

In search of $\text{C S}_2 (\text{H}_2\text{O})_n$ $n = 1 - 4$ clusters

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In search of $\text{CS}_2(\text{H}_2\text{O})_{n=1-4}$ clusters

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Gaussian-3 and MP2/aug-cc-pVnZ methods have been used to calculate geometries and thermochemistry of $\text{CS}_2(\text{H}_2\text{O})_n$, where $n=1-4$. An extensive molecular dynamics search followed by optimization using these two methods located two dimers, six trimers, six tetramers, and two pentamers. The MP2/aug-cc-pVDZ structure matched best with the experimental result for the $\text{CS}_2(\text{H}_2\text{O})$ dimer, showing that diffuse functions are necessary to model the interactions found in this complex. For larger $\text{CS}_2(\text{H}_2\text{O})_n$ clusters, the MP2/aug-cc-pVDZ minima are significantly different from the MP2(full)/6-31G* structures, revealing that the G3 model chemistry is not suitable for investigation of sulfur containing van der Waals complexes. Based on the MP2/aug-cc-pVTZ free energies, the concentration of saturated water in the atmosphere and the average amount of CS_2 in the atmosphere, the concentrations of these clusters are predicted to be on the order of $10^5 \text{ CS}_2(\text{H}_2\text{O})$ clusters·cm⁻³ and $10^2 \text{ CS}_2(\text{H}_2\text{O})_2$ clusters·cm⁻³ at 298.15 K. The MP2/aug-cc-pVDZ scaled harmonic and anharmonic frequencies of the most abundant dimer cluster at 298 K are presented, along with the MP2/aug-cc-pVDZ scaled harmonic frequencies for the $\text{CS}_2(\text{H}_2\text{O})_n$ structures predicted to be present in a low-temperature molecular beam experiment.

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INTRODUCTION

A key atmospheric reaction is the oxidation of carbon disulfide by the hydroxyl radical to produce carbonyl sulfide,¹ an important atmospheric molecule.² OCS is the most abundant sulfur containing compound in the atmosphere and further oxidation of this molecule leads to acid rain formation.³ Water clusters can catalyze reactions with sulfur species,⁴⁻⁹ and various theoretical and experimental studies have shown the importance and existence of water clusters in the atmosphere.^{2,10-19} While thorough studies of water clusters with other important sulfur species have been performed,²⁰⁻²⁶ we are unaware of any theoretical work on carbon disulfide and water clusters. Gaussian-3 (G3) model chemistry²⁷ has proven very reliable for describing water cluster structures and thermochemistry, as benchmarked against experimental and high level *ab initio* calculations.^{19,28-35} In this paper we present the structures and energies for $\text{CS}_2(\text{H}_2\text{O})_n$ complexes, where $n=1-4$, at 298.15 K. We used both G3 model chemistry and MP2 theory to investigate structure and thermochemistry and compare them to available experimental results.³⁶

METHODS

Multiple structures of $\text{CS}_2(\text{H}_2\text{O})_n$, where $n=1-4$, were built with SPARTAN.³⁷ All structures were optimized with the semiempirical Parametric Method Number 3 (PM3),³⁸ and unique structures were further optimized using Hartree-Fock (HF) theory and the 6-31G* basis set.³⁹ Energies, enthalpies, and free energies were obtained with the G3 model chemis-

try. In the G3 model chemistry, vibrational zero-point energy is obtained with a geometry optimization at the HF/6-31G* level, followed by scaling the frequencies by 0.8929. Then geometries are refined with an MP2(full)/6-31G* optimization, followed by a series of calculations used for various energetic corrections.²⁷

For the $\text{CS}_2(\text{H}_2\text{O})_n$ clusters, gas-phase molecular dynamics (MD) simulations were performed using the AMBER 8 suite of programs⁴⁰ to generate a wide range of input structures. In the first step of each MD simulation, the temperature was gradually increased from 5 K to the production temperature over 1 ns. Production temperatures were 40 K except where $n=1$, where the temperature was 35 K. The production simulation lasted for 9 ns. The nonbonded cutoff was 20 Å, and the GAFF force field was used.⁴¹ The water molecules were assigned to the TIP5P water model⁴² to ensure correct orientation of hydrogen bonding. The ensemble of structures from each simulation was examined, and while the simulation generated no new structures where $n=1-3$, the simulations produced two novel $\text{CS}_2(\text{H}_2\text{O})_4$ configurations.

The MP2(full)/6-31G* geometries from the G3 output were used as input structures for optimizations and calculations with the MP2/aug-cc-pVDZ model.⁴³ Single-point energy calculations were then carried out using the aug-cc-pVTZ basis set on the double zeta geometries. MP2/aug-cc-pVTZ geometry optimizations were performed on the two $\text{CS}_2(\text{H}_2\text{O})$ and three of the $\text{CS}_2(\text{H}_2\text{O})_2$ clusters. Anharmonic frequencies⁴⁴ of the lowest energy dimer were calculated at the MP2/aug-cc-pVDZ level. Scaled harmonic frequencies of the most likely clusters to be observed in a low-temperature molecular beam experiment were also calculated, using a scale factor of 0.9604 for the MP2/aug-cc-pVDZ minima.⁴⁵

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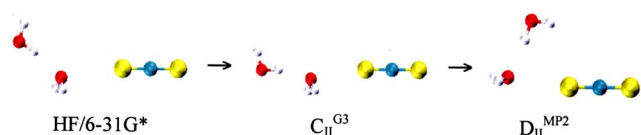


FIG. 1. Structures shown left to right: HF/6-31G* optimized structure from step 1 of the G3 model chemistry, MP2(full)/6-31G* optimized structure from step 3 of the G3 model chemistry (C_{II}^{G3}), and MP2/aug-cc-pVDZ optimized structure (D_{II}^{MP2}). The HF structure was used as input for the MP2(full) optimization that produced C_{II}^{G3} , and the MP2(full) C_{II}^{G3} structure was used as input that produced the D_{II}^{MP2} structure.

RESULTS

We observed significant differences between the G3 model chemistry and MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ results. MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ calculations obtained a structure for $CS_2(H_2O)_2$ similar to the single experimental structure found by Ogata and Lovas,³⁶ while the G3 calculations gave a very different lowest energy structure. Figure 1 exemplifies this by showing how the HF geometry optimized structure for a $CS_2(H_2O)_2$ cluster in step 1 of the G3 calculation changes slightly in step 3 of the G3 procedure, which is an MP2(full)/6-31G* optimization. More importantly, the G3 MP2(full)/6-31G* geometry, labeled C_{II}^{G3} , changes dramatically once the basis set is increased. The MP2/aug-cc-pVDZ structure that results, labeled D_{II}^{MP2} , is significantly different than the MP2(full)/6-31G* starting structure. This is a general problem with all of the minima located by these different methods; the MP2/aug-cc-pVDZ structures vary significantly from the MP2(full)/6-31G* structures, which affects the thermochemistry results. Selected optimizations at the MP2/aug-cc-pVTZ level for $n=1$ and $n=2$ structures support the aug-cc-pVDZ structures. The MP2(full)/6-31G* structures generated as part of the G3 model chemistry can be found in Figs. S1–S4 in the supplementary information,⁴⁶ while the MP2/aug-cc-pVDZ structures are presented in Figs. 2–5. We found two dimers, six trimers, six tetramers, and two pentamers. The structures are named to show order of stability, number of waters, and optimization method. The letters A–F in the figures signify stability, with A being the most stable according to the free energy at 298 K. The subscript Roman numeral signifies the number of water molecules in the complex, and the superscripts G3 and MP2 describes the method used to determine the structure [G3: MP2(full)/6-31G* optimization; MP2: MP2/aug-cc-pVDZ optimization]. The thermochemical values for these structures can be found in Table I. Table II contains the free energies, equilibrium con-

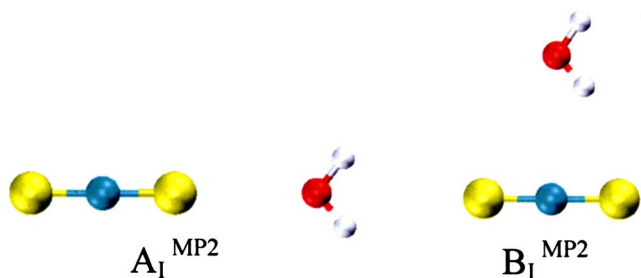


FIG. 2. MP2/aug-cc-pVDZ geometries of $CS_2(H_2O)$.

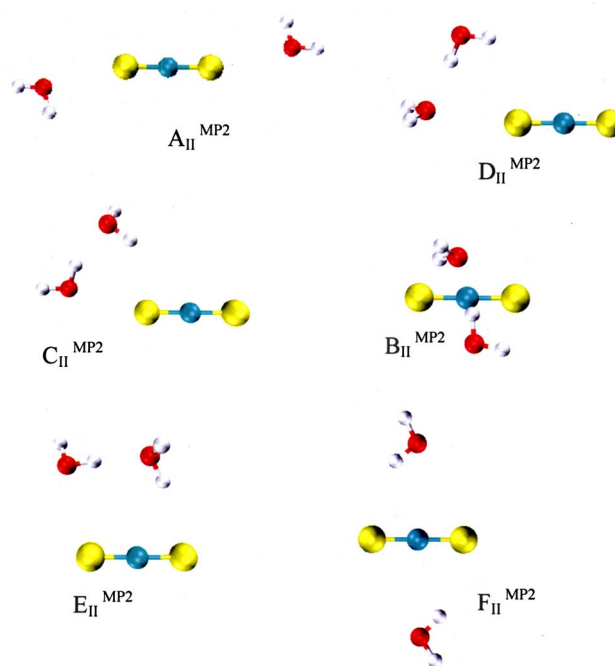


FIG. 3. MP2/aug-cc-pVDZ geometries of $CS_2(H_2O)_2$.

stants, and number of complexes per cubic centimeter predicted to be present in the atmosphere on a humid warm day. This assumes a CS_2 concentration of $3.17 \times 10^{-12} \text{ mol} \cdot \text{l}^{-1}$ ($1.91 \times 10^9 \text{ molecules} \cdot \text{cm}^{-3}$) (Ref. 3), a water concentration of $1.54 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ ($9.30 \times 10^{17} \text{ molecules} \cdot \text{cm}^{-3}$),^{19,47} and a temperature of 298 K. Scaled harmonic⁴⁵ and anharmonic frequencies for structure A_I^{MP2} can be found in Table III. Tables IV–VII contain the MP2/aug-cc-pVDZ scaled harmonic frequencies for the lowest energy clusters; those that are most likely to be observable in a low-temperature molecular beam experiment.

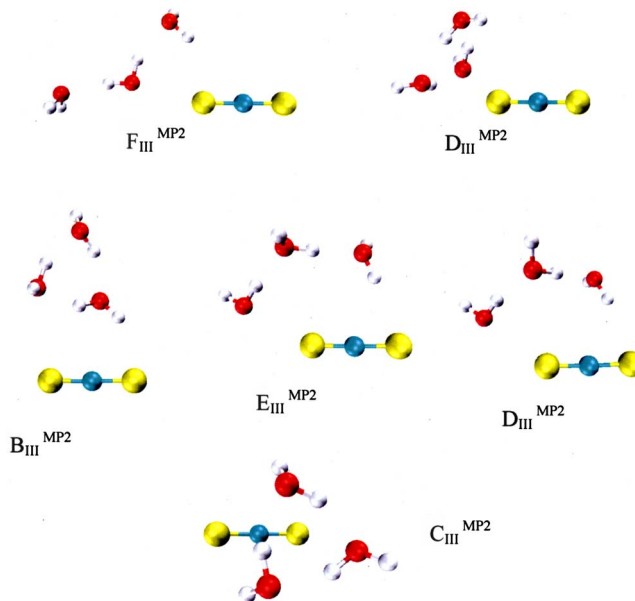
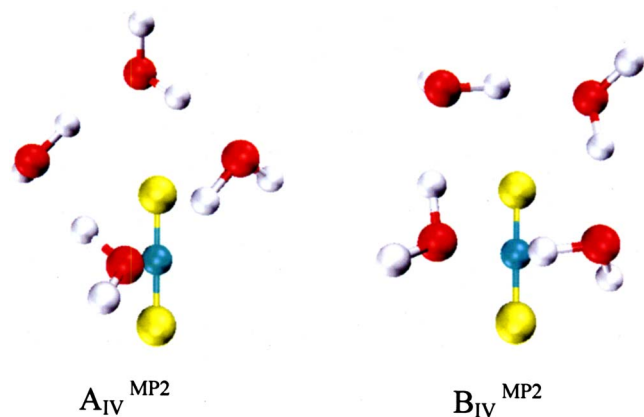


FIG. 4. MP2/aug-cc-pVDZ geometries of $CS_2(H_2O)_3$.

FIG. 5. MP2/aug-cc-pVDZ geometries of CS₂(H₂O)₄.

DISCUSSION

Structures

Two types of structures were found for CS₂(H₂O): a linear alignment of the heavy atoms found in A_I^{MP2} and B_I^{G3}, and the T shape found in B_I^{MP2} and A_I^{G3}.⁴⁶ The linear geometry is similar to the experimental structure obtained via Fourier transform microwave spectroscopy.³⁶ In the experimental structure the S···O distance is 3.197 Å, while the MP2/aug-cc-pVDZ distance is 3.116 Å and the MP2/aug-cc-pVTZ distance is 3.119 Å. Unlike the experimental structure, the MP2 structures have the hydrogen atoms in the same plane as the heavy atoms. In the experiment, the angle formed between water's rotational axis and the S–C–S molecular axis is 37°. This angle was determined assuming C_{2v} symmetry of the complex, no perturbation of the individual monomers, and a linear S–C–S···O geometry. This indicates that the hydrogen atoms on the water are not in the plane of the heavy atoms. Two spectroscopic constants, *B* and *C*, were determined from the microwave spectrum. The values of 1030.1109 and 1026.2912 MHz are modeled fairly well by the MP2/aug-cc-pVDZ results, which are 1029.83 and 1027.40 MHz. The value of *A* was assumed to be 366.4 GHz because it was the best value for the least-squares fitting procedure, although the authors comment that for a C_{2v} planar equilibrium structure they expected the *A* rotational constant to be equal to 437 GHz (the *B* rotational constant for water).³⁶ The MP2/aug-cc-pVDZ value for *A* is 428 GHz. The experimental dipole moment is 2.078 D, while the calculated result is 2.802 D.

The linear structure using the G3 method, B_I^{G3}, is not the theoretical global energy minimum, whereas the global minimum for the MP2/aug-cc-pVDZ method is the linear structure A_I^{MP2}. The A_I^{G3} structure (Fig. S1 in supplementary information) is qualitatively similar to the B_I^{MP2} structure displayed in Fig. 2. While qualitatively the structures are similar, the two methods produce different bond lengths and angles. In the T-shaped geometries, the S···O distances for A_I^{G3} and B_I^{MP2} are 2.972 and 2.754 Å, respectively. In addition to the different interaction distances, the S···H–O angle in the T-shaped structures is 125° for the MP2(full)/6-31G* geometry and 156° for the MP2/aug-cc-pVDZ structure. The addition of diffuse functions in the geometric optimizations

accounts for the structural differences and for the reversal of stability, significantly altering the enthalpy and entropy of interaction.

The six structures for CS₂(H₂O)₂ were composed of either the low energy water dimer²⁸ or two separate water molecules. The G3 MP2(full)/6-31G* optimized geometries underwent significant structural changes upon the addition of diffuse functions to the basis set. Structures A_{II}^{G3} and C_{II}^{G3} (Fig. S2) each contained water dimers, one perpendicular to the linear CS₂ molecule and the other extending away from one of the sulfur atoms. After MP2 optimization with diffuse functions, these water molecules reoriented to form the five-membered ring structures C_{II}^{MP2} and D_{II}^{MP2} (Fig. 3). The global minima for both methods are similar to their respective global minima for CS₂(H₂O). A_{II}^{G3} (Fig. S2) consists of a four-membered ring with an extra dangling water, and A_{II}^{MP2} is a linear structure with a S···O interaction on each end similar to that of A_I^{MP2}. The diffuse functions also affected the orientation of the free (noninteracting) hydrogens in the MP2/aug-cc-pVDZ optimizations. For the A_{II}^{MP2}, C_{II}^{MP2}, D_{II}^{MP2}, and F_{II}^{MP2} structures, a free hydrogen of one or more water molecules is in the plane defined by the heavy atoms.

Optimizations of CS₂(H₂O)₃ resulted in two common formations of the water molecules: a linear water trimer and a cyclic water trimer, similar to the (H₂O)₃ global energy minimum.^{28,30} In A_{III}^{G3}, the cyclic water trimer spans across CS₂ to create a S···O van der Waals interaction with each S atom. The global minimum from MP2/aug-cc-pVDZ calculations, A_{III}^{MP2}, contains a linear water trimer bound to one sulfur atom. The C_{III}^{MP2} structure is composed of the water trimer poised above CS₂. In G3 methodology the cyclic water trimer is a key feature of these complexes' stability as three of the four lowest energy structures contain the cyclic water trimer. In the MP2/aug-cc-pVDZ calculations, however, the cyclic water trimer no longer appears as the global minimum for CS₂(H₂O)₃. In the structures without cyclic water trimers, the MP2/aug-cc-pVDZ optimizations placed some noninteracting hydrogens in the plane with the heavy atoms of the complex, as shown in A_{III}^{MP2}, D_{III}^{MP2}, and E_{III}^{MP2}. The G3 calculations, however, show no tendency towards a planar orientation of hydrogen in any structures. Instead, geometries such as E_{III}^{G3} and F_{III}^{G3} (Fig. S3) have all noninteracting hydrogens out of the plane of the heavy atoms.

CS₂(H₂O)₄ shows two nearly identical structures optimized with G3 MP2/aug-cc-pVDZ. All structures contained the cyclic S₄ water tetramer³⁰ centered over one of the sulfur atoms. The A_{IV}^{MP2} minimum has one of the tetramer's hydrogen bonds passing over CS₂. The C···O interaction distance in this geometry is 3.382 Å. The B_{IV}^{MP2} structure has one water of the tetramer above the CS₂, with a S···H interaction distance of 3.450 Å.

Thermochemistry

Calculations for CS₂(H₂O)_n, where *n*=1–4, gave very different thermochemical results for the two methods, G3 and MP2/aug-cc-pVDZ. The differences are clear in Table I as some nearly identical structures have very different thermochemistry. The G3 results have to be discounted, as the

TABLE I. ΔE_0 , ΔH_{298}° , and ΔG_{298}° for incremental association energies using G3 and MP2 model chemistries at 298.15 K (All values are given in kcal/mol).

<i>n</i>	G3			MP2/aug-cc-pVDZ ^a				MP2/aug-cc-pVTZ ^b			
	Structure	ΔE_0	ΔH_{298}°	ΔG_{298}°	Structure	ΔE_0	ΔH_{298}°	ΔG_{298}°	ΔE_0	ΔH_{298}°	ΔG_{298}°
CS ₂ (H ₂ O) _{<i>n</i>-1} + (H ₂ O) → CS ₂ (H ₂ O) _{<i>n</i>} : incremental association energetics ^c											
1	A _I ^{G3}	-0.86	-0.40	0.87	A _I ^{MP2}	-0.47	-1.06	2.90	-0.38	-0.97	2.98
	B _I ^{G3}	-0.91	-0.50	3.21	B _I ^{MP2}	-0.41	-1.00	3.46	-0.38	-0.97	3.49
2	A _{II} ^{G3}	-3.79	-3.92	3.43	A _{II} ^{MP2}	0.23	-0.36	2.41	0.39	-0.21	2.57
	B _{II} ^{G3}	-5.03	-5.31	3.90	B _{II} ^{MP2}	-3.90	-4.50	3.47	-3.97	-4.57	3.40
	C _{II} ^{G3}	-3.33	-3.48	4.46	C _{II} ^{MP2}	-4.40	-4.99	3.39	-4.34	-4.93	3.45
	D _{II} ^{G3}	-4.20	-4.48	4.68	D _{II} ^{MP2}	-3.24	-3.83	3.52	-3.13	-3.72	3.63
	E _{II} ^{G3}	-4.57	-4.91	4.72	E _{II} ^{MP2}	-4.54	-5.13	3.87	-4.59	-5.18	3.82
	F _{II} ^{G3}	-0.95	-0.78	6.01	F _{II} ^{MP2}	-0.07	-0.66	5.04	-0.01	-0.61	5.10
3	A _{III} ^{G3}	-8.96	-10.1	0.48	A _{III} ^{MP2}	-12.8	-13.4	1.91	-12.8	-13.3	1.91
	B _{III} ^{G3}	-7.77	-8.24	1.72	B _{III} ^{MP2}	-12.5	-13.1	2.09	-12.6	-13.2	1.98
	C _{III} ^{G3}	-7.51	-8.64	1.78	C _{III} ^{MP2}	-13.3	-13.9	2.51	-13.4	-14.0	2.43
	D _{III} ^{G3}	-7.51	-8.67	2.50	D _{III} ^{MP2}	-11.0	-11.6	2.88	-11.1	-11.7	2.79
	E _{III} ^{G3}	-3.61	-3.66	3.89	E _{III} ^{MP2}	-11.3	-11.9	2.98	-11.4	-12.0	2.85
	F _{III} ^{G3}	-0.46	0.21	4.40	F _{III} ^{MP2}	-7.13	-7.72	4.36	-7.06	-7.65	4.43
4	A _{IV} ^{G3}	-10.1	-10.8	-0.99	A _{IV} ^{MP2}	-10.7	-11.3	-0.71	-10.6	-11.2	-0.61
	B _{IV} ^{G3}	-9.96	-10.7	-0.40	B _{IV} ^{MP2}	-10.8	-11.4	-0.26	-10.8	-11.4	-0.18

^aG3 output served as input for MP2/aug-cc-pVDZ optimization and frequency calculations.^bMP2/aug-cc-pVDZ output served as input for MP2/aug-cc-pVTZ single self-consistent field calculations.^cFor the CS₂(H₂O)₂ species, the A_I^X energy was used in determining the free energy of the reaction where X indicates G3 or MP2. Similarly, the A_{II}^X was used for CS₂(H₂O)₃ species, and the A_{III}^X energy was used for CS₂(H₂O)₄ species.

first optimization in the G3 method uses the HF/6-31G* method for the frequency information essential for the zero-point and entropic corrections, while the second uses the MP2(full)/6-31G* method. These two structures are often different from each other, and as shown in the previous section the lack of diffuse functions in the second geometry optimization produces quite different structures compared to the MP2/aug-cc-pVDZ method. Single-point energy calculations with the triple zeta basis set on the double zeta basis set geometries show a clear pattern, giving confidence that further increases of the basis set would lead to energy convergence.

The values in Table I show that the combination of a water molecule with a carbon disulfide molecule to form the most stable complex is only slightly exothermic (ΔH_{298}°), and including entropy results in a 3.0 kcal·mol⁻¹ free energy for formation of this complex at 298 K. Addition of another water to the A_I^{MP2} structure to form the A_{II}^{MP2} structure requires a free energy of 2.6 kcal·mol⁻¹ at 298 K. Building on the A_{II}^{MP2} structure to form the A_{III}^{MP2} structure is exothermic by 13.4 kcal·mol⁻¹ because of hydrogen bonding between the waters, but requires a free energy of 1.9 kcal·mol⁻¹ because of the entropic cost of ordering the three water molecules on one side of the carbon disulfide molecule. Adding one more

TABLE II. Free energies,^a equilibrium constants, and number of complexes per cubic centimeter predicted in the atmosphere at 298.15 K.

<i>n</i>	Structure	ΔG_{298}°	K_p	K_c	molec·cm ⁻³
CS ₂ (H ₂ O) _{<i>n</i>-1} + H ₂ O → CS ₂ (H ₂ O) _{<i>n</i>}					
1	A _I ^{MP2}	2.98	6.51 × 10 ⁻³	1.59 × 10 ⁻¹	4.69 × 10 ⁵
	B _I ^{MP2}	3.49	2.75 × 10 ⁻³	6.73 × 10 ⁻²	1.98 × 10 ⁵
	Total				6.68 × 10 ⁵
2	A _{II} ^{MP2}	2.57	1.31 × 10 ⁻²	3.20 × 10 ⁻¹	3.29 × 10 ²
	B _{II} ^{MP2}	3.40	3.22 × 10 ⁻³	7.88 × 10 ⁻²	8.12 × 10 ¹
	C _{II} ^{MP2}	3.45	2.98 × 10 ⁻³	7.29 × 10 ⁻²	7.52 × 10 ¹
	D _{II} ^{MP2}	3.63	2.20 × 10 ⁻³	5.37 × 10 ⁻²	5.54 × 10 ¹
	E _{II} ^{MP2}	3.82	1.58 × 10 ⁻³	3.85 × 10 ⁻²	3.97 × 10 ¹
	F _{II} ^{MP2}	5.10	1.83 × 10 ⁻⁴	4.47 × 10 ⁻³	4.61
	Total				5.85 × 10 ²

^aFree energies (kcal/mol) calculated with MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ.

TABLE III. MP2 scaled harmonic and anharmonic frequencies (all values in cm⁻¹) for the CS₂(HO) structure A_I^{MP2}.

Vibrational mode ^a	MP2/aug-c-pVDZ		Harmonic intensities		
	Scaled ^b	Anharm	IR	R	Expt.
ν_3 (a)	3772	3736	m	s	
ν_1 (a)	3645	3616	w	vs	
ν_2 (a)	1559	1575	m	m	
ν_3 (b)	1532	1576	vs	w	
ν_1 (b)	640	648	w	vs	
In plane ν_2 (b)	364	395	w	w	
Out of plane ν_2 (b)	363	394	w	w	
Rock	95	68	m	w	
Wag	88	88	s	w	
Intermol stretch	81	73	w	w	67 ^c
Out-of-plane bend	29	40	w	m	
In-plane bend	24	22	w	m	

^aModel motion: ν_1 for symmetric stretching, ν_2 for bending, and ν_3 for asymmetric stretching. (a) signifies the water and (b) signifies the carbon disulfide.

^bScaling factor for MP2/aug-cc-pVDZ was 0.9604 (Ref. 45).

^cReference 36.

water to produce the A_{IV}^{MP2} structure is exothermic by 11.2 kcal·mol⁻¹ and releases 0.61 kcal·mol⁻¹ of free energy. The S₄ water tetramer is quite stable, releasing much heat, but at the cost of greater entropy.³⁰

We note that more accurate thermochemical values could be obtained by using the MP2/aug-cc-pVDZ geometries and

frequencies as starting points for G3-like calculations or by calculating single-point energies at the CCSD(T)/aug-cc-pVnZ levels of theory. In addition, corrections for basis set superposition error would improve the thermochemical values. Such calculations would improve the absolute numbers

TABLE IV. MP2/aug-cc-pVDZ scaled harmonic frequencies (all values are in cm⁻¹) for the CS₂(H₂O)₂ structure C_{II}^{MP2}.

Vibrational mode ^a	MP2/aug-cc-pVDZ Scaled ^b	Intensity IR
ν_3 (d)	3754	s
ν_3 (a)	3744	s
ν_1 (d)	3622	m
ν_1 (a)	3535	s
ν_2 (a)	1578	m
ν_2 (d)	1559	m
ν_3 (c)	1530	vs
ν_1 (c)	639	w
ω (bonded H on a)	604	s
ρ (a), ω (bonded H on d)	414	m
In-plane ν_2 (c)	364	m
Out-of-plane ν_2 (c)	362	w
ρ (a), ω (bonded H on d)	209	vs
ω (free H d)	176	m
Intermolecular stretch (da)	170	m
Nonconcerted ω (free H a), ρ (d)	122	s
Nonconcerted ω (free H a), ω (bonded H on d)	94	m
Intermolecular stretch (ce)	80	w
Intermolecular stretch (dc)	75	m
Out-of-plane intermolecular bend	29	w
In-plane intermolecular bend	21	w

^aMode motion: ν_1 for symmetric stretching, ν_2 for bending, ν_3 for asymmetric stretching, ω for wag, and ρ for rock. (a) signifies the water with an S···O interaction, (d) signifies the water with an OH···S interaction, (c) signifies the carbon disulfide, and (e) signifies water dimer.

^bMP2/aug-cc-pVDZ scaling factor was 0.9604.

TABLE V. MP2/aug-cc-pVDZ scaled harmonic frequencies (all values are in cm⁻¹) for the CS₂(H₂O)₂ structure E_{II}^{MP2}.

Vibrational mode ^a	MP2/aug-cc-pVDZ Scaled ^b	Intensity IR
ν_3 (d)	3744	s
ν_3 (a)	3738	m
ν_1 (d)	3616	w
ν_1 (a)	3526	s
ν_2 (a)	1584	w
ν_2 (d)	1564	m
ν_3 (c)	1533	vs
ν_1 (c)	641	w
ω (bonded H on a)	626	m
ρ (a), ρ (bonded H on d)	383	m
In-plane ν_2 (c)	357	w
Out-of-plane ν_2 (c)	353	w
Asymmetric ρ (d,a)	267	s
ω (free H on d), ω (a)	197	w
Intermolecular stretch (d,a)	177	w
Nonconcerted ω (free H on a), ω (free H on d)	158	w
Concerted ω (free H on a), ω (free H on d)	122	w
Intermolecular stretch (d,c)	91	w
Intermolecular stretch (a,c)	74	w
In-plane intermolecular bend	36	w
Out-of-plane intermolecular bend	17	w

^aMode motion: ν_1 for symmetric stretching, ν_2 for bending, ν_3 for asymmetric stretching, ω for wag, and ρ for rock. (a) signifies the water with a S···O interaction, (c) signifies the carbon disulfide, and (d) signifies the water with an OH···S interaction.

^bMP2/aug-cc-pVDZ scaling factor was 0.9604.

TABLE VI. MP2/aug-cc-pVDZ scaled harmonic frequencies (all values are in cm^{-1}) for $\text{CS}_2(\text{H}_2\text{O})_3$ structure $\text{C}_{\text{III}}^{\text{MP2}}$.

Vibrational mode ^a	MP2/aug-cc-pVDZ Scaled ^b	Intensity IR
ν_3 (n)	3731	w
ν_3 (d)	3726	w
ν_3 (a)	3725	m
ν_3 (bonded H on d/n)	3487	s
ν_3 (bonded H on a/dn)	3475	s
ν_1 (bonded H on dan)	3415	w
ν_2 (dan)	1589	w
ν_2 (dn/a)	1571	s
ν_2 (d/n)	1568	m
ν_3 (c)	1531	s
ω (bonded H on dan)	846	w
ν_1 (c)	642	w
ω (an)	632	s
ω (da)	553	m
ρ (da)	428	m
in-plane ν_2 (c)	356	w
out-of-plane ν_2 (c)	351	w
ρ (dn/a)	341	w
ρ (dan)	330	w
ω (dna)	235	w
ω (an/d)	213	m
Heavy atom ring stretch	206	w
Heavy atom ring distortion	191	m
Heavy atom ring distortion	177	w
Heavy atom ring distortion	166	w
Intermolecular stretch (ce)	68	w
Intermolecular bend (ce)	61	w
Intermolecular stretch (ce)	51	w
Intermolecular bend (ce)	37	w
Intermolecular twist (ce)	15	w

^aMode motion: ν_1 for symmetric stretching, ν_2 for bending, ν_3 for asymmetric stretching, ω for wag, ρ rock, and / separates nonconcerted motions. (a) signifies the water with a $\text{S}\cdots\text{O}$ interaction, (d) signifies the water with $\text{OH}\cdots\text{S}$ interaction, (n) signifies the water with no direct interaction with CS_2 , (c) signifies the carbon disulfide, and (e) signifies the water trimer.

^bMP2/aug-cc-pVDZ scaling factor was 0.9604.

but most likely not change the trends, so that the MP2/aug-cc-pVTZ values effectively capture the minimum energy structures.

Based on the MP2/aug-cc-pVTZ free energies for forming the complexes in Table I, the concentration of saturated water in the atmosphere and the average amount of CS_2 in the atmosphere, the concentrations of the different dimer and trimer clusters are predicted in Table II. We predict that under these conditions at 298 K, 10^5 $\text{CS}_2(\text{H}_2\text{O})$ clusters· cm^{-3} and 10^2 $\text{CS}_2(\text{H}_2\text{O})_2$ clusters· cm^{-3} are present. Under the same conditions, it has been predicted that the total number of water dimers, trimers, tetramers, pentamers, and hexamers is on the order of 10^{14} , 10^{12} , 10^{11} , 10^{10} , and 10^4 clusters· cm^{-3} , respectively.¹⁹

Frequencies

Table III contains the MP2/aug-cc-pVDZ anharmonic and scaled harmonic frequencies for the A_1^{MP2} $\text{CS}_2(\text{H}_2\text{O})$ cluster. The anharmonic frequencies are computationally expensive, and it is reassuring that there is fairly good agree-

TABLE VII. MP2/aug-cc-pVDZ scaled harmonic frequencies (all values are in cm^{-1}) for the $\text{CS}_2(\text{H}_2\text{O})_4$ structure $\text{B}_{\text{IV}}^{\text{MP2}}$.

Vibrational mode ^a	MP2/aug-cc-pVDZ Scaled ^b	Intensity IR
ν_3 (a2)	3727	w
ν_3 (a1)	3722	w
ν_3 (free H on d2)	3721	w
ν_1 (free H on a1)	3713	w
ν_3 (bonded H on a1 d1/a2 d2)	3375	w
ν_3 (bonded H on a1/d1)	3344	vs
ν_3 (bonded H on a2/d2)	3327	vs
ν_1 (bonded H on a1 a2 d1 d2)	3247	w
ν_2 (a1 a2 d1 d2)	1616	w
ν_2 (a2 d2)	1589	w
ν_2 (a1 d1)	1584	w
ν_2 (a1 d1/a1 d2)	1571	m
ν_3 (c)	1537	vs
ω (bonded H on a1 a2 d1 d2)	951	w
ω (bonded H on a1 d2)	795	m
ω (bonded H on d1 d2)	787	m
ω (bonded H on a1 a2/d1 d2)	724	s
ν_1 (c)	643	w
ρ (a2 d2)	423	w
ρ (a1 d1)	430	w
ρ (a1 a2/d1 d2)	405	w
ν (a1 a2 d1 d2)	383	w
ν_2 (c)	356	w
ν_2 (c)	349	w
ω (a1 free H a2 d1 d2)	297	w
ω (a1 free H on d1/a2 d2)	255	m
ω (a1 free H on d2/a2)	252	s
ω (a1 free H on d2/a2 d1)	249	m
ω (a1 free H on d1/a2 d2)	234	w
ω (a1 free H on d1/a2)	230	w
Heavy atom ring stretch (f)	202	w
ω (free H on d1/a1 d2)	200	m
heavy atom ring ν_2 (f)	85	w
heavy atom ring ν_2 (f)	76	w
Heavy atom ring distortion (f)	59	w
Intermolecular stretch (cf)	50	w
Intermolecular bend (cf)	45	w
Intermolecular bend (cf)	33	w
Intermolecular twist (cf)	16	w

^aMode motion: ν_1 for symmetric stretching, ν_2 for bending, ν_3 for asymmetric stretching, ω for wag, ρ for rock, and / separates nonconcerted motions. (a1) signifies the water with $\text{C}\cdots\text{O}$ interaction, (a2) signifies the water with $\text{S}\cdots\text{O}$ interaction. (c) signifies the carbon disulfide, (d1) signifies the water that donates to a1, (d2) signifies the water that donates to a2, and (f) signifies the water tetramer.

^bMP2/aug-cc-pVDZ scaling factor was 0.9604.

ment between the scaled harmonic and anharmonic frequencies in the intermolecular infrared region below 1000 cm^{-1} . Ogata and Lovas used Fourier transform microwave spectroscopy to determine the intermolecular stretch of the $\text{CS}_2(\text{H}_2\text{O})$ cluster at 67 cm^{-1} . This frequency corresponds to the calculated values of 81 cm^{-1} (scaled MP2) and 73 cm^{-1} (anharmonic MP2) in Table III. The strongest intensity bands, according to the MP2 scaled harmonic data, are at 1532 and 88 cm^{-1} . These two modes correspond to the asymmetric stretch of carbon disulfide (redshifted by 10 cm^{-1}) and a wagging motion of the intermolecular com-

plex. The 88 cm⁻¹ peak is in a unique region of the spectrum relative to water clusters.³³ There is a weak intensity vibration for the water tetramer predicted at 66 cm⁻¹, and a few weak peaks below 50 cm⁻¹ for the water pentamer, and all of the other intermolecular modes for the water dimer, trimer, tetramer, and pentamer are predicted to be above 140 cm⁻¹. Thus we expect that this peak could be observed experimentally.

Based on the MP2 values for ΔE_0 in Table I, which approximate the values for ΔG_{5K} in a cold molecular beam, we would expect the A_I, B_I, B_{II} through E_{II}, A_{III} through F_{III}, A_{IV} and B_{IV} species to predominate in a low-temperature experiment. Tables III–VII contain the scaled harmonic frequencies for some of these clusters. Each vibrational mode is described in each table, along with the predicted frequency and relative IR intensity. The frequencies for the remaining clusters can be found in supplemental information.

Methodology

Despite the failures in the present work on van der Waals clusters of CS₂ and water, the G3 model chemistry is an excellent predictor of structures and thermochemistry for pure water clusters, water clusters associated with the hydroxyl and hydroperoxyl radicals, and ion/water clusters.^{19,28–35} The G3 method does not use diffuse functions in its geometric optimizations, an inherent weakness for calculations of sulfur-containing van der Waals clusters governed by London dispersion forces. The HF/6-31G* and MP2(full)/6-31G* optimizations cannot describe the long-range interactions with the third period sulfur atom. The G3 thermochemical calculations include various correcting factors for diffuse functions, polarization functions, and other effects, which are all based on the MP2(full)/6-31G* optimized structure.²⁷ As the MP2(full)/6-31G* global minimum for the G3 calculations does not match the linear experimental structure for CS₂(H₂O), or the MP2/aug-cc-pVDZ structures for the larger CS₂(H₂O)_n clusters, this model chemistry is not suitable for van der Waals complexes with sulfur, particularly CS₂.

CONCLUSION

We have performed an extensive molecular dynamics search for structures of CS₂(H₂O)_n, where $n=1-4$, locating two dimers, six trimers, six tetramers, and two pentamers with the G3 model chemistry and with MP2/aug-cc-pVDZ geometry optimizations. The MP2/aug-cc-pVDZ results match best with the experimental result for the CS₂(H₂O) dimer, showing that diffuse functions are necessary to model the interactions found in this complex. The MP2(full)/6-31G* global minimum for CS₂(H₂O) in the G3 calculations does not match the linear experimental structure for CS₂(H₂O), or the MP2/aug-cc-pVDZ structure. In addition, for the larger CS₂(H₂O)_n clusters, the MP2/aug-cc-pVDZ minima are significantly different from the MP2(full)/6-31G* structures. We conclude that the G3 model chemistry is not suitable for investigation of van der Waals complexes with sulfur. Based on the MP2/aug-cc-pVTZ free energies, the concentration of saturated water in

the atmosphere and the average amount of CS₂ in the atmosphere, the concentrations of CS₂(H₂O) and CS₂(H₂O)₂ clusters are predicted to be on the order of 10⁵ CS₂(H₂O) clusters·cm⁻³ and 10² CS₂(H₂O)₂ clusters·cm⁻³ at 298 K. The most abundant clusters at 298 K are not necessarily the most abundant found in a cold molecular beam, and we predict that most of the structures should be observable in the laboratory and predict the intermolecular infrared frequencies to observe them.

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