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The HSO−SOH Isomers Revisited: The Effect of Tight d Functions†

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The tight d-augmented correlation consistent basis sets, cc-pV(n+d)Z, and standard correlation consistent basis sets, cc-pVnZ, where n = D(2), T(3), Q(4), and 5, for the second-row atoms have been used to re-examine the relative energy of the HSO and SOH isomers using Hartree−Fock, coupled cluster with single and double excitation, and coupled cluster with single, double, and perturbative triple excitation levels of theory. Geometries, dissociation energies, and vibrational frequencies have also been determined for each species. The relative energies of the two isomers converge more rapidly and smoothly for the new tight *d*-augmented sets than for the standard sets. The impact of the tight *d* function is most significant upon dissociation energies at the double-ζ and triple-ζ levels for HSO, with differences of 5.46 and 2.57 kcal/mol, respectively, and less significant for SOH, with differences of 1.90 and 1.20 kcal/mol. The impact of the additional d functions in the basis set upon vibrational frequencies and zero-point energies is minor.

I. Introduction

The chemistry of atmospheric sulfur has been long-studied due to its significant role in environmental problems such as acid rain, ozone destruction, and chemical air pollution. To address such problems, a greater understanding of the underlying processes involved in the atmospheric sulfur cycle is needed. One potentially important reactive intermediate is the thioperoxy radical, HSO, which can be formed by several different pathways and, once formed, can play a catalytic role in ozone destruction as shown by several experiments according to the following sequence of reactions[1−3]

$$HS + O_3 \rightarrow HSO + O_2 \qquad (1)$$

$$HSO + O_3 \rightarrow HS + 2O_2 \qquad (2)$$

Though HSO and its isomer, SOH, have been well studied in the past,[4−6] it was not until 1993 that the HSO radical was shown by computation to be more stable than its isomer SOH.[7,8] This was the first theoretical study that gave predictions in agreement with experimental results,[9,10] as all earlier theoretical studies predicted SOH to be the more stable isomer. By use of multireference ab initio methods (CASSCF and CASSCF+1+2) and a sequence of correlation consistent basis sets (cc-pVnZ),[11,12] Xantheas and Dunning found that the SOH−HSO energy difference converged remarkably slowly with increasing basis-set size, with small basis sets (cc-pVDZ and cc-pVTZ) predicting SOH to be the more stable isomer.[7,8] This cast considerable doubt on the results of previous computational studies of HSO/SOH (and undoubtedly other sulfur species) that used small basis sets. Since this time, there have been a number of additional computational studies of the isomers.[13−20] However, none of the studies addressed the issues associated with the slow convergence of the SOH−HSO energy difference, although Denis and Ventura noted a similar problem in DFT (B3LYP and B3PW91) calculations with the correlation-consistent sets in their study of the enthalpy of formation of HSO.[14]

Over the past decade, the correlation consistent basis sets have shown their utility in numerous studies of atmospheric sulfur processes.[13,14,21,22] In particular, we note the work by Schaefer et al., which was an extended coupled cluster with single and double excitation (CCSD) and coupled cluster with single, double, and perturbative triple excitation (CCSD(T)) study of the $[2H,S,O]^+$ system using the correlation consistent basis sets.[13] Recent studies, however, revealed deficiencies in the composition of the correlation consistent basis sets for sulfur.[23−26] Unacceptable errors (~6 kcal/mol) in the binding energy of SO_2 were noted in 1995 by Bauschlicher and Partridge upon extrapolation of the results of CCSD(T) calculations with cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets to the complete basis-set (CBS) limit.[23] As binding energies for CCSD(T) combined with the correlation consistent basis sets typically approach chemical accuracy (~1 kcal/mol) at the CBS limit, this finding was surprising. Bauschlicher and Partridge observed that this error was significantly reduced with the addition of tight (high exponent) d functions to the sulfur basis sets. This problem was also noted for SO by Martin, who investigated the impact of adding tight functions to the correlation consistent sets in order to reduce the observed errors.[24] The problems were not limited to sulfur, as Martin and Uzan observed that similar errors occurred for other second-row atoms.[25]

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TABLE 1: Optimized Geometries for the Ground States of HSO and SOH Using CCSD(T) in Combination with the cc-pV*n*Z and cc-pV(*n*+*d*)Z Basis Sets

	HSO			SOH		
basis set	r_e(S−H), Å	r_e(S−O), Å	θ_e(H−S−O), deg	r_e(S−O), Å	r_e(O−H), Å	θ_e(S−O−H), deg
cc-pVDZ	1.3829	1.5594	103.53	1.6828	0.9724	105.65
cc-pVTZ	1.3711	1.5165	104.32	1.6481	0.9650	106.94
cc-pVQZ	1.3686	1.5043	104.47	1.6386	0.9636	107.82
cc-pV∞Z[a]	1.368	1.499	104.5	1.635	0.963	109.7
cc-pV(D+*d*)Z	1.3793	1.5324	104.42	1.6683	0.9723	106.14
cc-pV(T+*d*)Z	1.3689	1.5036	104.82	1.6407	0.9650	107.21
cc-pV(Q+*d*)Z	1.3687	1.4977	104.69	1.6350	0.9636	107.83
cc-pV(∞+*d*)Z[a]	1.369	1.496	(104.7)	1.634	0.963	108.7
exp[b]	1.389	1.494	106.6			
exp[c]	1.35	1.54	102			

[a] CBS limits were obtained using the exponential extrapolation scheme, eq 3. [b] Experimental values were obtained from ref 30. [c] Experimental values were obtained from ref 31.

In an earlier study, we re-examined the deficiencies in the standard correlation consistent basis sets.[27] As any arbitrary addition to the basis set always improves the total energy, and generally improves the dissociation energy (correlation effects are usually larger in molecules than in atoms), the challenge was to eliminate the deficiencies in the basis sets while maintaining the systematic behavior needed to provide accurate extrapolations to the CBS limit. We found that the deficiencies in the standard correlation consistent sets were due to two problems in the *d* sets: (1) a near duplication of the M-shell exponents in the (3*d*) and (4*d*) sets and (2) a deficiency in the L-shell region in the early members of the *d* sets needed to describe molecular core polarization effects as well as valence orbital correlation effects. The result of this work was the development of a new family of basis sets, the cc-pV(*n*+*d*)Z, "tight *d*-augmented correlation consistent basis sets," for second-row atoms. These sets are unique in that they maintain the systematic behavior needed to provide accurate extrapolations to the complete basis set limit.

In studies to date, it has been found that the use of the cc-pV(*n*+*d*)Z basis sets can have a dramatic effect upon the convergence of molecular properties computed with a sequence of such basis sets. The impact can be particularly significant upon properties (e.g., dissociation energies) determined using the lower-level basis sets, as demonstrated in earlier studies of SO and SO_2.[21,22,27] However, the overall convergence limit obtained using either series of basis sets can be similar, provided the extrapolation method and basis sets for inclusion in the extrapolation have been selected appropriately.

In this study, we recompute the energies of the HSO and SOH isomers to assess the impact of the new basis sets upon the once-troublesome theoretical description of the relative energies of the two isomers. The impact of the new sets upon the structures, frequencies, and dissociation energies of the isomers is also assessed.

II. Computational Details

All calculations were performed using the Gaussian 98 program.[28] Numerical optimizations were done using CCSD(T) for each level of basis set. Zero-point energies were computed at the double-ζ and triple-ζ levels of basis set.

The exponential extrapolation scheme, as shown below and first published by Feller to extrapolate to the CBS limit for the correlation consistent basis sets,[29] has been used

$$E(n) = E(\infty) + \mathrm{A}\, e^{-B(n-1)} \tag{3}$$

where, *n* stands for the cardinal number of the basis set and *E*(*n*) is the energy calculated with the cc-pV*n*Z or cc-pV(*n*+*d*)Z basis set.

III. Results and Discussion

A. Optimized Geometries of the HSO and SOH Isomers. The optimum geometries of the ground states ($^2A''$) of HSO and SOH obtained with the CCSD(T) method in combination with the cc-pV*n*Z and the cc-pV(*n*+*d*)Z basis sets are listed in Table 1. As seen in Table 1, convergence of the S−H and S−O bond lengths in HSO and the S−O bond length in SOH is significantly more rapid for the tight *d*-augmented basis sets than for the standard sets. For example, the difference between r_e(SO) for SOH calculated with the TZ and QZ basis sets is −0.0095 Å for the standard sets and just −0.0057 Å for the tight *d*-augmented TZ and QZ sets. As expected, the convergence of the O−H bond length in SOH is similar for the tight *d*-augmented sets as for the standard sets, as there is essentially no difference between r_e(OH) calculated with the $n =$ T and Q basis sets.

Although the bond angle is slightly larger for the tight *d*-augmented sets than for the standard sets, the convergence rates are very similar. In HSO, the bond angle is much less sensitive to the basis set than the S−H and S−O bond lengths; in SOH, they are more comparable.

Our best estimates for the HSO geometry are in reasonable agreement with experiment. The S−O equilibrium bond length predicted by the CCSD(T) method at the complete basis set (CBS) limit, 1.496 Å (eq 1 with the tight *d*-augmented sets)), is near the value of 1.494 Å obtained from one experiment,[30] though below the 1.54 Å value obtained in another experiment.[31] The extrapolated H−S bond length of 1.369 Å falls between the two experimental determinations of 1.35 and 1.389 Å.[30,31] The cc-pVQZ and cc-pV(Q+*d*)Z predictions of the bond angle, 104.5° and 104.7°, respectively (the bond angle in HSO does not converge smoothly), also fall between the values of 106.6 and 102° obtained from experiment.[30,31]

Note that isomerization of HSO to SOH results in a substantial lengthening of the S−O bond, from 1.369 Å in HSO to 1.634 Å in SOH.

B. Vibrational Frequencies. The tight *d*-augmented basis sets result in only a few percent change in the computed vibrational frequencies when compared with the standard basis sets as shown in Table 2. For example, ω_1, which corresponds to the S−O stretch of HSO, is calculated to be 1008 cm^{-1} with the cc-pVTZ set and 1027 cm^{-1} with the cc-pV(T+*d*)Z set. These predictions are within a few wavenumbers of experiment (1013 and 1026 cm^{-1}).[30,31] Our predictions for ω_3, the S−H

TABLE 2: Harmonic Vibrational Frequencies (in cm^{-1}) and Zero-Point Energies (in kcal/mol) from CCSD(T) Calculations with the cc-pV*n*Z and cc-pV(*n*+*d*)Z Basis Sets

	SOH				HSO			
basis set	ω_1 (SO str)	ω_2 (SOH bend)	ω_3 (OH str)	ZPE	ω_1 (SO str)	ω_2 (HSO bend)	ω_3 (HS str)	ZPE
cc-pVDZ	807.08	1172.46	3767.94	8.217	917.94	1054.46	2463.54	6.342
cc-pVTZ	847.02	1199.96	3792.29	8.348	1007.80	1089.23	2451.56	6.502
cc-pV(D+*d*)Z	810.50	1174.61	3766.47	8.222	948.28	1074.79	2458.29	6.406
cc-pV(T+*d*)Z	851.28	1200.13	3791.19	8.352	1027.41	1101.59	2447.90	6.543
exp[a]					1026	1164	2271	
exp[b]					1013	1063	2570	

[a] Experimental data were obtained from ref 30. [b] Experimental data were obtained from ref 31.

stretching frequencies of HSO, are 2452 cm^{-1} (cc-pVTZ) and 2448 cm^{-1} (cc-pV(T+*d*)Z) and, again, fall within the observed experimental values (2271 and 2570 cm^{-1}).[30,31] The H−S−O bending frequency, ω_2, is calculated to be 1089 cm^{-1} (cc-pVTZ) and 1102 cm^{-1} (cc-pV(T+*d*)Z) as compared to the experimental values 1063 and 1164 cm^{-1}.[30,31]

There is also little difference between the zero-point energies computed with the tight *d*-augmented basis sets and those computed with the standard basis sets for SOH, as shown by differences of 0.005 kcal/mol at the double-ζ level and 0.004 kcal/mol at the triple-ζ level. The change in zero-point energy for HSO arising from the tight *d*-augmented sets is slightly larger, with differences of 0.064 kcal/mol at the double-ζ level and 0.0041 kcal/mol at the triple-ζ level. SOH has a larger zero-point energy than HSO, 8.35 vs 6.54 kcal/mol, largely due to the difference in the ω_3 frequencies; the frequency of the O−H stretch in SOH is over 1300 cm^{-1} larger than the frequency arising from the S−H stretch in HSO. The S−O stretching frequency in SOH is only 175 cm^{-1} lower that the corresponding frequency in HSO.

C. Atomization Energies. The impact of the tight *d*-augmented basis sets is more significant for the calculation of the atomization energies for HSO and SOH than for the frequencies, which, as seen above, are relatively insensitive to the improvements in the basis sets. As shown in earlier studies, the most significant impact is observed for the lower-level basis sets.[21,22,27] Interestingly, the improvements resulting from the new sets are substantially larger for HSO than for SOH. For the atomization energy of HSO calculated using the CCSD(T) method, the improvements are 5.46 (cc-pV(D+*d*)Z), 2.57 (cc-pV(T+*d*)Z), 2.02 (cc-pV(Q+*d*)Z), and 0.40 (cc-pV(5+*d*)Z) kcal/mol, whereas the corresponding differences for SOH are only 1.90, 1.20, 0.76, and 0.16 kcal/mol. As we shall see below, these differences are very significant when calculating the HSO−SOH isomerization energy.

CBS limits for the atomization energy resulting from the combination of each method and basis set series have been determined using the exponential extrapolation scheme shown in eq 3. The HF and CCSD calculations were carried out at the optimum geometries obtained from the CCSD(T) calculations with the corresponding basis sets. The calculations with the cc-pV5Z and cc-pV(5+*d*)Z basis sets were performed at the optimum geometry obtained from CCSD(T) calculations with the corresponding quadruple-ζ (QZ) basis set. Note that the differences between the extrapolated values of the atomization energies of either SOH and HSO using either the cc-pV*n*Z or cc-pV(*n*+*d*)Z series never differ by more 0.6 kcal/mol.

At the CBS limit, the correlation effects included in the CCSD method increase the atomization energies of SOH and HSO by 70.0 and 72.8 kcal/mol, respectively. The connected triples correction included in the CCSD(T) method further increases the atomization energies by 6.1 kcal/mol in SOH and 6.9 kcal/mol in HSO.

TABLE 3: Atomization Energies for HSO and SOH in kcal/mol (Zero-Point Corrections Have Been Included)

method	basis set	D_0 (SOH)	D_0 (HSO)
HF	cc-pVDZ[a]	84.65	79.70
	cc-pVTZ[a]	97.45	95.23
	cc-pVQZ[a]	99.73	98.71
	cc-pV5Z[a,b]	100.75	100.99
	cc-pV∞Z[a,c]	100.7	101.1
	cc-pV(D+*d*)Z[a]	87.37	85.23
	cc-pV(T+*d*)Z[a]	99.03	98.78
	cc-pV(Q+*d*)Z[a]	100.63	100.74
	cc-pV(5+*d*)Z[a,b]	101.01	101.31
	cc-pV(∞+*d*)Z[a,c]	101.0	101.3
CCSD	cc-pVDZ[a]	143.73	138.76
	cc-pVTZ[a]	161.79	160.89
	cc-pVQZ[a]	167.60	168.71
	cc-pV5Z[a,b]	170.05	172.76
	cc-pV∞Z[a,c]	171.0	174.6
	cc-pV(D+*d*)Z[a]	145.67	144.16
	cc-pV(T+*d*)Z[a]	163.04	164.34
	cc-pV(Q+*d*)Z[a]	168.38	170.74
	cc-pV(5+*d*)Z[a,b]	170.23	173.14
	cc-pV(∞+*d*)Z[a,c]	171.0	174.1
CCSD(T)	cc-pVDZ	147.65	143.15
	cc-pVTZ	167.41	167.00
	cc-pVQZ	173.60	175.30
	cc-pV5Z[b]	176.22	179.55
	cc-pV∞Z[c]	177.2	181.4
	cc-pV(D+*d*)Z	149.55	148.61
	cc-pV(T+*d*)Z	168.61	170.43
	cc-pV(Q+*d*)Z	174.36	177.32
	cc-pV(5+*d*)Z[b]	176.38	179.95
	cc-pV(∞+*d*)Z[c]	177.1	181.0

[a] From single-point calculations at the optimized structures from CCSD(T) calculations with the corresponding basis sets. [b] From single-point calculations at the optimized structures from the corresponding quadruple-ζ basis set. [c] CBS limits were obtained using the exponential extrapolation scheme, eq 3.

D. Relative Energies of HSO and SOH. Relative energy differences between the HSO and SOH isomers are reported in Table 4. ΔE_e corresponds to the electronic energy difference, and ΔE_e from CCSD(T) calculations with both the cc-pV*n*Z and cc-pV(*n*+*d*) sets are plotted in Figure 1. ΔE_0 is the energy difference including harmonic zero-point energy corrections; for calculations with the QZ and 5Z basis sets, the zero-point corrections were taken from the calculations with the corresponding TZ sets. The energy difference is calculated relative to HSO, and thus, a negative ΔE_0 indicates that SOH is the more stable species. Experimental studies predict that HSO is the more stable species, i.e., ΔE_0 is positive.[9,10]

As shown in the table, the HF method only makes a qualitatively correct prediction of ΔE_0 when combined with the cc-pV5Z, cc-pV(Q+*d*), or cc-pV(5+*d*)Z basis sets. Even for the largest basis set, however, HF calculations predict that HSO is more stable than SOH by just 0.5 kcal/mol. For both the CCSD and CCSD(T) methods, HSO is predicted to be the more stable species using the cc-pVQZ or cc-pV5Z sets, while the

TABLE 4: Total Energy and Energy Separation (with respect to HSO) between the HSO and SOH Isomers

		E_h		ΔE_e (HSO−SOH)	ΔE_0 (HSO−SOH)
method	basis set	*E* (SOH)	*E* (HSO)	kcal/mol	kcal/mol
HF	cc-pVDZ[a]	−472.927 617	−472.916 740	−6.83	−4.95
	cc-pVTZ[a]	−472.977 665	−472.971 180	−4.07	−2.22
	cc-pVQZ[a]	−472.989 645	−472.985 083	−2.86	−1.02
	cc-pV5Z[a,b]	−472.993 190	−472.990 631	−1.61	0.24
	cc-pV(D+*d*)Z[a]	−472.932 000	−472.925 699	−3.95	−2.14
	cc-pV(T+*d*)Z[a]	−472.980 216	−472.976 923	−2.07	−0.26
	cc-pV(Q+*d*)Z[a]	−472.991 109	−472.988 397	−1.70	0.11
	cc-pV(5+*d*)Z[a,b]	−472.993 613	−472.991 218	−1.50	0.31
	cc-pV(∞+*d*)Z[c]			−1.3	0.5
CCSD	cc-pVDZ[a]	−473.249 725	−473.238 831	−6.84	−4.96
	cc-pVTZ[a]	−473.389 766	−473.385 389	−2.75	−0.90
	cc-pVQZ[a]	−473.430 422	−473.429 242	−0.74	1.10
	cc-pV5Z[a,b]	−473.444 420	−473.445 798	0.86	2.71
	cc-pV(D+*d*)Z[a]	−473.256 126	−473.250 839	−3.32	−1.50
	cc-pV(T+*d*)Z[a]	−473.392 680	−473.391 869	−0.51	1.30
	cc-pV(Q+*d*)Z[a]	−473.432 303	−473.433 178	0.55	2.36
	cc-pV(5+*d*)Z[a,b]	−473.445 076	−473.446 816	1.09	2.90
	cc-pV(∞+*d*)Z[c]			1.7	3.5
CCSD(T)	cc-pVDZ	−473.257 979	−473.247 831	−6.37	−4.49
	cc-pVTZ	−473.406 618	−473.403 022	−2.26	−0.41
	cc-pVQZ	−473.449 862	−473.449 626	−0.15	1.70
	cc-pV5Z[b]	−473.464 817	−473.467 194	1.49	3.34
	cc-pV(D+*d*)Z	−473.264 581	−473.260 181	−2.76	−0.95
	cc-pV(T+*d*)Z	−473.409 616	−473.409 635	0.01	1.82
	cc-pV(Q+*d*)Z	−473.451 803	−473.453 649	1.16	2.97
	cc-pV(5+*d*)Z[b]	−473.465 492	−473.468 298	1.76	3.57
	cc-pV(∞+*d*)Z[c]			2.4	4.2

[a] From single-point calculations at the optimized structures from CCSD(T) calculations with the corresponding basis sets. [b] From single-point calculations at the optimized structures from the corresponding quadruple-ζ basis set. [c] CBS limits were obtained using the exponential extrapolation scheme, eq 3.

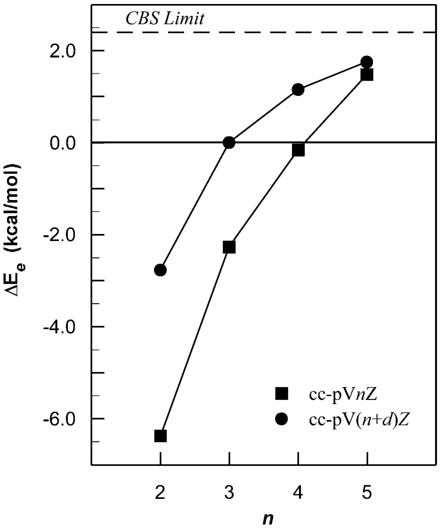

Figure 1. Energy differences, ΔE_e, between HSO and SOH from CCSD(T) calculations with the standard and tight *d*-augmented basis sets. Negative values mean that SOH is the more stable isomer.

tight *d*-augmented sets enable this to occur as early as with the cc-pV(T+*d*)Z basis set. CCSD calculations with the cc-pV(5+*n*)Z set yield a ΔE_0 of 2.90 kcal/mol; the triples correction increases this by another 1.3 kcal/mol to 4.2 kcal/mol. Note that the value of 4.2 kcal/mol obtained by extrapolating ΔE_0 differs by just 0.3 kcal/mol from that obtained by extrapolating the two atomization energies (3.9 kcal/mol). This HSO−SOH energy difference does, however, differ by 1.2 kcal/mol from that calculated by Xantheas and Dunning[7,8] (5.4 kcal/mol). Although the change in the nature of the wave function from HSO to SOH (the wave function for SOH has more multireference character than that for HSO) may account for part of this difference, the coupled-cluster method is remarkably robust in this regard, and it is likely that the difference in the two predictions is a result of other attributes of the two wave functions.

We found it impossible to reliably extrapolate the calculated ΔE values for the cc-pV*n*Z sets; the dependence on *n* was just too steep to obtain reasonable values of the CBS limits. For example, exponential extrapolation of the CCSD(T)/cc-pV*n*Z calculations for $n = 3-5$ yields a predicted ΔE_e of 7.2 kcal/mol, an increase over the cc-pV5Z result that is 3.5 times larger than the change in ΔE_e between the cc-pVQZ and cc-pV5Z basis sets. Extrapolation of the results from the cc-pV(*n*+*d*)Z sets, on the other hand, produced very reasonable CBS limits, e.g., 2.4 and 4.2 kcal/mol for ΔE_e and ΔE_0 with the CCSD(T) method.

When the standard basis sets are used, convergence behavior similar to that seen in the earlier work of Xantheas and Dunning[7,8] is found. This illustrates the importance of the use of the tight *d*-augmented sets.

IV. Conclusion

Use of the newly revised correlation consistent basis sets, the tight *d*-augmented correlation consistent basis sets, cc-pV(*n*+*d*)Z, for the second-row atoms (Al−Ar), can have a pronounced effect upon structure and property determinations for molecules containing these atoms. For HSO and SOH, the impact upon the computed atomization energies is not as dramatic as has been observed for other second-row species such as SO_2. The largest differences observed in the CCSD(T) prediction of the atomization energy of HSO are 5.46 and 2.57 kcal/mol, with the cc-pV(D+*d*)Z and cc-pV(T+*d*)Z basis sets, respectively. The impact is less significant for the atomization energy of SOH, with differences of 1.90 and 1.20 kcal/mol at the double- and triple-ζ levels.

Properties computed with the new tight *d*-augmented sets converge much more smoothly than those obtained with the standard correlation consistent basis sets. For example, reasonable values of the energy difference between HSO and SOH could not be obtained using the exponential extrapolation procedure and the cc-pV*n*Z sets. No such problem was encountered with the cc-pV(*n*+*d*)Z sets.

Extrapolation of the results of the CCSD(T) calculations to the CBS limit predict equilibrium geometries of 1.369 Å (S−H), 1.496 Å (S−O), and 104.7° (H−S−O) for HSO and 0.963 Å (O−H), 1.634 Å (S−O), and 108.7° (S−O−H) for SOH. The calculated frequencies at the CCSD(T)/cc-pV(T+*d*) level are 1027 (S−O stretch), 1102 (H−S−O bend), and 2448 cm^{-1} (S−H stretch) for HSO and 851 (S−O stretch), 1200 (S−O−H bend), and 3791 cm^{-1} (O−H stretch) for SOH. These results are in reasonable accord with the available experimental data; however, these data are not conclusive. The extrapolated atomization energies of HSO and SOH from CCSD(T) calculations and harmonic zero-point corrections are 181.0 and 177.1 kcal/mol, respectively. Finally, extrapolation of the computed, CCSD(T) energy differences predicts that HSO is more stable than SOH by 4.2 kcal/mol.

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