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The Protonation of CF_3SO_3H: Preparation and Characterization of Trifluoromethyldihydroxyoxosulfonium Hexafluoridoantimonate, $CF_3SO_3H_2{}^+SbF_6{}^-$

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Dedicated to Prof. Dr. Peter Klüfers on the occasion of his 60th birthday

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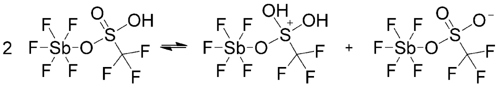
Trifluoromethanesulfonic anhydride reacts with superacidic solutions AF/SbF_5 (A = H, D) to form their corresponding salts $CF_3SO_3A_2{}^+SbF_6{}^-$, which are protonated forms of trifluoromethanesulfonic acid and CF_3SO_2F as by-product. The salts have been characterized by vibrational spectroscopy and single-crystal structural analysis. $CF_3SO_3H_2{}^+SbF_6{}^-$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell: a = 709.29(5) pm, b = 763.46(5) pm, c = 882.15(6) pm; α = 71.884(6)°, β = 72.488(6)°, γ = 84.509(6)°; V = 432.97(5) Å^3. The cations are linked with two strong hydrogen bonds to $SbF_6{}^-$ anions to form chains. The experimental data were also compared to quantum chemical calculations for the $CF_3SO_3H_2(HF)_2{}^+$ cation.

Introduction

Trifluoromethane sulfonic acid (triflic acid) was discovered in 1954 and has been investigated intensively since then.[1] The acid, its salts, and its organic derivatives (commonly known as triflates) are substances with a wide range of applications in organic syntheses and polymerization reactions.[2] Recently it was shown by Schulz et al. that $CF_3SO_3(SiMe_3)_2{}^+B(C_6F_5)_4{}^-$ can be utilized as a silylating agent.[3] Triflic acid is one of the strongest monoprotic organic acids. Its acidity (H_0 = –14.1) is comparable to perchloric acid ($H_0 \approx$ –13), and it is classified as a superacid by definition since its H_0 value is lower than that of concentrated sulfuric acid (H_0 = –12).[4] A study of the molecular structure in the gaseous phase has been implemented and, despite the low melting point (–40 °C) of triflic acid, a single-crystal X-ray structure is known.[5] The self-ionization equilibrium of triflic acid is described by Equation (1).

$$2\,CF_3SO_3H \rightleftharpoons CF_3SO(OH)_2{}^+ + CF_3SO_3{}^- \qquad (1)$$

In this equilibrium, the $CF_3SO_3{}^-$ anion can be bound by strong Lewis acids to form triflates, thereby increasing the concentration of the acidic species. The highest acidities (H_0 = –18.5) have been measured with Lewis acids $B(OSO_2CF_3)_3$ and SbF_5.[4a] Due to the limited solubility of $B(OSO_2CF_3)_3$ in triflic acid, the highest acidity in the triflic system is most likely reached with SbF_5. At high SbF_5 concentrations, the equilibrium described in Equation (2) competes with the one described in Equation (1).[4a]



(2)

Indeed, Mootz et al. described a reaction of triflic acid with SbF_5 that forms an adduct, which has been identified by a single-crystal structure.[6] The acidic cationic species of the triflate superacidic system has not yet been identified.

Results and Discussion

Synthesis and Properties of $CF_3SO_3H_2{}^+SbF_6{}^-$

The salt was prepared in three steps in quantitative yield according to Equations (3), (4), and (5).

$$2\,HF + SbF_5 \xrightarrow{-40\ ^\circ C} H_2F^+SbF_6{}^- \qquad (3)$$

$$(CF_3SO_2)_2O + HF \xrightarrow{-40\ ^\circ C,\ H_2F^+SbF_6^-} CF_3SO_3H + CF_3SO_2F \qquad (4)$$

$$CF_3SO_3H + H_2F^+SbF_6{}^- \xrightarrow{-50\ ^\circ C} CF_3SO(OH)_2{}^+SbF_6{}^- + HF \qquad (5)$$

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In the first step, the superacid was formed to ensure the highest possible concentration of $H_2F^+SbF_6^-$ in an HF solution, see Equation (3). In the second step, triflic anhydride, which is more volatile than CF_3SO_3H and therefore easier to condense quantitatively on a vacuum line, was condensed onto the frozen superacid. During the warm-up process of the reaction mixture, the superacid melted, and then at –40 °C the HF reacted with triflic anhydride to form CF_3SO_2F and CF_3SO_3H, with SbF_5 catalyzing the cleavage. CF_3SO_3H was then protonated according to Equation (5). After removal of the excess amount of HF and CF_3SO_2F at –78 °C, only colorless crystals of $CF_3SO_3H_2^+SbF_6^-$, which were stable up to –50 °C and suitable for single-crystal X-ray structure analysis, remained [Equations (4) and (5)]. Efforts to crystallize the cation as perfluoridoarsenate or perfluoridogermanate salts using superacid systems HF/AsF_5 and HF/GeF_4 were not successful. Clearly, the acidic strength of these systems is not sufficient to protonate triflic acid. The formation of an adduct of CF_3SO_3H with SbF_5, which was observed in the previous work of Mootz et al., was not found in the presence of HF.[6]

Crystal Structure of $CF_3SO_3H_2^+SbF_6^-$

Selected data of the X-ray data collection and refinement are summarized in Table 1. $CF_3SO_3H_2^+SbF_6^-$ crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two formula units in a unit cell. Bond lengths and selected angles are summarized in Table 2. The structure of the $CF_3SO_3H_2^+$ cation and the hydrogen bonds to the nearest fluorine atoms of the anions are shown in Figure 1. Figure 2 shows a section of the crystal structure.

Table 1. Crystal data and structure refinement for $CF_3SO_3H_2^+SbF_6^-$.

Empirical formula	$CH_2F_9O_3SSb$
M_r	386.836
T [K]	100(2)
λ [pm]	71.073
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a [pm]	709.29(5)
b [pm]	763.46(5)
c [pm]	882.15(6)
α [°]	71.884(6)
β [°]	72.488(6)
γ [°]	84.509(6)
V [Å^3]	432.97(5)
Z	2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0144$; $wR_2 = 0.0342$
R indices (all data)	$R_1 = 0.0164$; $wR_2 = 0.0345$
Largest diff. peak/hole [e Å^{-3}]	0.619/–0.526

As expected, the $CF_3SO_3H_2^+$ cation contains one short S=O double bond with a distance of 140.5(2) pm, which is comparable to the S=O bonds of the CF_3SO_3H molecule. The two S–O bonds with lengths of 148.3(2) and 150.5(2) pm are short for a formal single bond but, due to the electron-withdrawing CF_3 group, are in the expected re-

Table 2. Selected bond lengths [pm] and angles [°] for CF_3SO_3H, $CF_3SO_3H_2^+SbF_6^-$, and the calculated $CF_3SO_3H_2(HF)_2^+$.

	CF_3SO_3H obsd.[5b]	$CF_3SO_3H_2^+$ SbF_6^- obsd.	$CF_3SO_3H_2^+$ calcd.[a]	$CF_3SO_3H_2(HF)_2^+$ calcd.[b]
C(1)–S(1)	183.5(4)	185.5(2)	188.8	187.3
S(1)–O(1)	153.4(3)	150.5(2)	153.7	151.2
S(1)–O(2)	142.7(3)	148.3(2)	152.3	151.2
S(1)–O(3)	141.4(4)	140.5(2)	139.8	140.5
C(1)–F(1)	131.6(5)	130.5(2)	130.6	130.4
C(1)–F(2)	131.3(4)	130.7(2)	130.1	130.4
C(1)–F(3)	131.3(5)	132.0(2)	129.5	130.7
O(1)–H(1)	99(9)	84(4)	97.5	100.5
O(2)–H(2)		73(3)	97.5	100.5
O(1)···F(4a)		252.5		254.1
O(2)···F(9b)		242.6		254.1
O(1)–S(1)–C(1)	101.2(2)	102.26(9)	103.8	104.4
O(2)–S(1)–C(1)	105.2(2)	101.1(2)	105.3	104.4
O(3)–S(1)–C(1)	107.4(2)	111.8(2)	113.2	111.0
F(1)–C(1)–S(1)	109.2(3)	109.7(2)	106.7	108.6
F(2)–C(1)–S(1)	109.5(3)	107.5(2)	106.2	106.8
F(3)–C(1)–S(1)	110.2(3)	107.6(2)	107.1	106.8
S(1)–O(1)–H(1)	115(5)	117(3)	114.6	115.3
S(1)–O(2)–H(2)		114(2)	117.3	115.3
O(1)–H(1)···F(4a)		173.09		177.7
O(2)–H(2)···F(9b)		162.84		177.7

[a] Calculated at the PBE1PBE/6-311G(3df,3pd) level of theory. [b] Calculated at the PBE1PBE/6-311++G(3df,3pd) level of theory. Symmetry operations: a: x, y, $z + 1$; b: x, $y + 1$, z.

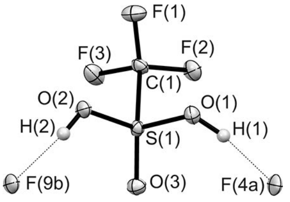

Figure 1. Fragment of the crystal structure of $CF_3SO_3H_2^+SbF_6^-$ showing the $CF_3SO_3H_2^+$ cation with interionic contacts (50% probability ellipsoids for the non-hydrogen atoms). Symmetry operations: a: x, y, $z + 1$; b: x, $y + 1$, z).

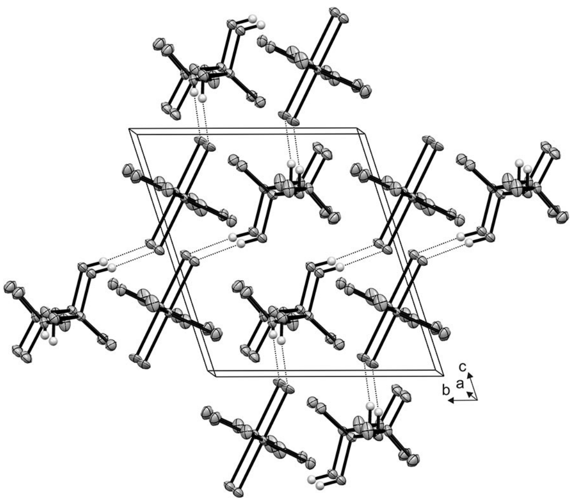

Figure 2. Crystal structure of $CF_3SO_3H_2^+SbF_6^-$ with interionic contacts (50% probability ellipsoids for the non-hydrogen atoms).

gion [*d*(S–O) = 170 pm, *d*(S=O) = 146 pm]. The C–S distance of 185.5(2) pm is only slightly longer than that of unprotonated triflic acid [183.2(3) pm]. Similarly, the CF_3 group of the cation has typical C–F bonds and angles that are almost unaffected by the protonation.

Each cation is connected to two neighboring SbF_6^- anions through strong, almost linear hydrogen bonds with an O···F distance of 242.7(2) and 252.5(2) pm. This linkage leads to $(CF_3SO_3H_2^+SbF_6^-)_n$ chains along the [011] axis. The ideal octahedral structure of the SbF_6^- anion is distorted to a quadratic bipyramid. The Sb–F distances in the equatorial plane are almost identical [185.1(2) to 186.6(2) pm], whereas the *trans*-bridging Sb–F distances are about 6 pm longer [190.6(2) and 192.7(2) pm].

Vibrational Spectra of $CF_3SO_3A_2^+SbF_6^-$ (A = H, D)

The infrared and Raman spectra of $CF_3SO_3H_2^+SbF_6^-$ and $CF_3SO_3D_2^+SbF_6^-$ are shown in Figure 3. The observed frequencies are listed in Table 3, together with the quantum-chemical-calculated frequencies for $CF_3SO_3A_2(HF)_2^+$ (A = H, D). The cation has C_1 symmetry and therefore should exhibit 24 fundamental vibrations. For the assignment of the vibrational spectra, the spectra of triflic acid and the theoretical calculations for $CF_3SO_3A_2(HF)_2^+$ were considered.[7] The 24 internal $CF_3SO_3A_2^+$ vibrations have been selected from the $CF_3SO_3A_2(HF)_2^+$ unit by inspection of the Cartesian displacement coordinates of the vibrational modes (A = H, D).

All spectra show frequencies for the CF_3 group in regions comparable to CF_3SO_3H. The *ν*(OH) band is detected at 3076 cm^{-1} and the *ν*(OD) band at 2162 cm^{-1}. Both frequencies agree well with the calculated values, and the broad band shapes are typical for the OH stretching modes that are involved in hydrogen bonds.[8]

The S=O stretching vibration is observed at nearly constant wavenumbers around 1400 cm^{-1}, which is comparable to that observed for the $H_3SO_4^+$ and $H_2SO_3F^+$ cations.[8,9] This is expected due to the similarity of the cations and the absence of interionic interactions. The two S–O stretching vibrations at 1073 and 956 cm^{-1} are better described as modes between the sulfur atom and the hydroxy group, which itself participates in the S–O–H···F bonds found in the crystal structure. The C–S stretching vibration occurs at a notably low wavenumber of 267 cm^{-1}. This is a lower value than that observed for the triflic acid (312 cm^{-1}). Clearly, the protonation of the triflic acid leads to a weaker C–S bond, which is in accord with the crystallographic results.[5a,7b]

For the SbF_6^- anion with ideal octahedral symmetry, two vibrations in the infrared and three vibrations in the Raman spectra with mutual exclusions are expected. As found in the crystal structure, the SbF_6^- is at least distorted to D_{4h} symmetry for which five vibrations in the infrared and five vibrations in the Raman spectrum with mutual exclusions are expected. This lowered symmetry suffices to explain the number of observed vibrations. However, the infrared spectra have only been measured in the spectral region above 450 cm^{-1}, and therefore only one infrared band at 691 cm^{-1} was detected.

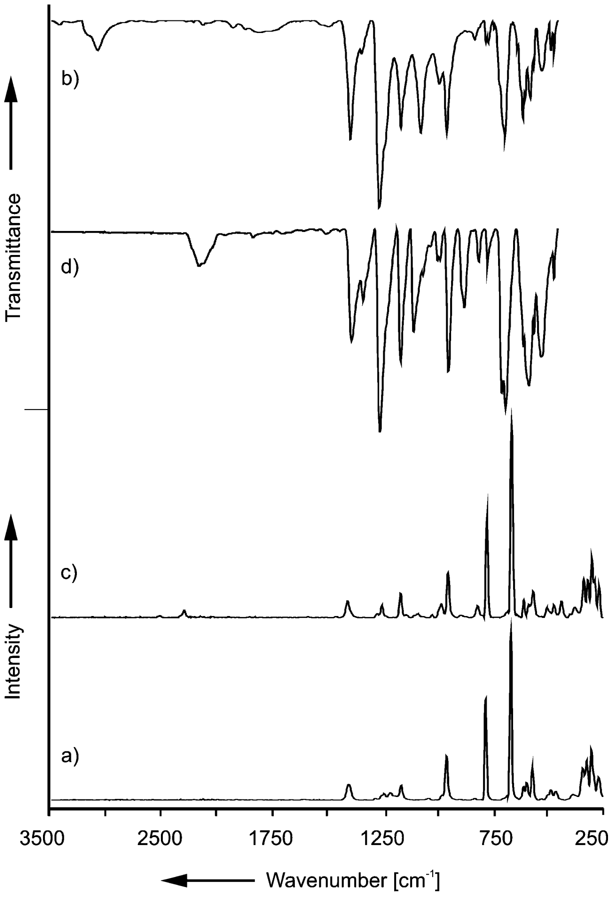

Figure 3. Vibrational spectra of $CF_3SO_3H_2^+SbF_6^-$: (a) Raman spectrum, (b) IR spectrum; and of $CF_3SO_3D_2^+SbF_6^-$: (c) Raman spectrum, (d) IR spectrum.

Theoretical Calculations

The calculation of the gas-phase structure of the free $CF_3SO_3A_2^+$ cation (A = H, D) was performed with the PBE1PBE method using the 6-311G(3df,3pd) basis set. Subsequently, vibrational frequencies in the harmonic approximation as well as IR and Raman intensities were calculated. The calculated geometry of the free cation shows a fair agreement with the one experimentally found in the crystal structure (Table 2), but large differences occur between the calculated and experimental frequencies. The O–H stretching vibrations (ν_s = 3589 and ν_{as} = 3578 cm^{-1}) in particular were overestimated by up to 500 cm^{-1} compared to the experimental data (ν_s = 3076 cm^{-1}). This is due to the strong hydrogen bonds confirmed by the crystal structure, since the formation of hydrogen bonds usually leads to a decrease of the corresponding O–A stretching frequency. To validate this, we added two HF molecules to the free $CF_3SO_3A_2^+$ cation, and this $CF_3SO_3A_2(HF)_2^+$ unit was calculated by the PBE1PBE method using a 6-

Table 3. Experimental vibrational frequencies [cm^{-1}] of $CF_3SO_3A_2^+SbF_6^-$ and calculated vibrational frequencies [cm^{-1}] of $CF_3SO_3A_2(HF)_2^+$ (A = H, D).

$CF_3SO_3H_2^+SbF_6^-$		$CF_3SO_3H_2(HF)_2^+$	$CF_3SO_3D_2^+SbF_6^-$		$CF_3SO_3D_2(HF)_2^+$	Assignment
IR	Raman	calcd.[a]	IR	Raman	calcd.[a]	
3076 w, br.		3059 (302/100)		2295 (10)	2241 (152/100)	ν_s(OA)
		3006 (3793/11)	2162 w, br.	2333 (2)	2192 (1977/11)	ν_{as}(OA)
1392 s	1400 (22)	1421 (205/5)	1389 m	1408 (15)	1420 (184/10)	ν(S=O)
1261 vs		1288 (223/0.1)	1260 vs		1288 (205/1)	$\nu_{as}(CF_3)$
	1239 (7)	1288 (198/1)		1252 (7.4)	1285 (253/0.5)	$\nu_{as}(CF_3)$
		1234 (38/1)		818 (8.6)	887 (73/2)	δ(SOA)
	1211 (10)	1212 (121/1)	813 w		874 (104/0.3)	δ(SOA)
1163 m	1162 (14)	1145 (153/3)	1167 m	1167 (15)	1144 (148/7)	$\nu_s(CF_3)$
1073 m		1029 (311/1)	1108 m		1077 (135/3)	ν_{as}(S–O)
989 w			989 vw	982 (10)		
956 s	957 (41)	959 (252/5)	950 s	952 (25)	955 (238/11)	ν_s(S–O)
777 vw	779 (62)	778 (64/5)	774 w	776 (42)	775 (22/15)	$\delta(CF_3)$
		757 (81/2)	585 s		575 (48/12)	δ(SOA)
		714 (14/0.1)			533 (16/0.1)	δ(SOA)
610 m	607 (10)	593 (143/1)	610 m	609 (7)	591 (170/2)	$\delta(SO_3)$
576 m	567 (20)	560 (5/1)	562 m	566 (14)	563 (1/2)	$\delta(CF_3)$
524 w	525 (0.9)	558 (1/1)	530 m		554 (6/1.0)	$\delta(CF_3)$
483 vw	483 (11)	490 (25/1)	472 w	472 (7)	457 (31/1)	$\delta(SO_3)$
469 w	461 (8)	471 (0.2/1)		438 (10)	445 (6/1)	$\delta(SO_3)$
	338 (34)	329 (3/1)		336 (24)	327 (2/2)	$\delta(SO_3/CF_3)$
	321 (28)	325 (5/1)		318 (22)	323 (6/2)	$\delta(SO_3/CF_3)$
	267 (15)	275 (8/3)		267 (13)	274 (8/5)	ν(C–S)
		173 (2/0.1)			173 (2/0.2)	$\delta(SO_3/CF_3)$
		171 (7/0.01)			169 (7/0.03)	$\delta(SO_3/CF_3)$
		37 (0.01/0.01)			37 (0/0.03)	τ
691 s			691 vs			SbF_6^-
	665 (100)			664 (100)		
	592 (9)			585 (8)		
				504 (8)		
	384 (10)			378 (9)		
	299 (46)			300 (42)		

[a] Calculated at the PBE1PBE/6-311++G(3df,3pd) level of theory. Frequencies are scaled with an empirical factor 0.98. IR intensity in km mol^{-1}. Raman activity is relative to a scale on which the most intense band is 100.

311++G(3df,3pd) basis set. The calculated geometry of the $CF_3SO_3A_2^+$ cation in the $CF_3SO_3A_2(HF)_2^+$ unit is comparable to that found in the crystal structure. The addition of the two HF molecules to the free cation leads only to small changes of the geometric parameters of the cation, but significantly influences of the vibrational modes observed. In particular, the O–H stretching modes of the cation (ν_s = 3059 and ν_{as} = 3006 cm^{-1}) were redshifted, due to the formation of S–O···H···F–H hydrogen bonds into a region that agrees fairly well with the experimental data. Overall, we find a satisfying agreement between the experimentally observed frequencies and those calculated for the $CF_3SO_3A_2(HF)_2^+$ cation, although the $CF_3SO_3A_2(HF)_2^+$ unit represents a very simplified model of the solid state.

Conclusion

The $CF_3SO_3H_2^+$ cation was prepared and identified for the first time. The synthesis was successfully executed through the reaction of $(CF_3SO_2)_2O$ with a superacidic solution of HF/SbF_5, which formed CF_3SO_3H in situ and was instantly protonated. The resulting $CF_3SO_3H_2^+SbF_6^-$ salt was characterized by vibrational spectroscopy and a single-crystal structure analysis. In the solid state, strong hydrogen bonds (O–H···F) between the cation and the fluorine atoms of the anions were observed. Therefore, theoretical calculations of the free $CF_3SO_3A_2^+$ cation did not describe the experimental vibrational spectra sufficiently. To consider the influences of the hydrogen bonds, an $CF_3SO_3H_2(HF)_2^+$ unit was calculated, which contains two hydrogen bonds (O–H···F) between the hydroxy groups of the cation and the fluorine atom of the HF molecules. This simplified model of the solid state led to a sufficient agreement between calculated and experimentally obtained vibrational spectra and geometric parameters.

The formation of $CF_3SO_3H_2^+SbF_6^-$ can be seen as a result of a competitive reaction between CF_3SO_3H/SbF_5 and HF/SbF_5, and it therefore indicates that CF_3SO_3H/SbF_5 is a weaker conjugated Brønsted–Lewis superacid than the HF/SbF_5 system.

Experimental Section

Caution! Avoid contact with any of these compounds and note that HF burns skin and causes irreparable damage. Safety precautions should be taken when using and handling these materials.

Chemicals: Trifluoromethanesulfonic anhydride (99%, ABCR) was used without further purification. SbF_5 (ABCR) was distilled three times through a Vigreux column under a flow of dry nitrogen at atmospheric pressure, then purified by trap-to-trap distillation under vacuum. HF (Linde) was first trap-to-trap-distilled under vacuum and then dried with fluorine for two weeks in a stainless-steel pressure cylinder. DF was prepared from dried CaF_2 and D_2SO_4, distilled under vacuum, and then dried with fluorine for two weeks in a stainless-steel pressure cylinder. D_2SO_4 was obtained by a reaction of D_2O with SO_3, which was trap-to-trap-condensed from oleum (65% SO_3, Merck).

Equipment and Instrumentation: All synthetic work and sample handling was performed by employing standard Schlenk techniques using a stainless-steel vacuum line. Superacid reactions were carried out in FEP ampules, which were sealed at one end and closed with a stainless-steel valve. All reaction vessels as well as the stainless-steel line were dried with fluorine prior to use. Infrared spectra of dry powders were recorded at –100 °C with a Bruker Vertex 80V FTIR spectrometer (3500–450 cm^{-1}). The infrared spectra were obtained using a single-crystal CsBr plate coated with the neat sample in a cooled cell. Raman spectra of the solids in a glass cell cooled with liquid nitrogen were recorded with a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation (λ = 1064 nm, 3500–250 cm^{-1}).

Crystal Structure Determination: X-ray diffraction studies were carried out with an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector (Mo-K_α, λ = 0.71073 Å, graphite monochromator) at 100 K. Single crystals were placed on a glass fiber coated with PFPE oil in a cooled stream of dry nitrogen. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97 and finally checked using PLATON.[10] The absorptions were corrected by a SCALE3 ABSPACK multiscan method.[11] All atoms, including protons, were found in the difference Fourier synthesis and were refined freely. All non-hydrogen atoms were refined anisotropically.

Synthesis of $CF_3SO_3H_2^+SbF_6^-$: In a typical reaction, SbF_5 (1.00 mmol, 220 mg) was condensed into an FEP reactor at –196 °C, followed by the addition of a large excess amount of anhydrous HF (3 mL, SbF_5/HF = 1:300). The mixture was warmed to –40 °C to form the superacid. The vessel was then cooled to –196 °C, and $(CF_3SO_2)_2O$ (1.00 mmol, 282 mg) was condensed onto the frozen superacid. The reaction mixture was warmed up to –60 °C for 5 min, then cooled to –78 °C. The excess amounts of HF and CF_3SO_2F were removed in a dynamic vacuum at –78 °C. The resulting colorless crystals of $CF_3SO_3H_2^+SbF_6^-$ were obtained in quantitative yield (387 mg, 1.00 mmol). The solid is stable below –50 °C and hydrolyzes rapidly upon exposure to moisture. The obtained crystals were suitable for single-crystal X-ray diffraction.

CCDC-782908 (for $CF_3SO_3H_2^+SbF_6^-$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $CF_3SO_3D_2^+SbF_6^-$: $CF_3SO_3D_2^+SbF_6^-$ was prepared in a procedure analogous to $CF_3SO_3H_2^+SbF_6^-$, using DF instead of HF.

Theoretical Calculations: Theoretical calculations were carried out on the free $CF_3SO_3H_2^+$ cation and the $CF_3SO_3H_2(HF)_2^+$ unit using the Gaussian 03 program.[12] The highest level of theory employed for each system was the PBE1PBE density functional approach with a 6-311G(3df,3pd) basis set for $CF_3SO_3H_2^+$ and $CF_3SO_3D_2^+$, and a 6-311++G(3df,3pd) basis set for $CF_3SO_3H_2(HF)_2^+$ and $CF_3SO_3D_2(HF)_2^+$.[13] Structural optimizations were performed using the GDIIS algorithm with tight convergence criteria.[14] Optimized geometries and vibrational frequencies were calculated in each case. The calculation of the $CF_3SO_3H_2(HF)_2^+$ unit was considered to simulate the hydrogen bonds found in the crystal structure of $CF_3SO_3H_2^+SbF_6^-$. The resulting theoretical vibrational modes represent the experimental spectra more closely than that of the free cation.[9]

Supporting Information (see footnote on the first page of this article): Computational details.

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