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Enthalpy of Formation of $^2\Pi_{3/2}$ SH

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The standard enthalpy of formation, $\Delta_f H°$, of $^2\Pi_{3/2}$ SH has been determined at converged levels of ab initio electronic structure theory, including high-order coupled cluster and full configuration interaction benchmarks. The atomic Gaussian basis sets employed include the (aug)-cc-p(wC)VnZ family with $n = 3$, 4, 5, and 6. Extrapolations to the complete one-particle basis set and the full configuration interaction limits, where appropriate, have been performed to reduce remaining computational errors. Additional improvements in the enthalpy of formation of $^2\Pi$ SH were achieved by appending the valence-only treatment with core−valence correlation, scalar relativistic and spin−orbit effects, and the diagonal Born−Oppenheimer correction. The recommended values for $\Delta_f H_0^\circ$ and $\Delta_f H_{298}^\circ$ of $^2\Pi$ SH are $141.24^{+0.52}_{-0.46}$ and $141.87^{+0.52}_{-0.46}$ kJ mol^{-1}, respectively, corresponding to a recommended $D_e = 365.76^{+0.50}_{-0.42}$ kJ mol^{-1}. The corresponding enthalpy of formation of $^2\Pi$ SD is $\Delta_f H_0^\circ = 140.17^{+0.56}_{-0.50}$ kJ mol^{-1}.

1. Introduction

H_2S is the major source of sulfur compounds in the earth's atmosphere. This compound is generated naturally by volcanic activity, by bacteria, and mainly by man-made pollution due to the burning of fossil fuels containing large amounts of S. The major source of the mercapto radical, SH, in the earth's atmosphere is S−H bond fission following near-ultraviolet photoexcitation of H_2S. Thermochemical data for SH are of special importance because of the role SH plays as an intermediate in reactions generating sulfur-containing pollutants (e.g., acid rain) as well as in complex reaction mechanisms explaining fossil combustion processes.[1]

New, ever more efficient techniques for the solution of the electronic structure problem coupled with advances in computer architecture make possible, with unprecedented accuracy,[2−11] the theoretical reevaluation of thermochemical properties. Because of their crucial importance in reaction kinetics studies, temperature-dependent standard enthalpies of formation, $\Delta_f H_T^\circ$, are of the greatest interest. For the smallest radicals, the accuracy of the best ab initio computations (see, for example, refs 10 and 11) of $\Delta_f H_T^\circ$ can exceed that of traditional experimental determinations.[12−18]

The most straightforward way to determine the converged ab initio $\Delta_f H_0^\circ$ of $^2\Pi_{3/2}$ SH goes through the determination of its atomization energy, though there are more efficient computational routes for systems with more atoms. The best theoretical scheme for this study is offered by the focal-point approach.[19,20] The converged ab initio determination of the enthalpy of formation of $^2\Pi_{3/2}$ SH is made simpler by the relatively small size of the system, allowing for the utilization of full configuration interaction (FCI) techniques.[21] The calculations reported herein for the SH radical are the most extensive reported to date, though calculations with a similar purpose have been performed before.[22−25]

Major thermochemical tables and databanks recommend values for the atomization energy, $D_{0/e}$, and for $\Delta_f H_T^\circ$ of $^2\Pi_{3/2}$ SH. The best available value of the zero-point-corrected atomization energy of $^2\Pi_{3/2}$ SH is $D_e = 350.51 \pm 1.20$ kJ mol^{-1},[26] obtained from a careful experimental and theoretical analysis of the secondary photolysis of ground-state SH arising from the 218.2-nm photodissociation of H_2S. Note that this value corresponds to the $v'' = 0$, $J'' = 3/2$ level of the X $^2\Pi_{3/2}$ spin−orbit component and the lowest-energy products, S($^3P_2$) and H(^2S). The available enthalpies of formation[12,13,16,27−38] are summarized in Table 1. The available values for $\Delta_f H_{298}^\circ$(SH) scatter around 140 kJ mol^{-1}, with recent reviews (e.g., ref 37) settling at 139.3 ± 3.0 kJ mol^{-1}. A slightly higher mean value, 143.0 ± 3.0 kJ mol^{-1}, has also been suggested and accepted[13] on the basis of the high-quality work of Nicovich et al.[31] Both values are in accord with the value obtained by Nourbakhsh and co-workers.[30] Nevertheless, in the same study, Nourbakhsh et al. suggested that $\Delta_f H_0^\circ = 148.5 \pm 8.4$ kJ mol^{-1} for the enthalpy of formation of CH_3S, which is substantially different from the generally accepted low value of Nicovich,[31] 131.5 ± 2.3 kJ mol^{-1}. To resolve this discrepancy, it is also mandatory to have a highly dependable estimate of the enthalpy of formation of SH.

2. Computational Approach

The X $^2\Pi$ ground electronic state of the mercapto radical has a $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(5\sigma)^2(2\pi)^3$ electronic configuration. Single-reference methods are appropriate for the descrip-

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TABLE 1: Literature Data for the Enthalpy of Formation of $^2\Pi$ SH[a]

$\Delta_f H^\circ_{298}$	reference	year	method[b]	comments
		Measurements		
144.76 ± 16.7	Mackle[27]	1963	KE	*c*
140.58 ± 4.6	Hwang and Benson[28]	1977	KE	*d*
138.6 ± 0.4	Traeger[29]	1984	PIMS-IE	*e*
142.4 ± 6.3	Nourbakhsh et al.[30]	1991	PIMS-IE	*f*
143.0 ± 2.8	Nicovich et al.[31]	1992	KE	*g*
		Computations		
141.0	Curtiss et al.[32]	1998	G3	*h*
138.0	Curtiss et al.[33]	1999	AI	*i*
140.6	Parthiban and Martin[34]	2001	W2	*j*
137.6	Janoschek and Rossi[35]	2002	G3MP2B3	*k*
143.1	Peebles and Marshall[25]	2002	AI	
		Reviews and Evaluations		
149 ± 12	Kerr[38]	1966	CDE	*l*
140.6 ± 4.6	McMillen and Golden[36]	1982	CDE	*m*
140.4 ± 3.5	Gurvich et al.[12]	1989	CDE	
143.0 ± 3.0	Berkowitz et al.[13]	1994	CDE	*n*
139.3 ± 3.0	Chase et al.[16]	1998	CDE	*o*
139.3 ± 5.0	Burcat[37]	2001	CDE	*p*

[a] All values are in kJ mol^{-1}. [b] KE = kinetic equilibrium study. PIMS-IE = photoionization mass spectrometry- ionization energy determination. AI = ab initio computation using a model chemistry. CDE = critical data evaluation. [c] Average of three independent measurements: the dissociations of $H_2S \rightarrow HS + H$, the ionization potential of HS, and the appearance potential of HS^+ from H_2S. [d] Calculated from $H_2S + I_2$ reaction kinetics in the 555−595 K range. [e] PIMS has been used to measure the appearance energies of $[C_2H_5]^+$ from ethanethiol, $[C_3H_7]^+$ from 2-propanethiol, and $[C_3H_5]^+$ from 2-methylthiirane. [f] $\Delta_f H^\circ_0 = 141.8 \pm 6.3$ kJ mol^{-1} was deduced from time-of-flight measurements of CH_3 and SH photofragments from the photodissociation of CH_3SH in a supersonic molecular beam. [g] Kinetics of the reaction $Br(^2P_{3/2}) + H_2S \rightarrow SH + HBr$ using resonance fluorescence temperature-dependent experiments result in $\Delta_f H^\circ_0 = 142.55 \pm 3.01$ kJ mol^{-1} and $\Delta_f H^\circ_{298} = 143.01 \pm 2.85$ kJ mol^{-1}. [h] G2 and G3 model chemistry values are both reported. [i] G3(MP2/6-31G(d)) computation. [j] Weizmann model W2. The W1 value is 145.6 kJ mol^{-1}. [k] The estimated average error in the G3MP2B3 calculations is 8 kJ mol^{-1}. [l] The old value of Kerr is an uncertain estimate based on the dissociation energy of the H−S bond as 90 ± 2 kcal/mol from the pyrolysis of benzyl sulfide. [m] Refers to the value of Hwang and Benson.[28] [n] Extensive calculation of data (mainly kinetic determinations) published until 1992. The recommended value is that of Nicovich et al.[31] [o] Based on a photoionization appearance energy (AE) of SH^+ produced from H_2S (Dibeler, V. H.; Liston, S. K. *J. Chem. Phys.* **1968**, *49*, 482) and the spectroscopic ionization energy for the SH radical (Morrow, B. A. *Can. J. Phys.* **1966**, *44*, 2447). These data were not reviewed after 1977. As pointed out by Traeger,[29] using a better estimate for the AE of SH^+ (14.300 ± 0.0024 eV; Prest, H. F.; Tzeng, W.-B.; Brom, J. M., Jr.; Ng, C. Y. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *50*, 315) increases $\Delta_f H^\circ_{298}$ to 142 ± 3 kJ mol^{-1}, in perfect agreement with our recommended (computational) value of $141.87^{+0.52}_{-0.46}$ kJ mol^{-1}. [p] Thermochemical database for combustion. The old calculation was based on 1977 JANAF[16] tables.

tion of the electronic structures of H, S, and SH. Because electronic energy calculations based on the correlation-consistent (cc) family of Gaussian basis sets (aug)-cc-p(C)VXZ (with cardinal number $X = 2(D)$, $3(T)$, $4(Q)$, 5, and 6) of Dunning and co-workers[39−42] usually approach the complete basis set limit in a systematic fashion, these basis sets were employed in the focal-point basis set extrapolations of the present study. Nevertheless, several problems with the original correlation-consistent basis sets for S have been observed (see, for example, refs 43 and 44). Convergence problems at the Hartree−Fock level led to the development of a new standard set of cc basis sets, denoted (aug)-cc-pV(X+d)Z,[41,42] which have been employed in this study instead of the original cc basis sets. Since no core-correlated basis sets are available in ref 41, CVXZ basis sets, with $X = 4$, 5, and 6, were constructed[45] as an even-tempered extension, with a factor of 3, of the corresponding completely uncontracted cc-pVX Z sets by adding two tight functions to each shell beyond p. A lack of optimization of the exponents in the CVXZ basis sets leads to convergence problems. Therefore, an unpublished set[46] of polarization-weighted basis sets for S has also been employed, denoted cc-pwCVXZ, with $X = 3$, 4, and 5. Complete basis set limit energies have been estimated through the equations $E^X = E_{\text{limit}} + a\exp(-bX)$[47] and $E^X = E_{\text{limit}} + cX^{-3}$[48] for the HF and correlation energy limits, respectively, employing the best three and two energies available, in order. Reference electronic wave functions have been determined by the single-configuration restricted (open-shell) Hartree−Fock [R(O)HF] method. Dynamical electron correlation was accounted for by the coupled cluster (CC) method including all single and double (CCSD)[49] and triple excitations (CCSDT).[50] The CCSD(T) method,[51,52] which estimates the effect of connected triple excitations through a perturbative term [(T)], was also employed extensively. The full configuration interaction (FCI) computations[21] utilized an ROHF reference wave function. During valence correlation energy computations, the 1s, 2s, and 2p core orbitals of sulfur were excluded from the active space. No virtual orbitals were frozen in any of the calculations. The experimental equilibrium bond distance $r_e/\text{Å} = 1.3409$[53] was adopted for all electronic structure computations in the valence focal-point analysis and during the auxiliary energy calculations. Core-correlation effects were determined by means of all-electron and frozen-core treatments up to CCSDT with (pw)CVXZ ($X = 3$, 4, and 5) and CVXZ ($X = 4$, 5, and 6) basis sets. Scalar relativistic effects[54,55] were gauged by first-order perturbation theory applied to the one-electron mass−velocity and Darwin terms (MVD1). The computation of the diagonal Born−Oppenheimer (DBOC) correction[56,57] was performed at the Hartree−Fock level within the formalism of Handy, Yamaguchi, and Schaefer.[56] Different versions of the program packages ACES II[58] and PSI[59] were used for the electronic structure computations.

The total energies computed as part of this study for $H(^2S)$, $S(^3P)$, and SH ($^2\Pi$) are given in Tables 4S−6S of the Supporting Information.

3. Discussion

Tables 2 and 3 summarize the atomization energy results obtained using the focal-point scheme[19,20] for the valence-only and core−valence treatments, respectively. The symbol δ in

TABLE 2: Valence Focal-Point Analysis of the Dissociation Energy of $^2\Pi$ SH in kJ mol^{-1}[a]

basis	ROHF	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[FCI]	FCI
aug-cc-pV(D+d)Z(9/32)	252.12	+84.47	+3.67	+0.33	+0.18	340.77
cc-pwCVTZ(14/59)	254.76	+95.23	+3.87			
aug-cc-pV(T+d)Z(23/55)	255.82	+97.65	+4.17	+0.09	+0.18[b]	357.91
cc-pwCVQZ(30/109)	256.32	+101.53	+4.23	+0.01		
aug-cc-pV(Q+d)Z(46/89)	256.39	+102.44	+4.30	+0.07	+0.18[b]	363.38
CVQZ(30/134)	256.34	+101.76	+4.25	+0.01		
cc-pwCV5Z(55/181)	256.57	+103.30	+4.37			
aug-cc-pV(5+d)Z(80/136)	256.59	+103.99	+4.47			
CV5Z(55/185)	256.54	+103.31	+4.37			
aug-cc-pV(6+d)Z(127/185)	256.68	+104.19	+4.48			
CV6Z(91/273)	256.65	+104.03	+4.44			
extrapolated[4−6]	256.73	+104.47	+4.49	+0.05	+0.18	365.92

[a] See text for an explanation of column headings and basis sets and for details about the extrapolation to the basis set limit for ROHF, δ[CCSD], and δ[CCSD(T)]. After each basis set, the number of contracted Gaussian basis functions for H/S is given in parentheses. Reference geometry: r(S−H) = 1.3409 Å. [b] Obtained using SHOC factors (see text for details).

TABLE 3: Core−Valence Correlation Corrections (kJ mol^{-1}) to the Total Atomization Energy of $^2\Pi$ SH[a]

basis	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	ΔE_e(CC)
cc-pwCVTZ	+0.615	+0.291	+0.013	+0.919
cc-pwCVQZ	+0.493	+0.304	+0.021	+0.818
cc-pwCV5Z	+0.472	+0.307		
extrapolated[4,5]	+0.450	+0.310	[+0.021]	+0.781
CVQZ	+0.447	+0.298	+0.022	+0.767
CV5Z	+0.559	+0.301		

[a] See text for an explanation of column headings and basis sets and for details about the extrapolation to the basis set limit for ROHF, δ[CCSD], and δ[CCSD(T)]. Reference geometry: r(S−H) = 1.3409 Å.

these Tables denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory, as given by the hierarchy ROHF → CCSD → CCSD(T) → CCSDT → FCI.

In a recent study,[60] a simple multiplicative procedure, termed scaled higher-order correlation or SHOC, was suggested to estimate higher-order correlation (HOC) energies not covered, for example, in CCSD(T) or CCSDT treatments. This procedure utilizes the observation that HOC energy increments show limited basis set dependence and thus even at the complete basis set limit they can be estimated from explicit small basis set FCI and CCSD(T) or CCSDT calculations. From our extensive previous computations, it became clear that the augmented basis sets are more amenable for this correction. The aug-cc-pVXZ CCSDT SHOC scale factors for S(^{3}P) are 1.001508 and 1.001124 for X = 2 and 3, respectively. The aug-cc-pVDZ CCSDT SHOC scale factor for SH($^2\Pi$) is 1.001634. As expected, it is very similar to the corresponding S(^{3}P) SHOC factor. The SHOC factors at the CCSD(T) level are substantially larger; using the aug-cc-pV(D+d)Z basis set, they are 1.005967 and 1.005926 for S(^{3}P) and SH($^2\Pi$), respectively. To make a balanced treatment, the CCSDT SHOC factors of 1.001124 and 1.001250 were employed for the valence-only treatments of S(^{3}P) and SH($^2\Pi$), respectively, where the latter factor was obtained by scaling the former one by 1.001634/1.001508. Using the best CCSD(T) and CCSDT sets of SHOC factors shows agreement within 0.1 kJ mol^{-1} for the atomization energy of $^2\Pi$ SH.

The directly computed valence-only atomization energies provide lower limits to the correct result, as an extension of the basis set as well as the electron correlation treatment increases, as expected, the calculated atomization energies. The valence-only complete basis set ROHF atomization energy is 256.73 ± 0.04 kJ mol^{-1}, obtained after averaging the extrapolated aug-cc-pVXZ and CVXZ, X = 4, 5, and 6 estimates and multiplying their deviation from the average by 2 to attach an error estimate to the recommended value. Estimating δ[CCSD] at the complete basis set limit presents, as usual, some difficulty. Nevertheless, the complete basis set CCSD value obtained from the aug-cc-pVXZ, X = 5 and 6, basis set results differs from the aug-cc-pV(6+d)Z and CV6Z values by only 0.28 and 0.44 kJ mol^{-1}, respectively, which are comfortably small. Our best estimate for δ[CCSD] is $+104.47^{+0.30}_{-0.15}$ kJ mol^{-1}. The extrapolated CCSD(T) increment, obtained the same way, is $+4.49^{+0.05}_{-0.01}$ kJ mol^{-1}. It is impossible to estimate the δ[CCSDT] and δ[FCI] increments accurately from the limited data available. Our best estimate for their combined effect is +0.23 ± 0.10 kJ mol^{-1}. Therefore, the valence-only complete basis set FCI atomization energy of $^2\Pi_{3/2}$ SH (see Table 2) is $365.92^{+0.32}_{-0.19}$ kJ mol^{-1}. As seen in Table 3, the core contribution to the atomization energy of SH($^2\Pi$) is rather small. The best estimate is +0.78 ± 0.15 kJ mol^{-1} at the estimated complete basis set FCI limit, obtained from the extrapolated cc-pwCVXZ, X = 4 and 5 results. It is notable how different the convergence characteristics of the CVXZ and cc-pwCVXZ δ[CCSD] results are. This is most likely due to weaknesses in our design of the CVXZ basis sets.

The scalar relativistic correction to the atomization energy of $^2\Pi$ SH has been computed at the HF and CCSD(T) levels using the pwCVQZ basis set and the MVD1 formalism. The correction is −0.85 kJ mol^{-1}. The correlation contribution included in this value is +0.23 kJ mol^{-1}. The fact that two-electron relativistic energy corrections are usually comparable to the electron correlation contribution to the MVD1 energy correction[55] indicates that relativistic corrections beyond MVD1 should have a small effect even at the level of precision sought in this study. Therefore, we set the scalar relativistic correction to −0.85 ± 0.30 kJ mol^{-1}. SH and S have inverted ground electronic states, $^2\Pi_{3/2}$ and $^3P_2$, respectively. For open-shell states, traditional nonrelativistic electronic structure calculations yield the weighted average of the available multiplets. To obtain the energy of the lowest states of S and SH, the next relativistic energy correction, the spin−orbit effect must be considered. We are employing literature values for these quantities; the experimental weighted-average spin−orbit splitting constants are 2.345 kJ mol^{-1} for the ^{3}P state of sulfur[61,62] and 2.254 kJ mol^{-1} for SH.[63] The spin−orbit correction to the dissociation energy is thus −0.091 ± 0.010 kJ mol^{-1}. Therefore, the total relativistic correction is −0.94 ± 0.30 kJ mol^{-1}, to be added to the computed nonrelativistic atomization energy.

The DBOC corrections, in cm^{-1}, computed at the Hartree−Fock level using a medium-sized TZ2Pf+dif basis set are +59.65, +1243.03, and +1302.90 for H(^{2}S), S(^{3}P), and SH($^2\Pi$), respectively, resulting in an overall DBOC correction to the atomization energy of 0.2 cm^{-1}. Therefore, this correction is negligible for this study. Collecting all of the terms and assuming independent error bars for the different terms, we obtain our best estimate for the equilibrium atomization energy of $^2\Pi_{3/2}$ SH as $365.92^{+0.32}_{-0.19} + 0.78^{+0.15}_{-0.15} - 0.94^{+0.30}_{-0.30} = 365.76^{+0.46}_{-0.39}$ kJ mol^{-1}. The molecular zero-point energy (ZPE) of $^{32}S^1H$ is 16.04 kJ mol^{-1},[53] obtained as $(1/2)\omega_e - (1/4)\omega_e x_e$ with $\omega_e = 2711.6$ cm^{-1} [53] and $\omega_e x_e = 60$ cm^{-1}.[64] The error bar that can be attached to this quantity is perhaps ±0.20 kJ mol^{-1}. This brings the computed zero-point-corrected atomization energy, corresponding to the lowest-energy spin multiplet, to $349.72^{+0.50}_{-0.44}$ kJ mol^{-1}. This value is in agreement with (a) the best experimental values of 350.51 ± 1.20 kJ mol^{-1} [26] and 349.4 ± 2.9 kJ mol^{-1},[65] though it has a considerably lower error bar and (b) the best previous direct theoretical estimate of D_0(S−H) = 349.9 ± 2.0 kJ mol^{-1} [25] based principally on coupled-cluster computations. (Half of the difference between the computed mean D_0 values is due to the use of slightly different ZPE corrections.)

The calculation of the enthalpy of formation from the atomization energy requires a knowledge of the enthalpy of formation of atoms H and S in their respective ground states. The relevant data, when available, were taken from ref 14 and are given, in kJ mol^{-1}, as $\Delta_f H^\circ_{298}[S(^3P)] = 277.17 \pm 0.15$, $\Delta_f H^\circ_{298}[H(^2S)] = 217.998 \pm 0.006$, $H_{298} - H_0[H] = 6.197 \pm 0.001$, $H_{298} - H_0[H_2] = 8.468 \pm 0.001$, $H_{298} - H_0[S_{cr,rhombic}] = 4.412 \pm 0.006$, and $H_{298} - H_0[S_{gas}] = 6.657 \pm 0.001$. The resulting 0 K atomic enthalpies of formation are $\Delta_f H^\circ_0[H(^2S)] = 216.034 \pm 0.006$ kJ mol^{-1} and $\Delta_f H^\circ_0[S(^3P)] = 274.925 \pm 0.150$ kJ mol^{-1}. The $H_{298} - H_0$ value for SH was taken from ref 16 as 9.274 kJ mol^{-1}. On the basis of these experimental values, the final computational value for $\Delta_f H^\circ_0$ of $^2\Pi_{3/2}$ SH is $141.24^{+0.52}_{-0.46}$ kJ mol^{-1}. The best recommended computational value for $\Delta_f H^\circ_{298}$ is $141.87^{+0.52}_{-0.46}$ kJ mol^{-1}. Our mean value is significantly higher than 139.3 ± 3.0 kJ mol^{-1} recommended by JANAF[16] and somewhat lower than 143.0 ± 3.0 kJ mol^{-1} recommended in other databases[13] on the basis of the work of Nicovich et al.[31] Our final recommended values are also significantly different from the $\Delta_f H^\circ_0$(SH) and $\Delta_f H^\circ_{298}$(SH) values recommended in ref 25, 142.9 ± 0.8 kJ mol^{-1} and 143.1 ± 0.8 kJ mol^{-1}, respectively, on the basis of a certain combination of computed and measured energy values.

4. Conclusions

In this paper, we have calculated ab initio the equilibrium and zero-point-energy-corrected dissociation energies of $^2\Pi_{3/2}$ SH with recommended values of $365.76^{+0.46}_{-0.39}$ and $349.72^{+0.50}_{-0.44}$ kJ mol^{-1}, respectively. These results allow us to estimate the standard enthalpy of formation, $\Delta_f H^\circ_T$, of $^2\Pi_{3/2}$ SH. The results obtained, $141.24^{+0.52}_{-0.46}$ and $141.87^{+0.52}_{-0.46}$ kJ mol^{-1} for $\Delta_f H^\circ_0$ and $\Delta_f H^\circ_{298}$, respectively, are somewhat different from the best available experimental results and have smaller error bars. Our final results for the enthalpy of formation of $^2\Pi_{3/2}$ SH shows that we can reliably calculate $\Delta_f H^\circ_T$ for such small species within about 0.5 kJ mol^{-1}.

To get a converged theoretical estimate of the enthalpy of formation of $^2\Pi$ SD, only a few extra data points are necessary over the benchmark-quality results obtained for SH. The difference in the zero-point energies of SH and SD is 4.85 ± 0.20 kJ mol^{-1} based on $\omega_e = 1885.6$ cm^{-1} [53] and $\omega_e x_e = 31$ cm^{-1} [64] for SD. The difference in the spin−orbit splitting constants of SH and SD[18] is only 0.001 kJ mol^{-1}, which is negligible for this study. Since the DBOC correction was found to be negligible for SH, the same can safely be assumed for SD. The enthalpy of formation of D(^{2}S) can be obtained from standard tables: $\Delta_f H^\circ_0[D(^2S)] = 219.81$ kJ mol^{-1}. Therefore, we obtain the result $\Delta_f H^\circ_0[SD(^2\Pi)] = 140.17^{+0.56}_{-0.50}$ kJ mol^{-1}.

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Supporting Information Available: ROHF energies for H(^{2}S), valence-only and all-electron energies for S(^{3}P), and valence-only and all-electron energies for $^2\Pi$ SH. This material is available free of charge via the Internet at http://pubs.acs.org.

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