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PAPER

AsS₂Cl—an Arsenic(v) Compound? Formation, Stability and Structure of gaseous AsSCl and AsS₂Cl—a combined experimental and theoretical study†

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By reaction of solid As_4S_4 with gaseous Cl_2 at a temperature of 410 K gaseous AsSCl and AsS₂Cl are formed. Unexpectedly in AsS₂Cl the arsenic is not of formal oxidation state +V but +III: the molecular structure of AsS₂Cl is arranged as a 1-chloro-dithia-arsirane and comprises an hitherto unknown AsS_2 three-membered ring. Thermodynamic data on AsSCl and AsS₂Cl are obtained by mass spectrometry (MS). The experimental data are extended and confirmed by *ab initio* quantum chemical calculations (QC). The following values are given: $\Delta_f H^0_{298}(AsSCl) = -5.2$ kJ mol^{-1} (MS), $\Delta_f H^0_{298}(AsSCl) = 1.7$ kJ mol^{-1} (QC), $S^0_{298}(AsSCl) = 296.9$ J K^{-1} mol^{-1} (QC) and $c_p^0{}_T(AsSCl) = 55.77 + 3.97 \times 10^{-3}\,T - 4.38 \times 10^5\,T^{-2} - 1.83 \times 10^{-6}\,T^2$ and $\Delta_f H^0_{298}(AsS_2Cl) = -39.0$ kJ mol^{-1} (MS), $\Delta_f H^0_{298}(AsS_2Cl) = -20.2$ kJ mol^{-1} (QC), $S^0_{298}(AsS_2Cl) = 321.3$ J K^{-1} mol^{-1} (QC) and $c_p^0{}_T(AsS_2Cl) = 80.05 + 5.09 \times 10^{-3}\,T - 7.61 \times 10^5\,T^{-2} - 2.35 \times 10^{-6}\,T^2$ (298.15 K $< T <$ 1000 K) (QC). The ionization energies are determined (IP(AsSCl) = 10.5, IP(AsS₂Cl) = 10.2 eV). The IR spectrum of AsSCl is detected by means of matrix isolation spectroscopy. The estimated force constant f(As=S) = 4.47 mdyn·Å^{-1} gives rise to an As=S double bond.

1 Introduction

We have investigated the reaction of arsenic sulphides with halogens by means of mass spectrometry. In accordance with ref. 1 we found $AsCl_3$ and S_2Cl_2 to be the main reaction products. But the mass spectra showed that in addition to these two, up to now unknown gaseous sulphide halides AsSCl and AsS₂Cl are formed. The existence of AsSCl could be expected in principle as analogous gaseous molecules like AsOCl and PSCl have been described earlier.[2] Absolutely unexpected is, however, AsS₂Cl. At first sight this molecule seems to be an arsenic(v)-compound. Due to the well known instability of simple arsenic(v)-compounds like $AsCl_5$ [3] or As_2O_5 [4] and the tendency of sulfur to form stable sulfur/sulfur-bonds we have been in doubt about the speculation of AsS₂Cl to be an arsenic(v)-compound.

Here we report mass spectrometric and infrared spectroscopic results, the determination of thermodynamic data by means of experimental and theoretical methods and the structures of AsSCl and AsS₂Cl.

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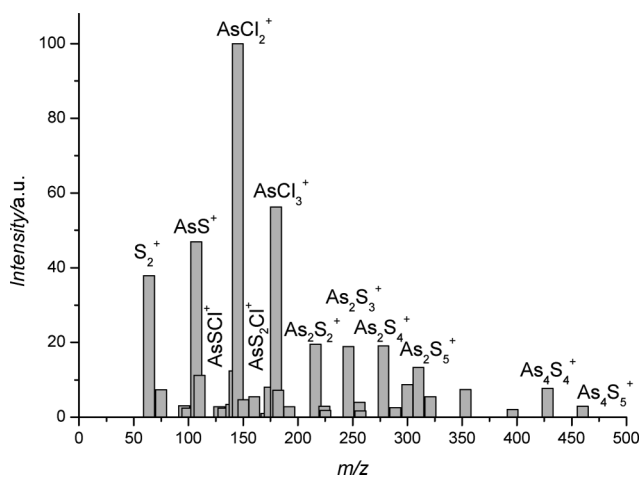† Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

2 Results and discussion

2.1 Experimental part

2.1.1 Mass spectrometry. In a first experiment, As_2S_3 was placed in a double Knudsen cell and a stream of chlorine originated by thermal decomposition of $CuCl_2$ passed over it ($T = 513$ K). The molecular beam leaving the Knudsen cell was analyzed using a mass spectrometer (electron impact ionisation). Ions were identified by the observed m/z values and isotopic patterns. They were consistent with the theoretically expected values (m/z and intensities). The following mass spectrum ($m/z > 50$) has been observed (intensities in brackets, Fig. 1):

As$^+$(7.3), S$_3$$^+$(3), S$_2Cl^+$(2.4), AsS$^+$(46.9), AsCl$^+$(11.2), S$_4$$^+$(2.8), S$_2Cl_2$$^+$(2.4), AsS$_2$$^+$(3.4), AsSCl$^+$(12.4), AsCl$_2$$^+$(100), As$_2$$^+$(4.7), S$_5$$^+$(5.5), AsS$_3$$^+$(1), AsS$_2Cl^+$(8), AsCl$_3$$^+$(56.3), As$_2S^+$(7.2), S$_6$$^+$(2.8), As$_2S_2$$^+$(19.5), S$_7$$^+$(2.9), As$_3$$^+$(1.8), As$_2S_3$$^+$(18.9), S$_8$$^+$(4), As$_3S^+$(1.7), As$_2S_4$$^+$(19.1), As$_3S_2$$^+$(2.5), As$_4$$^+$(8.7), As$_2S_5$$^+$(13.3), As$_3S_3$$^+$(5.5), As$_3S_4$$^+$(7.4), As$_4S_3$$^+$(2.1), As$_4S_4$$^+$(7.7), As$_4S_5$$^+$(2.9).

The spectrum shows several As$_x$S$_y$$^+$-ions due to the evaporation of As_2S_3 and fragmentation during electron impact. The exact decomposition of As_2S_3 is complicated and remains unresolved until now. Besides these $AsCl_3$, S_2Cl_2, AsSCl and AsS₂Cl and several sulfur-species ($S_2 \ldots S_8$) are formed. After electron impact the novel gas species AsSCl and AsS₂Cl form the parent ions AsSCl$^+$ and AsS₂Cl$^+$. Expected fragments like AsS$^+$ and As$^+$ (parent neutral AsSCl), AsS$_2$$^+$, AsS$^+$ and As$^+$ (parent neutral AsS₂Cl) cannot be distinguished from fragments of other As/S-species. Therefore it is impossible to specify the exact amount

Fig. 1 Mass spectrum obtained after the reaction of As_2S_3 with Cl_2.

of these species in the gas phase. Approximately, the partial pressures of AsSCl and AsS_2Cl are about 10% compared to the most abundant species $AsCl_3$. In a second experiment we followed the reaction between As_4S_4 and Cl_2. The evaporation behaviour of As_4S_4 is not as complicated as that of As_2S_3. As_4S_4 evaporates predominantly congruently. Besides gaseous As_4S_4-molecules only small amounts of other species are formed during the evaporation process.[5] Therefore this system is perfectly suitable for a quantitative evaluation of the gas phase composition in order to derive approximate values for the heats of formation of AsSCl and AsS_2Cl.

Within a Knudsen cell solid As_4S_4 reacts with chlorine as described above. The reaction products are detected by means of mass spectrometry. At 453 K the following mass spectrum was obtained (intensities in brackets, Fig. 2 and 3).
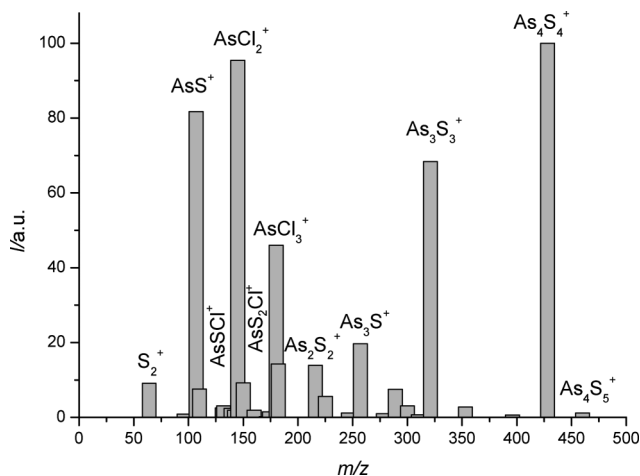

Fig. 2 Mass spectrum obtained after the reaction of As_4S_4 with Cl_2.

S_2^+(9.1), As^+(6.4), S_3^+(0.9), S_2Cl^+(2.5), AsS^+(81.7), $AsCl^+$(7.6), $S_2Cl_2^+$(3.1), AsS_2^+(2.4), $AsSCl^+$(1.9), $AsCl_2^+$(95.4), As_2^+(9.2), S_5^+(1.9), AsS_3^+(0.2), AsS_2Cl^+(1.5), $AsCl_3^+$(46), As_2S^+(14.3), $As_2S_2^+$(13.9), As_3^+(5.6), $As_2S_3^+$(1.2), As_3S^+(19.7), $As_2S_4^+$(1), $As_3S_2^+$(7.5), As_4^+(3.1), $As_2S_5^+$(0.7), $As_3S_3^+$(68.4), $As_3S_4^+$(2.8), $As_4S_3^+$(0.6), $As_4S_4^+$(100), $As_4S_5^+$(1.2).
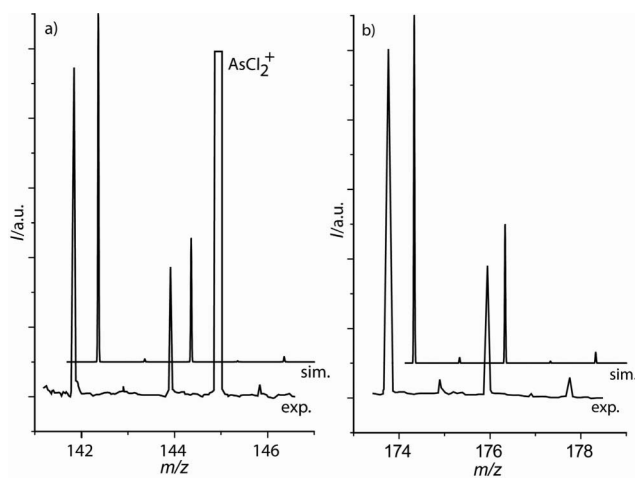

Fig. 3 Ion signals (experimental and simulated) in the mass spectrum after the reaction of As_4S_4 with Cl_2 associated to a) AsSCl and b) AsS_2Cl.

The attribution of ions to neutral molecules is not unambiguous in all cases. So the origin of As^+ is unclear, as this ion may be a fragment of all arsenic containing molecules. To minimize errors, As^+ has not been considered in the following evaluation of thermodynamic data. In accordance with literature data[5] and our experience in this field we have assigned the ions to neutral molecules as given in Table 1. During the reaction of As_4S_4 with Cl_2 the following gaseous compounds are formed: S_x, S_2Cl_2, As_4, $AsCl_3$, AsSCl and AsS_2Cl. AsSCl and AsS_2Cl are up to now unknown gaseous molecules.

With the help of appearance potential (AP) measurements (using the threshold technique) the ionization energies (IP) of AsSCl and AsS_2Cl were determined (IP(AsSCl) = 10.5 eV; IP(AsS_2Cl) = 10.2 eV; limit of error ±0.5 eV). By comparison with quantum chemically calculated values (*i*) we ensure that the ions $AsSCl^+$ and AsS_2Cl^+ were directly formed by ionization of the neutral molecules. Appearance potentials of ions obtained by fragmentation of parent ions are expected to be several eV higher. (*ii*) Comparison of calculated ionization potentials of different isomers with experimental values can further substantiate the structure of the molecules under discussion.

The intention of this work is the characterization of these reactive high temperature molecules that are not accessible by standard chemical procedures. The thermodynamic data are

Table 1 Results of the mass spectrometric analysis of the reaction of As_4S_4 with Cl_2

Molecule	Ion(s)	ΣI_i	p/bar
S_2	S_2^+	9.1	5.1×10^{-8}
S_3	S_3^+	0.9	5.0×10^{-9}
S_5	S_5^+	1.9	1.1×10^{-8}
S_2Cl_2	S_2Cl^+, $S_2Cl_2^+$	5.6	3.1×10^{-8}
As_4	As_2^+, As_3^+, As_4^+	27.9	1.6×10^{-7}
As_4S_4	AsS^+, AsS_2^+, As_2S^+, $As_2S_2^+$, $As_2S_3^+$, As_3S^+, $As_2S_4^+$, $As_3S_2^+$, $As_3S_3^+$, $As_3S_4^+$, $As_4S_3^+$, $As_4S_4^+$	313.7	1.8×10^{-6}
As_4S_6	$As_4S_5^+$	1.2	6.7×10^{-9}
$AsCl_3$	$AsCl^+$, $AsCl_2^+$, $AsCl_3^+$	149	8.3×10^{-7}
AsSCl	$AsSCl^+$	>1.9	$>1.1 \times 10^{-8}$
AsS_2Cl	AsS_2Cl^+	>1.5	$>8.4 \times 10^{-9}$

determined both by means of experimental (Knudsen cell) and theoretical methods (*ab initio* calculations).

Evaluation of data. The sum of the intensities ΣI_i of all ions formed by ionisation and fragmentation processes from a neutral molecule is related to the partial pressure p_i by eqn (1).

$$p_i = c \frac{\Sigma I_i \cdot T}{\sigma_i \cdot S_i} \qquad (1)$$

c = calibration factor/bar K^{-1}
$T = T$/K
σ_i = ionisation cross section
S_i = multiplier gain for a specific ion

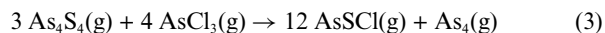Because σ_i and S_i are usually not known the approximate eqn (2) is used in most cases.

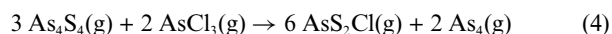$$p_i = c \cdot \Sigma I_i \cdot T \qquad (2)$$

The partial pressure of As$_4$S$_4$ within the Knudsen cell is defined by the evaporation equilibrium. The vapour pressure is given by the equation $\lg p(\text{As}_4\text{S}_4)/1\ \text{bar} = 8.470 - 6445/T$.[5] We use the measured value of $\Sigma I(\text{As}_4\text{S}_4)$, the vapour pressure at 453 K (1.75×10^{-6} bar) in order to determine the calibration factor c.

$$c = 1.23 \times 10^{-11}\ \text{bar} \cdot \text{K}^{-1}$$

Using this value the vapour pressures, as given in Table 1, were calculated. In order to determine the heats of formation of the unknown molecules AsSCl and AsS$_2$Cl, we calculated the equilibrium constants for the following equilibria

$$3\ \text{As}_4\text{S}_4(g) + 4\ \text{AsCl}_3(g) \rightarrow 12\ \text{AsSCl}(g) + \text{As}_4(g) \qquad (3)$$

$$K_p(3) = 1.23 \times 10^{-61}\ \text{bar}^6$$

$$3\ \text{As}_4\text{S}_4(g) + 2\ \text{AsCl}_3(g) \rightarrow 6\ \text{AsS}_2\text{Cl}(g) + 2\ \text{As}_4(g) \qquad (4)$$

$$K_p(4) = 2.26 \times 10^{-33}\ \text{bar}^3$$

The equilibrium constant is related to the reaction enthalpy, reaction entropy and temperature by the van't Hoff-equation:

$$\ln K = -\frac{\Delta_r H^0}{R \cdot T} + \frac{\Delta_r S^0}{R} \qquad (5)$$

$$\Delta_r H^0 = -R \cdot T \cdot \ln K + T \cdot \Delta_r S^0$$

The re-evaluation of the thermodynamic data of As$_4$S$_4$ was necessary due to inconsistencies in the literature. Britzke has determined the heat of formation of arsenic sulphides by means of combustion calorimetry.[6] A heat of formation of a compound with the formula As$_2$S$_2$ is given in this paper to be −121 kJ mol^{-1}. Today we know the formula As$_2$S$_2$ to be wrong, the correct formula has to be written as As$_4$S$_4$ due to the tetrameric nature of this 1:1 compound. Therefore the heat of formation based on the value given by Britzke is −2·121 kJ mol^{-1}. Unfortunately the factor of 2 has obviously not been considered even in the tabular compilation of Barin.[7] He gives a value of −142.3 kJ mol^{-1} for As$_2$S$_2$, whatever this is, −138.1 kJ mol^{-1} for the mineral realgar and −134.7 kJ mol^{-1} for As$_4$S$_4$, probably β-As$_4$S$_4$, three similar values for compounds with quite different numbers of atoms. Britzke reports the products of the combustion reaction to be As$_2$O$_3$, As$_2$O$_5$, As$_2$O$_4$·As$_2$O$_5$, SO$_3$ and As$_2$O$_3$·SO$_3$. This means that the reaction within the calorimeter is rather complicated and it seems to be almost impossible to derive correct values for the heat of formation of As$_4$S$_4$. In our opinion the oxygen combustion calorimetry seems to be an unsuitable method in this case. This holds for a paper of Johnson too.[8] O'Hare published a value of −127.5 ±5.3 kJ mol^{-1} for the heat of formation of β-As$_4$S$_4$ derived from fluorine combustion calorimetry.[9] The very experienced group of Kleppa showed that values derived from fluorine combustion experiments may be in error.[9] He gives a value of −117.6 ±1.6 kJ mol^{-1} for α-As$_4$S$_4$ derived from direct-synthesis calorimetry. In our opinion this value seems to be the best one and we take this for our evaluation. In combination with the heat of sublimation of α-As$_4$S$_4$, $\Delta_f H^0(\text{As}_4\text{S}_4)$ = 132.2 ±8.4 kJ mol^{-1} given by Hildenbrand,[11] we calculate a heat of formation of gaseous As$_4$S$_4$ of $\Delta_f H^0(\text{As}_4\text{S}_{4,g})$ = 14.6 ±10 kJ mol^{-1}.

Using help from the entropy data of As$_4$S$_4$(g), AsCl$_3$(g) and As$_4$(g) given in the literature,[12] the calculated value of AsSCl(g) (Table 2) and the K_p-value given above one calculates a heat of reaction $\Delta_r H^0(3)$ = 1091.2 kJ mol^{-1} and from this a heat of formation $\Delta_f H^0(\text{AsSCl})$ = −5.2 kJ mol^{-1} (as of the reaction temperature is not far from room temperature the heat capacities have not been taken into account, the error resulting from this approximation is negligible).

In the same way the heat of reaction $\Delta_r H^0(4)$ = 589.7 kJ mol^{-1} and from this a heat of formation $\Delta_f H^0(\text{AsS}_2\text{Cl})$ = −39.0 kJ mol^{-1} is calculated. We assume the error of these values to be ± 20 kJ mol^{-1} due to uncertainties in the determination of partial pressures, entropies and temperature measurement.

2.1.2 Matrix Isolation Infrared spectroscopy. To gain further insight into the molecular structures of AsSCl and AsS$_2$Cl we

Table 2 Thermodynamic data obtained by experimental and theoretical methods

Compound	$\Delta_f H^0_{298}$/kJ mol^{-1} (exp.//theory)	S^0_{298}/J mol^{-1} K^{-1} (exp.//theory)	$C^0_{p,T} = a + b \cdot 10^{-3} \cdot T + c \cdot 10^5 \cdot T^{-2} + d \cdot 10^{-6} \cdot T^2$				Ionization energy/eV (exp.//theory)
			a	b	c	d	
As$_4$S$_4$(g)	14.4[10,11]//−26.1	446.1[12]//445.7	178.69	6.95	−17.44	−3.20	
AsCl$_3$(g)	−261.5[12]//−267.6	327.3[12]//325.2[a]					10.55[27]//10.79[a]
As$_4$(g)	153.3[12]//-	327.4[12]//325.4[a]					
AsSCl(g)	−5.2[a]//1.7[a]	—//296.9[a]	55.77	3.97	−4.38	−1.83	10.5[a]//10.04[a]
AsS$_2$Cl(g)	−39.0[a]//−20.2[a]	—//321.3[a]	80.05	5.09	−7.61	−2.35	10.2[a]//10.75[a]

[a] this work.

condensed the gaseous reaction products of As_2S_3 as well as of As_4S_4 with Cl_2 together with a huge surplus of argon onto a copper mirror cooled to 10 K and recorded the matrix isolation IR spectra. In this special system the interpretation of the spectra is presumably very tedious as (*i*) the stretching vibrations of the As–S and of the As–Cl bonds are both expected in the small range around 380 ± 20 cm^{-1}, (*ii*) the expected intensities will be small and (*iii*) the bands will be broad as isotopic splitting related to $^{32/34}$S or $^{35/37}$Cl is not expected to be resolvable. Despite these difficulties we followed the high temperature reactions by matrix isolation infrared spectroscopy to gain structural information. In such a case *ab initio* frequency calculations provide valuable support to interpret the obtained experimental IR spectra.

Matrix IR spectra of the gas phase over As_4S_4 and As_2S_3

As only limited knowledge is available on the gas phase composition over solid As_2S_3 and As_4S_4, we recorded in advance their hitherto unknown matrix isolation IR spectra. As_4S_4 is vaporized congruently at about 410 K. The IR absorptions of this molecule (symmetry D_{2d}) are observed at 385 (representation b_2), 355 (e) and 230 cm^{-1} (e) (Table 3, Fig. 4). After heating solid As_2S_3 to 510 K a

Table 3 Theoretical IR spectra (RI-MP2, def2-QZVPP) of AsCl$_3$, AsSCl, AsS$_2$Cl, As$_4$S$_4$ and As$_4$S$_6$

Symmetry	ν(calc.)/cm^{-1}	Int.(calc.)/km mol^{-1}	ν(exp. [this work])/cm^{-1}
AsCl$_3$ (C$_{3v}$)			
e	156.21	1	
a$_1$	200.35	3	
e	413.02	190	390 (vs)
a$_1$	437.32	21	415 (m)
AsSCl (C$_s$)			
a'	181.17	2	
a'	383.82	103	365 (m)
a'	577.86	28	552 (m)
AsS$_2$Cl (1-chloro-dithia-arsirane, C$_s$)			
a''	150.85	1	
a'	163.54	1	
a''	363.89	8	
a'	373.66	21	
a'	409.05	69	
a'	550.83	9	
As$_4$S$_4$ (D$_{2d}$)			
a$_2$	107.13	0	
b$_1$	147.35	0	
e	169.48	3	
b$_2$	188.24	1	
a$_1$	195.29	0	
e	223.06	2	
a$_1$	229.80	0	
b$_2$	233.89	4	230 (w)
a$_2$	354.12	0	
e	369.76	41	355 (s)
b$_1$	383.11	0	
a$_1$	398.12	0	
b$_2$	400.19	14	385 (m)
e	408.07	0	
As$_4$S$_6$ (T_d)			
t$_1$	102.87	0	
e	115.73	0	
t$_2$	146.92	2	
a$_1$	250.40	0	
t$_2$	336.03	2	334.3 (m)(?)
e	348.62	0	
t$_1$	354.94	0	
a$_1$	355.59	0	
t$_2$	426.26	160	396 (vs)

Table 4 Structural data, total energies, thermal energies and entropies of the calculated molecules

Molecule[a]	E_{tot}(MP2)/a.u.[b]	$E^{therm.}{}_{298}$/kJ mol^{-1}	$S^0{}_{298}$/J mol^{-1} K^{-1}
As$_4$	−8939.254609	24.37	325.4
Cl$_2$	−919.429335	10.13	222.8
S$_2$	−795.449964	10.82	219.2
AsCl$_3$	−3614.074942	25.13	325.2
As$_4$S$_4$	−10530.32397	59.26	445.7
As$_4$S$_6$	−11325.81092	75.9	499.4
AsSCl	−3092.291706	17.13	296.9
AsS$_2$Cl (C$_s$)	−3490.047682	25.86	327.1
AsS$_2$Cl (C$_{2v}$)	−3490.023737	26.45	324.2
SAsSCl (cis)	−3490.014429	26.05	334.8

[a] Structural data: AsCl$_3$: r(As–Cl) = 214.8 pm, <(Cl–As–Cl) = 98.8°; As$_4$S$_4$: r(As–S) = 220.3, r(As–As) = 254.3, r(S–S) = 324.6 pm, <(As–S–As) = 101.3°; As$_4$S$_6$: r(As–S) = 221.9 pm, <(S–As–As) = 115.3°; AsSCl: r(As–S) = 201.1, r(As–Cl) = 218.3 pm, <(S–As–Cl) = 107.4°; AsS$_2$Cl (C$_s$): r(S–S) = 211.0, r(As–Cl) = 216.4, r(As–S) = 220.2 pm, <(Cl–As–S) = 102.9°; ClAsS$_2$ (C$_{2v}$): r(As–Cl) = 213.2, r(As=S) = 200.2 pm, <(S–As–S) = 135.5°; S=As–S–Cl (cis): r(As=S) = 201.9, r(As–S) = 222.7, r(Cl–S) = 199.7 pm, <(S=As–S) = 106.8, <(Cl–S–As) = 105.1°; [b] 1.a.u. = 2625.5 kJ mol^{-1}
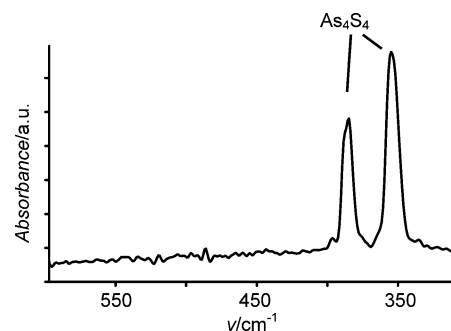

Fig. 4 Argon matrix IR spectrum obtained after passing argon over As_4S_4 heated to 410 K.

single highly intense absorption is found at 396.1 cm^{-1} (Fig. 5). In different experiments no further signal with an identical intensity ratio to this band is measured. Despite the lack of structural information on the primary vaporization product of As_2S_3 we assume that this signal may be attributable to the highly symmetric species As_4S_6 (symmetry T_d). This assumption is strengthened by theoretical frequency calculations on this species (v.i.) although its molecular peak was not detectable by mass spectrometry—presumably due to its spontaneous fragmentation after electron
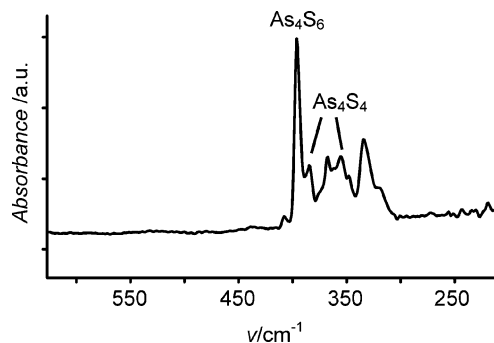

Fig. 5 Argon matrix IR spectrum obtained after passing argon over As_2S_3 heated to 510 K.

impact.[14] Further absorptions found at 384.4 and 355.5 cm^{-1} are attributed to the decomposition product As$_4$S$_4$.

The origin of signals at 334.3 cm^{-1} and 368.0 cm^{-1} remains unclear. By comparison of the experimental with the theoretical IR spectra of As$_4$S$_6$ and As$_4$S$_4$ (v.i., Fig. 6) we estimate the amount of As$_4$S$_6$ in the gas phase over solid As$_2$S$_3$ to be less than 50%.
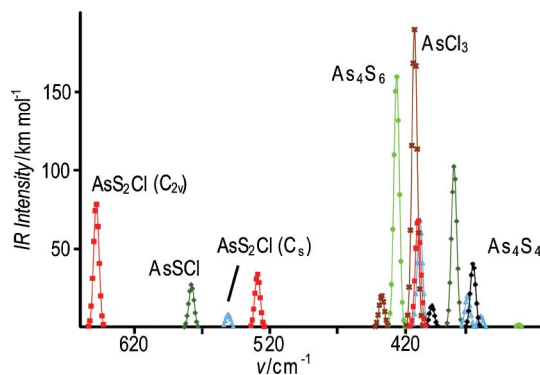

Fig. 6 Comparison of the calculated IR spectra of AsCl$_3$, AsSCl, AsS$_2$Cl (C_s), AsS$_2$Cl (C_{2v}), As$_4$S$_4$ and As$_4$S$_6$ (equal amounts).

Reaction of As$_2$S$_3$ with Cl$_2$

From the analysis of the high temperature mass spectrometric experiments only a minor amount of the gas phase is expected to be due to AsSCl and AsS$_2$Cl. This is especially true for the reaction of As$_4$S$_4$ with Cl$_2$ we performed at 410 K, so that this reaction is inappropriate for the analysis by matrix isolation spectroscopy. This expected behavior was found in several test experiments. Therefore we investigated intensively the reaction of As$_2$S$_3$ with Cl$_2$ at a temperature of 510 K. The advantage of the higher reaction temperature is unfortunately accompanied by a certain amount of byproducts related to the decomposition of As$_2$S$_3$ as proven before by mass spectrometry and IR spectroscopy.

After passing a mixture of Cl$_2$ in argon (0.5 to 2% Cl$_2$/Ar) over solid As$_2$S$_3$ at 510 K signals associated to As$_4$S$_6$ and its decomposition products are observed in the matrix IR spectrum. Two further absorptions at 552.8 and 367.1 cm^{-1} can be attributed to a single species due to their constant intensity ratio in different experiments (Fig. 7). By comparison with the stretching vibration of Ge=S (575.8 cm^{-1}),[15] which is isoelectronic to As=S$^+$ as well as with the AsCl stretching mode in O=AsCl (378.7 cm^{-1}),[15] and due to our knowledge from the mass spectrometric investigation these signals are attributed to the stretching motions of AsSCl (symmetry C$_s$). Theoretical calculations substantiate this assignment (v.i.). Depending on the concentration of Cl$_2$ in argon we recorded spectra representing mixtures of AsSCl together with AsCl$_3$ or with As$_4$S$_6$, respectively (Fig. 7).

For a C_{2v} symmetric molecule AsS$_2$Cl with the realization of two As=S double bonds normal modes between 670 and 560 cm^{-1} (of symmetric and anti-symmetric nature) are expected. We found no hints for such a molecule in the matrix IR spectra. For a possible isomer comprising a S$_2$As three-membered ring intense stretching vibrations are expected to overlap with strong absorptions related to As$_4$S$_6$, As$_4$S$_4$ and AsCl$_3$ (between 396 und 385 cm^{-1}). Furthermore the IR intensity of the S–S stretching mode of this molecule is calculated to be only 1/3 of the intensity
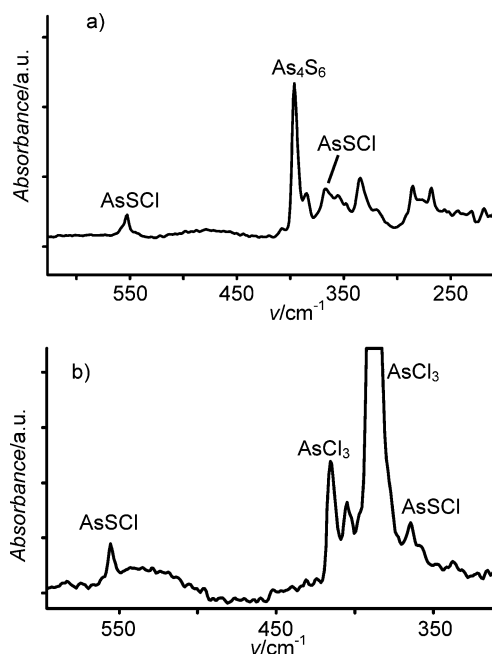

Fig. 7 Argon matrix IR spectrum obtained after passing a mixture of chlorine and argon over As$_2$S$_3$ heated to 510 K: (a) 0.5%, (b) 2% Cl$_2$/Ar.

of the As=S stretching mode of AsSCl. As the amount of AsS$_2$Cl is determined to be less than that of AsSCl (MS, Table 1), it is not unexpected that we were not able to detect hints on this species by IR spectroscopy (AsSCl: calc.: 578 cm^{-1} (int. 28 km mol^{-1}), obs.: 552 cm^{-1}; AsS$_2$Cl: calc. 551 cm^{-1} (int. 9 km mol^{-1}), expected close to 525 cm^{-1}; (Table 3, v.i.)).

2.2 Quantum chemical calculations

To confirm and extend the experimentally deduced values (heat of formation, entropy, structure, vibrational spectrum) on AsSCl and AsS$_2$Cl quantum chemical calculations were performed (Table 3, Fig. 8 and 9). The geometries, energies and IR spectra of the
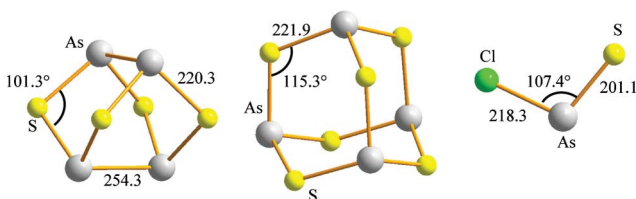

Fig. 8 Molecular structures of As$_4$S$_4$, As$_4$S$_6$ and AsSCl (RI-MP2, def2-QZVPP, distances (pm), angles (°)).
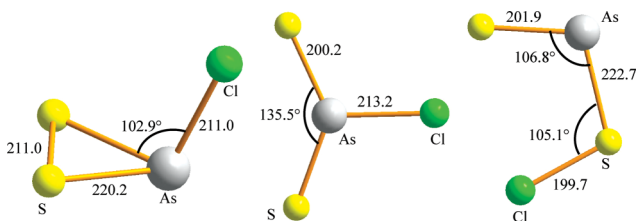

Fig. 9 Molecular structures of the isomers of AsS$_2$Cl (RI-MP2, def2-QZVPP, distances (pm), angles (°)).

molecules under discussion were computed on the RI-MP2 level using basis sets of def2-QZVPP quality. Ionization energies were obtained as differences of total energies of the neutral and the cationic species calculated on the RI-CC2 level by means of the RI-MP2 geometry (Franck–Condon principle).

AsCl$_3$ served as a test molecule to check the accuracy of the theoretical method. The calculated parameters chosen for comparison with experimental data (MS, IR) were thermodynamic values of $\Delta_f H^0_{298}$, S^0_{298} and ionization potentials as well as vibrational frequencies. The electronic structure of AsCl$_3$ was determined under C_{3v}-symmetry. The calculated and the experimental matrix IR spectra agree nicely (exp.: 415 (repr. a$_1$), 390 (e); calc. 437.3 (a$_1$), 413.0 (e) cm^{-1}). Therefore we estimate the stretching modes of the molecules under discussion calculated on this level of theory to be usually about 20 cm^{-1} too high. The theoretical value of the standard heat of formation of AsCl$_3$ was obtained by means of the theoretical investigation of the following reaction:

$$1/4 \ As_4(g) + 3/2 \ Cl_2(g) \rightarrow AsCl_3(g) \qquad (6)$$
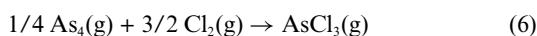
After determination of the theoretical harmonic vibrational frequencies thermal energies and entropies were derived using standard expressions of statistical thermodynamic. The standard heat of formation $\Delta_f H^0_{298}$(AsCl$_3$, calc.) was calculated taking into account the theoretically computed reaction enthalpy $\Delta_r H^0_{298}$(6, calc.) = −306.0 kJ mol^{-1} (difference of the electronic energies corrected by zero point and thermal energies, Table 1) and the well known experimental values for the heat of formation of As$_4$:

$$\Delta_f H^0_{298}(AsCl_3, \ calc.) = -\Delta_r H^0_{298}(6, \ calc.) +$$
$$1/4 \Delta_f H^0_{298}(As_4, \ exp.^{12})$$

By means of this procedure the following theoretical thermodynamic values of AsCl$_3$ are obtained:

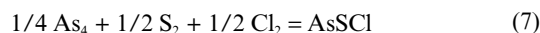$$\Delta_f H^0_{298}(AsCl_3 \ (MP2)) = -267.6 \ kJ \cdot mol^{-1}$$

and

$$S^0_{298}(AsCl_3 \ (MP2)) = 325.2 \ J \cdot K^{-1} \cdot mol^{-1}$$

$\Delta_f H^0_{298}$(AsCl$_3$ (MP2)) deviates only 6.1 kJ mol^{-1} from the experimental value (exp. −261.5 kJ mol^{-1}, Table 2). From this test calculation we estimate the uncertainty of $\Delta_f H^0_{298}$ to be less than 20 kJ mol^{-1}. The quantum chemically calculated ionization energy of AsCl$_3$ agrees well with the experimental value (exp. 10.55,[27] calc. 10.79 eV).

Due to the complicated vaporization behaviour of solid As$_4$S$_4$ and As$_2$S$_3$, the structures and the theoretical IR spectra of gaseous As$_4$S$_4$ and As$_4$S$_6$ as valuable support for the interpretation of the experimental-hitherto unknown-argon matrix IR spectra were calculated. The electronic structure of As$_4$S$_4$ was determined under D_{2d}-symmetry. This is in line with the solid state structure of realgar, the molecular crystal structure of As$_4$S$_4$. The calculated IR active stretching modes at 400 and 370 cm^{-1} are in perfect agreement with the experimental data (385, 355 cm^{-1}, Table 3). Under the assumption of As$_4$S$_6$ to be of T_d symmetry with an analogous shape to that of As$_4$O$_6$, the calculated IR spectrum agrees very well with a single intense signal obtained after the vaporization of As$_2$S$_3$ (exp. 396, calc. 426 cm^{-1}).

The structure of the molecule AsSCl is expected to be of C$_s$ symmetry. The isomer comprising an As–Cl single and a As=S double bond is found to be the one of lowest energy. The heat of formation is calculated by means of the reaction

$$1/4 \ As_4 + 1/2 \ S_2 + 1/2 \ Cl_2 = AsSCl \qquad (7)$$

$$\Delta_f H^0_{298}(AsSCl, MP2) = -\Delta_r H^0_{298}(7, \ calc.) +$$
$$1/4\Delta_f H^0_{298}(As_4, \ exp.^{12}) + 1/2\Delta_f H^0_{298}(S_2, \ exp.^{12})$$

From the reaction enthalpy $\Delta_r H^0_{298}$(7, calc.) = −100.9 kJ mol^{-1} the heat of formation is determined to be $\Delta_f H^0_{298}$(AsSCl, MP2) = +1.7 kJ mol^{-1} which is in perfect agreement with the experimental value (−5.2 kJ mol^{-1}). Within the error limits the experimentally deduced ionization energy of AsSCl (10.5 eV) agrees with the calculated value (10.04 eV) (Table 2) confirming that the ion AsSCl$^+$ was formed by direct ionization of the AsSCl molecule and not by fragmentation of a different parent ion. The calculated vibrational spectrum (Table 3, Fig. 6) is nicely confirmed by the observed As=S- and As–Cl-stretching vibrations found in the matrix IR spectrum. S^0_{298}(AsSCl, MP2) is calculated to be 296.9 J mol^{-1} K^{-1}.

For the molecule AsS$_2$Cl several structural isomers (Fig. 9) are conceivable: (i) a C_{2v} symmetric structure realizing arsenic(v) including two As=S double and a As–Cl bond, (ii) S=As–S–Cl as cis and trans isomers, and (iii) 1-chloro-dithia-arsirane with arsenic(iii), a S$_2$As three-membered ring and an As–Cl bond.

All these isomers represent true minima on the potential hypersurface; their heats of formation are calculated exploring the theoretical reaction

$$AsSCl + 1/2 \ S_2 = AsS_2Cl \qquad (8)$$

taking into account differences of electronic, zero point and thermal energies. This type of reaction is particularly suitable for the solution of our problem as the value for the heat of formation of the starting molecule AsSCl is determined in the same set of experiments.

$$\Delta_f H^0_{298}(AsS_2Cl, \ calc.) = -\Delta_r H^0_{298}(8, \ calc.)$$
$$+ \Delta_f H^0_{298}(AsSCl, \ exp.[this \ work]) + \frac{1}{2}\Delta_f H^0_{298}(S_2, \ exp.^{12})$$

We find that the chloro-dithia-arsirane is the most stable isomer: from the reaction enthalpy $\Delta_r H^0_{298}$(8, calc.) = −79.3 kJ mol^{-1} $\Delta_f H^0_{298}$(AsS$_2$Cl, MP2) is determined to be −20.2 kJ mol^{-1} which is in satisfying agreement with the experimental value (−39.0 kJ mol^{-1}). The C_{2v} symmetric isomer with arsenic(v) and the C_s isomer S=As–S–Cl (cis) are disfavored by 63.5 and 87.5 kJ mol^{-1}. Due to these large discrepancies isomers other than the cyclic dithia-arsirane can definitively be ruled out as reaction product. The experimental ionization energy of AsS$_2$Cl (10.2 eV, Table 2) confirms the calculated value for the most stable isomer (10.75, AsS$_2$Cl (C_s): 9.44, AsS$_2$Cl (C_{2v}): 9.94 eV).

Due to the lack of sufficient vibrational data a normal coordinate analysis on AsSCl is not possible. But as a first estimate of the bond strength in the molecules described here for the first time, we calculated the theoretical internal force constants by transformation of the cartesian force constant matrices into

the internal coordinate system. The diagonal force constants of the molecule AsSCl are calculated to be f(As=S) = 4.47, f(As–Cl) = 2.09 and d(S=As–Cl) = 3.56 mdyn·Å^{-1}. The diagonal force constant values of the most stable isomer of AsS$_2$Cl are f(As–Cl) = 2.40, f(As–S) = 2.18, f(S–S) = 2.36 and d(S–As–Cl) = 3.35 mdyn·Å^{-1}.

2.3 Conclusion

Molecular sulphide halides of arsenic were observed for the very first time. By means of high temperature mass spectrometry the chemical equilibria of As$_4$S$_4$ and Cl$_2$ with AsSCl as well as with AsS$_2$Cl were investigated. The heats of formation and ionization energies of both species were determined and compared to results of high level *ab initio* calculations. The calculated thermodynamic values perfectly confirm the formation of AsSCl but completely disagree with the formation of a C_{2v} symmetric arsenic(v) compound AsS$_2$Cl comprising two As=S double bonds by more than 80 kJ mol^{-1}. Actually sound agreement is found for the most stable isomer 1-chloro-arsirane with arsenic of the formal oxidation state III. To the best of our knowledge AsS$_2$Cl is the first example of a species with a S$_2$As three-membered ring. Obviously As–S (p–p)π-bonding in the system AsS$_2$ is less stable than the realisation of two As–S and a S–S single bond leading to arsenic +III instead of +V. By means of matrix isolation IR spectroscopy the As=S- and AsCl-stretching modes of AsSCl were detected. Theoretical frequency calculations confirm the experimental findings. Signals attributable to the molecule AsS$_2$Cl were not detected due to the very low intensity of the ν(S–S) and overlapping of ν(As–S) and ν(As–Cl) with those of AsCl$_3$, As$_4$S$_6$ and As$_4$S$_4$. Comparison of the As–S stretching force constants is in line with the expectation of a double bond in AsSCl and two single bonds in AsS$_2$Cl.

3 Experimental

The mass spectrometric measurements were performed with a modified mass spectrometer MAT 212 (Finnigan MAT). The gas phase molecules were ionized by electron impact. The reaction of As$_4$S$_4$ with Cl$_2$ was conducted in a double Knudsen cell. In the front part of the Knudsen cell As$_4$S$_4$ was heated to 453 K, in the back part solid copper(II)-chloride that decomposed to copper(I)-chloride served as Cl$_2$ source. The experimental setup was described elsewhere.[13] As$_4$S$_4$ and As$_2$S$_3$ were synthesized by reaction of elemental arsenic (Riedel de Haen) and sulfur (Merck) in a quartz ampoule at 513 K. The products were sublimed in a temperature gradient from 513 to 473 K. Their quality was tested by powder X-ray diffractometry.

The matrix IR spectrum of AsSCl was obtained by passing a mixture of 0.5 to 2% Cl$_2$/Ar over As$_2$S$_3$ (T = 510 K). The gas phase was condensed onto a polished copper mirror cooled to 10 K by means of a closed cycle helium cryostat (Leybold). The IR spectrum was taken with a FT-IR spectrometer Bruker IFS 113v (mylar beamsplitter, DTGS detector, CsI windows, resolution 1 cm^{-1}) with the help of a reflection unit.

The quantum chemical calculations of the geometries and energies of the molecules under discussion were performed on the RI-MP2 level[17] (basis sets of def2-QZVPP quality [18–21]). All the calculations entailed the use of the TURBOMOLE

package.[22] MP2 frequencies were obtained by diagonalization of the numerically computed Hessian using the module NumForce. The values of the force constants in the system of internal coordinates were obtained after transformation of the cartesian force constant matrix into the system of symmetry adapted internal coordinates using the program code FCT.[23] The high quality of this theoretical procedure for the confirmation of experimental thermodynamic data has been proven before.[24] The molecule's temperature dependent molar heat capacity, entropy, internal energy and its zero point energy were calculated using procedures of statistical thermodynamics (module FREEH). The temperature dependence of the heat capacity $c_p^0{}_T$ is expressed by the following polynome:

$$c_p^0{}_T = a + b\ 10^{-3}\ T + c\ 10^5\ T^{-2} + d\ 10^{-6}\ T^2$$
$$(298.15\ \mathrm{K} < T < 1000\ \mathrm{K})$$

The coefficients were calculated by the mathematical program package MAPLE [25] choosing four values of $c_p^0{}_T$ (T = 298.15, 532.1, 766.05, 1000 K) as given from the FREEH module of the TURBOMOLE package. Accurate values for the heat of formation and the entropy at different temperatures can be obtained using Kirchhoff's law.

Ionization potentials were calculated according to the Franck–Condon principle as differences of the total energies of the neutral and the cationic species on the approximate coupled cluster model RI-CC2[26] using the RI-MP2 geometry of the neutral species.

Acknowledgements

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