Vibrational study of the CS 2 -H 2 O, CS 2 -(H 2 O) 2 , and (CS 2) 2 -H 2 O complexes isolated in solid neon. Highlighting the existence of two isomers for CS 2 -H 2 O

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Vibrational study of the CS_2-H_2O, CS_2-$(H_2O)_2$, and $(CS_2)_2$-H_2O complexes isolated in solid neon. Highlighting the existence of two isomers for CS_2-H_2O.

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Abstract

For the first time the investigation of water molecule complexed with CS_2 molecule in solid neon was performed in a large frequencies range from near to far infrared using Fourier transform infrared spectroscopy. From concentration effects and with the help of theoretical results we have identified several vibrational transitions for CS_2 dimer, CS_2-H_2O, CS_2-$(H_2O)_2$ and $(CS_2)_2$-H_2O complexes. We have also highlighted the presence of two isomers for CS_2-H_2O. Theoretical calculations at the second-order Møller-Plesset level (MP2) have been performed to obtain the equilibrium geometries and vibrational spectra at the harmonic level and comparison with experimental data allows us to give structures of observed complexes. Finally, the results are compared with thoses of the isolectronic complexes N_2O-H_2O, CO_2-H_2O, and OCS-H_2O previously published.

KEYWORDS: carbon disulfide, carbon disulfide-water complex, Hydrogen Bond, Infrared Spectroscopy, Neon Matrix Isolation, ab initio calculations, isomer.

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1. Introduction

Weakly bound complexes are important for describing the chemistry of Earth's atmosphere [1] and hydrogen bonding interaction, the most important non-covalent interaction, plays a key role in many chemical and biological processes and the structures of hydrogen-bonded complexes are of great theoretical and experimental interest [2]. That is why we have investigated in the last years hydrated complexes formed of CO2 [3], OCS [4], N_2O [5], and H_2S [6] and water molecules. Carbon disulfide is one of the simplest triatomic molecules as carbon dioxide, so it would be interesting to study the complex CS_2-H_2O and to compare the results with those obtained with its isoelectronic analogs CO_2, OCS, and N_2O. Therefore we have undertaken for the first time the infrared study in solid neon of $(CS_2)_n$-$(H_2O)_m$ complexes, noted n:m (n and m equal to 1 or 2). The advantage of noble gas matrix [7] and particularly the neon cage is its low interaction with the involved molecules, so the matrix cage effects are weak and it is important for such weak complexes as we have shown in previous studies [3-6].

Few studies exist in literature for this system. A microwave work [8] on 1:1 complex concludes to a C_{2v} planar geometry as the most stable one with a sulfur atom bonded to the oxygen atom of water. A theoretical work [9] calculated the equilibrium geometries of several hydrated complexes including CS_2-H_2O using CCSD(S,D,T) ab initio method and the authors have found a C_{2v} planar equilibrium in agreement with the microwave observation [8]. Another study [10] predicted geometries of CS_2-$(H_2O)_n$ complexes with n=1-4 and two isomers are predicted for the 1:1 complex, the C_{2V} structure already mentioned above and a C_S one with a hydrogen bond between H and S atoms. Frequencies and intensities are also given. A recent experimental and theoretical study [11] in the far infrared in solid para-hydrogen predicted two different isomers for the 1:1 as the previous work but only the C_{2V} structure is observed. There is no experimental data in literature for the 2:1 complex but the CS_2 dimer and trimer have been the subject of several theoretical and gas phase experimental works [12-15] notably recently for the ν_3 and the $\nu_1+\nu_3$ combination of the dimer [15]. A cross shaped structure D_{2h} is observed and calculated as the most stable conformer.

To the best of our knowledge there are no reported experimental infrared results for the $(CS_2)_n$-$(H_2O)_m$ complexes that is why we undertook this study to obtain vibrational data from the far infrared

(intermolecular vibrations region) to the near infrared (overtones and combinations bands region). We also want to prove or not the existence of the two isomers for the 1:1 complex in the matrix.

After a brief description of the experimental conditions, experimental spectra will be presented. We will report our calculations at the same level, MP2 aug-cc-pVTZ, for all the observed monomers, dimers and 1:1, 1:2, and 2:1 complexes. 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.

2. Experimental and theoretical details

2.1 Experimental apparatus

Samples were prepared by co-condensing CS_2-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/CS_2 molar ratio varies between 100 and 6000, and the neon/water molar ratio varies between 100 and 2000. In the experiments with water it is important to saturate the stainless steel vacuum line to measure accurate pressures. Absorptions spectra were recorded between 50 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. Some spectra were recorded after annealing at 12 K. Natural water and CS_2 (Aldrich, 99.0 % purity) samples were degassed under vacuum before use. Neon from Air Liquide with a purity of 99.995 % was used.

2.2 Computational details

To compare all the vibrational data for the 1:0, 0:1, 0:2, 2:0, 1:1, 1:2, and 2:1 complexes with each other we have performed calculations at second order Møller-Plesset (MP2) with the Gaussian09 package [16] and the augmented correlation-consistent basis set aug-cc-pVTZ (AVTZ) of Dunning and co-workers [17,18] to obtained equilibrium geometries, equilibrium (D_e) and ground state (D_0) binding energies with BSSE and zero point energy(ZPE) corrections, harmonic vibrational frequencies and infrared intensities.

3. Spectral data and assignments

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 [19,20]. Few studies [21,22] have been done on the CS_2 monomer in matrix and the only available experimental data on the CS_2 dimer [13,15] and trimer [12,15] were obtained by McKellar group in gas phase.

Our experiments were performed using different concentration ratios of CS_2/H_2O/Ne gas mixtures to identify the transitions of the n:m complexes. It is important to notice that the intensities of the ν_2 bending mode is weak and the ν_1 mode is inactive, so the concentration of CS_2 needed to observe all the signatures of $(CS_2)_n$ –$(H_2O)_m$ complexes in the frequency domain of CS_2 modes must be very high. Figures 1-8 illustrate the IR spectra in different frequency ranges. Table 1 and 2 summarize our measured vibrational frequencies of $(CS_2)_n$-$(H_2O)_m$ complexes for the H_2O and CS_2 spectral regions, respectively.

3.1 Intermolecular spectral region

We investigate the far infrared region (Fig. 1 and Table 1) and we observe, in addition to the water dimer (122 and 170 cm^{-1}) and trimer bands (150 cm^{-1}), four well-defined bands that appear when CS_2 is added to water and are attributed to the 1:1 complex because they linearly follow the concentration of CS_2 or H_2O. Two bands are close together at 110 and 116 cm^{-1} and two others ones at 192.5 and 209.5 cm^{-1}. We do not agree with the attribution of the two latter bands to the 1:2 complex as reported in reference 11. Even if the quality of the spectra performed in a para-hydrogen matrix allows to obtain narrow signals and good S/N ratio, the intensities of the bands at 192.5 and 209.5 cm^{-1} do not seem to follow the variation of concentration of the water dimer but that of the water monomer.

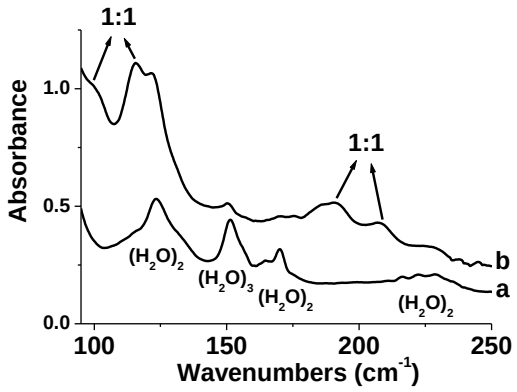

Fig. 1. Spectra in the 100-250 cm^{-1} region at 3 K deposition, with different CS_2/H_2O/Ne concentration ratios. (a) 0/0.5/1000, (b) 20/0.1/1000

3.2 H_2O spectral regions

Near the ν_2 bending mode of the H_2O nonrotating monomer (nrm) at 1595.6 cm^{-1} (Fig. 2), a new intense band appears at 1597.6 cm^{-1} when CS_2 is added to H_2O and it is assigned to the 1:1 complex. When the concentration of CS_2 is important a broad band at 1594.3 cm^{-1} that is attributed to 2:1 complex. At high water concentration a band at 1612.5 cm^{-1} appears near the rotation line $Q_+(1)$ of the ν_2 water monomer at 1614.2 cm^{-1} and this band follows the intensity evolution of the water dimer band at 1616.5 cm^{-1} and so belongs to 1:2 complex. Since the ν_2 region is congested at high water concentration, it is easier to see this band for a dilute water sample where an annealing is done at 12 K (Fig. 2d). Also, two broad bands are observed above the ν_2 fundamental at 1700 and 1716 cm^{-1} (Fig. S1) and follow the other signatures attributed to the 1:1 complex. These two bands are combinations of ν_2 bending mode with the intermolecular modes at 100 and 116 cm^{-1}.

Close to the $2\nu_2$ of $(H_2O)_2$ we observe the overtones of 2:1 and 1:1 complexes at 3152 and 3159.0 cm^{-1}, respectively. The deduced anharmonic coefficients are 18.3 and 18.1 cm^{-1}, respectively, close to the H_2O dimer, 17.7 cm^{-1}. In the ν_1 H_2O region (Fig. 3) two signatures at 3644.8 and 3658.9 cm^{-1} follow linearly the concentration of H_2O or CS_2 and are attributed to 1:1 complex. At higher water concentration an intense band at 3569.2 cm^{-1} grows like the signature of the ν_1 proton donor (PD) of the H_2O dimer observed at 3590.5 cm^{-1} and is attributed to the ν_1 PD of 1:2 complex. A weak band associated with it is observed at 3638.6 cm^{-1} near the ν_1 proton acceptor (PA) of the H_2O dimer at 3660.6 cm^{-1} and so it is the signature of the

ν_1 PA of 1:2 complex. A broad band at 3633.3 cm^{-1} is attributed to 2:1 complex because appears when CS_2 concentration becomes important. Others bands grow significantly at 3618.3 and 3626.1 cm^{-1} (not shown) and are signatures of complexes formed of more than two CS_2 molecules.

In the asymmetric ν_3 O-H stretching region (Fig. 4) two bands, one narrow and one weak, at 3728.7 and 3739.4 cm^{-1} are attributed to the 2:1 complex. We did not observe the ν_3 signature of 1:1 in this region but we can deduce a frequency interval for its value thanks to the observation of two bands at 3863 and 3877 cm^{-1} that follow the other signatures attributed to the 1:1 complex (Fig. 5). These two bands are combinations of ν_3 O-H stretching mode with the intermolecular modes at 100 and 116 cm^{-1} and so we deduce a frequencies range of 3750-3765 cm^{-1} for ν_3. We have a similar situation for the 1:2 complex since we do not observe the ν_3 signature but we can deduce a frequencies interval for its value thanks to the observation of the combination band $\nu_2+\nu_3$ at 5323 cm^{-1}. Using the anharmonicity constant of the water dimer [19], we can deduce a frequencies range of 3726-3730 cm^{-1} for ν_3.

Table 1

Observed frequencies (cm^{-1}) and assignments in intermolecular region and different H_2O regions of $(CS_2)_n$-$(H_2O)_m$ complexes isolated in solid neon.

n:m	Assignment	Frequencies (cm^{-1})
1:1	ν_{inter} [a]	100, 116, 192.5, 209.5
2:1	ν_2	1594.3
H_2O	ν_2 (nrm [b])	1595.6
1:1	ν_2	1597.6
1:2	ν_2	1612.5 PD
H_2O	ν_2 ($Q_+(1)$)	1614.2
$(H_2O)_2$	ν_2	1599.2 PA, 1616.5 PD
1:1	ν_2+100	1700
1:1	ν_2+116	1716
2:1	$2\nu_2$	3152.0
1:1	$2\nu_2$	3159.0
$(H_2O)_2$	$2\nu_2$	3163.0, 3193.7
1:2	ν_1	3569.2 PD
$(H_2O)_2$	ν_1	3590.5 PD, 3660.6 PA
n:1	ν_1	3618.3, 3626.1
2:1	ν_1	3633.3
1:2	ν_1	3638.6 PA

1:1	ν_1	3644.8 , 3658.9
H_2O	ν_1 (nrm)	3665.4
1:2	ν_3	3726-3730 PD [c]
2:1	ν_3	3728.7, 3739.4
1:1	ν_3	3750-3765 [d]
H_2O	ν_3 P(1)	3735.7
$(H_2O)_2$	ν_3	3733.7 PD , 3763.5 PA
H_2O	ν_3 (nrm)	3761.0
1:1	ν_3+100	3863
1:1	ν_3+116	3877
$(H_2O)_2$	$\nu_1+\nu_2$	5242.8 PA, 5191.2 PD
n:1	$\nu_2+\nu_3$	5300.0
1:2	$\nu_2+\nu_3$	5323.0 PD

[a] ν_{inter} : frequencies of the intermolecular modes.
[b] nrm : nonrotating monomer of H_2O (see text).
[c] Domain of values deduced from the combination mode ν_2+100 and ν_2+116 (see text).
[d] Domain of values deduced from the combination mode ν_3+100 and ν_3+116 (see text).

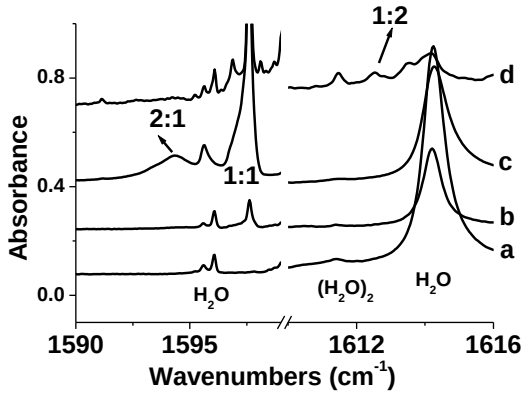

Fig. 2. Spectra in the H_2O bending ν_2 region at 3 K deposition, with different $CS_2/H_2O/Ne$ concentration ratios. (a) 0/1/1000, (b) 0.4/0.01/1000, (c) 10/0.02/1000, (d) annealing at 12 K of (b).

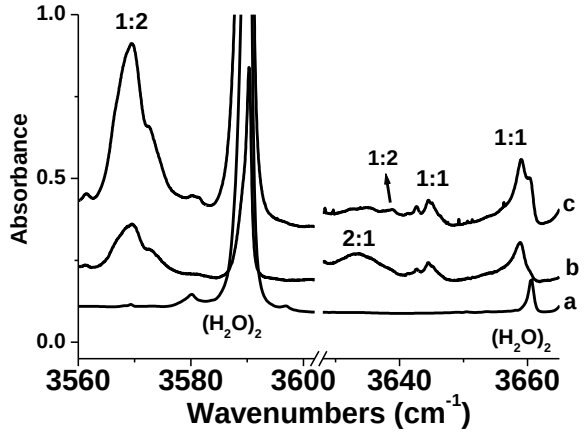

Fig. 3. Spectra in the H_2O stretching ν_1 region at 3 K deposition, with different $CS_2/H_2O/Ne$ concentration ratios. (a) 0/4/1000, (b) 20/3.75/1000, (c) 10/10/1000.

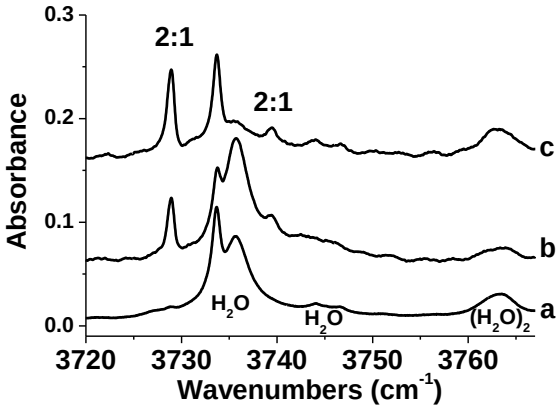

Fig. 4. Spectra in the H_2O stretching ν_3 region at 3 K deposition, with different $CS_2/H_2O/Ne$ concentration ratios. (a) 0/0.04/1000, (b) 0.8/0.04/1000, (c) 1/0.04/1000.

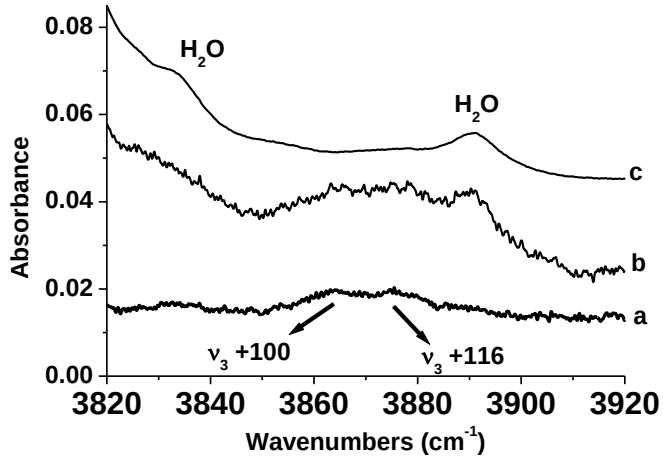

Fig. 5. Spectra in the H_2O $\nu_3 + \nu_{inter}$ combination region of 1:1 complex at 3 K deposition, with different $CS_2/H_2O/Ne$ concentration ratios. (a) 10/4/1000, (b) 10/10/1000, (c) 0/10/1000.

3.3 CS_2 spectral regions

Since there is no data on CS_2 isolated in solid neon, we first examine the spectrum of only CS_2/Ne deposition (Fig. 6-8). We observe the ν_2 band at 397.1 cm^{-1}, very near the gas phase value (396.0 cm^{-1}) [23], and in the region of the ν_3 vibration, we observe many bands, due to different sites, with a main band located at 1533.4 cm^{-1}, near the gas phase value [23] at 1535.4 cm^{-1}. We observe a similar multiple sites pattern on the combinations with the ν_3 mode (Table 2). Near the monomer's fundamentals we observe bands for the

CS_2 dimer, especially at higher concentration at 393.5, 657.7 and 1540 cm^{-1} for the ν_2, ν_1, and ν_3 modes, respectively. The observed CS_2 modes for the monomer, dimer, and $(CS_2)_n$-$(H_2O)_m$ complexes are reported in Table 2. In all this work, we will use the Hertzberg's convention for linear triatomic molecule: ν_3 and ν_1 for the S-C-S asymmetric and symmetric stretching modes, respectively, and ν_2 for the bending mode.

In the region of the CS_2 ν_2 bending mode (Fig. 6) a new band at 403.8 cm^{-1} appears when H_2O is added to CS_2 and follows linearly the concentration of CS_2 or H_2O so it belongs to the 1:1 complex. In the region of the ν_1 stretching mode (Fig. 7) on both sides of the band of the dimer at 657.7 cm^{-1} we observe two bands at 656.5 and 658.6 cm^{-1} attributed to 1:1 following concentration effects. A signature at 657.1 cm^{-1} appears when the concentration of CS_2 becomes high and belongs to 2:1.

In the region of the CS_2 ν_3 stretching mode (Fig. 8) a thin band at 1526.9 cm^{-1}, accompanied by many weaker bands due to different sites, and another one at 1531.3 cm^{-1} appear in the middle of the multi sites of CS_2 monomer band (Fig.8 b, c), both follow the same concentration dependent evolution and are attributed to the 1:1 complex. We observe a similar multiple sites pattern for the 1:1 complex on the $\nu_1+\nu_3$ combination band around 2175 cm^{-1} (not showed). A multi sites band with an intensity maximum at 1525.1 cm^{-1} becomes important when H_2O concentration is high and is attributed to 1:2 complex (Fig. 8c).

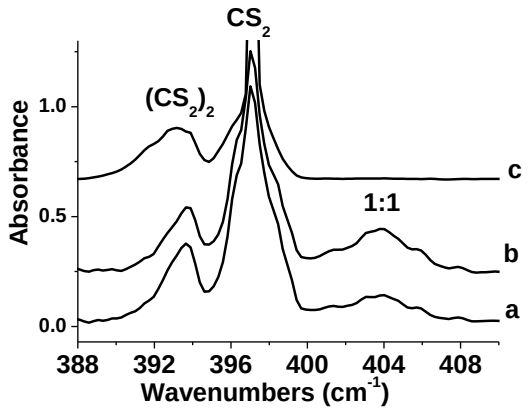

Fig. 6. Spectra in the CS_2 bending ν_2 region at 3 K deposition, with different $CS_2/H_2O/Ne$ concentration ratios. (a) 10/5/1000, (b) 10/10/1000, (c) 10/0/1000.

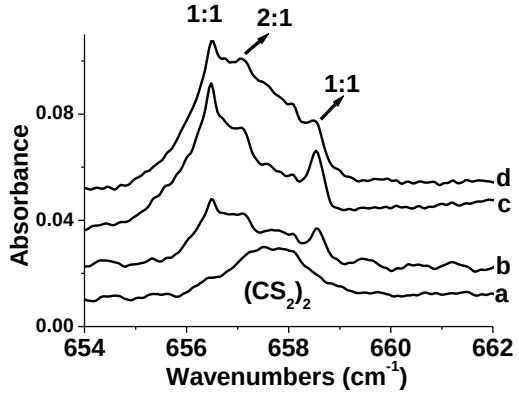

Fig. 7. Spectra in the CS_2 stretching ν_1 region at 3 K deposition, with different CS_2/H_2O/Ne concentration ratios. (a) 10/0/1000, (b) 10/5/1000, (c) 10/10/1000, (d) 20/5/1000.

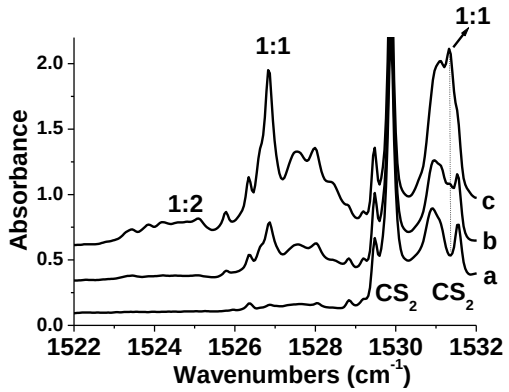

Fig. 8. Spectra in the CS_2 stretching ν_3 region at 3 K deposition, with different CS_2/H_2O/Ne concentration ratios. (a) 0.4/0/1000, (b) 0.4/1/1000, (c) 0.4/3/1000.

Table 2

Observed frequencies (cm^{-1}) and assignments in different CS_2 regions of $(CS_2)_n$-$(H_2O)_m$ complexes isolated in solid neon.

n:m	Assignment	Frequencies (cm^{-1})
$(CS_2)_2$	ν_2	393.5
CS_2	ν_2	397.1
1:1	ν_2	403.8
$(CS_2)_2$	ν_1	657.7
1:1	ν_1	656.5, 658.6
2:1	ν_1	657.1
1:2	ν_3	1525.1
1:1	ν_3	1526.9, 1531.3

CS_2	ν_3	1533.4
$(CS_2)_2$	ν_3	1540
CS_2	$\nu_1+\nu_3$	2183.6
1:1	$\nu_1+\nu_3$	2175.5, 2181.7
CS_2	$2\nu_2+\nu_3$	2324.5
1:1	$2\nu_2+\nu_3$	2330.0
CS_2	$2\nu_1+\nu_3$	2831.5
CS_2	$\nu_1+2\nu_2+\nu_3$	2961.9

4. THEORETICAL RESULTS

As mentioned in the introduction, we investigate calculations at MP2 level with the basis set aug-cc-pVTZ to find the most stable structures for the 1:1, 1:2, 2:0, and 2:1 complexes and to calculate frequencies and intensities to help to the assignment of the experimental spectra. For these complexes, data as D_0, frequencies and intensities are given in the supplementary material as well as the frequencies of the monomers. All the most stable calculated geometries are reported in Fig. 9.

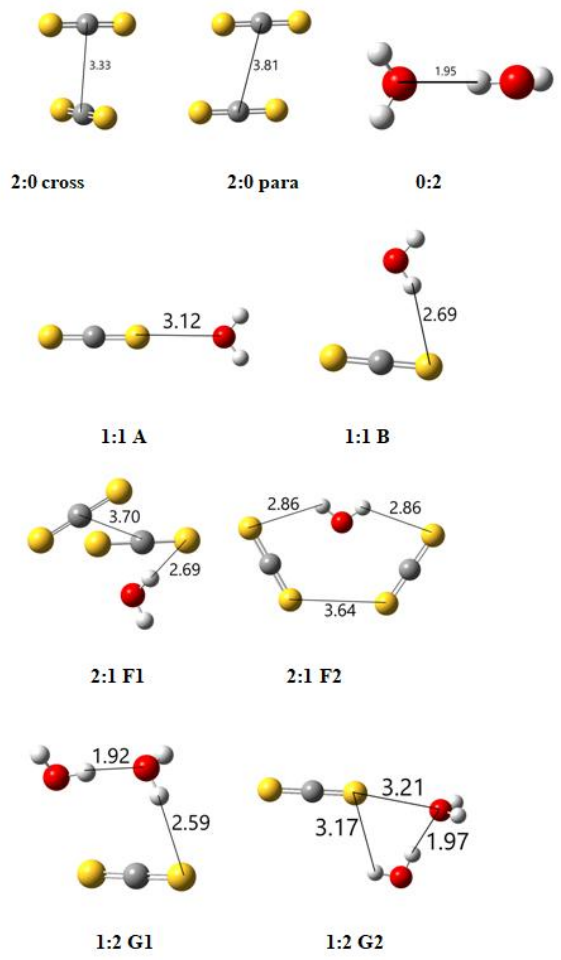

Fig. 9. The most stable calculated structures of different isomers of 0:2, 2:0, 1:1, 1:2, and 2:1complexes.

4.1. CS_2 dimer and CS_2-H_2O complex

For the CS_2 dimer two experimental infrared studies [13,15] conclude to the observation of a cross shaped structure. A theoretical study [14] compares different forms, notably a parallel and cross shape, with several levels of calculations and concludes at the same most stable isomer namely the cross one. So we calculate the geometries and frequencies of the two forms and the results are given in the Table S2 of supplementary material as well as the binding energy and Fig. 9 shows the most stable isomers. For the cross shaped structure, we find a D_0 equal to -4.2 kcal/mol and a C-C intermolecular distance of 3.33 Å. An experimental distance [13] of 3.54 Å is found and theoretical calculations [14] give 3.30 Å very near of our value. For the parallel structure, we find a D_0 equal to -3.7 kcal/mol.

For the CS_2-H_2O complex, two most stable isomers have a C_{2V} and C_S structure noted A and B, respectively (Fig. 9), with a binding energy D_0 of -1.42 and -1.20 kcal/mol, respectively. In Table S3 of the supplementary material we report all calculated frequencies and intensities. Our data are in agreement with the previous theoretical results [9-11] both for geometries and frequencies even for those calculated at the CCSD(T) level [11] reported in the supplementary material (Tables S1 and S3) .

4.2. $(CS_2)_2$-H_2O and CS_2-$(H_2O)_2$ complexes

For the $(CS_2)_2$-H_2O complex, we find a stable geometry noted F1 represented in Fig. 9 with a D_0 of - 1.92 kcal/mol. This structure is formed by a cross CS_2 dimer slightly distorted by the complexation with a water molecule. All frequencies and intensities are reported in Table S4. In the only theoretical study [11] on the 2:1 complex one structure is found and it corresponds to the one noted F2 in Fig. 9 formed by a parallel dimer deformed by a water molecule inserted between the two CS_2 molecules. We have optimized this geometry and we find a binding energy of - 0.2 kcal/mol so significantly higher compared to F1 so too high to be considered. It is difficult to compare our data obtained for the 2:1 complex with those of reference 11 because nowhere is there any mention of the geometry and binding energy of CS_2 dimer, data useful to study the 2:1 complex. The frequencies for these two isomers are reported in Table S4.

For the CS_2–$(H_2O)_2$ complex, the two most stable geometries, noted G1 and G2, are represented in Fig. 9 and all the frequencies are given in Table S4. The most stable one is G1 which has the same structure that 1:1 B complex where the water molecule is replaced by the water dimer, with a D_0 value of -2.84 kcal/mol while the G2 structure has a D_0 value of -1.68 kcal/mol. In the previous theoretical studies [10,11] many structures have been calculated and in reference 11 the two most stable ones have the same structures that ours with a reversal in stability, structure G2 very slightly more stable than G1 with a difference of binding energy of 0.17 kcal/mol. We do not use the same method of calculations that can explain this difference in the stability but the frequencies are comparable.

5. Vibrational assignments and discussion

5.1. CS_2-H_2O complex

From the concentration effects, attributions have been clearly established to the three n:m complexes. According to the calculations two isomers A and B for 1:1 complex can be observable because they have close binding energies, A is slightly more stable. So to go further in the assignment, thanks to the comparison of the theoretical and experimental values of the frequencies shifts between the monomer and 1:1 complex noted $\Delta\nu=\nu_{mono}-\nu_{complex}$ we can suggest an attribution of bands to isomer A or B. In Table 3 we report the calculated harmonic and observed frequencies and intensities and the corresponding $\Delta\nu$ for H_2O and CS_2 modes and for the intermolecular modes.

Table 3

Comparison of frequencies (cm^{-1}) and shifts ($\Delta\nu=\nu_{mono}-\nu_{complex}$) between observed and calculated data for the A and B isomers of the 1:1 complex. The intensities are in parenthesis.[a]

		Calculated				Experimental		
		A		B				
		ν	$\Delta\nu^b$	ν	$\Delta\nu^b$	ν	$\Delta\nu^b$	
H_2O	ν_3	3941 (84)	+7	3924 (154)	+24	3750-3765	+11 to -4	A
modes	ν_1	3816 (10)	+6	3795 (35)	+27	3644.8 (6)	+21	B
						3658.9 (12)	+7	A
	ν_2	1630 (51)	-2	1627 (40)	+1	1597.6 (93)	-2	A, B

CS_2	ν_3	1609 (1000)	+7	1616 (553)	0	1526.9 (1000)	+7	A
modes						1531.3 (380)	+2	B
	ν_1	672 (1)	+3	674 (0.3)	+1	656.5 (1.3)		A
						658.5 (0.5)		B
	ν_2	404 (5)	-8	394 (5)	+2	403.1 (40)	-7	A, B
		405 (6)	-9	401 (8)	-5			
inter[c]				209 (50)		209(23)		B
				162 (115)		192.5(94)		B
		94 (59)				116(350)		A
		89 (229)				100.5(105)		A

[a]Calculated and experimental intensities relative to CS_2 ν_3 (I ν_3=1000) in parenthesis.
[b]Rounded calculated and experimental values.
[c]Intermolecular modes.

For the intermolecular modes, we can conclude that the lowest observed frequencies are the signature of the A isomer and the two highest ones are that of the B isomer. For the ν_3 H_2O mode only an interval can be estimated thanks to the observation of combinations with intermolecular mode belonged to A so we can assign this ν_3 mode to the A isomer and the calculations agree well with this conclusion. For the ν_1 H_2O mode two observed bands are attributed to 1:1 complex and the comparison between experimental and calculated $\Delta\nu$ allows us to attribute the lower frequency to B and the higher one to A isomer. For the H_2O ν_2 mode we only observe one band and the difference between the calculated $\Delta\nu$ for A and B is too small to be able to conclude definitively.

For the CS_2 ν_3 mode two signatures are observed, separated by 4.4 cm^{-1}, we can assume that the lower band at 1526.9 cm^{-1} belongs to the A isomer and the other one at 1531.3 cm^{-1} belongs to the B isomer (Table 3). For the CS_2 ν_1 mode two signatures are also observed, separate by 2 cm^{-1}, but we cannot compare those values with the monomer since this mode is infrared inactive. However, since we observed two bands for the ν_1+ν_3 combination around 2175 cm^{-1}, separate by 6.2 cm^{-1}, we can assume that the lower band at 2175.5 cm^{-1} is the combination of 1526.9+656.5 cm^{-1} and the band at 2181.7 cm^{-1} is the combination of 1531.3+658.6 cm^{-1}. We conclude that the band at 656.5 cm^{-1} belongs to the A isomer and the one at 658.5

cm^{-1} belongs to the B isomer. These two attributions are also supported by the comparison of the intensities of the 2 isomers (Table 3).

For the CS_2 ν_2 mode, degenerated mode in the monomer, we only observe one band and the calculations give two very close bands for the two isomers since the complexation removes this degeneracy. As a small difference exists between the data of A or B, we are not able to conclude which isomer is observed.

We can conclude that the two isomers of 1:1 complex are present in the neon matrix. It is difficult to directly compare experimental and theoretical intensities because calculated ones don't take account of the probability to form the isomers according to the stability and influence of the cage even if it is weak. Experimentally the signatures of A isomer are always more intense probably because it can be more produce in the matrix due to its higher stability. This remark strengthens the attribution of water ν_2 mode to A isomer.

5.2. $(CS_2)_2$-H_2O complex

Our work is the first report on experimental data on the 2:1 complex. In Table 4 we report the experimental and calculated frequencies shifts for the water and CS_2 modes. The water vibrations are compared with those of the water monomer and the CS_2 one with that of the CS_2 dimer. Only the 2:1 F1 and the cross CS_2 dimer isomers are considered because they are clearly the most stable ones. For the water modes the two stretching ones are more perturbed for the bending one. We observe a very good match between experimental and calculated values.

Table 4

Experimental and calculated (MP2/AVTZ) frequencies shifts[a] (in cm^{-1}) between the 2:1 F1 complex and the H_2O monomer or the CS_2 dimer.

	H_2O modes		CS_2 modes	
	$\Delta\nu=\nu(H_2O)-\nu(2:1)$		$\Delta\nu=\nu(CS_2)_2-\nu(2:1)$	
	exp	calc	exp	calc
$\Delta\nu_3$	+32	+32		
$\Delta\nu_1$	+32	+35	+1	0

$\Delta\nu_2$	+1	-2

[a]Rounded calculated and experimental values.

5.3. CS_2-$(H_2O)_2$ complex

Our work is the first report on experimental vibrational data on the 1:2 complex since in literature there are only theoretical studies [10-11]. In Table 5 we compare the experimental and calculated $\Delta\nu$ of the two G1 and G2 isomers (Fig. 9). The water vibrations are compared with those of the water dimer and the CS_2 ones with those of the CS_2 monomer. For H_2O modes we can attribute the strong observed band at 3569.8 cm^{-1} to the signature of the O-H hydrogen bond ν_1 with a red shift of 21 cm^{-1} from the ν_1 PD of the H_2O dimer. We can conclude that we observe the ν_1 water signature of the G1 isomer since this mode is blue-shifted for the isomer G2. We have observed the same red shift for the OCS-$(H_2O)_2$ complex [4] which has a similar structure.

For the ν_1 PA mode, the observed $\Delta\nu$ value is 22 cm^{-1} and the calculated ones are 47 and 7 cm^{-1} for the G1 and G2 isomer, respectively, but since the intensity of this mode is five times higher for the isomer G1 compared to B (Table S4 in the supplementary information), we have assigned the observed value to the G1 isomer. For the two others observed modes, CS_2 ν_3 and H_2O ν_2, it is difficult to conclude because the $\Delta\nu$ between G1 and G2 are not significant. However as G1 isomer is the most stable we can conclude that we observe the structure G1, structure similar of the OCS-$(H_2O)_2$ and N_2O-$(H_2O)_2$ complexes previously published [4,5].

Table 5

Experimental and calculated (MP2/AVTZ) frequencies shifts[a] (in cm^{-1}) between the 1:2 complex and the H_2O dimer or the CS_2 monomer.

	H_2O modes			CS_2 modes		
	$\Delta\nu=\nu(H_2O)_2-\nu(1:2)$			$\Delta\nu=\nu(CS_2)-\nu(1:2)$		
	Exp	Calc		Exp	Calc	
		G1	G2		G1	G2
$\Delta\nu_3$	4-8	+12	+10	+8.3	+6	+7
$\Delta\nu_1$	+22 PA +21 PD	+47 PA +38 PD	+7 PA -12 PD			

$\Delta\nu_2$	+4 PD	-2 PD	-1 PD

[a]Rounded calculated and experimental values.

5.4. Comparison with isoelectronic analog water complexes.

We compare our CS_2-water results with those obtained with the CO_2, OCS, and N_2O molecules [3-5]. These four linear molecules (LM) are isoelectronic and comparison between the vibrational data for the water modes in the 1:1, 1:2, and 2:1 complexes is done in Table 6. For the 1:1 complex, the CS_2- and OCS-water complexes have the same structure with the oxygen atom of water near a sulfur atom (Fig. 9) and the frequencies shifts of the three water modes are very near [4]. For the CO_2- and N_2O-water complexes [3,5] their structures are completely different since the first one is a planar T-shaped complex with the water's oxygen atom near the carbon and the N_2O-H_2O complex has a tilted T shaped structure with the water's oxygen atom near the central nitrogen [3,5]. For this reason the frequencies shifts are different (Table 6) and we cannot compare these data with those of the CS_2 and OCS-water complexes. However the modes for the CO_2- and N_2O-water complexes are less affected than those of the CS_2- and OCS-water complexes.

The 1:2 complex is formed by a LM interacting with a water dimer and the structure is cyclic with a relatively conserved bond length inside the H_2O dimer (Fig. 9). One water molecule is hydrogen bonded to an atom at the extremity of the LM (O, N, or S). Since the structure is very similar for all complexes, the observed water vibrations are very near (Table 6). The only observation of the water signatures would not allow to distinguish the LM-water complexes to each other.

The 2:1 complex is formed by a water molecule interacting with a LM dimer. The water molecule is oxygen bounded to central atom above the plane formed by the CO_2 and N_2O dimer [3,5] or hydrogen bounded to atoms at the CS_2 and OCS dimer's extremity [4]. In addition the two molecules in the dimer are not always parallel. For these reasons the frequencies shifts are different (Table 6) and we cannot compare the data between them.

For all the n:m complexes, the ν_2 mode is the least affected and the largest differences in shifts are observed for 2:1 complexes (between 15 and 32 cm^{-1} for ν_1 and between 8 and 32 cm^{-1} for ν_3).

Table 6

Comparison of water frequencies shifts ($\Delta\nu=\nu_{monomer}-\nu_{complex}$) for the most stable LM-water complexes.

n:m complexes	Water modes	N_2O	CO_2	OCS	CS_2
1:1	ν_2	-0.3	+0.4	-2.4	-2.0
	ν_1	+1.4	+0.8	+6.6	+7.0
	ν_3	+2.0	+0.7	+7.7	[+11, -4]
1:2[a]	ν_2	+1.0	+1.4	+2.0	-
		-	+3.2	+0.9	+4.0
	ν_1	+23.6	+21.6	+19.0	+22.0
		+18.7	+29.3	+21.0	+20.7
	ν_3	+22.4	+24.0	+22.9	-
		-	-	+19.0	[+4, +8]
2:1	ν_2	-4.6	+1.0	+2.2	+1.0
	ν_1	+18.3	+15.0	+17.1	+32.1
	ν_3	+7.6	+9.0	+20.0	+32.3

[a] For the H_2O vibrations of the 1:2 complex, the frequencies shifts are given in comparison with the water dimer, the first value is for the proton acceptor (PA) and the second one for the proton donor (PD).

6. Conclusion

For the first time a vibrational analysis of the $(CS_2)_n$-$(H_2O)_m$ complexes has been carried in neon matrix isolation from the near to the far infrared. Using different concentration ratios of $CS_2/H_2O/Ne$ we assign the observed bands to the $(CS_2)_n$-$(H_2O)_m$ complexes. The existence of two isomers for CS_2-H_2O complex have been highlighted thanks to the comparison between theoretical and experimental vibrational shifts between monomers and complexes ($\Delta\nu=\nu_{mono}-\nu_{complex}$). We observe the ν_1 and ν_3 modes of CS_2 perturbed by a molecule of water for the two isomers. For the water modes perturbed by CS_2 we clearly identify ν_1 for the two isomers but we only observe one signature for ν_2 and ν_3. The study of the far infrared region allows the assignment of two 1:1 intermolecular modes for each isomer. The $(CS_2)_2$-H_2O and CS_2-$(H_2O)_2$ complexes have been also observed thanks to the attribution of five signatures for each complex. Bonding energy consideration and comparisons between the observed data and the calculated ones support our attributions of 2:1 and 1:2 to F1 and G1 structures, respectively. The comparison between the data

obtained for the isolectronic N_2O-H_2O, CO_2-H_2O, OCS-H_2O, and CS_2-H_2O n:m complexes shows that they have close vibrational data for the water modes when they have similar structure. This infrared work shows once more the interest to associate experimental studies in Ne matrix isolation and ab initio calculations to make a complete vibrational analysis and to obtain structures for some observed complexes on so weak hydrated complexes.

Declaration of competing interest

The authors declare that they have no conflict of interest.

CRediT authorship contribution statement

Pascale Soulard carried out the experiments, contributed to the data analysis, performed the ab initio calculations, and drafted the manuscript ; **Benoit Tremblay** carried out the experiments, performed the IR analysis and contributed to the manuscript drafting.

Supplementary materials

See the supplementary material for calculated Binding energies, Harmonic frequencies, Intensities for the monomers, dimers, and the most stable isomers of 1:1, 2:1 and 1:2, and a figure showing the H_2O $\nu_2 + \nu_{inter}$ combination region of 1:1 complex.

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