Synthesis and Characterization of the Mercaptosulfonium Cation, $HSSH_2^+$

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The synthesis of the first known mercaptosulfonium salts $H_3S_2^+AsF_6^-$, $H_3S_2^+SbF_6^-$, and $D_3S_2^+AsF_6^-$ is reported. The salts were prepared by protonation of H_2S_2 in the superacidic systems HF−AsF_5, HF−SbF_5, and DF−AsF_5, respectively. The solids decomposed at 213 K under formation of sulfur and H_3S^+ salts. The mercaptosulfonium salts are characterized by vibrational spectra. An ab initio and a general valence force field were calculated for the $H_3S_2^+$ cation. The calculations give a conformation with the S−H bond antiperiplanar to the lone pair of SH_2^+.

Introduction

The solution of AsF_5 and SbF_5 in HF belong to the strongest acid.[1] The superacidic systems have been used successfully for the protonation of very weak bases like H_2Se,[2] H_3As,[3] H_3Sb,[3] H_4P_2,[4] H_2O_2.[5] The known cations of hydrides with two basic centers are given in Chart 1. The $H_5N_2^+$ cation is a weak acid ($pK_A = 6.1$) but its basicity ($pK_B = 15.1$) is sufficient for a protonation to the $H_6N_2^{2+}$ cation.[6,7] In case of Diphosphan, the basicity is much lower and the protonation give the monocation which is only stable in solution.[4] Though H_2O_2 is in water a weak acid ($pK_A = 11.6$), stable peroxonium salts were prepared by Christie in the systems HF−AsF_5 and HF−SbF_5.[5] Analogous reactions with homologous H_2S_2, which is expected to be a weaker base, have not been studied yet.

Chart 1. Cations of Hydrides with Two Basic Centers

H_3N^+-NH_2 H_3N^+-$^+NH_3$	H_2O^+-OH
H_3P^+-PH_2	H_2S^+-SH

The thermodynamically unstable disulfane decompose very easy to H_2S and sulfur. The decomposition is catalyzed by traces of bases. Therefore the disulfane requires special conditions in preparation and handling.

Experimental Section

All synthetic work and sample handling were performed by employing standard Schlenk techniques and a standard vacuum line (stainless steel or glass, respectively). The glass vacuum line and the reaction vessels have been treated with concentrated hydrochloric acid and dried by vacuum. H_2S_2 was obtained by distillation of crude polysulfane.[9] AsF_5 and SbF_5 (Merck) were fractionally distilled. DF was prepared from D_2SO_4 and CaF_2.[10] DF and HF were dried with fluorine.

Infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra of dry powders were obtained between CsBr plates. The Raman spectra were recorded on a Coderg T800 using an Ar^+ laser tube (514.5 nm) from Spectra Physics. The spectra were recorded in a glass tube cooled with liquid nitrogen.

Preparation of $H_3S_2^+AsF_6^-$ and $H_3S_2^+SbF_6^-$. In a 30 mL KEL-F reactor, 220 mg (1 mmol) of SbF_5 or 170 mg (1 mmol) of AsF_5, respectively, was dissolved in 2 g of HF. The solution was frozen at 77 K and layered with HF (0.5 g). H_2S_2 (1 mmol) was condensed into the reaction mixture, and it was slowly warmed to 213 K. The mercaptosulfonium salt precipitated as a colorless solid on thawing. Excess of HF was removed under a dynamic vacuum at 213 K. The colorless mercaptosulfonium salts are not soluble in HF. The decomposition takes place at 233 K.

Preparation of $D_3S_2^+AsF_6^-$. An amount of 0.5 mmol of H_2S_2 was stirred with 2 g of DF. The mixture was frozen at 77 K and layered with 1 g of DF. AsF_5 (0.6 mmol) was condensed into the reaction mixture, and it was slowly warmed to 213 K. Further isolation was carried out as described above. A deuteration grade of 99% was obtained by this method.

Results and Discussion

Synthesis and Properties. The disulfane reacts with HF-MF_5 during the melting process of the mixture (−80 °C) almost

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Table 1. Vibrational Spectra (cm^{-1}) of $H_3S_2^+AsF_6^-$, $D_3S_2^+AsF_6^-$, $H_3S_2^+SbF_6^-$, H_2S_2, and Their Assignments

$H_3S_2^+AsF_6^-$		$D_3S_2^+AsF_6^-$		$H_3S_2^+SbF_6^-$	H_2S_2	
Raman	IR	Raman	IR	Raman	Raman	assignment[a]
	2531 m		1846 s		2495(30)	ν(SX)
2495(38)	2496 m	1826(35)	1819 s	2494(42)	2477(47)	ν(SX)
1182(1)	1189 w		851 w	1185(1)		$\delta(SX_2)$
	905 w		680 sh			δ(SSX)
865(25)		630(26)	620 sh	864(22)	884(5)	δ(SSX)
	817 w				870(2)	δ(SSX)
492(100)	491 w			492(100)	505(100)	ν(SS)
474(95)	470 mw	482(100)	480 w	474(90)		ν(SS)
247(9)	251 s	223(24)	231 m	250(14)	237(8)	τ
200(24)	202 m	198(19)	206 mw	196(9)	128(76)	lattice
159(16)		166(34)		161(12)	57(5)	lattice
	713 vs		711 vs			$\nu_3(MF_6^-)$
692(6)		691(4)		655(6)		$\nu_1(MF_6^-)$
580(2)				572(2)		$\nu_2(MF_6^-)$
	388 vs		388 vs			$\nu_4(MF_6^-)$
377(3)		377(2)		280(3)		$\nu_5(MF_6^-)$

[a] X = H, D.

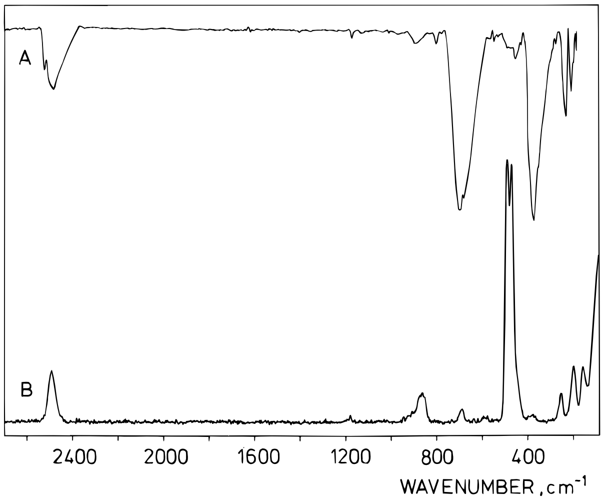

Figure 1. Vibrational spectra of $H_3S_2^+AsF_6^-$: trace A, infrared spectrum of the solid as a dry powder between CsBr plates recorded at −110 °C; trace B, Raman spectrum of the solid in a glass tube recorded at −196 °C.

quantitatively under formation of a colorless precipitate. According to the elemental analysis only a single protonation of the disulfane took place (reaction 1).

$$H_2S_2 + HF + MF_5 \rightarrow H_3S_2^+MF_6^- \qquad (M = As, Sb) \qquad (1)$$

The SbF_6^- salt is stable below −40 °C; the AsF_6^- salt, below −45 °C. The decomposition is similar to that of $H_3O_2^+$ (reaction 2). Both mercaptosulfonium salts decompose under formation of sulfur and SH_3^+ salts (reaction 3).

$$H_3O_2^+MF_6^- \rightarrow H_3O^+MF_6^- + {}^1/_2O_2 \qquad (M = As, Sb) \qquad (2)$$

$$H_3S_2^+MF_6^- \rightarrow H_3S^+MF_6^- + {}^1/_8S_8 \qquad (M = As, Sb) \qquad (3)$$

The mercaptosulfonium salts are not soluble in HF and in polar solvents like SO_2 and SO_2ClF a decomposition was observed. Because of the absence of a suitable solvent NMR spectra could not be obtained. Also the preparation of single crystals from the microcrystalline salts was not possible. Therefore more detailed vibrational studies of the mercaptosulfonium salts were carried out.

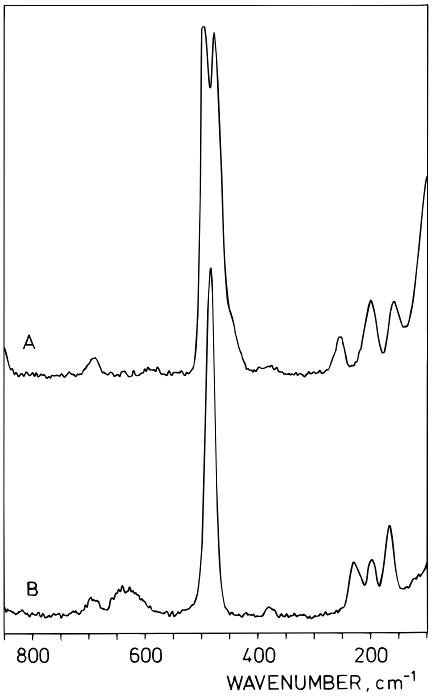

Figure 2. Vibrational spectra; trace A, Raman spectrum of $H_3S_2^+AsF_6^-$; trace B, Raman spectrum of $D_3S_2^+AsF_6^-$.

Vibrational Spectra. The infrared and Raman spectrum of $H_3S_2^+AsF_6^-$ is shown in Figure 1 and the observed frequencies are summarized in Table 1. The Raman spectra of $H_3S_2^+AsF_6^-$ and $D_3S_2^+AsF_6^-$ are shown in Figure 2. The assignments for $H_3S_2^+$ were made by comparison with similar compounds, since vibrational spectra of the isoelectronic compounds like H_2PSH, and H_2PPH^-, respectively, are not known.[1,11] An ab initio investigation which is discussed later give in accordance to the isoelectronic H_2PSH a structure of symmetry C_s. Consequently, nine fundamentals (6A′ + 3A) are expected for $H_3S_2^+$. These fundamentals should all be active in both the infrared and the Raman spectra. The observed and calculated frequencies of the $H_3S_2^+$ cation are summarized in Table 2.

Three hydrogen−sulfur stretching modes are expected in the region at 2500 cm^{-1}. The infrared spectrum shows a broad band at 2496 cm^{-1} split on the high-frequency side (2531 cm^{-1}). The sharp side band belongs to the −SH mode of H_2SSH^+.

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Table 2. Experimental and Calculated Vibrational Spectra[a] and Potential Energy Distribution[b] of the $H_3S_2^+$ Cation

$H_3S_2^+$			$D_3S_2^+$			assignment	
obsd	calcd	PED	obsd	calcd	PED		c
2531	2544	100 S_3	1846	1828	100 S_3	$\nu_3(A')$	$\nu(SX)$
2531	2543	100 S_7	1846	1829	100 S_7	$\nu_7(A'')$	$\nu(SX)$
2495	2511	100 S_2	1823	1799	100 S_2	$\nu_{2(A')}$	$\nu(SX')$
1185	1187	61 S_4 + 22 S_6 + 16 S_5	851	848	60 S_4 + 22 S_6 + 17 S_5	$\nu_4(A')$	$\delta(SX_{2})$
905	916	71 S_6 + 25 S_4	680	664	70 S_6 + 29 S_4	$\nu_6(A')$	$\delta(SSX')$
865	867	99 S_8	625	623	99 S_8	$\nu_8(A'')$	$\delta(SSX)$
817	829	76 S_5 + 24 S_4	625	607	79 S_5 + 20 S_4	$\nu_5(A')$	$\delta(SSX)$
482	483	92 S_1	481	480	92 S_1	$\nu_1(A')$	$\nu(SS)$
249	249	79 S_9 + 21 S_8	223	179	79 S_9 + 21 S_8	$\nu_9(A'')$	$\tau(XSSX')$

[a] Frequencies in cm^{-1}. [b] Percent contributions. Contribution of less than 10% to the PED are not listed. S_n are the symmetry coordinates, which represents the pure character of the corresponding vibrations ν_n. [c] X = H, D.

The broad part belongs to the symmetric and antisymmetric $-SH_2$ modes which are not resolved, because of the small difference in frequencies. In the Raman spectrum only one broad line was observed at 2495 cm^{-1}. A significant resolution of the stretching modes was not detectable.

Five deformation modes are expected for $H_3S_2^+$. The $-SH_2$ scissoring mode occurs in both the infrared (1189 cm^{-1}) and Raman spectrum (1182 cm^{-1}) as a weak band and line, respectively. The SSH deformation modes are usually weak and occur at 905 and 817 cm^{-1}. The Raman spectrum shows at this region a broad band. Such a band is observed in mercaptosulfonium salts and polysulfanes.[13,14] The torsional mode is expected to occur in the frequency region below 300 cm^{-1}. The line at 247 cm^{-1} has been assigned as the torsional mode and the residue lines as lattice vibrations. In comparison to the deutereted cation $D_3S_2^+$ this line shows the expected isotope shift to lower frequencies.

In the region of sulfur-sulfur stretching modes two very intense lines are observed instead of one. The unexpected two lines with almost equal intensity are caused by Fermi resonance of the sulfur-sulfur stretching mode ($(492 + 474)/2 = 483$ cm^{-1}) with the first torsional overtone ($2 \times 247 = 494$ cm^{-1}). Deuteration of the cation has almost no influence on the sulfur-sulfur stretching mode, but causes an isotope shift to the torsional mode. Consequently, the energy difference between the first overtone ($2 \times 223 = 446$ cm^{-1}) of the torsional mode and the sulfur-sulfur stretching mode (482 cm^{-1}) is to high for Fermi resonance and only one line is observed for the sulfur-sulfur stretching mode in $D_3S_2^+$ (Figure 2).

For the AsF_6^- anion two infrared and three Raman active modes are observed in agreement with an octahedral geometry.

Table 3. Force Constants[a] and Geometric Parameters[b] of $H_3S_2^+$, H_2S_2, H_2S, H_3S^+, $S(SH)_3^+$, H_2SF^+

	$H_3S_2^+$	H_2S_2[c]	H_2S[d]	H_3S^+[e]	$S(SH)_3^+$[f]	H_2SF^+[g]
f(SS)	2.438	2.766			2.29	
f(SH′)	3.722					
f(SH)	3.676	4.066	3.95	3.655	3.61	3.521
f(SH/SH)	−0.030	−0.003	−0.02	−0.001		−0.063
r(SS)	210.8	206.1			217.1	
r(SH)	133.8	134.2	133.6	134.1	135.4	134.0
r(SH′)	133.7					
∠(SH_{2})	95.80		92.12	95.71		95.1
∠(SSH)	100.34	97.51			91.5	
∠(SSH′)	92.48					

[a] Stretching constants in N/cm and stretch−bend interactions in N/cm rad. [b] Bond distances in pm and angles in degrees. [c] Data from ref 21. [d] Data from ref 22. [e] Data from ref 23. [f] Data from ref 19. [g] Data from ref 20.

Table 4. General Valence Force Field Matrix F_{ij} of the $H_3S_2^+$ Cation

	j								
i	1	2	3	4	5	6	7	8	9
1	2.438	0.032	−0.020	−0.002	0.365	0.253			
2		3.646	−0.005	−0.083	−0.004	0.013			
3			3.722	−0.003	−0.012	−0.045			
4				0.385	0.080	0.134			
5					0.782	0.108			
6						0.999			
7							3.706	0.060	−0.004
8								0.751	0.069
9									0.028

Ab Initio Calculations and Force Field. For the ion $S_2H_3^+$ ab initio calculations had been performed using the force method.[15−17] A 43-21G basis set with an additional d function (exponent 0.8)[18] was used for the sulfur atoms, which had proved to give good results for other similar compounds.[19,20] A periplanar syn and anti form was assumed, giving both potential minima, with the anti form of slightly lower energy. Bond distances are almost identical for both forms, only the SSH bond angles are slightly larger for the syn form (∠SSH 108.09°, ∠SSH′ 96.35°) than for the anti form because of repulsive effects between the H atoms. The anti form was adopted for further treatment. As Table 3 shows, bond distances and angles for $S_2H_3^+$ are almost the same as for similar molecules and ions. Compared with H_2S_2[21] a lengthening of the SS bond is observed, but not to the extent found for $S(SH)_3^+$.[19]

The ab initio calculated force field was iterated to fit the experimental frequencies. The mean value of the Fermi resonance splitting of ν_{SS} in $S_2H_3^+$ was used for the calculation. To get a good fit, F_{45}, F_{46}, and F_{56} connecting the strongly coupled SH deformational modes had to be iterated along with the diagonal terms. Table 4 shows the symmetry constant matrix obtained. The calculated frequency values and the main contributions to the potential energy distribution are given in Table 2. The calculated frequencies for the SH vibrations show the expected deviations from the experimental data due to anharmonicity effects. The SSH′ torsional mode was calculated as 227 cm^{-1} (163 cm^{-1} for the deuterium compound) for the free ion. Increase of the frequency (and perhaps also the

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decrease of the isotopic shift) might be caused by the impediment of this motion in the crystal filed.

Comparison of the valence force constants for $S_2H_3^+$ with values of similar molecules and ions show (Table 3) a decrease of $f_{(SS)}$ compared with H_2S_2, according to the difference of the bond distance. As for other cations, the $f_{(SH)}$ values are somewhat smaller than for the uncharged molecules (without a correlated significant change of bond lengths). This might be caused by a higher polarity of the SH bonds in the cations. The SH/SH coupling constant shows the usual small negative value.

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