

# Hydration of OCS with One to Four Water Molecules in Atmospheric and Laboratory Conditions

Gregory M. Hartt, George C. Shields,\* and Karl N. Kirschner\*

Hamilton College, Department of Chemistry, Center for Molecular Design,  
198 College Hill Road, Clinton, New York 13323

Received: January 10, 2008; Revised Manuscript Received: February 25, 2008

Carbonyl sulfide is the most abundant sulfur gas in the atmosphere. We have used MP2 and CCSD(T) theory to study the structures and thermochemistries of carbonyl sulfide interacting with one to four water molecules. We have completed an extensive search for clusters of  $\text{OCS}(\text{H}_2\text{O})_n$ , where  $n = 1-4$ . We located three dimers, two trimers, five tetramers, and four pentamers with the MP2/aug-cc-pVDZ method. In each of the complexes with two or more waters, OCS preferentially interacts with low-energy water clusters. Our results match current theoretical and experimental literature, showing correlation with available geometries and frequencies for the  $\text{OCS}(\text{H}_2\text{O})$  species. The CCSD(T)/aug-cc-pVTZ thermochemical values combined with the average amount of OCS and the saturated concentration of  $\text{H}_2\text{O}$  in the troposphere, lead to the prediction of  $10^6$   $\text{OCS}(\text{H}_2\text{O})$  clusters  $\cdot \text{cm}^{-3}$  and  $10^2$   $\text{OCS}(\text{H}_2\text{O})_2$  clusters  $\cdot \text{cm}^{-3}$  at 298 K. We predict the structures of  $\text{OCS}(\text{H}_2\text{O})_n$ ,  $n = 1-4$  that should predominate in a low-temperature molecular beam and identify specific infrared vibrations that can be used to identify these different clusters.

## Introduction

Carbonyl sulfide (OCS), with a lifetime of approximately seven years, is the most abundant atmospheric sulfur species and is believed to be responsible for the sulfate aerosol layer in the stratosphere.<sup>1</sup> Significant theoretical and experimental work has shown the existence and importance of sulfur species and water clusters in the atmosphere.<sup>2-11</sup> Water clusters have also been shown to catalyze reactions with sulfur species.<sup>12-17</sup> Experimental and computational research have thus far explored only the  $\text{OCS}(\text{H}_2\text{O})$  dimer.<sup>18-20</sup> In this paper, we present geometries and energies of  $\text{OCS}(\text{H}_2\text{O})_n$ , where  $n = 1-4$ , at 298.15 K. After an extensive initial search for input geometries using both molecular dynamics and quantum mechanics, we used the MP2 level of theory to predict structures and frequencies and the CCSD(T) level of theory to calculate accurate thermochemistries. We compared these values to available experimental and theoretical results.

## Methods

Several structures of  $\text{OCS}(\text{H}_2\text{O})_n$ , where  $n = 1-4$ , were created using SPARTAN,<sup>21</sup> followed by initial geometry optimizations using the semiempirical parametric method number 3 (PM3).<sup>22</sup> Unique PM3 structures were optimized at the Hartree–Fock (HF) and Møller–Plesset (MP2(full)) perturbation levels of theory using the 6-31G\* basis set. HF and MP2(full) optimization reduced the number of minima found by PM3. Molecular dynamics calculations were also used as an alternative approach for generating  $\text{OCS}(\text{H}_2\text{O})_n$  configurations, using a similar procedure as that outlined previously for  $\text{CS}_2(\text{H}_2\text{O})_n$  clusters.<sup>23</sup> The ensemble of structures was examined but provided no novel structures. A final set of optimizations

at the MP2/aug-cc-pVDZ level of theory provided geometries for further single-point energy calculations. (We have previously shown that the MP2/aug-cc-pVDZ method for geometry optimization reproduces microwave rotational constants for  $\text{CS}_2(\text{H}_2\text{O})$  well, suggesting that this is a suitable level of theory for sulfur–water system.<sup>23</sup> As a reviewer pointed out, the aug-cc-pV(D+d)Z is an alternative basis set that could be used, which we will employ in future studies.) Single-point energy calculations were performed at the MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVTZ levels of theory to obtain more accurate energies. The  $\text{OCS}(\text{H}_2\text{O})_n$  interaction energies for clusters with  $n \geq 2$  water molecules were determined by subtracting the most stable  $\text{OCS}(\text{H}_2\text{O})_{n-1}$  cluster from the  $\text{OCS}(\text{H}_2\text{O})_n$  cluster, as elaborated in Table 1. The MP2/aug-cc-pVDZ frequencies were scaled by a factor of 0.9604;<sup>24</sup> the resulting thermodynamic values were combined with the MP2 and CCSD(T) energies to obtain zero-point-corrected energy changes ( $\Delta E_0$ ), enthalpy changes at 298 K ( $\Delta H^\circ_{298}$ ), and free-energy changes at 298 K ( $\Delta G^\circ_{298}$ ). We have shown in previous studies that a single scaling factor for MP2/aug-cc-pVDZ frequencies adequately reproduces the experimental frequencies for the water dimer and expensive anharmonic frequencies calculated for the  $\text{CS}_2 \cdot \text{H}_2\text{O}$  dimer.<sup>23,25</sup> Additional calculations using the Gaussian-3 (G3)<sup>26</sup> model chemistry were also executed but proved inadequate in describing the van der Waals forces around the sulfur atom. The failure of G3 to model nonbonded complexes involving sulfur has been previously reported and is not discussed further in this paper.<sup>23</sup>

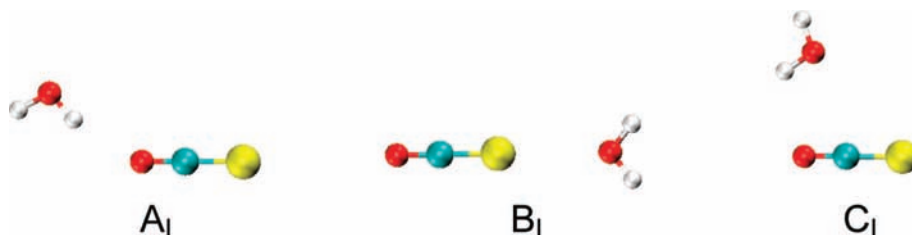
Complete basis set (CBS) limit extrapolations for the lowest-energy structures using the HF and correlated single-point energies were determined using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The extrapolation procedure was explained in greater detail previously.<sup>27-29</sup> Briefly, for each structure, the calculations yield four energetic values  $E_2^{\text{RHF}}$ ,  $E_2^{\text{cor}}$ ,  $E_3^{\text{RHF}}$ ,  $E_3^{\text{cor}}$ , each corresponding to the RHF and correlated energetic values

\* To whom correspondence should be addressed. E-mail: gshields@hamilton.edu. Telephone: 315-859-4367(K.N.K.); E-mail: kkirschn@hamilton.edu. Telephone: 315-859-4728(G.C.S.). Fax: 315-859-4807.

**TABLE 1:  $\Delta E_0$ ,  $\Delta H^\circ_{298}$ , and  $\Delta G^\circ_{298}$  Values for Incremental Association Energies Using the MP2 and CCSD(T) Methods and the CCSD(T) CBS-Limit Extrapolation at 298.15 K (All Values in kcal·mol<sup>-1</sup>)**

<i>n</i>	structure	MP2/aug-cc-pVDZ			MP2/aug-cc-pVTZ <sup>a</sup>			CCSD(T)/aug-cc-pVTZ <sup>b</sup>			CCSD(T) CBS-limit <sup>c</sup>		
		$\Delta E_0$	$\Delta H^\circ_{298}$	$\Delta G^\circ_{298}$	$\Delta E_0$	$\Delta H^\circ_{298}$	$\Delta G^\circ_{298}$	$\Delta E_0$	$\Delta H^\circ_{298}$	$\Delta G^\circ_{298}$	$\Delta E_0$	$\Delta H^\circ_{298}$	$\Delta G^\circ_{298}$
OCS(H <sub>2</sub> O) <sub><i>n</i>-1</sub> + H <sub>2</sub> O → OCS(H <sub>2</sub> O) <sub><i>n</i></sub> : Incremental Association Energetics <sup>d</sup>													
1	A <sub>I</sub>	-1.25	-1.05	2.95	-1.26	-1.06	2.94	-1.31	-1.11	2.89	-1.27	-1.08	2.92
	B <sub>I</sub>	-1.72	-1.26	2.86	-1.63	-1.16	2.96	-1.54	-1.08	3.05	-1.52	-1.06	3.06
	C <sub>I</sub>	-1.39	-1.29	3.87	-1.27	-1.16	3.99	-1.29	-1.19	3.97	-1.25	-1.15	4.01
2	A <sub>II</sub>	-5.35	-5.81	3.62	-5.23	-5.69	3.74	-5.28	-5.74	3.69	-5.33	-5.80	3.64
	B <sub>II</sub>	-4.58	-4.95	3.51	-4.27	-4.64	3.82	-4.29	-4.66	3.80	-4.27	-4.63	3.83
3	A <sub>III</sub>	-6.51	-7.33	-1.13	-6.55	-7.37	-1.16	-6.49	-7.31	-1.11	-6.63	-7.45	-1.25
	B <sub>III</sub>	-7.63	-8.48	0.56	-7.46	-8.31	0.73	-7.36	-8.22	0.82	-7.47	-8.33	0.72
	C <sub>III</sub>	-7.22	-7.98	0.77	-7.09	-7.86	0.89	-6.95	-7.72	1.03	-7.05	-7.81	0.94
	D <sub>III</sub>	-7.39	-8.24	1.15	-7.16	-8.01	1.39	-6.94	-7.79	1.60	-7.00	-7.85	1.55
	E <sub>III</sub>	-8.02	-8.96	1.37	-7.74	-8.68	1.65	-7.65	-8.59	1.75	-7.67	-8.61	1.72
4	A <sub>IV</sub>	-11.3	-12.3	0.74	-10.9	-11.9	1.07	-10.7	-11.7	1.29	-10.6	-11.7	1.35
	B <sub>IV</sub>	-11.4	-12.4	1.08	-11.0	-12.0	1.46	-10.7	-11.8	1.72	-10.6	-11.7	1.81
	C <sub>IV</sub>	-11.1	-12.1	1.31	-10.8	-11.8	1.60	-10.4	-11.4	2.02	-10.4	-11.4	2.03
	D <sub>IV</sub>	-10.6	-11.5	1.60	-10.2	-11.1	2.04	-9.89	-10.8	2.35	-9.76	-10.6	2.48

<sup>a</sup> MP2/aug-cc-pVDZ geometries served as input for MP2/aug-cc-pVTZ single-point energy self-consistent field calculations. <sup>b</sup> MP2/aug-cc-pVDZ geometries served as input for CCSD(T)/aug-cc-pVTZ single-point energy self-consistent field calculations. <sup>c</sup> Extrapolation of CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ energies. See text for equation. <sup>d</sup> For the OCS(H<sub>2</sub>O)<sub>2</sub> species, the A<sub>I</sub> energy was used in determining the free energy of the reaction. Similarly, the A<sub>II</sub> energy was used for OCS(H<sub>2</sub>O)<sub>3</sub>, and the A<sub>III</sub> energy was used for the OCS(H<sub>2</sub>O)<sub>4</sub> species.

**Figure 1.** MP2/aug-cc-pVDZ geometries of OCS(H<sub>2</sub>O).

for both basis sets ( $n = 2$  and  $3$  for the aug-cc-pVnZ basis sets). The extrapolation is then performed using the following expression

$$E_{\infty}^{\text{tot}} = \frac{3^{\alpha}}{3^{\alpha} - 2^{\alpha}} E_3^{\text{RHF}} - \frac{2^{\alpha}}{3^{\alpha} - 2^{\alpha}} E_2^{\text{RHF}} + \frac{3^{\beta}}{3^{\beta} - 2^{\beta}} E_3^{\text{cor}} - \frac{2^{\beta}}{3^{\beta} - 2^{\beta}} E_2^{\text{cor}}$$

where  $\alpha$  and  $\beta$  are empirical parameters, equal to 3.39 and 2.02, respectively.<sup>30,31</sup>

## Results

Figures 1–4 present the calculated structures for OCS(H<sub>2</sub>O)<sub>*n*</sub>, where  $n = 1$ –4, respectively. We found three dimers, two trimers, five tetramers, and four pentamers. The structures are named in the order of stability and the number of participating waters. Letters A–E signify the free-energy stability at 298 K based on the CCSD(T)/aug-cc-pVTZ single-point energy. The subscript Roman numeral signifies the number of waters. We found geometries for OCS(H<sub>2</sub>O) that match experimental and theoretical structures in the literature; B<sub>I</sub> matches the structure found by Tatamitani and Ogata,<sup>18</sup> while C<sub>I</sub> matches that calculated by Wójcik and co-workers.<sup>20</sup> Table 1 presents the relative zero-point-corrected energies, enthalpies, and free energies for all OCS(H<sub>2</sub>O)<sub>*n*</sub> clusters. Table 2 presents the free energies, equilibrium constants, and predicted observable complexes per cubic centimeter in the lower troposphere. This assumes an OCS concentration of  $2.04 \times 10^{-11}$  mol·L<sup>-1</sup> ( $1.23 \times 10^{10}$  molecules·cm<sup>-3</sup>),<sup>1</sup> a saturated water concentration of

**TABLE 2: Free Energies,<sup>a</sup> Equilibrium Constants, and Number of Complexes Per Cubic Centimeter in the Atmosphere at 298.15 K**

<i>n</i>	structure	$\Delta G^\circ_{298}$	$K_p$	$K_c$	clusters·cm <sup>-3</sup>
OCS(H <sub>2</sub> O) <sub><i>n</i>-1</sub> + H <sub>2</sub> O → OCS(H <sub>2</sub> O) <sub><i>n</i></sub>					
1	AI	2.92	$7.2 \times 10^{-3}$	$1.8 \times 10^{-1}$	$3.35 \times 10^6$
	BI	3.06	$5.7 \times 10^{-3}$	$1.4 \times 10^{-1}$	$2.64 \times 10^6$
	CI	4.01	$1.1 \times 10^{-3}$	$2.8 \times 10^{-2}$	$5.32 \times 10^5$
	total				$6.52 \times 10^6$
2	AII	3.64	$2.1 \times 10^{-3}$	$5.3 \times 10^{-2}$	$5.27 \times 10^2$
	BII	3.83	$1.6 \times 10^{-3}$	$3.8 \times 10^{-2}$	$3.83 \times 10^2$
	total				$9.10 \times 10^2$

<sup>a</sup> Free energies (kcal·mol<sup>-1</sup>) calculated with CCSD(T)/CBS-limit values from Table 1. Standard state of 1 atm.

$1.54 \times 10^{-3}$  mol·L<sup>-1</sup> ( $9.30 \times 10^{17}$  molecules·cm<sup>-3</sup>),<sup>32</sup> and a temperature of 298.15 K. Table 3 contains the unique infrared frequencies for low-energy clusters of OCS(H<sub>2</sub>O)<sub>*n*</sub>, where  $n = 1$ –4. We have previously shown that scaled MP2 frequencies give good values for pure water clusters<sup>11,25</sup> and have applied this method successfully for HO<sub>2</sub>(H<sub>2</sub>O)<sub>*n*</sub>, OH(H<sub>2</sub>O)<sub>*n*</sub>, and CS<sub>2</sub>(H<sub>2</sub>O)<sub>*n*</sub> clusters.<sup>23,33,34</sup>

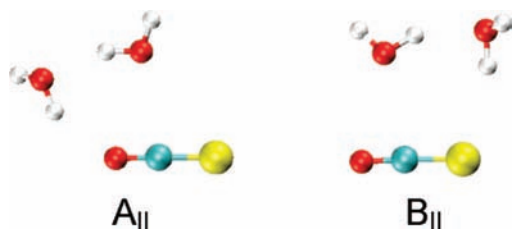
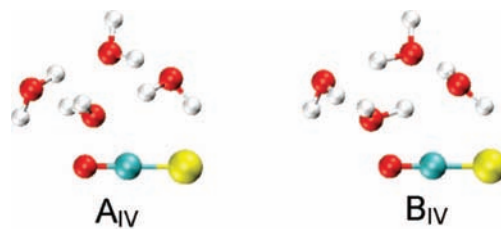
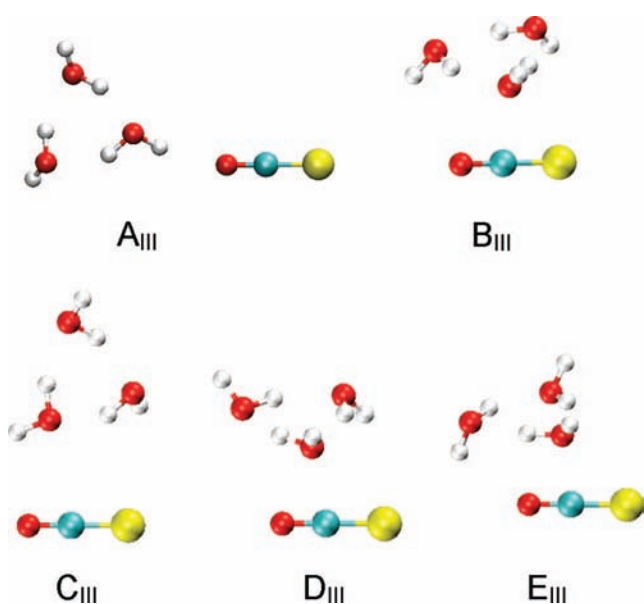
## Discussion

**A. Structures.** Three structures were found for OCS(H<sub>2</sub>O). The B<sub>I</sub> structure corresponds to the linear dimer geometry observed via FT microwave spectroscopy.<sup>18</sup> The association free energies ( $\Delta G^\circ_{298}$ ) of B<sub>I</sub> and A<sub>I</sub> are within 0.14 kcal·mol<sup>-1</sup>, suggesting that both structures are equally stable at 298 K since this energy difference is likely within the error range of the

**TABLE 3: Unique Infrared Frequencies for Low-Energy Clusters of OCS(H<sub>2</sub>O)<sub>n</sub>, n=1–4<sup>a,b</sup>**

mode <sup>c</sup>	B <sub>I</sub>	A <sub>II</sub>	E <sub>III</sub>	A <sub>IV</sub> and B <sub>IV</sub>
Unique Frequencies				
$\omega$	55 (15%)			
$\rho$ (waters)			361 (8%) +34 (7%)	
$\omega$ (waters)		598 (7%) -16 (7%)		804 (8%) and 806 (9%) +17 (12%) and +19 (12%)
$\nu_1$ (waters) - only B <sub>IV</sub>				3220 (12%) -41 (0%)
$\nu_1$ (waters)		3625 (7%) -21 (1%)	3470 (22%) -19 (35%)	3298 (92%) and 3308 (75%) -43 (100%) and -33 (100%)
$\nu_3$ (waters)				3703 (6%), 3705 (6%), and 3705 (6%) -27 (9%), -25 (9%), and -25 (9%)
$\nu_3$ (waters)				3716 (6%), 3719 (6%), and 3715 (5%), 3717 (6%) -14 (9%), -11 (9%), and -15 (9%), -13 (9%)
Other Important Frequencies <sup>d</sup>				
$\omega$ (waters)		239 (20%) +62 (9%)		272 (22%) and 272 (23%) +30 (14%), +30 (14%)
$\rho$ (waters)			440 (8%) +16 (10%)	
$\nu_{\text{asym}}$ (OCS)	1969 (49%) -11 (47%)	1970 (56%) -10 (47%)	1967 (46%) -13 (47%)	1961 (42%) and 1961 (42%) -19 (47%) and -19 (47%)

<sup>a</sup> Infrared intensities are presented as a percentage, relative to the greatest intensity found in all systems studied (italics). Frequency shifts from the corresponding pure water complex are indicated by a minus (red-shifted) or a plus (blue-shifted), along with the relative intensity of that peak. <sup>b</sup> All values are in cm<sup>-1</sup>, and all mode motions are assigned from examination of MP2/aug-cc-pVDZ frequencies. The five complexes' geometries and the corresponding pure water clusters were optimized with the keyword `opt = verytight` prior to the frequency calculation. <sup>c</sup> Only the most significant mode motion is indicated:  $\nu_1$  for symmetric stretching;  $\omega$  for wag;  $\rho$  for rock. Reference 25 has the frequencies for the pure water complexes; note that the geometries used within this reference were calculated without `opt = verytight` during the optimization. <sup>d</sup> These frequencies will also be unique if the corresponding species can be isolated from the other clusters. The OCS asymmetric stretch is presented as a reference point for the spectrum.

**Figure 2.** MP2/aug-cc-pVDZ geometries of OCS(H<sub>2</sub>O)<sub>2</sub>.**Figure 4.** MP2/aug-cc-pVDZ geometries of OCS(H<sub>2</sub>O)<sub>4</sub>.**Figure 3.** MP2/aug-cc-pVDZ geometries of OCS(H<sub>2</sub>O)<sub>3</sub>.

theory. However, in a molecular beam at low temperatures, B<sub>I</sub> will likely be the most stable structure as indicated by the  $\Delta E_0$  values presented in Table 1 (see Thermochemistry in the

Discussion). In the experimental structure, the S $\cdots$ O distance is 3.138(17) Å, while the MP2/aug-cc-pVDZ distance is 3.077 Å. Kjaergaard and co-workers determined B<sub>I</sub>'s S $\cdots$ O distance to be 3.094 Å at the CCSD(T)/aug-cc-pV(T+d)Z level of theory; only after counterpoise optimization at this high level did the S $\cdots$ O distance come into closer agreement with a value of 3.139 Å.<sup>19</sup> With the exception of the S $\cdots$ O distance, the MP2/aug-cc-pVDZ-optimized geometry possesses distances that are within 0.017 Å of the optimized CCSD(T)/aug-cc-pV(T+d)Z values and within 0.025 Å of the experimental value.<sup>18,19</sup> Thus, we expect the MP2/aug-cc-pVDZ geometries of the cluster containing 2–4 waters to be a decent estimate of their actual structures.

A notable difference between the calculated structure (MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pV(T+d)Z<sup>19</sup>) and the experimental B<sub>I</sub> structure is that the hydrogens in the theoretical structure are in the plane with the heavy atoms. The angle

between the O–C–S molecular axis and the water's rotational axis is  $17^\circ$  in the experimental structure, for which the authors assumed a linear OCS $\cdots$ O geometry and no perturbation of the individual monomers. Two rotational constants,  $B$  and  $C$ , were determined spectroscopically as 1522.0115(2) and 1514.3302(2) MHz, respectively. These values are predicted by the MP2/aug-cc-pVDZ method as 1528.72 and 1523.33 MHz, respectively, in excellent agreement with the experimental values. The rotational constant  $A$  is predicted as 432.50 GHz, while the experimental approximated value is 366.400 GHz. The experiment could not directly determine the rotational constant  $A$ , which was ultimately decided upon through a least-squares fitting of the spectra.<sup>18</sup> Various values of the rotational constant  $A$  are all consistent with the values for  $B$  and  $C$ , and the authors note that the value of the  $A$  rotational constant varies from 50 to 450 GHz, leading to a high degree of uncertainty in  $A$ . On the basis of the accuracy of our calculated  $B$  and  $C$  rotational constants, both overestimating the experimental values by 7 MHz, the theoretically determined  $A$  rotational constant of 432.50 GHz is likely a better estimate of the true value.

The other two predicted structures,  $A_I$  and  $C_I$ , show no interactions between the water and the sulfur atom.  $A_I$  contains a hydrogen bond interaction between the OCS oxygen and the water hydrogen with a heavy-atom O<sub>OCS</sub> $\cdots$ O distance of 3.133 Å (O<sub>OCS</sub> $\cdots$ H distance of 2.192 Å) and an O<sub>OCS</sub> $\cdots$ H–O angle of  $164.0^\circ$ . The third structure,  $C_I$ , is best described as T-shaped with respect to the heavy atoms. It is bound by London dispersion forces, with a C<sub>OCS</sub> $\cdots$ O distance of 3.073 Å (O<sub>OCS</sub> $\cdots$ H distance of 2.464 Å) and an O<sub>OCS</sub> $\cdots$ H–O angle of  $110.6^\circ$ . Like  $B_I$ , both  $A_I$  and  $C_I$  have the hydrogen in the plane with the heavy atoms.

For OCS(H<sub>2</sub>O)<sub>2</sub>, two trimers were predicted, both containing a slightly distorted water dimer. These structures are similar, with one H<sub>2</sub>O forming a van der Waals interaction with OCS's carbon atom, while the second H<sub>2</sub>O is either forming a hydrogen bond with OCS's oxygen atom ( $A_{II}$ ) or with OCS's sulfur atom ( $B_{II}$ ). The heavy-atom O<sub>OCS</sub> $\cdots$ O distance in  $A_{II}$  is 3.023 Å (O<sub>OCS</sub> $\cdots$ H distance of 2.149 Å), and the C<sub>OCS</sub> $\cdots$ O distance is 2.989 Å. For  $B_{II}$ , the S<sub>OCS</sub> $\cdots$ O distance is 3.586 Å (S<sub>OCS</sub> $\cdots$ H distance of 2.648 Å), and the C<sub>OCS</sub> $\cdots$ O distance is 2.978 Å. The O<sub>OCS</sub> $\cdots$ H–O angle in  $A_{II}$  is  $149.3^\circ$ , while the S<sub>OCS</sub> $\cdots$ H–O angle in  $B_{II}$  is  $162.9^\circ$ .

Five tetramers were predicted for OCS(H<sub>2</sub>O)<sub>3</sub>, all containing one of the enantiomers of the low-energy cyclic water trimer. The lowest-energy cyclic water trimer has two dangling hydrogens (those not part of the hydrogen-bonded network of the trimer) pointing to one side of the trimer ring and the other one pointing to the opposite side of the ring.<sup>35</sup> The global free-energy minimum for  $n = 3$ ,  $A_{III}$ , is a cyclic water trimer at the end of OCS, forming a hydrogen bond with OCS's oxygen atom that has an O<sub>OCS</sub> $\cdots$ O distance of 3.115 Å (O–H $\cdots$ O distance of 2.167 Å) and an O<sub>OCS</sub> $\cdots$ H–O angle of  $166.7^\circ$ . The other four structures are composed of the water trimer forming a van der Waals interaction above OCS. In the  $B_{III}$ ,  $D_{III}$ , and  $E_{III}$  structures, each of the waters interacts with OCS.  $C_{III}$  is unique among these four structures, as the trimer ring is on edge, allowing for similarity to  $C_I$  in that a slightly distorted water dimer is interacting with OCS; the third water does not interact with OCS and inhibits the other two waters from forming the hydrogen bond seen in  $A_{II}$  and  $B_{II}$ . The closest heavy-atom distances between OCS and a H<sub>2</sub>O molecule within the cyclic water trimer are a C<sub>OCS</sub> $\cdots$ O distance of 3.112 Å for  $B_{III}$ , an O<sub>OCS</sub> $\cdots$ O distance of 3.000 Å for  $C_{III}$ , a C<sub>OCS</sub> $\cdots$ O distance of 3.088 Å for  $D_{III}$  and a C<sub>OCS</sub> $\cdots$ O distance of 3.113 Å for  $E_{III}$ .

The four pentamers of OCS(H<sub>2</sub>O)<sub>4</sub> show three types of structures, all possessing a cyclic water tetramer forming van der Waals interactions with OCS.  $A_{IV}$  and  $B_{IV}$  are nearly identical with the S<sub>4</sub> water tetramer centered about the OCS's oxygen, with the primary differences lying in the direction of proton donation within the water tetramer. Looking down upon the water (Figure 1),  $A_{IV}$  has a clockwise proton donation within the (H<sub>2</sub>O)<sub>4</sub> tetramer, while  $B_{IV}$  has a counterclockwise proton donation. An alternative description for the difference between  $A_{IV}$  and  $B_{IV}$  is that the S<sub>4</sub> tetramer is rotated  $180^\circ$  along its axis that parallels the OCS molecular axis.  $C_{IV}$  and  $D_{IV}$  have the water tetramer centered above the sulfur atom. As seen in  $A_{IV}$  and  $B_{IV}$ ,  $C_{IV}$ 's water tetramer has S<sub>4</sub> symmetry, while  $D_{IV}$ 's water tetramer has the higher energy C<sub>i</sub> symmetry. There are most likely higher energy pentamer structures present that combine higher energy tetramers (e.g., Pyramid or Lasso)<sup>35</sup> with OCS, but these are expected to be much higher in energy than the pentamers presented here.

**B. Thermochemistry.** All thermal correction values were calculated using the MP2/aug-cc-pVDZ method. For improved thermochemistry accuracy, single-point energies were computed using the MP2/aug-cc-pVnZ and CCSD(T)/aug-cc-pVnZ methods, where  $n = D$  and  $T$ . The results showed convergence, and thus, a CBS-limit extrapolation should yield the most accurate results. We will focus this part of the discussion on the values calculated with the CCSD(T)/aug-cc-pVTZ method and the CBS-limit two-point extrapolation.

Table 1 shows the incremental association of hydrated carbonyl sulfide. The combination of OCS and one water molecule is exothermic ( $\Delta H^\circ_{298}$ ) by approximately 1.1 kcal·mol<sup>-1</sup> for all three structures but has a positive free energy of reaction at 298 K ( $\Delta G^\circ_{298}$ ) of 2.9 kcal·mol<sup>-1</sup> for the most stable structure. The three dimer structures have similar enthalpy values, but the entropy caused by the single interaction between the water and OCS makes  $A_I$  the most thermodynamically favorable, with  $B_I$  slightly energetically higher. The geometry of  $C_I$  is slightly more constrained than the  $A_I$  and  $B_I$  geometries, causing the entropy to be lower and the free energy of reaction to be nearly 1 kcal·mol<sup>-1</sup> greater (i.e., 4.0 kcal·mol<sup>-1</sup>). The addition of a water to  $A_I$  is exothermic by 4.6–5.8 kcal·mol<sup>-1</sup>, but after accounting for entropy, the free energy of this reaction is 3.6–3.8 kcal·mol<sup>-1</sup>.

While  $A_{III}$  is the least enthalpically favorable tetramer, significant entropic effects of the dangling water trimer cause the binding of a third water to  $A_{II}$  to be thermodynamically favorable at 298 K, with a free-energy value of  $-1.25$  kcal·mol<sup>-1</sup>. This is the only instance where the free energy for the addition of a water to OCS results in a negative free energy. The addition of the fourth water to  $A_{III}$  is enthalpically very favorable due to the formation of the water tetramer from the water trimer and has a free energy between 1.4 to 2.5 kcal·mol<sup>-1</sup>.

On the basis of the free-energy values in Table 1 and the atmospheric concentrations of OCS and H<sub>2</sub>O at 298 K in the atmosphere on a 100% humid day, we have calculated the concentrations at 298 K of OCS(H<sub>2</sub>O) <sub>$n$</sub>  where  $n = 1-2$ . Tropospheric concentrations were calculated on the order of 10<sup>6</sup> and 10<sup>2</sup> clusters·cm<sup>-3</sup> for the dimer and trimer complexes, respectively (Table 2). This concentration is much less than the predicted concentrations of pure water dimers, trimers, tetramers, and pentamers,<sup>11</sup> as well as the predicted concentrations of small ion–water clusters.<sup>36,37</sup> It is unlikely that these clusters will form in the stratosphere where the water concentration is much lower.

In the laboratory, under molecular beam conditions at very low temperatures (e.g., 10 K), the structures that are predicted to be present will closely follow the  $\Delta E_0$  trends, which is a good approximation of the free energy at very low temperatures (e.g.,  $\Delta G_{10K}$ ). On the basis of the values for  $\Delta E_0$ , we predict that each of the proposed hydration schemes with one to four waters can be generated in a cold molecular beam. As discussed earlier, the reaction to form  $B_I$  has the lowest  $\Delta E_0$  with a value of  $-1.5 \text{ kcal}\cdot\text{mol}^{-1}$ , and it is the structure that was experimentally determined for a single water interacting with OCS.<sup>18</sup> For the larger clusters, we predict that structures  $A_{II}$  ( $-5.3 \text{ kcal}\cdot\text{mol}^{-1}$ ),  $E_{III}$  ( $-7.7 \text{ kcal}\cdot\text{mol}^{-1}$ ) and  $A_{IV}$  and  $B_{IV}$  ( $-10.6 \text{ kcal}\cdot\text{mol}^{-1}$ ) will predominate. The energies of other structures are close enough that it is quite likely that a low-temperature beam will have more than one structure for a given  $\text{OCS}(\text{H}_2\text{O})_3$  or  $\text{OCS}(\text{H}_2\text{O})_4$  cluster.

**C. Frequencies.** Tatamitani and Ogata estimated the intermolecular stretch of the  $\text{OCS}(\text{H}_2\text{O})$  cluster at  $122 \text{ cm}^{-1}$  for the linear dimer.<sup>18</sup> This value corresponds fairly well with the calculated frequency (scaled MP2) at  $86 \text{ cm}^{-1}$ . The strongest band in all structures is located at approximately  $1969 \text{ cm}^{-1}$ , representing the asymmetric stretching of OCS, which is red-shifted from free OCS by approximately  $11 \text{ cm}^{-1}$ .

On the basis of the values for  $\Delta E_0$ , we predict that structures  $B_I$ ,  $A_{II}$ ,  $E_{III}$ ,  $A_{IV}$ , and  $B_{IV}$  will predominate at very low temperatures and will be identifiable in the infrared due to unique frequencies for each cluster (Table 3).  $B_I$  would be detectable at  $55 \text{ cm}^{-1}$  by the wagging of the hydrogens. For  $A_{II}$ , there is a unique frequency at  $598 \text{ cm}^{-1}$ , an out-of-plane bend or wagging motion between the two water molecules, and a second unique frequency that occurs at  $3625 \text{ cm}^{-1}$ , corresponding to a symmetric water stretch.  $E_{III}$  is characterized at  $361 \text{ cm}^{-1}$  by a concerted rocking motion of the waters and at  $3470 \text{ cm}^{-1}$  by a nonconcerted symmetric stretching of the waters.  $A_{IV}$  and  $B_{IV}$  have several predicted water stretching modes that are unique, each red-shifted from the  $S_4$  water tetramer. The most predominate frequencies, which also have the largest red shifts, are the water stretching modes at  $3298 \text{ cm}^{-1}$  ( $A_{IV}$ ) and  $3308 \text{ cm}^{-1}$  ( $B_{IV}$ ). Note that the calculated pure  $S_4$  water spectrum gives these modes the highest infrared intensities of all of the systems studied here. There is also a unique wagging mode of the waters at  $804 \text{ cm}^{-1}$  ( $A_{IV}$ ) and  $806 \text{ cm}^{-1}$  ( $B_{IV}$ ), which are blue-shifted from the  $S_4$  water tetramer.  $B_{IV}$  may be uniquely distinguished from  $A_{IV}$  at  $3220 \text{ cm}^{-1}$ , corresponding to a symmetric stretching in all of the waters. Table 3 also presents additional vibrations that can be used to identify these clusters, with the condition that the individual clusters and their corresponding pure water clusters can be isolated from the other clusters (i.e., a molecular beam containing only  $E_{III}$  and the water trimer).

**D. Use in Atmospheric and Climate Modeling.** To our knowledge, atmospheric and climate models do not include specific molecular clusters or their larger constituent aerosols composed of a specific chemical makeup. Often, these models consider all aerosols grouped into major families and do not address their specific molecular composition. Akin to the chemical field of molecular dynamics, understanding the approximations, assumptions, and sources of error in the modeling will lead to improved simulations. Improving our understanding of the chemical and thermodynamic mechanisms of how molecules form clusters and continue their growth to aerosols may improve atmospheric simulations if the information can be incorporated into the models.

Aerosols interact with the earth's climate through direct and indirect effects. Direct effects include scattering and absorption of radiation, while indirect effects include changing the size and abundance of cloud droplets, a cloud's lifetime, and a cloud's ability to reflect radiation.<sup>38,39</sup> Understanding the formation mechanisms of molecular clusters will lead to a better understanding of the mechanism of for aerosol formation. This in turn will lead to a better understanding of how aerosols impact the climate because of improving the models for cloud microphysics.<sup>40</sup> To this end, we have published several papers concerning the structures, frequencies, thermodynamics, and concentrations of several atmospherically important molecular clusters,  $(\text{H}_2\text{O})_n$ ,<sup>11,25,35,41-47</sup>  $\text{CS}_2(\text{H}_2\text{O})_n$ ,<sup>23</sup> the hydration of ions,<sup>36,37,48</sup> and the hydration of radical species.<sup>33,34</sup> This paper has explored  $\text{OCS}(\text{H}_2\text{O})_n$  and suggests an upper limit on cluster size; for continued cluster growth, a third chemical species will be needed, such as an ion, which is the logical next step in the continuation of this cluster work.

## Conclusion

We have completed an extensive search for clusters of  $\text{OCS}(\text{H}_2\text{O})_n$ , where  $n = 1-4$ . Using MP2/aug-cc-pVDZ methods, we found three dimers, two trimers, five tetramers, and four pentamers. In each of the complexes with two or more waters, OCS preferentially interacts with low-energy water clusters; in these complexes, there were no instances where a water was bound to a different topological part of OCS, isolating it from the remaining waters. Our results match current theoretical and experimental values, showing correlation with available geometries and frequencies. Using the CCSD(T) CBS thermochemical values in Table 1, the average amount of OCS in the atmosphere, and the saturated concentration of  $\text{H}_2\text{O}$  in the troposphere at 298 K, the concentrations of  $\text{OCS}(\text{H}_2\text{O})$  and  $\text{OCS}(\text{H}_2\text{O})_2$  are predicted to be on the order of  $10^6 \text{ OCS}(\text{H}_2\text{O})$  clusters  $\cdot \text{cm}^{-3}$  and  $10^2 \text{ OCS}(\text{H}_2\text{O})_2$  clusters  $\cdot \text{cm}^{-3}$ . All hydration patterns are likely to be present in a low-temperature molecular beam experiment. In addition to  $B_I$ , previously observed experimentally, we predicted that structures  $A_{II}$ ,  $E_{III}$ ,  $A_{IV}$ , and  $B_{IV}$  will predominate in a low-temperature molecular beam and will be distinguishable through specific infrared vibrations.

**Acknowledgment.** Acknowledgment is made to NSF, NIH, DOD, and Hamilton College for support of this work. This project was supported, in part, by the U.S. Army Medical Research and Materiel Command's Breast Cancer Project Grant W81XWH-05-1-0441, NIH Grant 1R15CA115524-01, NSF Grant CHE-0457275, and by NSF Grants CHE-0116435 and CHE-0521063 as part of the MERCURY high-performance computer consortium (<http://mercury.chem.hamilton.edu>).

**Supporting Information Available:** Optimized geometries, strong harmonic frequency electronic energies, enthalpies, and free energies in Hartrees for all structures reported in this paper. The single-point MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVTZ electronic energies are also available for each structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1st ed.; John Wiley & Sons, Inc.: New York, 1998.
- Vaida, V.; Headrick, J. E. *J. Phys. Chem. A* **2000**, *104*, 5401.
- Vaida, V.; Kjaergaard, H. G.; Feierabend, K. J. *Int. Rev. Phys. Chem.* **2003**, *22*, 203.

- (4) Jayne, J. T.; Pöschl, U.; Chen, Y.-M.; Dai, D.; Molina, L. T.; Worsnop, D. R.; Kolb, C. E.; Molina, M. J. *J. Phys. Chem. A* **1997**, *101*, 10000.
- (5) Aloisio, S.; Francisco, J. S.; Friedl, R. R. *J. Phys. Chem. A* **2000**, *104*, 6597.
- (6) Loerting, T.; Klaus, R. L. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 8874.
- (7) Loerting, T.; Kroemer, R. T.; Liedl, K. R. *Chem. Commun.* **2000**, 999.
- (8) Vaida, V.; Daniel, J. S.; Kjaergaard, H. G.; Goss, L. M.; Tuck, A. F. *Q. J. R. Meteorol. Soc.* **2001**, *127*, 1627.
- (9) Pfeilsticker, K.; Lotter, A.; Peters, C.; Bösch, H. *Science* **2003**, *300*, 2078.
- (10) Huneycutt, A. J.; Saykally, R. J. *Science* **2003**, *299*, 1329.
- (11) Dunn, M. E.; Pokon, E. K.; Shields, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 2647.
- (12) Morokuma, K.; Maguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.
- (13) Hofmann-Sievert, R.; Castleman, A. W. *J. Phys. Chem.* **1984**, *88*, 3329.
- (14) Kolb, C. E.; Jayne, J. T.; Worsnop, D. R.; Molina, M. L.; Meads, R. F.; Viggiano, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 10314.
- (15) Akhmatkaya, E. V.; Apps, C. J.; Hillier, I. H.; Masters, A. J.; Watt, N. E.; Whitehead, J. C. *Chem. Commun.* **1997**, 707.
- (16) Ignatov, S. K.; Sennikov, P. G.; Razuvaev, A. G.; Schrems, O. *J. Phys. Chem. A* **2004**, *108*, 3642.
- (17) Standard, J. M.; Buckner, I. S.; Pulsifer, D. H. *J. Mol. Struct.: THEOCHEM* **2004**, *673*, 1–16.
- (18) Tatamitani, Y.; Ogata, T. *J. Chem. Phys.* **2004**, *121*, 9885.
- (19) Garden, A. L.; Lane, J. R.; Kjaergaard, H. G. *J. Chem. Phys.* **2006**, *125*, 144317.
- (20) Wójcik, M. J.; Boczar, M.; Ford, T. A. *Chem. Phys. Lett.* **2001**, *348*, 126.
- (21) SPARTAN, 5.1.3 ed.; Wavefunction, Inc.: Irvine, CA 92612, 1998.
- (22) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.
- (23) Kirschner, K. N.; Hartt, G. M.; Evans, T. M.; Shields, G. C. *J. Chem. Phys.* **2007**, *126*, 154320.
- (24) Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. *J. Phys. Chem. A* **2005**, *108*, 9213.
- (25) Dunn, M. E.; Evans, T. M.; Kirschner, K. N.; Shields, G. C. *J. Phys. Chem. A* **2006**, *110*, 303.
- (26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
- (27) Butler, P. R.; Ellis, A. M. *Mol. Phys.* **2001**, *99*, 525.
- (28) Wheeler, M. D.; Ellis, A. M. *Chem. Phys. Lett.* **2003**, *374*, 392.
- (29) Patel, K.; Butler, P. R.; Ellis, A. M.; Wheeler, M. D. *J. Chem. Phys.* **2003**, *119*, 909.
- (30) Truhlar, D. G. *Chem. Phys. Lett.* **1998**, *294*, 45.
- (31) Fast, P. L.; Sanchez, M. L.; Truhlar, D. G. *J. Chem. Phys.* **1999**, *111*, 2921.
- (32) Stull, R. B. *Meteorology for Scientists and Engineers*, 2nd ed.; Brooks/Cole: Pacific Grove, CA, 2000.
- (33) Alongi, K. S.; Dibble, T. S.; Shields, G. C.; Kirschner, K. N. *J. Phys. Chem. A* **2006**, *110*, 3686.
- (34) Allodi, M. A.; Dunn, M. E.; Livada, J.; Kirschner, K. N.; Shields, G. C. *J. Phys. Chem. A* **2006**, *110*, 13283.
- (35) Day, M. B.; Kirschner, K. N.; Shields, G. C. *J. Phys. Chem. A* **2005**, *109*, 6773.
- (36) Pickard, F. C.; Pokon, E. K.; Liptak, M. D.; Shields, G. C. *J. Chem. Phys.* **2005**, *122*, 024302.
- (37) Pickard, F. C.; Dunn, M. E.; Shields, G. C. *J. Phys. Chem. A* **2005**, *109*, 4905.
- (38) Nöber, F. J.; Graf, H. F.; Rosenfeld, D. *Global Planet. Change* **2003**, *37*, 57 and references within.
- (39) Stier, P.; Seinfeld, J. H.; Kinne, S.; Boucher, O. *Atmos. Chem. Phys.* **2007**, *7*, 5237 and references within.
- (40) Lohmann, U.; Stier, P.; Hoese, C.; Ferrachat, S.; Kloster, S.; Roeckner, E.; Zhang, J. *Atmos. Chem. Phys.* **2007**, *7*, 3425.
- (41) Jurema, M. W.; Shields, G. C. *J. Comput. Chem.* **1993**, *14*, 89.
- (42) Jurema, M. W.; Kirschner, K. N.; Shields, G. C. *J. Comput. Chem.* **1993**, *14*, 1326.
- (43) Kirschner, K. N.; Shields, G. C. *Int. J. Quantum Chem.* **1994**, *Supplement 28*, 349.
- (44) Kirschner, K. N.; Sherer, E. C.; Shields, G. C. *J. Phys. Chem.* **1994**, *28*, 349.
- (45) Dunn, M. E.; Pokon, E. K.; Shields, G. C. *Int. J. Quantum Chem.* **1996**, *100*, 3293.
- (46) Day, M. B.; Kirschner, K. N.; Shields, G. C. *Int. J. Quantum Chem.* **2005**, *102*, 565.
- (47) Shields, G. C.; Kirschner, K. N. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2008**, *38*, 32.
- (48) Palascak, M. W.; Shields, G. C. *J. Phys. Chem. A* **2004**, *108*, 3692.