatically change the Raman intensity. For CF_3 groups bonded to sulfur, reduction of local symmetry from C_{3v} to C_s replaces a weak depolarized band in the 215–310-cm^{-1} region[32a,c,37a] by a medium to very strong polarized band near 300 cm^{-1} and a weak depolarized band near 200 cm^{-1}.[32b,d] Thus a CF_3 rock, the SCF_3 wag, and CS stretch are candidates for the three prominent bands between 300 and 350 cm^{-1} in the Raman

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(46) Lowering the C_{3v} symmetry of the SO_3 segment of the $CF_3SO_3^-$ ion to the C_s symmetry of the SO_2 group in XSO_2Y splits $\nu_d(SO_3)$ into $\nu_s(SO_2)$ and $\nu_{as}(SO_2)$. Extending to $\nu_d(SO_3)$ in $CF_3SO_3^-$ the concept that $\nu_s(SO_2)$ and $\nu_{as}(SO_2)$ and their average in an XSO_2Y system increase with the electronegativity of Y at constant X[29] suggests the sequence $CH_3SO_3^-$ 1193 cm^{-1}, $CCl_3SO_3^-$ 1250 cm^{-1}, and $CF_3SO_3^-$ 1285 cm^{-1} using the Raman data of MDCT for $Na[CX_3SO_3]$. However, both BBB and MDCT assign $\nu_d(SO_3) < 1200$ cm^{-1} and $\nu_d(CF_3) > 1200$ cm^{-1} in the $CF_3SO_3^-$ ion. For CF_3SO_2F and CF_3SO_2OH, $\nu_{as}(SO_2)$ is more intense than $\nu_d(CF_3)$ in our Raman spectra, consistent with the 1285-cm^{-1} band being more intense than the 1188-cm^{-1} band in the Raman spectra of MDCT for $Na[CF_3SO_3]$. Although BBB do list $\nu_d(CF_3) > \nu_d(SO_3)$ in their Table 3, they have found in their normal-coordinate analysis that either $\nu_d(CF_3) > \nu_d(SO_3)$ or the reverse is in good agreement with frequencies calculated from two different chemically plausible sets of force constants. We consider that the weight of the evidence presented here favors $\nu_d(CF_3) < \nu_d(SO_3)$ for the $CF_3SO_3^-$ ion.

(47) The original assignment of MDCT has the following three cases where a single band or a system of two overlapping bands assigned to the overlap for an A_1 mode and an E mode has a disturbingly high depolarization ratio: $\delta_s(SO_3)$ and $\delta_d(SO_3)$ at 580 cm^{-1} with 0.88 in $CF_3SO_3^-$; $\delta_s(SO_3)$ and $\delta_d(SO_3)$ at 548 cm^{-1} with 1.08 in $CCl_3SO_3^-$; and $2\nu_s(CCl_3)$ and $\nu_{as}(CCl_3)$ at 829/814 cm^{-1} with 0.94 in $CCl_3SO_3^-$. The assignment shown in Table III does retain the third problem since 829 cm^{-1} is now $\nu(CS)A_1$ and 814 cm^{-1} is $\nu_d(CCl_3)E$. However, the first two difficulties are removed. In addition the low intensity of the Raman band at 621 cm^{-1} in $Na[CCl_3SO_3]$ is surprising for its original assignment to $\nu(CS)$ by MDCT but plausible for $\delta_s(SO_3)$ as assigned in Table III.

(48) For a CF_3S group of local C_s symmetry it is reasonable that the symmetric CF_3 stretching, symmetric CF_3 (umbrella) deformation and CS stretching symmetry coordinates may couple strongly to form a complicated normal coordinate as in $CF_3SO_3^-$.[34,35] For CF_3SO_2OCl there is probably no normal mode that is a symmetric CF_3 (umbrella) deformation group frequency.[35,36]

(49) In CF_3SO_2OH $\nu(SO)$ and $\nu(OH)$ would be essentially uncoupled. However, as pointed out by a referee, in CF_3SO_2OCl $\nu(SO)$ and $\nu(OCl)$ would probably couple strongly so that the 821- and 685-cm^{-1} bands would be more accurately described by $\nu_{as}(SOCl)$ and $\nu_s(SOCl)$, respectively. An analogous situation probably occurs in FSO_2OCl.

(50) A referee has suggested that the 411-cm^{-1} band in CF_3SO_2OCl be assigned to $\delta(SOCl)$ rather than $\delta(SCF_3$ wag). The high intensity of the bands at 411 and 363 cm^{-1} in CF_3SO_2OCl and FSO_2OCl, respectively, makes such an assignment for CF_3SO_2OCl and its extension to the FSO_2OX series data of Aubke and DesMarteau[3] attractive. We believe the two most intense bands below 500 cm^{-1} in the Raman spectra of the liquid FSO_2OX compounds are most reasonably assigned as the $\delta(SO(X)$ wag) and the $\delta(SOX)$ modes. The frequencies (cm^{-1}) and relative intensities in parentheses for FSO_2OX, where X = F, Cl, or Br, and for CF_3SO_2OCl are as follows (all bands are polarized): FSO_2OF 395 (40), 242 (30); FSO_2OCl 363 (80), 212 (25); FSO_2OBr 317 (100), 175 (40); CF_3SO_2OCl 411 (57), 211 (20). Since the $\delta(SOX)$ mode should have the larger extent of X atom motion, its frequency should show the larger percentage decrease with increasing mass of the X atom providing the force constants do not change in such a way as to alter this expected trend. Consequently, the lower frequency band is selected as $\delta(SOX)$ or at least as having the larger contribution from an SOX bending motion. Then the higher frequency band is selected as $\delta(SO(X)$ wag). We recognize that complex coupling effects may be operating here and that the higher frequency band might have a larger SOX bending contribution than the lower frequency band. It is also possible that there is no mode which has SOX bending as its major contributor but that the referee's description is closer to the truth than ours. However, with the current state of information we prefer to retain the assignment consistent with the FSO_2OX assignments of Aubke and DesMarteau[3] rather than revise the FSO_2OX assignments without results from a normal-coordinate analysis to provide additional insight.

spectrum of liquid CF_3SO_2OCl.

The band at 336 cm^{-1} for CF_3SO_2OCl is assigned to the SCF_3 wag by analogy to this same assignment for the bands at 333 and 340 cm^{-1} in CF_3SO_2F and CF_3SO_2OH, respectively.[43] The SO_2 twist for CF_3SO_2OCl either is too weak to observe or is degenerate with the SCF_3 wag at 336 cm^{-1}. The SO_2 twist in FSO_2OCl is assigned to a weak band at 389 cm^{-1}. The band at 302 cm^{-1} for CF_3SO_2OCl is assigned to the CS stretch by analogy to CF_3SO_2F and CF_3SO_2OH where the CS stretch is assigned at 301 and 312 cm^{-1}, respectively.[38,43] Then the band at 321 cm^{-1} in CF_3SO_2OCl can be assigned to the CF_3 rock of A' symmetry for C_s. It would, of course, be possible to reverse our CS stretch and CF_3 rock assignments. The bands are of almost equal intensity (the third and fourth most intense bands in the Raman spectrum) with the 302-cm^{-1} band being slightly more intense and having the lower depolarization ratio. It seems reasonable for the CS stretch,[38,43] which would be polarized in any case, to have a lower depolarization ratio than the CF_3 rock which is depolarized in C_{3v} local symmetry but becomes polarized under C_s local symmetry. Consequently, we have chosen this assignment.[51]

The band at 211 cm^{-1} in CF_3SO_2OCl seems too intense for a CF_3 rock of A'' symmetry under C_s local symmetry and is assigned to the SOCl bend.[50] A band at 212 cm^{-1} with very similar relative intensity is so assigned in FSO_2OCl.[50] Either the band at 184 cm^{-1} or the shoulder at $\sim$198 cm^{-1} must be the CF_3 rock. The shoulder on the Rayleigh line near 90 cm^{-1} must surely be a torsion. Since no evidence for a band assignable to the CF_3 torsion was obtained for CF_3SO_2F or CF_3SO_2OH, we assume the CF_3 torsion is too weak to observe and assign 90 cm^{-1} as the OCl torsion. Although no OCl torsion has been found in FSO_2OCl, an OF torsion is assigned at 137 cm^{-1} in FSO_2OF[3,42]. Since the 184-cm^{-1} band is near twice 90 cm^{-1} and $\Delta\nu = 2$ transitions for torsions may be more prominent than $\Delta\nu = 1$ transitions,[52] we tentatively assign the 184-cm^{-1} band as 2 τ_{OCl}. Then the shoulder near 198 cm^{-1} remains to be assigned to the CF_3 rock of A'' symmetry for local C_s symmetry of the CF_3 group in CF_3SO_2OCl.

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Registry No. CF_3SO_2OCl, 65597-24-2; CF_3SO_2OBr, 70142-16-4; $CF_3SO_2OCF_3$, 3582-05-6; $CF_3SO_2OSO_2OCF_3$, 72214-10-9; CF_3SO_2F, 335-05-7; CF_3SO_2OH, 1493-13-6.

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(51) In CF_3SO_2OCl, coupling could occur among three modes giving bands between 300 and 350 cm^{-1} so the situation could be even more complex than in CF_3SO_2F and CF_3SO_2OH. However, in the absence of further information we prefer to retain our description of $\delta(SCF_3)$ and ν(C–S) with proper qualification of the later[38] as done in CF_3SO_2F and CF_3SO_2OH[43] and list the band at 321 cm^{-1} as a CF_3 rock.

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Infrared and Raman Spectra of Ammonium, Potassium, Rubidium, and Cesium Metavanadates

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The infrared and Raman spectra of five metavanadates, MVO_3 (M = NH_4, ND_4, K, Rb, Cs), have been measured. The observed bands for KVO_3 in the aqueous solution were assigned to the vibrations of the $(VO_3)_n^{n-}$ ionic chain with C_{2v} symmetry. The vibrational assignments to the chain in the crystalline salts were given tentatively by taking into consideration a different arrangement of atoms in the chain from that in aqueous solution. The internal vibrations of the ammonium ions in NH_4VO_3 and ND_4VO_3 at 77 and 100 K were also discussed. The rule of alternative inhibition has been adapted to the librations of the ammonium ions at 77 K.

In the previous paper,[1] the far-infrared spectra of five metavanadates, MVO_3 (M = NH_4, ND_4, K, Rb, Cs), were reported with the discussions concerning the bending vibrations of the VO_3 anion chain, the cation translations, and the NH_4^+ librations. It was suggested that these salts have similar force constants for the translational modes of the cations. According to the X-ray analyses of NH_4VO_3 and KVO_3,[2] the unit cell in a crystal with space group *Pmab*-D_{2h}^{11} contains four MVO_3 molecules including four equivalent cations, and the VO_3 anions constitute a chain arrangement in which the VO_4 groups are tetrahedral. Few vibrational studies for the anion chain are found in the literature.[3,4]

In order to investigate the fundamental vibrations of the anion chain, we measured the infrared and Raman spectra of the powdered salts at room temperature. Since the stereochemical structure of the VO_4 tetrahedral chain in aqueous solution has been assumed to be different from that in crystal,[5] the spectra of the aqueous solution were also examined for KVO_3, which is soluble in water. This paper deals with the assignments for these observed bands. Internal motions and librations of the ammonium ions are also discussed for the spectra of NH_4VO_3 and ND_4VO_3 measured at room and low temperatures.

Experimental Section

The materials measured were NH_4VO_3, ND_4VO_3, KVO_3, $RbVO_3$, and $CsVO_3$, all of which were prepared as previously reported.[1] Infrared spectra were measured with a Perkin-Elmer Model 125

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