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Relative proton affinities of hydrogen sulfide and water

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The difference in proton affinities for H_2S and H_2O has been measured in a photoionization mass spectrometer by studying the following equilibrium $H_3S_{(g)}^{+}+H_2O_{(g)}\rightleftarrows H_3O_{(g)}^{+}+H_2S_{(g)}$. Mixtures of H_2S and H_2O are photolyzed at 10.63 eV in the source of the mass spectrometer. H_2S^+, which is the only ion produced, reacts with H_2S to produce H_3S^+. H_3S^+ reacts with water to produce H_3O^+ which further hydrates to $H(H_2O)_n{}^+$. The equilibrium constant is measured as a function of temperature and a van't Hoff plot produces $\Delta H^\circ = 2.9$ kcal/mole $\Delta S^\circ = 5.5$ eV. Thus the proton affinity of H_2S is 3 kcal/mole greater than the proton affinity of H_2O. Species such as $H_3S(H_2S)_n{}^+$ and $H_3S(H_2O)_n{}^+$ are not observed while $H(H_2O)_n{}^+$ hydrates are highly favored. A possible explanation is offered which involves the weakness of hydrogen bonds to sulfur.

INTRODUCTION

The heats of formation of H_3O^+ and H_3S^+ or their counterparts, the proton affinities of H_2O and H_2S, are important in determining the energetics of reactions involving these species. For this reason numerous mass spectrometric investigations have been made to determine these quantities.

Van Raalte and Harrison[1] place the proton affinity of H_2O at 152 kcal/mole based on appearance potentials of H_3O^+ by electron impact on various organic compounds. Haney and Franklin[2] using similar techniques found P.A.(H_2O) to be 165 kcal/mole. Using electron impact appearance potentials of H_3S^+ from organic sulfides Hobrock and Kiser[3] found P.A.(H_2S) to be 199 kcal/mole; while Haney and Franklin[2] determined P.A.(H_2S) = 170 kcal/mole using similar techniques and organic thiols. Several other workers[4-8] have used ion–molecule reactions to set limits on the proton affinities of H_2S and H_2O. Tal'rose and Frankevich[4] and Long and Munson[5] used a magnetic mass spectrometer equipped with an electron impact ionization source, while Chupka and Russell[6] used a similar instrument except with a photoionization source. Chong, Meyers, and Franklin[7] used a quadrupole mass spectrometer with electron impact ionization and Beauchamp and Buttrill[8] used an ion cyclotron double resonance spectrometer in conjunction with electron impact. Previous values for P.A.(H_2S) and P.A.(H_2O) are shown in Table I.

As can be seen from Table I, the values for the proton affinities of H_2S and H_2O are not well established. Some of the reasons for the uncertainty in the results deduced from ion molecule reactions may result from the internal energy of ions created by electron impact or the kinetic energy of ions reacting in an electric or rf field. A serious difficulty in basing thermochemical data on appearance potential studies is the identification of the neutral fragments and the determination of the energy of the fragments.

We have developed a photoionization mass spectrometer which is particularly well suited to reinvestigate the proton affinities of H_2S and H_2O since both the internal energy and the translational energy of the reactant ion are very low. Reactant ions are produced by photoionization near threshold and react in a field free region. As a result thermodynamic quantities can be determined by measuring equilibrium constants as function of temperature without energy contributions from other sources.

TABLE I. Reported values for the proton affinities of H_2S and H_2O

P.A.(H_2S) kcal/mole	P.A.(H_2O) kcal/mole	Ref.
···	152	1
170	165	2
199	···	3
···	163–172	4
···	164	5
···	>161	6
170	168	7
178	164	8

EXPERIMENTAL

The instrument used in this study is a Du Pont Instruments Model 21-440 quadrupole mass spectrometer which has been modified to operate with a photoionization source. The instrument, depicted schematically in Fig. 1, has been described previously.[9] H_2S and H_2O, which are premixed in a 2-liter bulb in the

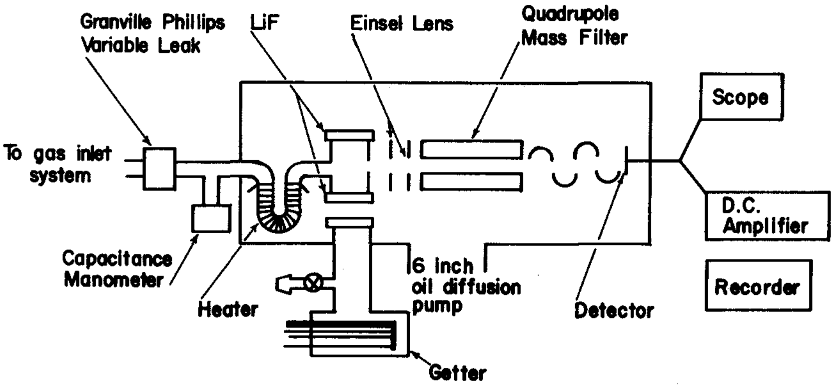


FIG. 1. Schematic drawing of the mass spectrometer.

inlet system at total pressures between 40 and 100 torr, are introduced under controlled pressure into the ion source through a Granville–Phillips variable leak. The ion source is a stainless steel cube, approximately 1 cm per side. Lithium fluoride windows, 1 mm thick, are attached to two sides of the source with silicon rubber cement. The ion exit hole, which is 1/25 in. diameter in these experiments, is centered on a removable face plate at the front of the source. Gases inside the source are photolyzed with a Krypton resonance lamp at 10.03 and 10.63 eV. H_2S^+ (I.P.=10.46 eV), which is produced by the upper line, is the only ion produced by the radiation.

Ions thus produced are allowed to react under field free conditions. Reactant and product ions drift out of the source through the ion exit hole where they are accelerated to a maximum of 320 eV by the ion focus plate and subsequently decelerated to 20 eV at the aperture of the quadrupole mass filter. The ions are mass analyzed by the quadrupole filter and detected by the electron multiplier.

The entire stainless steel housing is evacuated to less than 10^{-5} torr by a liquid nitrogen trapped Norton 3317 pumping system which uses a 6-in. oil fractionating diffusion pump backed by a 10.6 CFM Welch mechanical pump. Pressure inside the ion source is measured with a Granville–Phillips capacitance manometer calibrated from 0 to 10 torr. The capacitance manometer was calibrated with known vapor pressure sulfuric acid–water solutions which were maintained at 293°K during the calibration. Pressure in the gas inlet system is measured with a Wallace and Tiernan gauge which reads from zero to one hundred inches of water.

Temperature control is established using a heater which was designed specifically for this instrument.

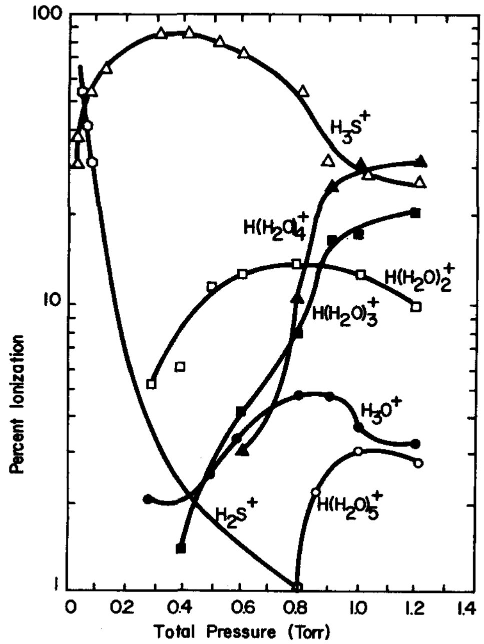


FIG. 2. Ion distribution as a function of pressure. Mole fraction of water=0.50, T=298°K.

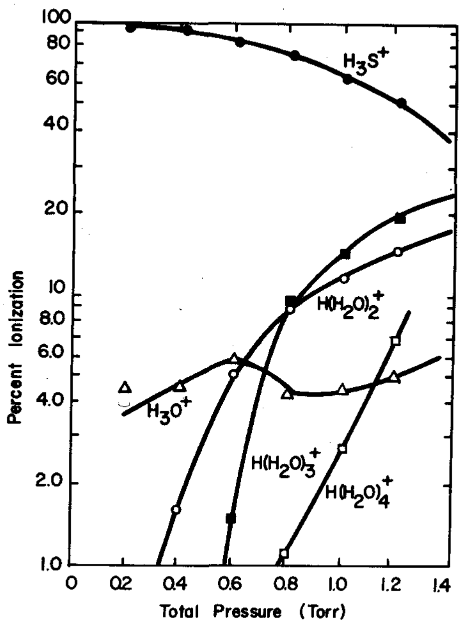


FIG. 3. Ion distribution as a function of pressure. Mole fraction of water=0.17, T=355°K.

Gas temperatures inside the source are measured with an iron–constantan thermocouple. The source temperature was never measured simultaneously with data collection because of the perturbing effect of the thermocouple inside the source. Temperature measurements were always taken in experiments exactly like those where data were collected except that the mass spectrometer and the Kr lamp were not turned on. A Keithly electrometer was used to measure the thermocouple emf against an identical thermocouple in an ice–water bath. It was determined that the source temperature did not decrease more than two degrees as a result of adiabatic expansion through the leak at source pressures up to 1.5 torr.

The hydrogen sulfide used in these experiments was Matheson Company CP grade and was used without further purification. The water was distilled in a Corning AG-3 still and passed through two Barnstead Sybron ion exchange columns. Neither of these compounds produced any unexpected ions in the mass spectrometer under irradiation with the Krypton resonance lines.

RESULTS

Experiments have been performed at three different temperatures; 296, 355, and 426°K and at a variety of mole fractions of H_2O ranging from 0.07 to 0.50. Typical experiments at each temperature are shown in Figs. 2–4. The logarithm of the percent of total ionization is shown as a function of total pressure in the source. Since an increase in source pressure increases the reaction time of an ion in the source, a plot of ion population vs source pressure is analogous to a more familiar plot of product yield vs time and may be used as such in deducing a reaction mechanism.

The data in Fig. 2 confirm that the major ion at very low pressure is H_2S^+ since the krypton resonance lamp (10.03 and 10.63 eV) will ionize only H_2S (ionization potential 10.46 eV) without ionizing water (ionization potential 12.61 eV).[10] It is also important to note that the close match of the more energetic Kr line to the ionization potential of H_2S assures the production of ground state ions. As the source pressure is increased, $[H_3S^+]$ grows rapidly to a maximum at which point the intensity of H_3O^+ begins to increase. As the pressure is increased further $[H_3S^+]$ declines slowly, being compensated by the rise of $[H_3O^+]$. Finally $[H_3O^+]$ maximizes and begins to decline due to formation of higher proton hydrates such as $H(H_2O)_2^+$ and $H(H_2O)_3^+$, which are the predominant species at high pressure.

Results at higher temperatures agree with those at 296°K except that H_2S^+ disappears so rapidly that it is never observed and H_3S^+ is the predominant ion at low pressure. It can be noted that H_3O^+ is produced at a lower pressure in the high temperature experiments and that fewer proton hydrates are observed. From all of these observations the following mechanism can be deduced:

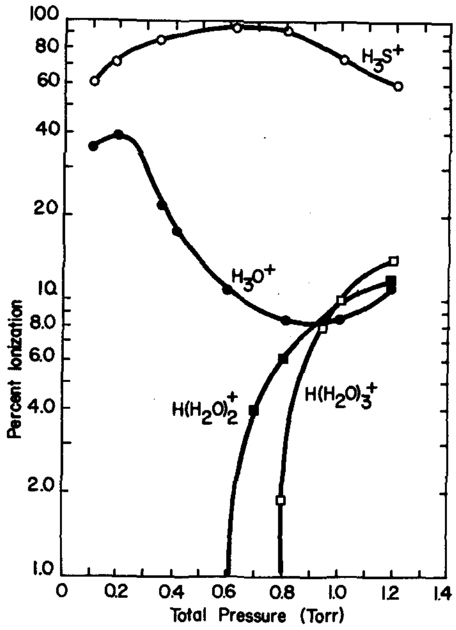


FIG. 4. Ion distribution as a function of pressure. Mole fraction of water=0.50, T=426°K.

$$H_2S^+ + H_2S \xrightarrow{k_1} H_3S^+ + HS, \qquad (1)$$

$$H_2S^+ + H_2O \xrightarrow{k_2} H_3O^+ + HS, \qquad (2)$$

$$H_3S^+ + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_3O^+ + H_2S, \qquad (3)$$

$$H_3O^+ + H_2O + M \overset{k_4}{\rightleftharpoons} H(H_2O)_2^+ + M, \qquad (4)$$

$$H(H_2O)_n^+ + H_2O + M \rightleftharpoons H(H_2O)_{n+1}^+ + M, \qquad (5)$$

where M represents any third body.

Figure 4, as well as other data at 426°K, shows that Reaction (2), which is not observed at low temperature, appears to occur at 426°K. At low pressure where $[H_2S^+]$ has not yet been depleted by Reaction (1), Reaction (2) produces H_3O^+ as indicated by the rise of $[H_3O^+]$ to an early maximum. At intermediate pressure H_3O^+ reacts with H_2S to produce H_3S^+ by the reverse of Reaction (3) and with H_2O to produce $H(H_2O)_2^+$ by Reaction (4), and thus H_3O^+ declines. At the highest pressures shown, proton hydrates such as $H(H_2O)_2^+$ produce H_3O^+ by collisional decomposition outside the ion exit hole of the source in a region where they are accelerated to high kinetic energy. Thus, $[H_3O^+]$ begins to increase at high pressure.

DISCUSSION

An attempt to calculate equilibrium constants directly from the H_3O^+:H_3S^+ ratio and the mole fraction

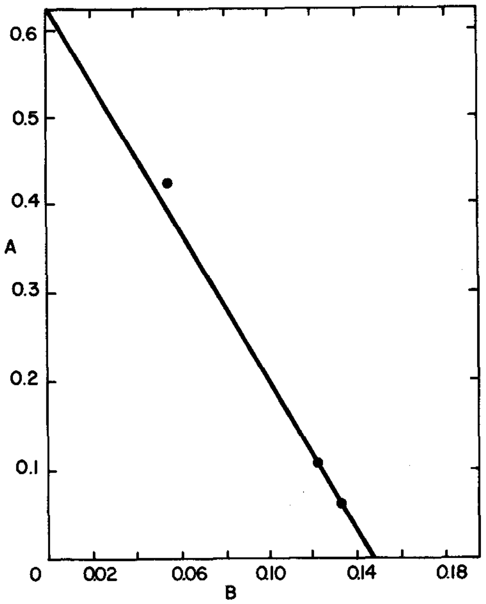


FIG. 5. Determination of K_{eq} at 298°K from $K_{eq}=(k_1/k_{-3})A+B$ where $A=[H_2S^+][H_2S]/[H_3S^+][H_2O]$ and $B=[H_3O^+][H_2S]/[H_3S^+][H_2O]$.

proved to be impossible. If the pressure in the source could be raised sufficiently to establish equilibrium in Reaction (3), H_3O^+ would be completely converted to higher hydrates. Attempts to use high pressures with very low mole fractions of water to diminish hydration of H_3O^+ yielded very erratic results presumably because of desorption of water from surfaces exposed to gas mixture.

A steady state kinetics assumption was used to calculate the equilibrium constant for Reaction (3). At 296°K H_3S^+ passes through a readily recognizable steady state fitting the following mathematical expression:

$$k_{-3}[H_3O^+][H_2S]+k_1[H_2S^+][H_2S]=k_3[H_3S^+][H_2O]$$

and, therefore,

$$\begin{aligned}K_{eq}&=k_3/k_{-3}\\&=(k_1/k_{-3})[H_2S^+][H_2S]/[H_3S^+][H_2O]\\&\qquad+[H_3O^+][H_2S]/[H_3S^+][H_2O]\end{aligned}$$

or for convenience,

$$K_{eq}=(k_1/k_{-3})A+B.$$

A plot of A vs B at the H_3S^+ steady state for experiments at 296°K is shown in Fig. 5. The $A=0$ intercept determines the equilibrium constant to be 0.15. The slope also indicates that k_1 is 4 times larger than k_{-3} and, therefore, 27 times larger than k_3.

The same steady state treatment cannot be readily applied to the data at the other two temperatures since (H_2S^+) disappears too rapidly to be measured, and at least at the highest temperature, Reaction (2) is occurring. Therefore, a steady state assumption based on the H_3O^+ maximum was used.

All experiments at 355 and 426°K show H_3O^+ passing through an easily recognizable steady state fitting the following mathematical expression:

$$\begin{aligned}&k_2(H_2S^+)(H_2O)+k_3(H_3S^+)(H_2O)\\&\qquad=k_{-3}(H_3O^+)(H_2S)+k_4(H_3O^+)(H_2O)(M)\end{aligned}$$

and, therefore,

$$K_{eq}=\frac{k_4}{k_{-3}}\frac{(H_3O^+)(M)}{(H_3S^+)}+\frac{(H_3O^+)(H_2S)}{(H_3S^+)(H_2O)}-\frac{k_2(H_2S^+)}{k_{-3}(H_3S^+)}.$$

Since (H_2S^+) is near zero at this steady state this expression can be conveniently written as

$$K_{eq}=(k_4/k_{-3})CM+B.$$

A plot of C times the pressure (M) in torr vs B is shown in Fig. 6 for experiments at 355°K and in Fig. 7 for 426°K. From these two figures it is determined that $K_{eq}=0.36$ at 355°K and 0.62 at 426°K. It can also be observed that the line has a near zero slope since Reaction (4) is third order while k_{-3} is a second order rate constant.

Values of the equilibrium constant are plotted as a function of inverse temperature in a conventional van't Hoff plot (Fig. 8) and the thermodynamic functions for the reaction are found to be

$$\Delta H°=2.9\pm0.2\ \text{kcal/mole},$$

$$\Delta S°=5.5\pm0.2\ \text{eu},$$

thus indicating that the proton affinity of H_2S is 2.9 kcal higher than that of H_2O.

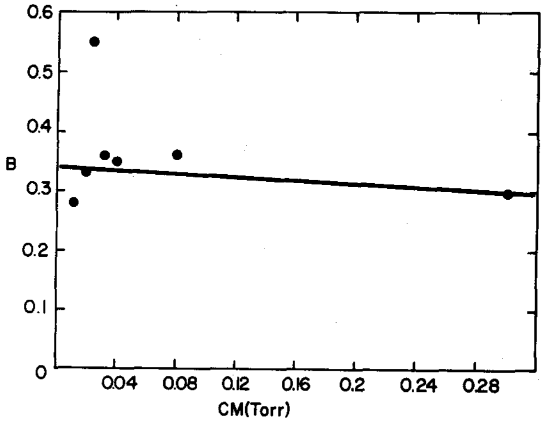


FIG. 6. Determination of K_{eq} at 355°K from $K_{eq}=(k_4/k_{-3})CM+B$ where M is the total pressure, $C=[H_3O^+]/[H_3S^+]$, and $B=[H_3O^+][H_2S]/[H_3S^+][H_2O]$.

Chong, Meyers, and Franklin[7] studied Reaction (3) at 340°K and found $\Delta G^\circ = 1.8 \pm 0.44$ kcal/mole, but they did not determine ΔS°. Beauchamp and Buttrill[8] report a proton affinity difference of 14 kcal/mole for H_2S and water by using an ion–molecule limit-setting technique. Their[8] reported value of P.A.(H_2O) of 164 kcal/mole agrees reasonably well with the value of Chong, Meyers, and Franklin.[7] Since this study is in better agreement with the P.A. difference of Chong, Meyers, and Franklin, it appears that P.A.(H_2S) may be in doubt. Beauchamp and Buttrill's value of 178 kcal/mole for P.A.(H_2S) may be too high due to reactant excitation since Haney and Franklin[2] report that Beauchamp and Buttrill's upper limit setting reaction for $\Delta H_f(H_3S^+)$,

$$H_2S_{(g)}^+ + CD_{4(g)} \rightarrow H_2DS_{(g)}^+ + CD_{3(g)}, \qquad \text{(V-1)}$$

will proceed spontaneously only if H_2S^+ is excited. Beauchamp and Buttrill[8] also report that they observe the spontaneous reaction

$$H_2S_{(g)}^+ + H_2O_{(g)} \rightarrow H_3O_{(g)}^+ + HS_{(g)}, \qquad \text{(V-2)}$$

which is seen by this study [Reaction (2)] to proceed only at elevated temperature. These two observations could explain the larger proton affinity difference observed by Beauchamp and Buttrill[8] for H_2S and water since excited H_2S^+ will cause the lower limit for P.A.(H_2S) to be too high. Haney and Franklin[2] are the only other workers who have measured the proton affinities of both H_2S and water in the same series of experiments. They report the difference in proton affinities of these two compounds to be 5 kcal/mole using appearance potential measurements found by electron impact on alcohols and organic thiols. It would thus seem that our work best supports values of P.A.(H_2O) = 166±2 kcal/mole and P.A.(H_2S) = 169±2 kcal/mole.

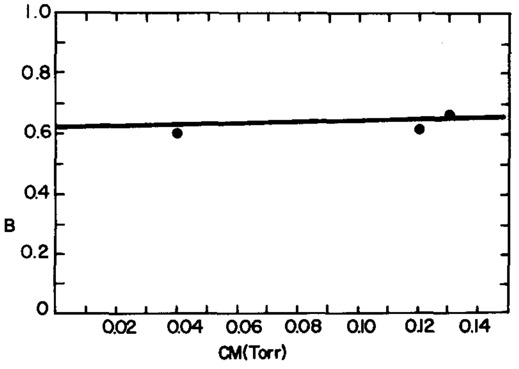


FIG. 7. Determination of K_{eq} at 426°K from $K_{eq} = (k_4/k_{-3})CM + B$ where M is the total pressure, $C = [H_3O^+]/[H_3S^+]$ and $B = [H_3O^+][H_2S]/[H_3S^+][H_2O]$.

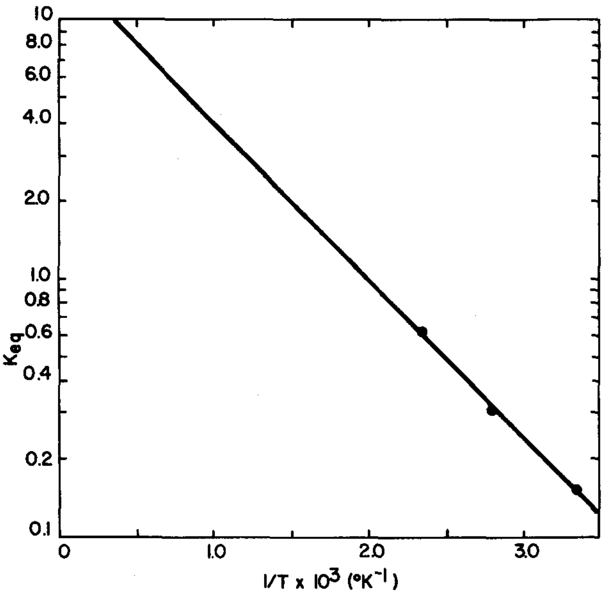


FIG. 8. Van't Hoff plot for the equilibrium $H_3S_{(g)}^+ + H_2O_{(g)} \rightleftharpoons H_3O_{(g)}^+ + H_2S_{(g)}$.

The standard entropy change ΔS° for the Reaction (3) was found to be small as expected, although somewhat larger than might have been predicted for a proton transfer reaction. The fact that the proton affinity of H_2S is greater than that for water indicates that the proton is more tightly bound by H_2S in agreement with a positive entropy change for Reaction (3).

The technique of threshold photoionization coupled with field-free ion source conditions can be an extremely powerful tool in the study of the thermodynamics of gaseous ionic systems. The only serious limitation in extending this work is the limited number of molecules whose ionization potentials closely match the energy of existing resonance lamps.

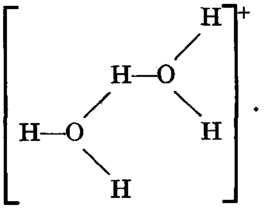
It is interesting to note that in none of the recorded spectra of the mixtures were species such as

$$H(H_2S)_2^+,\ H(H_2O)(H_2S)^+,\ H(H_2O)_2(H_2S)^+,\ \cdots$$

ever observed while species such as

$$H(H_2O)_2^+,\ H(H_2O)_3^+,\ H(H_2O)_4^+,\ \cdots$$

were observed in great abundance. Newton and Ehrenson[11] and McAdams and Bone[9] have suggested that the structure for $H(H_2O)_2^+$ is



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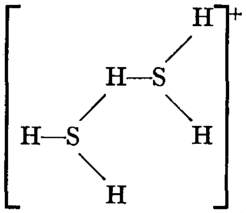
If this hydrogen bonded structure is correct for $H(H_2O)_2^+$ then it becomes apparent why similar structures involving H_2S were never observed. Assuming that H_2S is constrained to behave like H_2O, the structures of $H(H_2S)_2^+$ and $H(H_2O)(H_2S)^+$ would be



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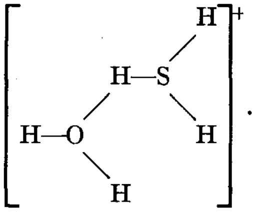

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These require that sulfur form hydrogen bonds of sufficient strength to stabilize the ion against decomposition. Since sulfur is known to form only weak hydrogen bonds, it is unlikely that these structures are stable enough to be observed in the mass spectrometer. This argument suggests that hydrogen bonding is extremely important in ion cluster formation.

ACKNOWLEDGMENTS

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