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

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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 OCS(H₂O)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 OCS(H₂O) species. The CCSD(T)/aug-cc-pVTZ thermochemical values combined with the average amount of OCS and the saturated concentration of H₂O in the troposphere, lead to the prediction of 10⁶ OCS(H₂O) clusters·cm⁻³ and 10⁶ OCS(H₂O)₂ clusters·cm⁻³ at 298 K. We predict the structures of OCS(H₂O)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.

Methods

Several structures of OCS(H₂O)ₙ, where n = 1–4, were created using SPARTAN,¹ followed by initial geometry optimizations using the semiempirical parametric method number 3 (PM3).² 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 OCS(H₂O)ₙ configurations, using a similar procedure as that outlined previously for CS₂(H₂O)ₙ clusters.²³ 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 CS₂(H₂O) well, suggesting that this is a suitable level of theory for sulfur–water systems.²⁴ As a reviewer pointed out, the aug-cc-pV(D+dz)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 OCS(H₂O)ₙ interaction energies for clusters with n ≥ 2 water molecules were determined by subtracting the most stable OCS(H₂O)ₙ–1 cluster from the OCS(H₂O)ₙ cluster, as elaborated in Table 1. The MP2/aug-cc-pVDZ frequencies were scaled by a factor of 0.9604;²⁴ the resulting thermodynamic values were combined with the MP2 and CCSD(T) energies to obtain zero-point-corrected energy changes (ΔE₀), enthalpy changes at 298 K (ΔH₂⁹⁸), and free-energy changes at 298 K (ΔG₂⁹⁸). 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 CS₂·H₂O dimer.²⁵ Additional calculations using the Gaussian-3 (G3)²⁶ 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.²³

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.²²,²⁷ Briefly, for each structure, the calculations yield four energetic values E₂(RHF), E₂(CSV), E₄(RHF), E₄(CSV), each corresponding to the RHF and correlated energetic values

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TABLE 1: \( \Delta E_0, \Delta H^0_{298}, \) and \( \Delta G^0_{298} \) 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 \( \cdot \) mol\(^{-1}\))

<table>
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<th>( n )</th>
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<th>( \Delta E_0 )</th>
<th>( \Delta H^0_{298} )</th>
<th>( \Delta G^0_{298} )</th>
<th>( \Delta E_0 )</th>
<th>( \Delta H^0_{298} )</th>
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<td>2.04</td>
<td>-9.89</td>
<td>-10.8</td>
<td>2.35</td>
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\( ^{a} \) MP2/aug-cc-pV(n)Z geometries served as input for MP2/aug-cc-pVTZ single-point energy self-consistent field calculations. \( ^{b} \) MP2/aug-cc-pV(n)Z geometries served as input for CCSD(T)/aug-cc-pVTZ single-point energy self-consistent field calculations. \( ^{c} \) Extrapolation of CCSD(T)/aug-cc-pV(n)Z and CCSD(T)/aug-cc-pVTZ energies. See text for equation. \( ^{d} \) For the OCS(H\(_2\)O)\(_n\) species, the A\(_1\) energy was used in determining the free energy of the reaction. Similarly, the A\(_3\) energy was used for OCS(H\(_2\)O)\(_3\), and the A\(_4\) energy was used for the OCS(H\(_2\)O)\(_4\) species.

**Results**

Figures 1—4 present the calculated structures for OCS(H\(_2\)O)\(_n\), 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\(_2\)O)\(_n\) that match experimental and theoretical structures in the literature; B\(_1\) matches the structure found by Tatamini and Ogata,\(^{18}\) while C\(_1\) matches that calculated by Wójcik and co-workers.\(^{20}\) Table 1 presents the relative zero-point-corrected energies, enthalpies, and free energies for all OCS(H\(_2\)O)\(_n\) 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 \( \cdot \) L\(^{-1} \) (1.23 \( \times \) \( 10^{10} \) molecules \( \cdot \) cm\(^{-3} \)),\(^{1}\) a saturated water concentration of \( 1.54 \times 10^{-3} \) mol \( \cdot \) L\(^{-1} \) (9.30 \( \times \) \( 10^{17} \) molecules \( \cdot \) cm\(^{-3} \)),\(^{22}\) and a temperature of 298.15 K. Table 3 contains the unique infrared frequencies for low-energy clusters of OCS(H\(_2\)O)\(_n\), where \( n = 1—4 \). We have previously shown that scaled MP2 frequencies give good values for pure water clusters and have applied this method successfully for HO\(_2\)(H\(_2\)O)\(_n\), OH(H\(_2\)O)\(_n\), and CS\(_2\)(H\(_2\)O)\(_n\) clusters.\(^{23,33,34}\)

**Discussion**

**A. Structures.** Three structures were found for OCS(H\(_2\)O). The B\(_1\) structure corresponds to the linear dimer geometry observed via FT microwave spectroscopy.\(^{18}\) The association free energies (\( \Delta G^0_{298} \)) of B\(_1\) and A\(_1\) are within 0.14 kcal \( \cdot \) mol\(^{-1} \), suggesting that both structures are equally stable at 298 K since this energy difference is likely within the error range of the
theory. However, in a molecular beam at low temperatures, $B_I$ will likely be the most stable structure as indicated by the $\Delta E_0$ values presented in Table 1. 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 $B_I$'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.$^{19}$ 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.$^{18,19}$ 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.

### Table 3: Unique Infrared Frequencies for Low-Energy Clusters of OCS(H$_2$O)$_n$, $n=1–4$$^{a,b}$

<table>
<thead>
<tr>
<th>mode$^c$</th>
<th>$B_I$</th>
<th>$A_{II}$</th>
<th>$E_{II}$</th>
<th>$A_{IV}$ and $B_{IV}$</th>
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<tr>
<td>$\omega$</td>
<td>55 (15%)</td>
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<td></td>
<td></td>
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<tr>
<td>$\rho$ (waters)</td>
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<td></td>
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<tr>
<td>$\omega$(waters)</td>
<td></td>
<td>361 (8%)</td>
<td>$+34$ (7%)</td>
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<tr>
<td>$\nu_1$ (waters) - only $B_{IV}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\nu_1$ (waters)</td>
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<td>3625 (7%)</td>
<td>3470 (22%)</td>
<td></td>
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<tr>
<td>$\nu_1$ (waters)</td>
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<td>$-21$ (1%)</td>
<td>$-19$ (35%)</td>
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<tr>
<td>$\nu_3$ (waters)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\nu_3$ (waters)</td>
<td></td>
<td>3703 (6%), 3705 (6%), and 3705 (6%)</td>
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<tr>
<td>$\nu_3$ (waters)</td>
<td></td>
<td>$-27$ (9%), $-25$ (9%), and $-25$ (9%)</td>
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<tr>
<td>$\nu_3$ (waters)</td>
<td></td>
<td>3716 (6%), 3719 (6%), and 3715 (5%), 3717 (6%)</td>
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</table>

$^a$ 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. $^b$ All values are in cm$^{-1}$, 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. $^c$ 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. $^d$ 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.

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 $B_I$’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.$^{19}$ 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.$^{18,19}$ 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)$^{19}$ and the experimental $B_I$ 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° in the experimental structure, for which the authors assumed a linear OCS⋯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.18 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, AIII and CII, show no interactions between the water and the sulfur atom. AII contains a hydrogen bond interaction between the OCS oxygen and the water hydrogen with a heavy-atom O−O−S distance of 3.133 Å (O−O−S−H distance of 2.192 Å) and an O−O−S−S−H angle of 164.0°. The third structure, CII, is best described as T-shaped with respect to the heavy atoms. It is bound by London dispersion forces, with a C−O−C−O distance of 3.073 Å (O−O−S−H distance of 2.464 Å) and an O−O−S−H−O angle of 110.6°. Like BII, both AII and CII have the hydrogen in the plane with the heavy atoms.

For OCS(H2O)2, two trimers were predicted, both containing a slightly distorted water dimer. These structures are similar, with one H2O forming a van der Waals interaction with OCS’s carbon atom, while the second H2O is either forming a hydrogen bond with OCS’s oxygen atom (AII) or with OCS’s sulfur atom (BII). The heavy-atom O−O−S−O distance in AII is 3.023 Å (O−O−S−H distance of 2.149 Å), and the C−O−C−O distance is 2.989 Å. For BII, the S−O−S−O distance is 3.586 Å (S−O−S−H distance of 2.648 Å), and the C−O−C−O distance is 2.978 Å. The O−O−S−H−O angle in AII is 149.3°, while the S−O−S−H−O angle in BII is 162.9°.

Five tetramers were predicted for OCS(H2O)3, 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.35 The global free-energy minimum for n = 3, AIII, is a cyclic water trimer at the end of OCS, forming a hydrogen bond with OCS’s oxygen atom that has an O−O−S−O distance of 3.115 Å (O−O−S−H distance of 2.167 Å) and an O−O−S−S−H angle of 166.7°. The other four structures are composed of the water trimer forming a van der Waals interaction above OCS. In the BIII, DIII, and EIII structures, each of the waters interacts with OCS. CIII is unique among these four structures, as the trimer ring is on edge, allowing for similarity to C 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 AIII and BIII. The closest heavy-atom distances between OCS and a H2O molecule within the cyclic water trimer are a C−O−C−O distance of 3.112 Å for BIII, an O−O−S−O distance of 3.000 Å for CIII, a C−O−C−O distance of 3.088 Å for DIII, and a C−O−C−O distance of 3.113 Å for EIII.

The four pentamers of OCS(H2O)4 show three types of structures, all possessing a cyclic water tetramer forming van der Waals interactions with OCS. AIV and BIV are nearly identical with the S4 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), AIV has a clockwise proton donation within the (H2O)4 tetramer, while BIV has a counterclockwise proton donation. An alternative description for the difference between AIV and BIV is that the S4 tetramer is rotated 180° along its axis that parallels the OCS molecular axis. CIV and DIV have the water tetramer centered above the sulfur atom. As seen in AIV and BIV, CIV’s water tetramer has S4 symmetry, while DIV’s water tetramer has the higher energy CI symmetry. There are most likely higher energy pentamer structures present that combine higher energy tetramers (e.g., Pyramid or Lasso)36 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 (ΔH° at 298) by approximately 1.1 kcal·mol⁻¹ for all three structures but has a positive free energy of reaction at 298 K (ΔG° at 298) of 2.9 kcal·mol⁻¹ 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 AII the most thermodynamically favorable, with BII slightly energetically higher. The geometry of CII is slightly more constrained than the AII and BII geometries, causing the entropy to be lower and the free energy of reaction to be nearly 1 kcal·mol⁻¹ greater (i.e., 4.0 kcal·mol⁻¹). The addition of a water to AII is exothermic by 4.6–5.8 kcal·mol⁻¹, but after accounting for entropy, the free energy of this reaction is 3.6–3.8 kcal·mol⁻¹.

While AII is the least enthalpically favorable tetramer, significant entropic effects of the dangling water trimer cause the binding of a third water to AII to be thermodynamically favorable at 298 K, with a free-energy value of −1.25 kcal·mol⁻¹. 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 AIII 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⁻¹.

On the basis of the free-energy values in Table 1 and the atmospheric concentrations of OCS and H2O at 298 K in the atmosphere on a 100% humid day, we have calculated the concentrations at 298 K of OCS(H2O)n where n = 1–2. Tropospheric concentrations were calculated on the order of 10^6 and 10^8 clusters·cm⁻³ 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,11 as well as the predicted concentrations of small ion–water clusters.36 It is unlikely that these clusters will form in the stratosphere where the water concentration is much lower.
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. 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. To this end, we have published several papers concerning the structures, frequencies, thermodynamics, and concentrations of several atmospherically important molecular clusters. This paper has explored OCS(H$_2$)$_n$ 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 OCS(H$_2$)$_n$, 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 H$_2$O in the troposphere at 298 K, the concentrations of OCS(H$_2$O) and OCS(H$_2$O)$_2$ are predicted to be on the order of 10$^3$ OCS(H$_2$O) clusters·cm$^{-3}$ and 10$^4$ OCS(H$_2$O)$_2$ clusters·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$_n$II, E$_n$II, A$_n$IV, and B$_n$ 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 Material 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**

JP800229K