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H_2S-CIMS: Theoretical calculations of the energies and structures of secondary ions in the ion source

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Abstract

For the first time, a study has been made of H_2S as a reactant gas in positive-ion chemical-ionization mass spectrometry. To this end, the mass spectrum of an H_2S plasma was recorded, and the energies and structures of the ions were examined.

The most stable structures of the plasma ions H_3S^+, S_2^+, $H_2S_2^+$, $H_3S_2^+$, $[H_2S\cdots H_3S]^+$, $H_2S_3^+$, $H_3S_4^+$ and HS_n^+ were obtained by the ab initio G3B3 method, in which the G3 method is extended with B3LYP/6-31G(*d*). Of the three isomers of $H_2S_3^+$, the C_{2V} structure, with terminal hydrogen atoms, proved to be the lowest energy. The structure of the adduct $[H_2S\cdots H_3S]^+$ was found to be comparable with that of the water adduct $[H_2O\cdots H_3O]^+$. An enthalpy of $-59.9\,\mathrm{kJ\,mol^{-1}}$ was calculated for the reaction $H_3S^+ + H_2S \rightarrow [H_2S\cdots H_3S]^+$ and the exothermic reaction enthalpies of the polysulfonium ions, formed according to the equation $HS_n^+ + S \rightarrow HS_{n+1}^+$, lie in the range 225–347 $\mathrm{kJ\,mol^{-1}}$ for $n = 1$–8.

Keywords: H_2S plasma; Chemical-ionization mass spectrometry; Ab initio; G3B3

1. Introduction

Methane, isobutane and ammonia are frequently used for soft ionization in chemical-ionization mass spectrometry (CIMS) [1]. Only when these gases fail to achieve the desired goal are alternative reactant gases considered.

The CI gas is chosen to have proton affinities (PA) lower than those of the analytes, so as to guarantee protonation. Therefore, it is important thereby that the PA difference between the reactant gas and the analyte is not too great, otherwise, as for example with isobutane ($\mathrm{PA} = 677.8\,\mathrm{kJ\,mol^{-1}}$), there is too much fragmentation of the analyte [2]. On the other hand, the very soft gas ammonia ($\mathrm{PA} = 853.6\,\mathrm{kJ\,mol^{-1}}$) is likely to lead to the formation of $[M + NH_4]^+$ ions instead of $[M + H]^+$ ions [3].

H_2S could be an alternative here. Its PA, $705.0\,\mathrm{kJ\,mol^{-1}}$, lies between those of isobutane and ammonia, so that fewer adducts should be formed than with the latter gas [4]. The toxicity of H_2S and its reactivity toward the steels, of which most ion sources are made, argue against this compound [5,6]. However, the gaseous state and relatively small molecular size, however, argue for H_2S.

Since chemical ionization with H_2S is still an unknown area, this article describes an experimental CI plasma of H_2S and offers an interpretation by means of theoretical calculations.

2. Experimental

An usual gas chromatograph/mass spectrometer (GC/MS) was used for the study of the ions in the H_2S CI plasma, a GC HP6890 being coupled over an interface with an MS HP5973 MSD. The interface was held at a temperature of 240 °C, the ion source at 200 °C and the quadrupole at 106 °C. For the regulation of the CI gas, the mass-flow controller (MFC) was adjusted to $1.0\,\mathrm{ml\,min^{-1}}$ (20% of the calibration flow recommended by the manufacturer for N_2). This resulted in a gas pressure of 22.7 Pa in the ion source and 13.3 mPa at the

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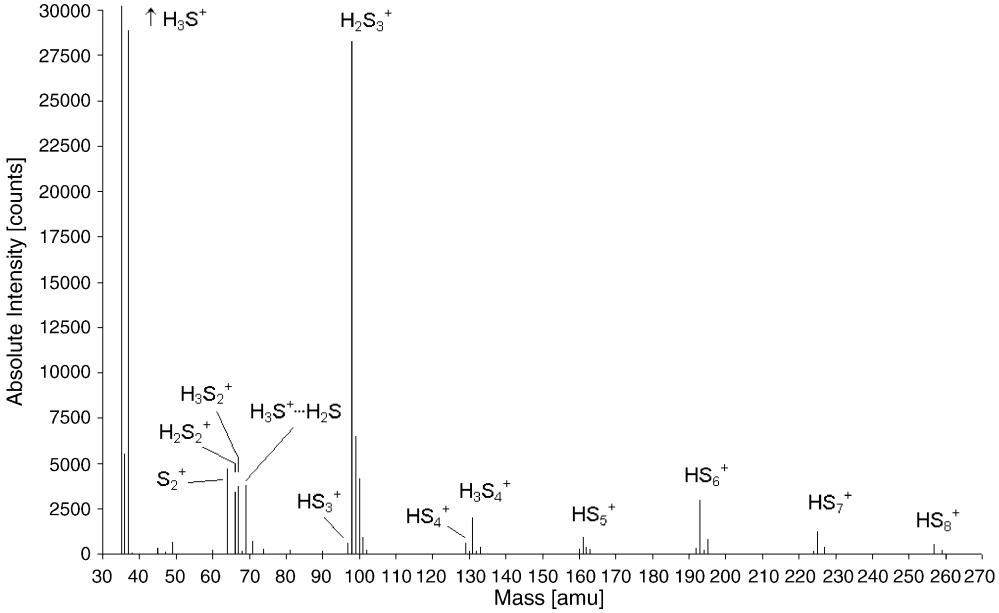

Fig. 1. Ions of the H_2S plasma. The base peak H_3S^+ is about 20 times as intense as depicted.

detector (electron multiplier). All temperatures and pressures are standard values and recommended by the manufacturer. A cylinder of H_2S gas (Merck, synthesis quality) was connected via a needle valve at the CI gas inlet directly with the CI-MFC of the mass spectrometer, and the pressure was set at 1 bar. In the CI ion source, a low-pressure plasma (22.7 Pa; 473.15 K, housing and plasma temperature) is always established. The ionized gas in the ion source is a plasma, i.e., it consists of free-moving neutral molecules, atoms, cations and electrons. The housing of the ion source is open to the MS side and to the filament, so that H_2S and electrons (70 eV) must be supplied constantly. When the system had equilibrated, the mass spectrum of the H_2S plasma was recorded and examined (Fig. 1).

The mass spectrum of the H_2S plasma is shown in Fig. 1. No peaks were observed with masses lower than 32 *m*/*z*. The signal groups appearing at a regular interval of 32 amu can be interpreted as the sulfonium cations $H_xS_n{}^+$. Like the H_3S^+ ion, the $H_2S_3{}^+$ ion has great stability in the CI plasma. Theoretical calculations were carried out to clarify possible reaction paths indicated by the mass spectrum. Some assumptions had to be made in order to explain the generation of the most important ions. The following primary reactions (electron ionization, EI) are expected to occur in the CI of H_2S [7].

$$H_2S + e^- \rightarrow H_2S^+ + 2e^- \quad (+1009.6\,\mathrm{kJ\,mol^{-1}}) \tag{1}$$

$$H_2S + e^- \rightarrow HS^+ + 2e^- + H \quad (+1390.3\,\mathrm{kJ\,mol^{-1}}) \tag{2}$$

$$H_2S + e^- \rightarrow S^+ + 2e^- + H_2 \quad (+1284.1\,\mathrm{kJ\,mol^{-1}}) \tag{3}$$

The primary ions H_2S^+, HS^+ and S^+ were not detectable under the CI conditions prevailing in the source. A series of reactions can be assumed to explain the secondary ions. The following are involved as educts and products:

$$H_2S,\ H_2S^+,\ HS^+,\ S^+ \rightarrow\ H_3S^+,\ S_2{}^+,\ H_2S_2{}^+,\ H_3S_2{}^+,$$
$$[H_2S\cdots H_3S]^+,\ H_2S_3{}^+,\ H_3S_4{}^+,\ HS_n{}^+$$

3. Computational method

The ab initio molecular-orbital calculations were carried out by the Gaussian-3-Becke's three-parameter functional (G3B3) method [8], a modification of the G3 method [9], which is a part of the GAUSSIAN 03 program package [10]. The G3B3 method differs from the G3 method in two modifications. The equilibrium geometry and the zero-point energy are obtained at the B3LYP/6-31G(*d*) level, and the zero-point energy is scaled by 0.96 to provide reliable thermodynamic data. The outstanding ability of these methods to reproduce the thermodynamic properties of small molecules is well established [11,12].

4. Structures

The structures of all the sulfonium ions found in the mass spectrum (Fig. 1) were calculated by the B3LYP/6-31G(*d*) theory used in G3B3. All structures are found by a systematic screening of the potential energy surface (PES). The larger molecules ($HS_n{}^+$, $n > 6$) showed some unexpectedly stable structures. A systematic search of possible conformers revealed that some conformers were not far from the global energy minimum of $HS_n{}^+$. Therefore, only already reported structures were used, up to three ring conformers [13,14] and one chain like conformer with the lowest energy (Fig. 2).

The geometries of the cations H_3S^+, $H_3S_2^+$, the three species of $H_3S_4^+$ and the various isomers of HS_n^+ ($n > 2$) have already been treated extensively in the work of Otto and Steudel [15,16], so that no extensive discussion of these is necessary here. $H_2S_3^+$, the most intense cation after H_3S^+, has three possible geometries ($H_2S_3^+$(a), $H_2S_3^+$(b), $H_2S_3^+$(c)). In all three, the hydrogen atoms are located above and below the plane described by the three sulfur atoms. Geometry (a) of this species, with C_{2v} symmetry, is the most stable conformation. Geometry (b) with C_S symmetry and geometry (c) with C_1 symmetry have progressively lower stability. The energy difference ΔG°_{298} amounts to 23.1 kJ mol^{-1} between (a) and (b) and 71.7 kJ mol^{-1} between (b) and (c). These energy differences are large in comparison with those between the three structures of $H_3S_4^+$ (both differences 0.1 kJ mol^{-1}) [15]. They may be traced to hyperconjugation between non-binding electron pairs on the triply coordinated sulfur atom and the S–H or S–S bonds. This is especially clear in the case of (b), where the S1–S2 bond, at 262.3 pm, is significantly longer than that of a typical S–S bond (205 pm) [17], while the S2–S3 bond, at 188.7 pm, is appreciably shorter. The cause of this may, in analogy with the sulfonium ions of type $H_3S_3^+$, be the negative hyperconjugation [15,18]. The non-binding 3p electron pair of S3 is here partly delocalized into the σ^* orbital of the S1–S2 bond. This weakens the S1–S2 bond and simultaneously strengthens the S2–S3 bond by an additional contribution to the π bond. In structures (a) (206.6 pm) and (c) (211.4 and 203.9 pm), the S–S bond lengths are normal and there is no indication of hyperconjugation.

The $H_2S_2^+$ ion, in contrast to uncharged H_2S_2, has *trans* geometry [19] instead of gauche [17]. Because the π^* orbital of the two $3p_\pi$ orbitals of the neighboring S atoms in $H_2S_2^+$ is only singly occupied, the π orbital has bonding character and the HSSH torsion angle is 180°. The bond length of 203.2 pm is only a little smaller than in uncharged H_2S_2. Both the HS bond length at 135.8 pm and the HSS angle at 97.7° are somewhat larger than in uncharged H_2S_2 [17].

Like NH_3 and H_2O [20,21], H_2S is able to solvate its ions in the gas phase. H_3S^+ can bind up to three H_2S molecules via hydrogen bonds [22]. Under the conditions prevailing in mass spectrometry, only the first solvation step $[H_2S \cdots H_3S]^+$ (Fig. 1) was observed.

The theoretically determined structure of $[H_2S \cdots H_3S]^+$ is directly comparable with that of the water cluster $[H_2O \cdots H_3O]^+$ [21]. The hydrogen is symmetrically positioned between the H_2S molecules, while the vector of the dipole moment of H_2S is not parallel to this bond. In further analogy to $[H_2O \cdots H_3O]^+$, the bridging hydrogen has a direct bond to either of the H_2S molecules. The hydrogen bond is formed along the non-bonding 3p electron pairs of S1–S2.

Homologues of the type HS_n^+ make up a large group of sulfonium cations in the CI plasma (see Fig. 1). The ions HS_3^+ to HS_8^+ were also identified in the mass spectrum, but HS^+ and HS_2^+ were not observed under our conditions because they react too quickly to give higher homologues.

All the HS bond lengths of chain-like $^3[HS_n^+]$ fall in the expected range 135.2–137.3 pm and correspond to those of known sulfonium cations [15]. Only in HS_4^+ and higher homologues is the familiar twisting or helical structure of sulfur chains seen in the anomeric delocalization of the non-bonding electron pairs [23,24]. Unlike $H_2S_3^+$ (b), HS_3^+ has no negative hyperconjugation. Among the homologues of HS_n^+, no hyperconjugation is clearly recognizable up to HS_4^+ and then it is largely limited to the last two bonds of the S–S chain.

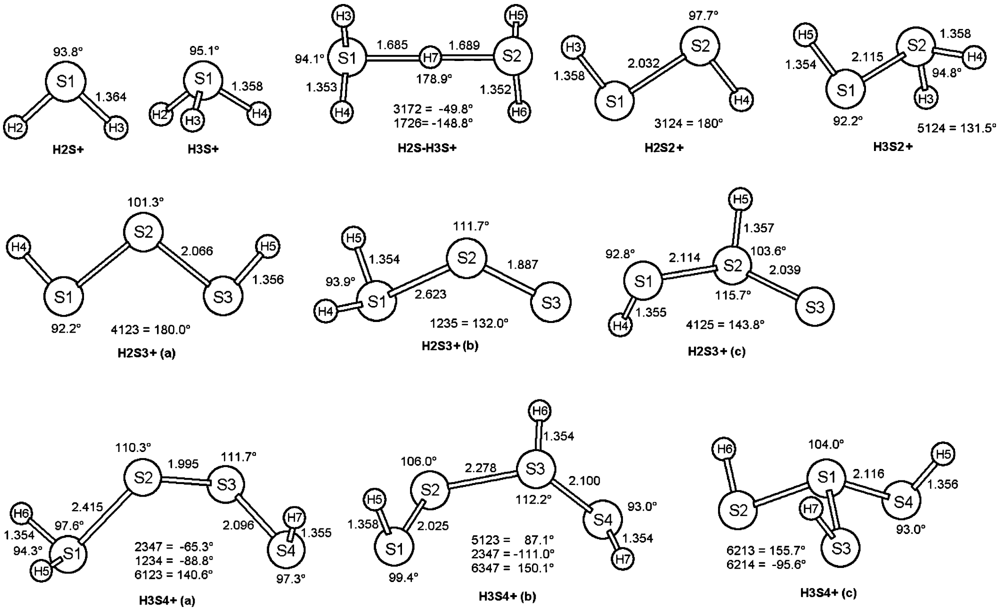

Fig. 2. Structures and bond lengths (in Å) and bond angles of the sulfonium ions calculated at the B3LYP/6-31G(*d*) level used in G3B3.

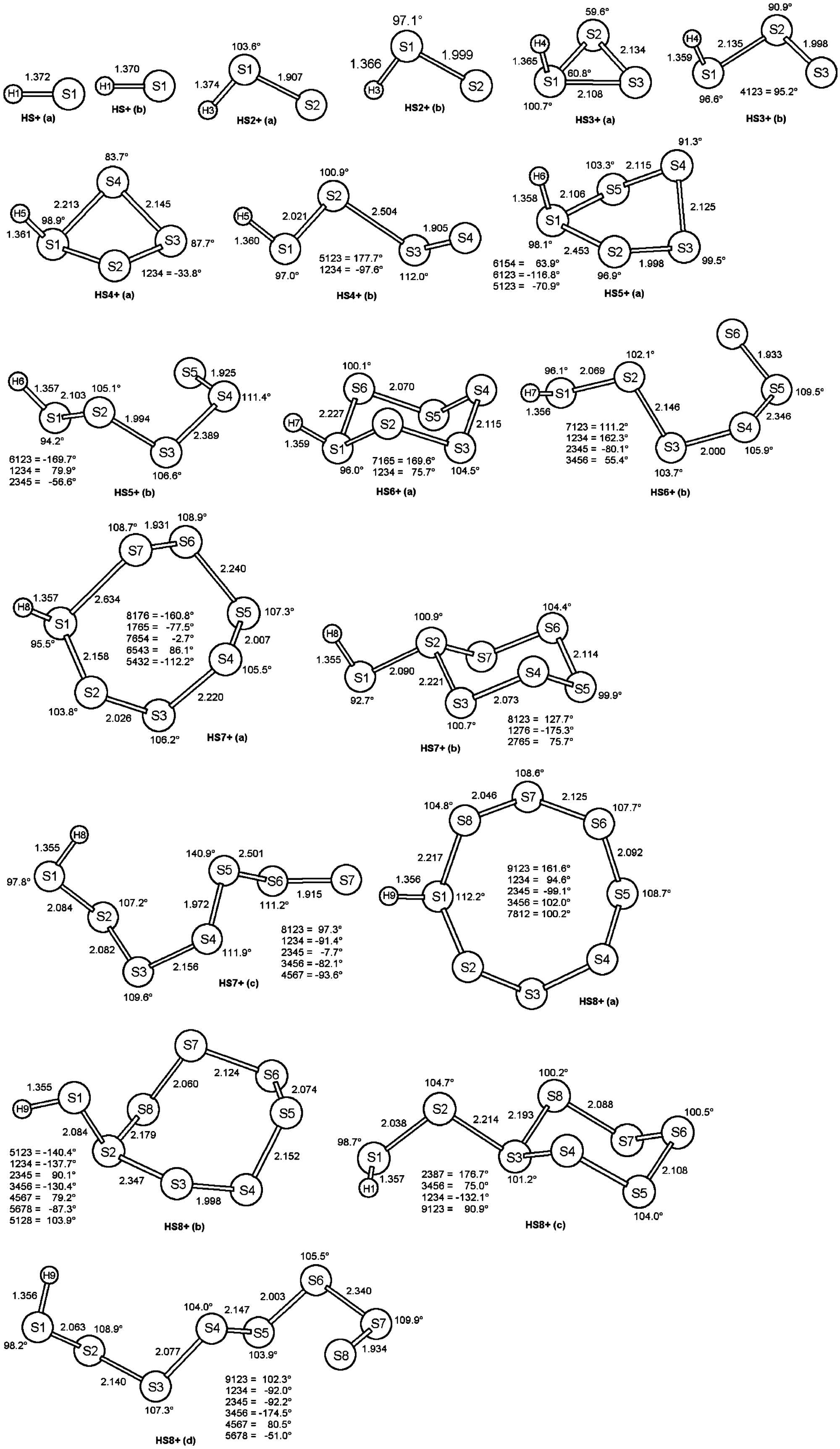

Fig. 2. (*Continued*).

This can be explained by the fact that both the charge and the unpaired electrons are located on the last sulfur atom of the chain. As mentioned above, this leads to a weakening of the penultimate S–S σ bond and a contribution to the π bonding of the last S–S bond of the chain. The growth of the $HS_n{}^+$ chain becomes easier as more S atoms are added.

5. Thermodynamics

The absolute enthalpy H° and the Gibbs free energy G° at 298 K were calculated by the G3B3 method for the sulfur compounds listed in Table 1. To describe the origin of the ions observed in the CI plasma of H_2S, a series of exothermic ion–molecule reactions were formulated (Table 2), with charge and multiplicity being taken into account. Ideally, such a description of the reaction system would include the activation energies. These energies were not calculated because of the unmanageable multiplicity of possible transition structures for the individual reactions. The reference values given in Table 2 were obtained at different temperatures, but they nevertheless provide a good comparison.

The first four entries in Table 2 are crucial, since H_3S^+ is formed exclusively from these secondary reactions of H_2S^+, HS^+ and H_2S. There is no way for the S^+ formed in the primary reaction to initiate the formation of H_3S^+, since it is not able to transfer any hydrogen. Noticeable are the low exothermicities of these secondary reactions. However, some of the ensuing reactions in Table 2, are pronouncedly exothermic. The formation of $S_2{}^+$ can be explained very well by the reactions of S^+ with S or H_2S, especially since H_2S is present in excess. Three reactions are conceivable for the formation of $H_2S_3{}^+$. Structures (a) and (b) may well make up most of the ions $H_2S_3{}^+$ because they require the fewest reaction steps from the primary ions. The formation of $H_2S_3{}^+$ (b) in particular, whose precursor $S_2{}^+$ is detected in the mass spectrum,

Table 1
G3B3 enthalpies and Gibbs free energies of the species in the plasma (in hartrees)

Species	Multiplicity	Symmetry	E_{elec}	ZPE	E°_{298}	H°_{298}	G°_{298}
H_2	1	$D_{\infty h}$	−1.177214	0.009744	−1.165110	−1.164166	−1.178957
S	3	C_1	−397.962412	0	−397.960996	−397.960051	−397.978345
S^+	4	C_1	−397.584546	0	−397.583130	−397.582186	−397.600751
HS	2	$C_{\infty v}$	−398.602493	0.005850	−398.594282	−398.593338	−398.615158
HS^+ (a)	1	$C_{\infty v}$	−398.170717	0.005679	−398.162677	−398.161733	−398.182922
HS^+ (b)	3	$C_{\infty v}$	−398.222893	0.005680	−398.214852	−398.213908	−398.236132
H_2S	1	C_{2v}	−399.254403	0.014564	−399.236990	−399.236046	−399.260063
H_2S^+	2	C_{2v}	−398.870472	0.014193	−398.853428	−398.852484	−398.876532
H_3S^{+a}	1	C_{3v}	−399.531885	0.025445	−399.503549	−399.502605	−399.527389
S_2	3	$D_{\infty h}$	−796.085020	0.001534	−796.081002	−796.080058	−796.106009
$S_2{}^+$	2	$D_{\infty h}$	−795.741464	0.001777	−795.737242	−795.736298	−795.761729
$H_2S_2{}^+$	2	C_{2h}	−796.973091	0.018104	−796.951620	−796.950676	−796.979806
$H_3S_2{}^{+a}$	1	C_S	−797.591305	0.027466	−797.559986	−797.559042	−797.589343
$H_2S_3{}^+$ (a)	2	C_{2v}	−1195.044012	0.019004	−1195.020540	−1195.019596	−1195.053957
$H_2S_3{}^+$ (b)	2	C_S	−1195.033795	0.019267	−1195.009099	−1195.008155	−1195.045125
$H_2S_3{}^+$ (c)	2	C_1	−1195.008465	0.019873	−1194.983753	−1194.982809	−1195.017849
$H_3S_4{}^+$ (a)[a]	1	C_1	−1593.719958	0.029211	−1593.683189	−1593.682245	−1593.724243
$H_3S_4{}^+$ (b)[a]	1	C_1	−1593.720831	0.029954	−1593.683733	−1593.682789	−1593.724289
$H_3S_4{}^+$ (c)[a]	1	C_3	−1593.720355	0.028782	−1593.684112	−1593.683168	−1593.724260
$[H_2S\cdots H_3S]^+$	1	C_S	−798.808008	0.039877	−798.762389	−798.761444	−798.796921
$HS_2{}^+$ (a)[b]	1	C_S	−796.343757	0.009139	−796.331609	−796.330665	−796.358794
$HS_2{}^+$ (b)[b]	3	C_S	−796.329874	0.008651	−796.318117	−796.317173	−796.346575
$HS_3{}^+$ (a)[b]	1	C_S	−1194.420579	0.012349	−1194.404435	−1194.403491	−1194.435608
$HS_3{}^+$ (b)	3	C_1	−1194.405311	0.010849	−1194.389982	−1194.389038	−1194.423799
$HS_4{}^+$ (a)[b]	1	C_S	−1592.466707	0.013332	−1592.447789	−1592.446845	−1592.483610
$HS_4{}^+$ (b)	3	C_1	−1592.478739	0.011972	−1592.460136	−1592.459191	−1592.501328
$HS_5{}^+$ (a)[b]	1	C_1	−1990.582454	0.015243	−1990.560163	−1990.559219	−1990.599760
$HS_5{}^+$ (b)	3	C_1	−1990.551473	0.013681	−1990.529638	−1990.528694	−1990.575037
$HS_6{}^+$ (a)[b]	1	C_S	−2388.647876	0.016545	−2388.622564	−2388.621619	−2388.666344
$HS_6{}^+$ (b)	3	C_1	−2388.619746	0.015069	−2388.594710	−2388.593765	−2388.644898
$HS_7{}^+$ (a)[b]	1	C_1	−2786.718486	0.017803	−2786.690023	−2786.689079	−2786.738790
$HS_7{}^+$ (b)	1	C_S	−2786.719495	0.017517	−2786.691207	−2786.690263	−2786.740044
$HS_7{}^+$ (c)	3	C_1	−2786.677093	0.006002	−2786.664192	−2786.663248	−2786.708753
$HS_8{}^+$ (a)[b]	1	C_S	−3184.789201	0.019589	−3184.757482	−3184.756538	−3184.809699
$HS_8{}^+$ (b)	1	C_1	−3184.792953	0.019205	−3184.761400	−3184.760456	−3184.814532
$HS_8{}^+$ (c)	1	C_1	−3184.785146	0.019082	−3184.753567	−3184.752623	−3184.807853
$HS_8{}^+$ (d)	3	C_1	−3184.747794	0.017926	−3184.716390	−3184.715446	−3184.776916

[a] Resembles the geometry in Ref. [15].

[b] Resembles the geometry in Ref. [16].

Table 2
G3B3 enthalpies and Gibbs free energies (kJ mol^{-1}) for the possible reactions in the plasma

Reaction	ΔH°_{298}	ΔG°_{298}	ΔH_{Ref}
$H_2S^+ + H_2S \rightarrow H_3S^+ + HS$	−19.5	−15.6	−29[a]
HS^+ (b) + $H_2S \rightarrow H_3S^+ + S$	−33.4	−25.1	−50[a]
HS^+ (b) + $H_2S \rightarrow {HS_2}^+ + H_2$	−82.5	−77.1	
${HS_2}^+ + H_2S \rightarrow H_3S^+ + S_2$	−77.4	−70.3	
$H_3S^+ + H_2S \rightarrow [H_2S\cdots H_3S]^+$	−59.9	−24.9	−64.5[b]
$S^+ + S \rightarrow {S_2}^+$	−509.8	−479.8	
$S^+ + H_2S \rightarrow {S_2}^+ + H_2$	−216.0	−209.8	−197[a]
$HS + HS^+$ (b) $\rightarrow {H_2S_2}^+$	−376.0	−337.6	
${HS_2}^+ + HS \rightarrow {H_2S_3}^+$ (A)	−286.6	−242.3	
${S_2}^+ + H_2S \rightarrow {H_2S_3}^+$ (B)	−94.1	−61.3	
${H_2S_2}^+ + S \rightarrow {H_2S_3}^+$ (C)	−189.4	−156.8	
$H_2S^+ + HS \rightarrow {H_3S_2}^+$	−297.5	−256.6	
${H_2S_3}^+$ (A) + $HS \rightarrow {H_3S_4}^+$ (C)	−184.5	−144.9	
${H_2S_3}^+$ (B) + $HS \rightarrow {H_3S_4}^+$ (A)	−212.2	−168.0	
${H_2S_3}^+$ (C) + $HS \rightarrow {H_3S_4}^+$ (B)	−280.2	−239.8	
HS^+ (b) + $S \rightarrow {HS_2}^+$ (b)	−376.3	−347.1	
${HS_2}^+$ (b) + $S \rightarrow {HS_3}^+$ (b)	−293.8	−259.8	
${HS_3}^+$ (b) + $S \rightarrow {HS_4}^+$ (b)	−289.3	−260.6	
${HS_4}^+$ (b) + $S \rightarrow {HS_5}^+$ (b)	−287.6	−250.5	
${HS_5}^+$ (b) + $S \rightarrow {HS_6}^+$ (b)	−275.9	−240.4	
${HS_6}^+$ (b) + $S \rightarrow {HS_7}^+$ (c)	−287.5	−224.7	
${HS_7}^+$ (c) + $S \rightarrow {HS_8}^+$ (d)	−242.1	−236.0	

[a] Reference value based on thermochemical data from Huntress and Pinizzotto [25].

[b] Reference value based on thermochemical data from Hiraoka and Kebarle [22].

may be formulated as in equation (4).

$$\begin{array}{l} S^+ + H_2S \rightarrow {S_2}^+ + H_2 \\ {S_2}^+ + H_2S \rightarrow {H_2S_3}^+(b) \\ \hline S^+ + 2H_2S \rightarrow {H_2S_3}^+(b) + H_2, \quad \Delta H^\circ_{298} = -310.1\,\mathrm{kJ\,mol^{-1}} \end{array} \tag{4}$$

The radicals HS and S are assigned special roles, as higher sulfonium cations can be formed from each. Thus, H_2S^+ and HS can lead to the ${H_3S_2}^+$ cation, which in its bond lengths and bond angles is comparable with H_2S_2 and H_3S^+ [15]. The structures already examined for the ${H_3S_4}^+$ cations result from the addition of HS to the three ${H_2S_3}^+$ species [15], while the sulfonium cations ${HS_n}^+$ observed in the spectrum can come from the sequential addition of sulfur atoms that are by-products of the formation of H_3S^+ (equation (5)), or by a disproportionation ${HS_n}^+$ itself (equation (6)) [16]. Spin conservation is the basis for both reactions.

$$ {HS_n}^+ + S \rightarrow {HS_{n+1}}^+, \quad \Delta H^\circ_{298} < 0 \tag{5}$$

$$ 2{HS_n}^+ \rightarrow {HS_{n-1}}^+ + {HS_{n+1}}^+, \quad \Delta H^\circ_{298} < 0 \text{ or } \Delta H^\circ_{298} > 0 \tag{6}$$

The conceivable reaction $S_n + H^+ \rightarrow {HS_n}^+$ is improbable because the necessary free protons were not be observed, nor could they be generated by any theoretical reaction. Another reaction, $S_n + H_3S^+ \rightarrow {HS_n}^+ + H_2S$ ($-\Delta H^\circ$ with $S_{n\geq 2}$), can also be removed from consideration: no elemental sulfur could be found in the ion source. If atomic sulfur is produced in the plasma, it reacts further to higher sulfonium ions.

Equation (6) describes the generation of $^1[{HS_n}^+]$ under superacidic conditions [16]; these reactions are partly endo- and exothermic. In equation (5), we postulate ${HS_n}^+$ reacting in the excited triplet state with atomic sulfur, but whether ${HS_n}^+$ reacts in the chain-like or cyclic structure is still unknown. This kind of gas-phase polymerization of ${HS_n}^+$ is essentially a cationic polymerization. It is remarkable that, although all the observations were carried out at 498 K and 22.7 Pa, the ${HS_n}^+$ cations were still stable. In this context, it must be pointed out that pressures over 15 MPa and temperatures up to 160 °C are often necessary for the synthesis of neutral polysulfanes H_2S_n [26].

6. Conclusion

In order to account for the mass distribution in the spectrum of the CIMS plasma of H_2S, theoretical calculations were carried out for the formation of the secondary ions. It is shown that not only the main component H_3S^+, but numerous other sulfonium ions are formed exothermally. The $[H_2S\cdots H_3S]^+$ ion plays a rather subordinate role in the plasma. More intense are the isomers of ${H_2S_3}^+$, which are formed from primary and secondary ions, and themselves serve as precursors of the isomers of ${H_3S_4}^+$. Furthermore, it is shown that the formation of the polysulfonium ions ${HS_n}^+$ is comparable with cationic polymerization.

We have compared H_2S with several more usual reactant gases under conditions typical for CIMS, and, in an article oriented more toward analytical applications, we will show that H_2S can be used with great success in the simultaneous CIMS analysis of a mixture of fatty alcohols.

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