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Vibrational study in neon matrix of H_2S-H_2O, H_2S-$(H_2O)_2$ and $(H_2S)_2$-H_2O complexes.

Identification of the two isomers: HOH-SH_2 (H_2O proton donor) and HSH-OH_2 (H_2S proton donor).

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Abstract

For the first time the investigation of water molecules complexed with hydrogen sulfide in solid neon was performed from 80 to 6000 cm^{-1} using Fourier transform infrared spectroscopy. In a first step we identify the ν_1 and ν_3 frequencies of the proton donor in the H_2S dimer. From concentration effects and with the help of theoretical results we have highlighted the presence of the two stable isomers, HOH-SH_2 where H_2O is proton donor and HSH-OH_2 where H_2S is proton donor. We also identify several transitions for $(H_2S)_2$-H_2O and H_2S-$(H_2O)_2$ complexes, the first step of the microsolvatation of H_2S, and we propose structures for these complexes with the help of theoretical calculations at MP2 level.

KEYWORDS: H_2S-water complex, Hydrogen Bond, Infrared Spectroscopy, Neon Matrix Isolation, microsolvatation of H_2S, ab initio calculations.

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I. INTRODUCTION

Weakly bound complexes are important for describing the chemistry of Earth's atmosphere[1], and molecular hydrates are significant candidates as pointed by Vaida and Headrick[2]. In addition, hydrogen bonding interaction, the most important noncovalent interaction, plays a key role in many chemical and biological processes and structures of hydrogen-bonded complexes are of great theoretical and experimental interest.[3] In this way, we have recently studied hydrated complexes composed of a proton donor water molecule and small molecules as CO_2[4], OCS[5] and NO_2[6], proton acceptors.

The complex formed by water with hydrogen sulfide, H_2O-H_2S, is an interesting example for studying the competition between proton donor and proton acceptor because water and hydrogen sulfide have the both characteristics[7]. Consequently two possible hydrogen bonded structures is possible. In one of the structure, HOH-SH_2, the water molecule acts as a proton donor and in the second one, H_2O-HSH, it acts as a proton acceptor. In solid phase, many infrared studies have been done on H_2S molecule in N_2, O_2, Kr, Xe and Ar.[8-13] It is necessary to mention the difficulty to assign unambiguously the fundamental modes of H_2S in rare gas matrix because of their very weak IR absorption and of the very small frequency difference between the two ν_1 and ν_3 stretching modes. In addition, in solid Ar, Kr and Xe, narrow bands have been interpreted as rotational structures[13] of the ν_3 band making attributions even more difficult. The H_2S dimer have also been studied in solid N_2, O_2, Kr, Xe and Ar and ν_1,ν_2 and ν_3 values are given.[8,10,14-16]

For the monomer in gas phase, the ν_2 mode[17-21] was found at 1182.6 cm^{-1} and ν_1 and ν_3[21-23] at 2614.4 and 2628.4 cm^{-1}, respectively. Very recently, a gas phase study of the H_2S dimer gives the vibrational frequencies ν_1 and ν_3 for each proton acceptor and proton donor[24], and a microwave study shows that the dimer is indeed hydrogen bonded.[25] For the heterocomplex H_2S-H_2O, experimental studies exist in solid N_2[26], Ar[27], Kr, and Xe[16], none in gas phase, and vibrational data are often incomplete. Vibrational theoretical studies were performed on the H_2S monomer and dimer and on the H_2S-H_2O complex at MP2 and CCSD(T) level.[11,28-32] For this complex, a study[31] gives data on stabilities, geometries and harmonic frequencies only for the H_2O proton donor complex, HOH-SH_2. Another recent one[32] gives these data for the two isomers HSH-OH_2 and HOH-SH_2 with in addition anharmonic frequencies and intensities and concludes that the two isomers are isoenergetic. With regard to experimental gaps and uncertainties found in literature for these complexes we have undertaken for the first time the infrared study in solid neon of (H_2S)n-(H_2O)m complexes, noted n:m, and in particular the 1:1 complex with the observation of the two isomers HOH-SH_2, noted A, and HSH-OH_2, noted B, and also $(H_2S)_2$-H_2O (noted 2:1) and H_2S-$(H_2O)_2$ (noted 1:2) complexes. The Fourier transform infrared spectrometer permits to obtain complete vibrational data from the far infrared (intermolecular vibrations region) to the near infrared (overtones and combinations bands region). The advantage of neon matrix cage is its weak interaction with the involved molecules or complexes and so observed vibrational data are close to the gas phase values.

After a brief description of the experimental conditions, the spectra will be presented. An assignment of the different observed bands to 1:1, 1:2, and 2:1 complexes and isomers will be proposed with the support of theoretical results found in literature[31,32] and of our own calculations for 1:2 and 2:1 complexes.

II. EXPERIMENTAL AND THEORETICAL DETAILS

A. Experimental apparatus

Samples were prepared by co-condensing H_2S-Ne and H_2O-Ne mixtures at a rate of 2-15 mmol/h onto one of six highly polished, rhodium-plated copper mirrors maintained at 3 K using a closed-cycle helium cryostat (Cryomech PT-405). The temperature was measured using silicon diodes. The Ne/H_2S molar ratio varies between 100 and 6000, and the neon/water molar ratio varies between 100 and 2000. We use a Baratron gauge to measure the gas pressures. In the experiments with water it is important to saturate the stainless steel vacuum line to measure accurate pressures. Absorptions spectra were recorded between 80 and 6000 cm^{-1} on the same sample using a Bruker 120 FTIR spectrometer equipped with suitable combinations of light sources (globar, W filament), beamsplitters (composite, KBr/Ge, Si/CaF_2) and detectors (liquid N_2-cooled InSb, liquid N_2-cooled HgCdTe photoconductor, liquid He-cooled Si-B bolometer). All the spectra have been recorded at 3 K and by co-adding 200 scans at 0.1cm^{-1} resolution.

Natural water sample was degassed under vacuum before use. Ne (Air Liquide, 99.995 % purity) and H_2S (Aldrich, 99.5 % purity) were used without purification.

B. Computational details

As there are no vibrational data in literature for 1:2 and 2:1 complexes we have performed calculations at the second order Møller-Plesset calculations (MP2) used with the Gaussian09 package[33] and the augmented correlation-consistent basis set aug-cc-pVTZ (AVTZ) of Dunning and co-workers[34,35] has been chosen. So energy calculations have been carried out at MP2/AVTZ optimized structures to compute equilibrium geometries, equilibrium (D_e) and ground state (D_0) binding energies with BSSE and zero point energy (ZPE) corrections, harmonic vibrational frequencies as well as infrared intensities.

We also recalculated for 0:2, 2:0 and 1:1 complexes the structures, binding energies D_0 and harmonic frequencies with their intensities at MP2aug-cc-pVTZ level and also at CCSD(T)pVTZ level performed with the Molpro2012 package[36,37] only for 1:1.

III. SPECTRAL DATA AND ASSIGNMENTS

Our experiments were performed using different concentration ratios of $H_2S/H_2O/Ne$ gas mixture to identify the transitions of the n:m complexes: low concentration, typically $H_2S/H_2O/Ne=1-4/0.5/1000$ for the 1:1 complex and $H_2S/H_2O/Ne=6/0.2-1/1000$ and 10/5/1000 for 1:m and n:1 complexes, respectively. Figures 1-6 illustrate the IR spectra for different frequency ranges. Table I and II summarize our measured vibrational frequencies of $(H_2S)_n$-$(H_2O)_m$ complexes for the H_2S and H_2O spectral regions.

A. Monomers and dimers

In a first step we study the spectra of each partner before studying complexes formed with H_2S and H_2O. The infrared absorptions of the H_2O monomer, dimer and trimer trapped in solid neon are well known for the fundamental modes and for many overtones and combinations.[38,39]

Since there is no data on H_2S isolated in solid neon, we first examine the spectrum of only H_2S/Ne deposition. It is very difficult to observe all the fundamental frequencies of the H_2S monomer for two reasons. First the infrared intensities for the ν_3, ν_1 and ν_2 fundamental modes at 2626, 2614, and 1183 cm^{-1} are very weak since the gas phase data are $I\nu_1=0.121$ and $I\nu_2=0.485$ $km.mol^{-1}$ and $I\nu_3=0.0294$ and $I\nu_1=0.1108$ $km.mol^{-1}$ at 296 K.[21,23] Secondly, the H_2S molecules aggregate very easily at low temperature as mentioned in the Reference 12. If the concentration of H_2S is high, the dimer or larger polymers are formed to the detriment of the monomer and we only observe the ν_2 bending mode at 1190.4 cm^{-1} (Fig. 1(a)) close to the 1182.7 cm^{-1} gas phase value.[17-21] For the H_2S dimer, with concentration effects we can observe bands at 2623.5, 2622.1, 2605.0, 2602.1, 2596.5, and 2596.0 cm^{-1} (Fig. 2(a)). The intensity of the 2596.0 cm^{-1} band is ten times greater than that of 2622.1 cm^{-1} band. The ν_2 mode is observable at 1179.2 cm^{-1} as well as several close bands at 1181.8, 1182.8, and 1184 cm^{-1} having approximately the same intensity (Fig. 1(a)). For each mode we often observe a multiple sites pattern in a small range less than 3 cm^{-1}. We also attribute signatures to the H_2S trimer at 2581.8, 2582.8, and 2584.2 cm^{-1} for ν_1 and at 2619.0 and 2617.9 cm^{-1} for ν_3. Polymers with more than three H_2S molecules are observable at 2567.6 and 2570.1 cm^{-1}.

B. $(H_2S)_n$-$(H_2O)_m$ complexes

1. H_2S spectral regions

In the region of the ν_2 bending mode, a new band at 1188.1 cm^{-1} appears near H_2S and $(H_2S)_2$ signatures when H_2O is added to H_2S (Figs. 1(b)-1(c)) and follows linearly the concentration of H_2S or H_2O so it belongs to the 1:1 complex. We observe a band at 1187.1 cm^{-1} that appears when the concentration of H_2S becomes high and we conclude that it belongs to 2:1.

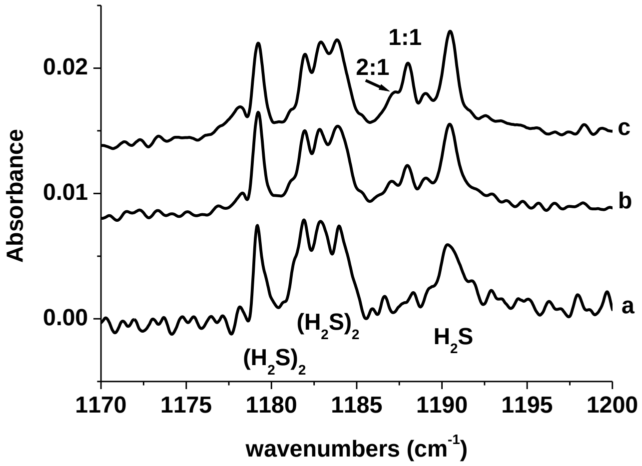

FIG. 1. Spectra in the H_2S ν_2 bending region at 3 K deposition, with different $H_2S/H_2O/Ne$ concentration ratios. (a) 4/0/1000, (b) 4/1/1000, (c) 4/3/1000.

In the ν_1 region (Fig. 2(a)) we observe a band at 2593.8 cm^{-1} and a smaller one at 2592.3 cm^{-1} attributed to 1:1 following concentration effects (Figs. 2(b)-2(d)) as well as a very weak signature at 2623.9 cm^{-1} near the ν_3 dimer. With a high H_2S concentration, we observe two groups of bands at 2567.4, 2568.4 cm^{-1}, and 2579.4, 2580.4 cm^{-1} attributed to ν_1 of 2:1 complex, probably due to proton donor (PD) and proton acceptor (PA) of H_2S dimer present in the 2:1 complex. With a high H_2O concentration, the bands at 2562.2 (the most intense) and 2610.6 cm^{-1} are attributed to ν_1 and ν_3 of the 1:2 complex, respectively, (Figs. 2(b)-2(d)).

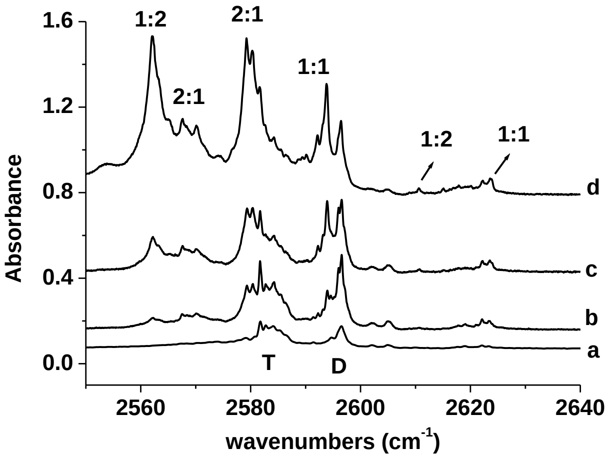

FIG. 2. Spectra in the H_2S ν_1 and ν_3 stretching region at 3 K deposition, with different $H_2S/H_2O/Ne$ concentration ratios. (a) 5/0/1000, (b) 6/1/1000, (c) 6/2/1000, (d) 6/10/1000. D and T are for H_2S dimer and trimer, respectively.

2. H_2O spectral regions

Near the ν_2 bending mode of the H_2O nonrotating monomer (nrm) at 1595.6 cm^{-1} (Fig. 3), two new intense bands appear at 1597.0 and 1602.0 cm^{-1} when H_2S is added to H_2O and they are assigned to the 1:1 complex. The observed band at 1598.7 is the signature of the 2:1 complex because of concentration effects. We observe the $2\nu_2$ overtone of 1:1 at 3157.8 and 3165.8 cm^{-1} and of 2:1 complex at 3258.8 cm^{-1} near the ones of H_2O dimer.[38]

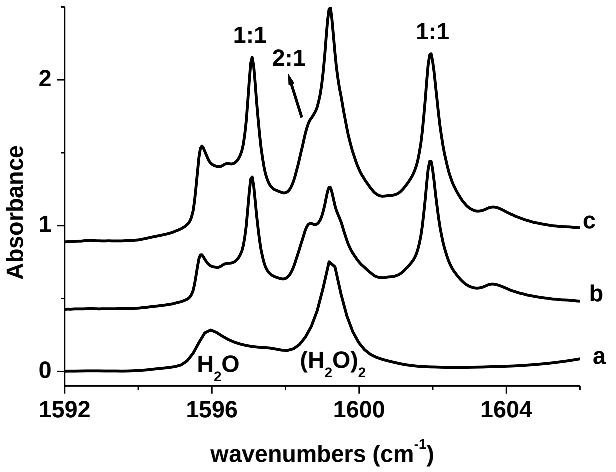

FIG. 3. Spectra in the H_2O ν_2 bending region at 3 K deposition, with different H_2S /H_2O/Ne concentration ratios. (a) 0/0.7/1000, (b) 6/0.7/1000, (c) 6/0.9/1000.

In the ν_1 PD region of the H_2O dimer observed at 3590.5 cm^{-1} (Fig. 4) one intense band at 3613.3 cm^{-1} appears as well as one at 3655.2 cm^{-1} (not showed) near the H_2O dimer ν_1 PA at 3660.6 cm^{-1}, both grow linearly with the water concentration and so belong to the 1:1 complex.

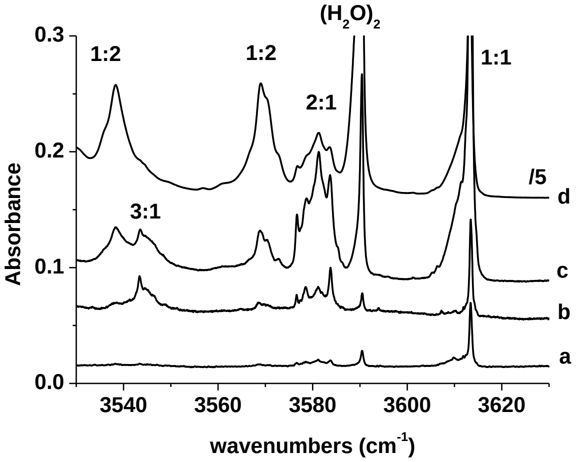

FIG. 4. Spectra in the H_2O stretching ν_1 region at 3 K deposition, with different $H_2S/H_2O/Ne$ concentration ratios. (a) 1.5/0.1/1000, (b) 3/0.1/1000, (c) 6/0.5/1000, (d) 6/10/1000, with absorbance scale divided by 5.

We observe two signatures at 3538.5 and 3569 cm^{-1} that follow the same intensity evolution of the water dimer bands and so are attributed to the 1:2 complex (Fig. 4(d)). At higher H_2S concentration, a broad band composed of several peaks at 3576.7, 3578.5, 3581.4 (the most intense), and 3583.8 cm^{-1} is attributed to the 2:1 complex (Figs. 4(b)-4(c)) and a signature at 3543.6 cm^{-1} also appears with even higher H_2S concentration and weak H_2O concentration and it is tentatively attributed to the 3:1 complex.

In the ν_3 asymmetric O-H stretching region (Fig. 5) the 1:1 complex is characterized by two bands: one at 3734.5 cm^{-1} that grows on the high frequency side of the PD water dimer at 3733.7 cm^{-1} and another one at 3743.5 cm^{-1}. A band at 3725.1 cm^{-1} is attributed to the 1:2 complex and the signature of the 2:1 is composed of four bands at 3716.0, 3718.0, 3720.2, and 3722.0 cm^{-1}**.** Two signatures at 3706.3 and 3745.5 cm^{-1} can be tentatively attributed to 3:1 and n:1 when H_2S concentration is high. All the signatures of n:1 complexes in the different spectral regions are composed of a set of several bands. We also observe combinations bands in the $\nu_1+\nu_2$ region at 5130.0, 5159.5, and 5198.0 cm^{-1} for the 1:2, 2:1, and 1:1 complexes, respectively, and two bands at 5306.0 and 5318.0 cm^{-1} in the $\nu_2+\nu_3$ region for 1:2 and 1:1 complexes (Table II).

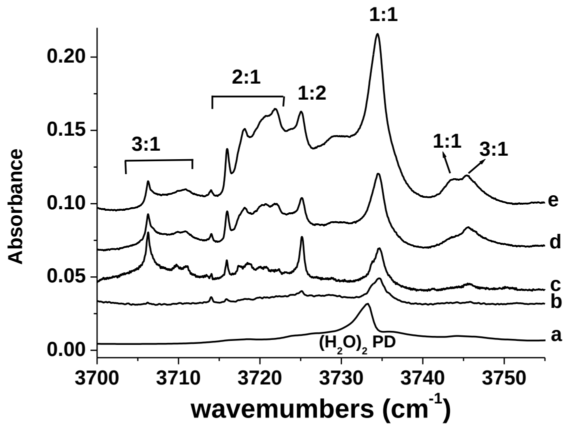

FIG. 5. Spectra in the H_2O stretching ν_3 region at 3 K deposition, with different $H_2S/H_2O/Ne$ concentration ratios. (a) 0/1/1000, (b) 1.5/0.1/1000, (c) 3/0.1/1000, (d) 6/0.1/1000, (e) 6/0.2/1000

3. Intermolecular spectral region

A very recent study[40] limited to the observation of H_2O libration motion in the FIR has been published about microsolvation of organic molecules in Ne matrix and in particular of H_2S-H_2O in a brief paragraph. The authors observed a band at 324.5 cm^{-1} attributed to a signature of 1:1 complex. Thanks to our experimental device we can probe the intermolecular region between 80 and 500 cm^{-1} where many signatures of H_2O dimer and trimer are present (Fig. 6(a)). We report the observed values (Fig. 6) in Table II. A well-defined intense band at 110 cm^{-1} and two weak broad ones at 291 and 333 cm^{-1} appear when H_2S is added to water especially visible on the spectrum with a lower water concentration (Fig. 6(b)) and are attributed to the 1:1 complex. A band at 195.4 cm^{-1} and a weak broad one at 360 cm^{-1} are observed when H_2S concentration is high and they are attributed to the 2:1 complex due to their concentration evolution. We can attribute signatures (Fig. 6(c)) to the 1:2 complex at 252 (the most intense), 283 and 325 cm^{-1} when H_2O concentration is high because they follow the H_2O dimer evolution. We do not agree with the attribution of the reference 40 for the band at 324.5 cm^{-1} to the 1:1 complex. We also observe a weak broad band at 3974 cm^{-1} that can be related to a combination between intra- and intermolecular of H_2O modes for the 1:2 complex: ν_3+252 = 3725+252=3977 cm^{-1}.

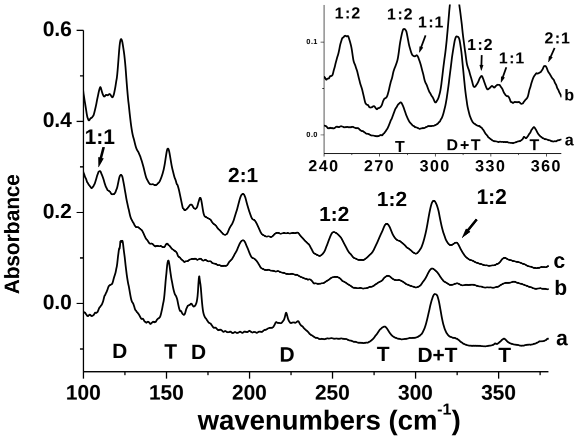

FIG.6. Spectra in the 100-400 cm^{-1} region at 3 K deposition, with different $H_2S/H_2O/Ne$ concentration ratios. (a) 0/2/1000, (b) 6/0.5/1000, (c) 6/2/1000. The 240-400 cm^{-1} range is enlarged in the inset. D and T are for H_2O dimer and trimer, respectively.

TABLE I. Observed frequencies (cm^{-1}) and assignments in different H_2S regions of $(H_2S)_n$-$(H_2O)_m$ complexes isolated in solid neon. The most intense bands are in bold.

n:m	Assignment	Frequencies (cm^{-1})
$(H_2S)_2$	ν_2	1179.2
		1181.8, 1182.8, 1184.0
2:1	ν_2	1187.1
1:1	ν_2	1188.1
H_2S	ν_2	1190.4
1:2	ν_1	2562.2
$(H_2S)_n$		2567.6, 2570.1
2:1	ν_1	**2567.4**, 2568.4 PD
		2579.4, 2580.4 PA
$(H_2S)_3$	ν_1	**2581.8**, 2582.8, 2584.2
1:1	ν_1	2592.3, **2593.8**
$(H_2S)_2$	ν_1	2596.0, **2596.5** PD
		2602.1, **2605.0** PA
1:2	ν_3	2610.6
$(H_2S)_3$	ν_3	2617.9, **2619.0**
$(H_2S)_2$	ν_3	**2622.1**, 2623.5 PD or PA
1:1	ν_3	2623.9

TABLE II. Observed frequencies (cm^{-1}) and assignments in the far-IR and in H_2O regions of $(H_2S)_n$-$(H_2O)_m$ complexes isolated in solid neon. Most intense bands are in bold.

n:m	Assignment	Frequencies (cm^{-1})
1:1	ν_{inter}	**110**, 291, 333
1:2	ν_{inter}	**252,** 283, 325
2:1	ν_{inter}	**195.4**, 360
H_2O	ν_2 (nrm)	1595.6
1:1	ν_2	1597.0, **1602.0**
2 :1	ν_2	1598.7
$(H_2O)_2$	ν_2	**1599.2** PA, 1616.5 PD
1 :1	$2\nu_2$	3157.8, **3165.8**
2 :1	$2\nu_2$	3158.8
$(H_2O)_2$	$2\nu_2$	3163.0, 3193.7
1:2	ν_1	**3538.5** PD, 3569 PA
3:1	ν_1	3543.6
2:1	ν_1	3576.7, 3578.5, **3581.4**, 3583.8
$(H_2O)_2$	ν_1	**3590.5** PD, 3660.6 PA
1:1	ν_1	**3613.3**, 3655.2
H_2O	ν_1 (nrm)	3665.4
H_2O	ν_1 R(0)	3696.6
3:1	ν_3	3706.3
2:1	ν_3	**3716.0**, 3718.0, 3720.2, 3722.0
1:2	ν_3	3725.1 PA
H_2O	ν_3 P(1)	3735.7
1:1	ν_3	**3734.5**, 3743.5
$(H_2O)_2$	ν_3	**3733.7** PD , 3763.5 PA
3:1	ν_3	3745.5
H_2O	ν_3 (nrm)	3761.0
H_2O	ν_3 R(0)	3783.3
1:2	ν_3+252	3974
1:2	$\nu_1+\nu_2$	5130.0
2:1	$\nu_1+\nu_2$	5159.5
1:1	$\nu_1+\nu_2$	5198.0
1:2	$\nu_2+\nu_3$	5306.0
1:1	$\nu_2+\nu_3$	5318.0

IV. VIBRATIONAL ASSIGNMENTS AND DISCUSSION

For such weak van der Waals complexes, following the effect of complexation by using the vibrational shift between the monomer and complexes ($\Delta\nu=\nu_{mono}-\nu_{complex}$) is a good spectroscopic diagnosis to match the observed bands with modes of the different complexes. The comparison between the theoretical and experimental $\Delta\nu$ values can confirm our experimental attributions and helps to deduce, if possible, the structure of the observed 1:1, 1:2, and 2:1 complexes. As mentioned in introduction, calculated vibrational data[32] have been performed for the two 1:1 isomers (H_2O and H_2S proton donor), so the harmonic CCSD(T)/ha(Q+d)Z data will be taken as reference to calculate the theoretical shifts. These data are in agreement with those of reference 31 and with our calculations (Table S1 in the supplementary material). For 0.1, 1:0, 0:2, 2:0, 1:2, and 2:1 we have performed harmonic calculations at MP2 PVTZ level for the geometries, dissociation energies D_0 (Table S2 of the supplementary material), harmonic frequencies, and intensities (Table S3 and S4 in the supplementary material).

A. H_2S dimer

We report in Table III the H_2S and $(H_2S)_2$ intramolecular frequencies in gas phase[23,24], in our solid neon work and given by the MP2 PVTZ calculations, and the shifts $\Delta\nu=\nu(H_2S)-\nu((H_2S)_2)$. As we do not observe the two stretching modes ν_1 and ν_3 for the H_2S monomer we take the gas values[23] to calculate $\Delta\nu$, knowing that differences between Ne matrix and gas frequencies are small. We report only the frequency of the main band having the higher intensity or the mean frequencies when they are many trapping sites.

TABLE III. H_2S and $(H_2S)_2$ experimental frequencies in gas phase, in solid Ne , $\Delta\nu=\nu(H_2S)-\nu((H_2S)_2)$, and harmonic calculated ones in cm^{-1}. Intensities are in parenthesis (in km/mol for calculated ones and relative values for experimental ones normalized on the most intense one to 100).

	H_2S			$(H_2S)_2$					
	Calculated[a]	Gas[b]	Ne[a]	Calculated[a]		Gas[c]		Ne[a]	
					$\Delta\nu$		$\Delta\nu$		$\Delta\nu$ (H_2S)g
ν_3	2793	2628.4		2789 (2) PA	+4	2618	+10.4	2622.1 (10)[d]	+6.3
				2784 (4) PD	+9	2618	+10.4	2622.1 (10)[d]	+6.3
ν_1	2773	2614.4		2769 (1) PA	+4	2605	+9.4	2605.0 (25)	+9.4
				2730 (82) PD	+43	2590	+24.4	2596.5 (100)	+17.9
ν_2	1211	1182.6	1190.4	1216 (1) PD	-5	-		1183 (25)	-0.3
				1209 (4) PA	+2	-		1179.2 (20)	+3.5

[a] This work.

[b] Ref 23 for ν_1 and ν_3 and Ref 19 for ν_2.
[c] Ref 24.
[d] the 2622.1 cm^{-1} value is the PA or the PD band (see text).

The H_2S dimer assignments are supported by the gas phase observation and calculations. We can attribute the observed bands at 2596.5 and 2605.0 cm^{-1} to ν_1 vibrations of the proton donor and proton acceptor, respectively, and the one at 2622.1 cm^{-1} is the signature of the ν_3 mode but it is not possible to attribute this band to the proton donor or acceptor (Table III).

B. H_2S-H_2O complex

In this paragraph we discuss the assignment of observed bands to the isomers, HOH-SH$_2$ noted A or HSH-OH$_2$ noted B. Our D_0 calculations (Table S2 in supplementary material) for these two isomers show that they are isoenergitic (-1.63 and -1.56 kcal/mol for A and B, respectively) as also mentioned in reference 32.

We report in Table IV intramolecular CCSD(T)[32] harmonic and experimental frequencies and intensities and corresponding $\Delta\nu$ values for A and B isomers. All the vibrations are given in Table S1 of the supplementary material. As we have mentioned above, we take the ν_1 and ν_3 gas phase values for the H_2S monomer to calculate $\Delta\nu$.

TABLE IV. Comparison of vibrational data (cm^{-1}) between observed and CCSD(T) calculated values for the two isomers of 1:1 complex. The intensities are in parenthesis (in km/mol for calculated ones and relative values for experimental ones normalized on the most intense one to 100).

		Calculated				Experimental		
		A		B				
			$\Delta\nu$		$\Delta\nu$		$\Delta\nu_{exp}$	assignment
H_2O	ν_3	3914 (112)	+31	3938 (72)	+7	3734.5 (60)	+26.5	A
						3743.5 (10)	+17.5	B
	ν_1	3781 (106)	+54	3828 (8)	+7	3613.3 (100)	+52.1	A
						3655.2 (7)	+10.2	B

	ν_2	1657 (38)	-7	1649 (73)	+1	1597.0 (90)	-1.4	B
						1602.0 (100)	-6.4	A
H_2S	ν_3	2735 (3)	+4	2733 (4)	+6	2623.9 (7)	+4.5	A or B
	ν_1	2719 (2)	+4	2700 (54)	+23	2593.8 (20)	+20.6	B
	ν_2	1208 (0.2)	+2	1218 (1)	-8	1188.1 (1)	-8.8	B

If we compare $\Delta\nu_{theo}$ with $\Delta\nu_{exp}$ we can conclude that the two observed more intense stretching modes of water perturbed by a H_2S molecule at 3734.5 and 3616.3 cm^{-1} belong to the ν_3 and ν_1 modes of isomer A. The signatures of B isomer are also observable at 3743.5 and 3655.2 cm^{-1}. The intensities of O-H bands attributed to A isomer are calculated stronger than those of the B isomer. This is in agreement with the well-known signature of the O-H hydrogen bond for a proton donor interaction.[41] For the water ν_2 bending mode we observe two bands at 1602.0 and 1597.0 cm^{-1} which are in agreement with the signature of A and B, respectively.

For the H_2S modes regions, the observed ν_2 and ν_1 bands can be attribute to B isomer, H_2S proton donor, because the $\Delta\nu_{theo}$ and $\Delta\nu_{exp}$ are very close and the intensities of the bands of this isomer are significantly stronger than those for A bands. The observed ν_3 band can be the signature of the A or B isomer. In conclusion we observe the signatures of H_2O ν_1, ν_2 and ν_3 modes perturbed by H_2S of the both A and B isomers and only the most intense ones of H_2S perturbed by H_2O.

For the multiquanta transitions, we observe the $2\nu_2$ overtone for the A and B isomers at 3165.8 and 3157.8 cm^{-1}, respectively, and the deduced anharmonicity coefficients are 19.1 and 18.1 cm^{-1}, close to the H_2O dimer values, 19.7 (PD) and 17.7 (PA) cm^{-1}. For the combination bands $\nu_1+\nu_2$ and $\nu_2+\nu_3$, the deduced anharmonicity coefficients are $X_{1,2}$ = -17.3 cm^{-1} and $X_{2,3}$= -18.5 cm^{-1}, similar to those of PD water dimer, -15.8 and 17.6 cm^{-1}, respectively.

For the intermolecular bands, we attribute a signature at 110 cm^{-1} and weak bands at 291 and 333 cm^{-1} to the 1:1 complex. The most intense calculated CCSD(T) harmonics intermolecular frequencies[32] with intensities in parenthesis are 123(53), 271(22) and 417(55) cm^{-1} for A isomer and 143(76) and 347(32) cm^{-1} for B isomer. It is very difficult to attribute the observable bands to A or B isomer. Indeed, the most intense signature observed at 110 cm^{-1} can be associated to the calculated ones at 123 or 143 cm^{-1} belonging to A and B, respectively. The band at 291 cm^{-1} can be associated to 271 or 347 cm^{-1}, and the band at 333 cm^{-1} can be compared to 417 cm^{-1}, or 347 cm^{-1}, signatures of A and B isomers, respectively. A better assignment is not possible.

C. $(H_2S)_2$-H_2O complex

As no theoretical data exist on the 2:1 complex we have performed calculations at MP2 pVTZ level to obtain the stable geometry and vibrational data (Tables S4 and S5 in the supplementary material). The Figure 7 displays the most stable structure with a D_0 value of -4.56 kcal/mol. The 2:1 complex is formed by a H_2S dimer and by a H_2O molecule through a hydrogen bond between one H atom of H_2S and the O atom of water, and a second weaker hydrogen bond exists between one H atom of water and the S atom. The 2:1 complex forms a ring where the H_2S dimer is bonded to the H_2O molecule with weak shortening of bonds (r_{HS}=2.74 Å in $(H_2S)_2$, r_{SH}=2.53 Å in A isomer and r_{HO}=2.18 Å in B isomer, values calculated at the same MP2 level as 2:1 complex).

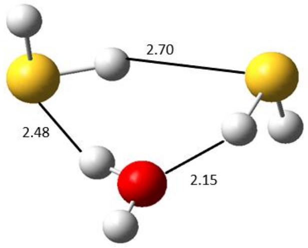

Fig. 7. Geometry of the most stable form of 2:1 complex at the MP2 level. The distances are in Å.

We compare the calculated and experimental frequencies shifts between the H_2S dimer and the 2:1 complex for the H_2S frequencies, $\Delta\nu=\nu(H_2S)_2-\nu(2:1)$, and between H_2O monomer and the 2:1 complex for H_2O frequencies, $\Delta\nu=\nu(H_2O)-\nu(2:1)$. All the values are reported in Table V, where we take the frequencies of the main bands and the mean value for multi sites bands. Our theoretical data (Table S1 in the supplementary material) are in agreement with literature for monomer and dimers.[28,29]

The observed bands at 2567.4 and 2579.4 cm^{-1} are correlated to ν_1 PD and PA vibrations in H_2S dimer perturbed by H_2O, respectively, essentially because the PD vibration is at low frequency. For the ν_2

bending mode, only one band is observed and it is impossible to attribute it to the PA or PD since the calculated Δν values are too close.

As well for the perturbation of water frequencies by the presence of a H_2S dimer, the two stretching modes are more perturbed in comparison with the bending mode. We observe a very good match between experimental and calculated values which confirms our attributions for the three H_2O modes. We observe the $2\nu_2$ overtone and the $\nu_1+\nu_2$ combination at 3258.8 and 5159.5 cm^{-1}, respectively, and the deduced anharmonicity coefficients are X_{22} = -19.3 cm^{-1} and X_{12} = -20.6 cm^{-1}.

Table V. Experimental and calculated (MP2/AVTZ) frequencies and shifts (cm^{-1}) for 0:1, 2:0 and 2:1 complexes. Intensities are in parenthesis (in km/mol for calculated ones and relative values for experimental ones normalized on the most intense one to 100).

H_2S	Calculated			Experimental		
	2:0	2:1	$\Delta\nu^a$	2:0	2:1	$\Delta\nu^b$
ν_1	2769 (1) PA	2716 (122)	+53	2605.0 PA	2579.4 (100) PA	+25
	2730 (82) PD	2692 (91)	+38	2596.5 PD	2567.4 (10) PD	+28
ν_2	1216 (4) PD	1215 (1)	+1	1183	1187.1 (1)	-4.1
	1209 (1) PA	1214 (3)	-5	1179.2	1187.1	-8.1
H_2O						
	0:1	2:1	$\Delta\nu^b$	0:1	2:1	$\Delta\nu^b$
ν_3	3948 (75)	3903 (141)	+45	3761.1	3716 (80)	+45.1
ν_1	3822 (5)	3716 (216)	+106	3665.4	3581.4 (50)	+84
ν_2	1628 (72)	1631 (45)	-3	1595.6	1598.7 (70)	-3.1

[a] $\Delta\nu=\nu(H_2S)_2-\nu(2:1)$

[b] $\Delta\nu=\nu(H_2O)-\nu(2:1)$

In the FIR, we observe two bands at 195 and 360 cm^{-1} for the 2:1 complex. The first one is very intense and can be assigned to the calculated one at 256 cm^{-1} which has the largest intermolecular calculated intensity (Table S4 in the supplementary material) and the weak one can be correlate to the calculated one at 319 or 441 cm^{-1} which have lower intensities.

D. H_2S-$(H_2O)_2$ complex

In literature[27] few experimental data can be found on the 1:2 complex. Like for the 2:1 one, we have performed calculations at MP2 pVTZ level to find the most stable structure and vibrational data. (Tables S4 and S5 in the supplementary material). The Figure 8 represents the most stable structure formed by a slightly disturbed water dimer, with a shorter length r_{OH}=1.90 Å, in regard to r_{OH}=1.94 Å in water dimer, where H_2S is added through a hydrogen bond between one H atom of H_2S and O atom of water. Another weaker hydrogen bond exists between one H atom of H_2O and the S atom. Bond dissociation energy D_0 calculated on the counterpoise (CP) correction and zero point energies at MP2 pVTZ harmonic level is found at - 4.81 kcal/mol. The water vibrations of 1:2 complex are compared with those of the water dimer and the H_2S vibrations with those of the H_2S monomer (Table VI).

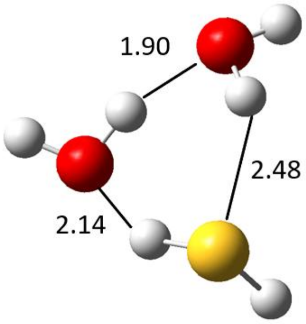

Fig. 8. Geometry of the most stable form of 1:2 complex at the MP2 level. The distances are in Å.

Table VI. Experimental and calculated (MP2/AVTZ) frequencies and shifts (cm^{-1}) for 1:0, 0:2, and 1:2 complexes. Intensities are in parenthesis (in km/mol for calculated ones and relative values normalized on the most intense one to 100 for experimental ones).

H_2O	Calculated			Experimental		
	0:2	1:2	$\Delta\nu$ [a]	0:2	1:2	$\Delta\nu$ [a]
ν_3	3935 PA	3897 (42) PA	+38	3763.5 PA	3725.1 (10) PA	+38.4

ν_3	3915 PD	3906 (31) PD	+9	3733.7 PD	-	
ν_1	3814 PA	3697 (100) PA	+117	3660.6 PA	3569.0 (100) PA	+91.6
ν_1	3719 PD	3648 (65) PD	+71	3590.5 PD	3538.5 (90) PD	+52
H_2S						
	0:1	1:2	$\Delta\nu$ [b]	0:1	1:2	$\Delta\nu$ [b]
ν_3	2793	2780 (1)	+13	2628.4	2610.6 (10)	+17.8
ν_1	2773	2687 (37)	+86	2614.4 [c]	2562.2 (40)	+52.2

[a] $\Delta\nu=\nu(H_2O)_2-\nu(1:2)$

[b] $\Delta\nu=\nu(H_2S)-\nu(1:2)$

[c] gas value (Ref 23)

We attribute without ambiguity the PD and the PA of the ν_1 H_2O vibrations and the PA of ν_3 vibration thanks to the comparison between the calculated and observed shifts that are in very good agreement, and the calculated intensities are in agreement with the observed intense bands. For the H_2S vibrations we do not observe the ν_2 bending mode but the attribution of the two stretching modes can be made with any ambiguity with the help of calculations (Table VI).

The intense observed signature of the 1:2 complex in the FIR is at 250 cm^{-1} and with regard to the calculations we can associate this band at the most intense harmonic calculated frequencies at 309 or 345 cm^{-1}. (Table S4 in the supplementary material). We observe the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ combinations at 5130.0 and 5306.0 cm^{-1}, respectively, but we cannot deduce the anharmonicity coefficients since we do not observe the ν_2 transition.

V. Conclusion

For the first time a neon matrix isolation infrared study of the $(H_2S)_n(H_2O)_m$ complexes has been carried out from 80 to 6000 cm^{-1}. Using different $H_2S/H_2O/Ne$ concentration ratios we identify several bands of the 1:1, 1:2, and 2:1 complexes. The existence of the two isomers for the 1:1 complex, H_2O proton donor (HOH-SH$_2$) and H_2O proton acceptor (HSH-OH$_2$), have been highlighted by comparing theoretical and experimental vibrational shifts between the monomer and complexes ($\Delta\nu=\nu_{mono}-\nu_{complex}$).

With the help of ab initio calculation the 1:2 and 2:1 complexes have been identified thanks to the observation of six frequencies of each of them. In the two cases these complexes are formed from a slightly distorted homodimer on which a H_2S or H_2O molecule is bound. Careful examination of the far infrared region allows the assignment of 1:1, 2:1, and 1:2 intermolecular modes. All these observed data and especially the intermolecular vibrations, difficult to observe without the matrix isolation technique, are important to improve theoretical approach for the study of very weak complexes.

Supplementary Material

See supplementary material for binding energies, Harmonic frequencies and Intensities calculated for monomers, dimers, the two isomers of 1:1, the most stable 1:2 and 2:1 complexes and Cartesian coordinates for 1:2 and 2:1 complexes.

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