High-accuracy coupled-cluster computations of bond dissociation energies in SH, H₂S, and H₂O

Lynda R. Peebles and Paul Marshall^{a)}

Department of Chemistry, University of North Texas, Denton, Texas 76203

(Received 5 February 2002; accepted 21 May 2002)

The first and second bond dissociation enthalpies of H₂S have been investigated at up to the CCSD(T)/aug-ccpV6Z level of theory. Corrections for core/valence electron correlation, anharmonic zero point vibrational energy and relativistic effects were followed by extrapolation to the complete basis set limit. Analysis of direct dissociation yields $D_0(\text{S-H})=349.9$ and $D_0(\text{HS-H})=375.8 \text{ kJ mol}^{-1}$. Together these imply an atomization enthalpy for H₂S about 1 kJ mol^{-1} larger than literature evaluations. Consideration of exchange of a second H atom from OH to SH yields $D_0(\text{HS-H})=376.2 \text{ kJ mol}^{-1}$. The two computations of $D_0(\text{HS-H})$ lie within 0.5 kJ mol^{-1} of a recent spectroscopic measurement of $D_0(\text{HS-H})=376.24\pm0.05 \text{ kJ mol}^{-1}$ [R. C. Shiell, X. K. Hu, Q. J. Hu, and J. W. Hepburn, *J. Phys. Chem. A* **104**, 4339 (2000)]. The deuterated analogs SD and D₂S are also considered. There is also accord to within 1.5 kJ mol^{-1} with $D_0(\text{S-H})=348.4\pm0.8 \text{ kJ mol}^{-1}$, which we derive from the experimental literature. We propose revised enthalpies of formation, $\Delta_f H_0(^2\Pi_{3/2}\text{SH})=142.6\pm0.8 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298.15}(\text{SH})=143.1\pm0.8 \text{ kJ mol}^{-1}$. The results suggest the dominant uncertainties in these high-level calculations come from the basis set extrapolation and scalar relativistic terms, and that both contribute about 1 kJ mol^{-1} uncertainty. We also obtain $D_0(\text{H-OH})=492.6 \text{ kJ mol}^{-1}$, which compares well with recent experiments. © 2002 American Institute of Physics. [DOI: 10.1063/1.1493175]

I. INTRODUCTION

The molecules SH and H₂S are the simplest species that contain S–H bonds. High quality thermochemical information about them is therefore crucial to benchmarking recent advances in computational methodology which offer the prospect of high accuracy energy calculations. These two molecules also play important roles in the chemistry of sulfur in flames and in the atmosphere.¹

There have been extensive prior studies, both experimental and computational, of bond dissociation energies D_e (measured from the equilibrium point in the potential energy surface) and D_0 (measured from the ground state at 0 K and which include zero point vibrational energy) for the following processes:

and the isotopic analogs,

Some of these studies are summarized in Tables I and II.^{2–20} It can be seen that the experimental D_0 values are in generally good accord, to within 5 kJ mol^{-1} or better. The 1993 photodissociation measurements carried out via photo-fragment translational spectroscopy gave determinations of

D_0 for reactions (1) and (2) of 350.7 ± 1.2 and $376.8\pm0.5 \text{ kJ mol}^{-1}$, respectively.⁵ Taken together, and with the error limits combined in quadrature, these data imply the 0 K atomization enthalpy of H₂S is $\Delta_{\text{at}}H=727.5\pm1.3 \text{ kJ mol}^{-1}$. This is significantly different from the precise and presumably accurate $\Delta_{\text{at}}H$ values of 724.7 ± 0.5 and $724.4\pm0.8 \text{ kJ mol}^{-1}$ derived from enthalpies in critically evaluated thermochemistry reviews.^{18,19} These reviews are based on evaluations from the 1970s and, as discussed later, the NIST-JANAF Tables contain errors.¹⁹ More recent spectroscopic studies confirmed the previous value of $D_0(\text{S-H})$ (Ref. 6) and determined $D_0(\text{H-SH})$ even more precisely, with values of 376.1 ± 0.2 , 376.24 ± 0.05 , and $\geq 376.0\pm0.2 \text{ kJ mol}^{-1}$.^{6–8} Combination of these later data now yields $\Delta_{\text{at}}H$ for H₂S of $726.7\pm1.2 \text{ kJ mol}^{-1}$, which reduces the discrepancy from the NIST-JANAF evaluation¹⁹ to around 2 kJ mol^{-1} . This is comparable to the uncertainty in $D_0(\text{S-H})$.

It was pointed out that an alternative evaluation of $\Delta_{\text{at}}H$ for H₂S is obtained via the appearance energy for $\text{H}_2\text{S} + h\nu \rightarrow \text{S}^+ + \text{H}_2 + e^-$, and notes that since the ionization potential of S is very well known, $999.58\pm0.01 \text{ kJ mol}^{-1}$,¹⁹ “this single measurement is tantamount to determining the atomization energy, if the thermal internal energy is excluded. Dibeler and Liston²¹ reported two numbers for this threshold, $13.40\pm0.01 \text{ eV}$ for S^+ and $13.36\pm0.01 \text{ eV}$ for the “metastable” S^+ . The study used room temperature H₂S; one expects exponential tailing at threshold due to thermal and statistical fragmentation effects. This is not evident in their S^+ measurement. Prest *et al.*²² used a supersonically cooled

^{a)}Electronic mail: marshall@unt.edu

TABLE I. S–H bond dissociation energies.

Method	$D_0(\text{S–H})^a$	$D_e(\text{S–H})^a$	$D_0(\text{HS–H})^a$	$D_e(\text{HS–H})^a$	$\Delta_{\text{at}}H(\text{H}_2\text{S})^a$
Expt., photodissociation, Ref. 2	357.9±6.8	...	376.5±0.5	...	734.4±6.8
Expt., photodissociation, Ref. 3	349.4±2.9	365.3±2.9	...	...	...
Expt., reaction/equilibration, Ref. 4	...	...	376.2±3.8	...	...
Expt., photodissociation, Ref. 5	350.7±1.2	...	376.8±0.5	...	727.5±1.3
Expt., photodissociation, Ref. 6	350.5±1.2	...	376.1±0.2	...	726.4±1.2
Expt., spectroscopy, (TIPPS), Ref. 7	...	...	376.24±0.05	...	...
Expt., photodissociation, Ref. 8	...	...	≥376.0±0.2	...	...
Calc., MRD CI, Ref. 9	322.3	337.7	...	...	...
Calc., MRD CI, Ref. 10	...	340.6	...	...	...
Calc., G2 theory, Ref. 11	346.6	...	377.4	...	724.1
Calc., Hamiltonian, Ref. 12	...	336.7	...	...	...
Calc., CAS-CI, Ref. 13	...	359.0	...	...	...
Calc., G3 theory, Ref. 14	349.7	...	373.0	...	722.7
Calc., CBS-Q, Ref. 15	350.6	...	380.3	...	731.0
Calc., aV5Z, ^b Ref. 16	...	369.0	...	...	...
Calc., aDTQ, ^c Ref. 16	...	...	...	...	726.8
Calc., aVDTQ, ^c Ref. 17	351.9	...	371.5	...	723.4
Expt., critical evaluation, Ref. 18	351.0±3.5	...	...	...	724.7±0.5
Expt., critical evaluation, Ref. 19	354.3±5.0	...	370.1±4.2	...	724.4±0.5
Ref. 19, corrected in this work	351.9±6.3	...	372.5±6.3	...	...
This work, Eq. (5)	349.1	365.1	375.1	398.5	724.2
This work, Eq. (6)	349.8	365.8	375.9	399.2	725.7
This work, Eq. (7) ^d	349.9	365.8	375.8	399.1	725.7
This work, Eq. (8)	348.4	364.4	374.6	397.9	723.0
This work, Eq. (9)	350.1	366.0	376.1	399.5	726.2
This work, Eq. (10)	...	...	376.2	399.5	...

^aAll units given in kJ mol^{−1}.^bCBS extrapolation through aug-cc-pV5Z including core/valence, scalar relativistic, and spin–orbit corrections.^cCBS extrapolation through aug-cc-pVQZ including core/valence, scalar relativistic, and spin–orbit corrections.^dBest estimate.

beam of H₂S, and reported 13.375±0.022 eV for this threshold. The temperature of H₂S was not specified, but from the tailing threshold of H₂S⁺, it may not have been very cold. Assuming a rotational temperature of 150 K, the observed threshold should be increased by 0.02 eV to arrive at a 0 K value of 13.395 eV, which roughly agrees with Dibeler and Liston.” With an increase of the error limit to reflect the uncertainty in temperature, the derived atomization energy is ≤724.9±2.9 kJ mol^{−1}, in good accord with the values discussed above.

It was also noted that a similar argument can be made to derive $D_0(\text{H–SH})$ from $\text{H}_2\text{S} + h\nu \rightarrow \text{SH}^+ + \text{H} + e^-$, because the ionization potential of SH is well-established as 10.4219±0.0004 eV.²³ The SH⁺ appearance potentials of

14.27±0.02 eV and 14.300±0.024 eV determined by Dibeler and Liston²¹ and Prest *et al.*,²² respectively, can be corrected to 0 K assuming 298 K and 150 K sample temperatures to yield 14.31±0.02 and 14.32±0.03 eV, respectively. These values lead to $D_0(\text{H–SH}) = 375.1 \pm 1.9$ and 376.1 ± 2.9 kJ mol^{−1}, consistent with the more recent spectroscopic values noted above, although less precise.

Here we re-examine the energetics of reactions (1) and (2) by independent, computational techniques. Two working reactions are considered: direct dissociation and H-atom exchange. Coupled cluster [CCSD(T)] theory is applied, which has been shown capable of high accuracy,^{24–26} with the largest basis sets employed to date and with extrapolation to the

TABLE II. S–D bond dissociation energies.

Method	$D_0(\text{S–D})^a$	$D_e(\text{S–D})^a$	$D_0(\text{DS–D})^a$	$D_e(\text{DS–D})^a$	$\Delta_{\text{at}}H(\text{D}_2\text{S})^a$
Expt., photodissociation, Ref. 5	355.5±1.2	...	383.4±0.6	...	738.9±1.3
Expt., critical evaluation, Ref. 19	356.6±5.0	...	378.7±5.0	...	735.3±0.8
Expt., photodissociation, Ref. 20	347.3	...	...	...	...
Expt., photodissociation, Ref. 8	...	...	≥381.3±0.3	...	...
This work, Eq. (5)	353.9	365.1	381.3	398.4	735.2
This work, Eq. (6)	354.5	365.7	382.0	398.9	736.5
This work, Eq. (7) ^b	354.7	365.8	381.9	399.1	736.6
This work, Eq. (8)	353.2	364.4	380.8	397.9	734.0
This work, Eq. (9)	355.1	366.2	382.1	399.3	737.2

^aAll units given in kJ mol^{−1}.^bBest estimate.

TABLE III. Equations used for extrapolation to the complete basis set limit.

Equation ^a	Number	RMS 1, ^b kJ mol ⁻¹	RMS 2, ^c kJ mol ⁻¹
$E(x) = E_{\text{CBS}} + b \exp(-cx)$	(5)	0.06	0.10
$E(x) = E_{\text{CBS}} + b \exp(-(x-1))$ $+ c \exp(-(x-1)^2)$	(6)	0.5	0.6
$E(x) = E_{\text{CBS}} + b/(x+0.5)^4$ $+ c/(x+0.5)^6$	(7)	0.05	0.07
$E(x) = E_{\text{CBS}} + b/(x+0.5)^4$	(8)	3.6	5.2
$E(x) = E_{\text{CBS}} + b/(x+0.1)^4$ $+ c/(x+1)^5$	(9)	0.15	0.08

^a x is an index associated with each basis set, $x=2$ (DZ), 3 (TZ), 4 (QZ), etc.^bRoot mean square deviation of fit to data for $D_e(\text{S-H})$.^cRoot mean square deviation of fit to data for $D_e(\text{HS-H})$.

complete basis set (CBS) limit. The results are compared to the available data for the S/H system, and the related S/D system. The S/D measurements are independent of the S/H results but of course the underlying potential energy surfaces are identical. An important goal of this comparison is assessment of likely uncertainties in S-H bond strengths obtained by high-level methods. Although not the main focus of this work, the *ab initio* data also permit assessment of the H-OH bond strength, whose tabulated values^{18,19} have recently been criticized.²⁷

II. METHODOLOGY

CCSD(T) energies were calculated using the GAUSSIAN 98 (Ref. 28) and MOLPRO 2000 (Ref. 29) programs, with correlation consistent basis sets from aug-cc-pVDZ through aug-cc-pV6Z.³⁰⁻³² Spin-restricted RCCSD(T)/RHF theory was applied to H_2S and spin-unrestricted UCCSD(T)/UHF theory to the open-shell species S and SH. The bond length of the SH molecule was optimized with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Then, single point energy calculations were performed with the aug-cc-pVQZ basis set and the minimum energy was interpolated from a graph of the bond length vs the energy. The same process was performed with the aug-cc-pV5Z and aug-cc-pV6Z basis sets. The geometry of H_2S was optimized with five basis sets, aug-cc-pVDZ through aug-cc-pV6Z.

Core electrons were excluded from the correlation treatments in all of these calculations. To correct for this, pairs of calculations were done for S, SH, and H_2S at the CCSD(T)/aug-cc-pVQZ geometry with the cc-pwCV5Z basis set of Peterson.³³ One calculation included core electrons, while the other excluded them. All computations for these core/valence corrections were made using MOLPRO (Ref. 29) at the UCCSD(T)/RHF level of calculation.

To minimize errors arising from basis set truncation in the CCSD(T) calculations we extrapolated our results to the infinite basis set limit. Several functions used to calculate such CBS limits have been summarized by Feller and Peterson.²⁴ In this study, five of these extrapolation functions were used to approach a CBS limit systematically for the dissociation energies, and they are listed in Table III. The first function used, Eq. (5), is a simple exponential function, and the second function, Eq. (6), is based on a combined

TABLE IV. Computed and experimental geometries for SH and H_2S .

Calculation	S-H bond length(Å)	HS-H bond length(Å)	H-S-H bond angle(deg)
CCSD(T)/aug-cc-pVDZ	1.361	1.356	92.5
CCSD(T)/aug-cc-pVTZ	1.346	1.342	92.3
CCSD(T)/aug-cc-pVQZ	1.344	1.340	92.3
CCSD(T)/aug-cc-pV5Z	1.342	1.338	92.4
CCSD(T)/aug-cc-pV6Z	1.342	1.338	92.4
Experiment ^a	1.345	1.328	92.2

^aEquilibrium geometries (r_e , θ_e) from Refs. 19 and 41.

Gaussian/exponential function. This method was used by Peterson *et al.*^{34,35} to extrapolate the dissociation energy of second row diatomic molecules. The third function, Eq. (7), and a simpler two-parameter expression, Eq. (8), were used by Martin³⁶ to calculate the atomization energy of HCN and by Martin and Lee³⁷ in their study of NH_3 . Wilson and Dunning³⁸ showed that a similar expression, Eq. (9), improved estimates of the CBS limit for the MP2 correlation energy.

An alternative analysis is based on consideration of the congeneric³⁹ reaction

where *ab initio* errors may be expected to cancel in part. The 0 K reaction enthalpy is equal to the difference between $D_0(\text{H-SH})$ and $D_0(\text{H-OH})$, and because the latter quantity is known accurately, 492.28 ± 0.06 kJ mol⁻¹,⁴⁰ the former bond strength may be obtained.

III. RESULTS AND DISCUSSION

A. Geometries and energies

The computed geometries obtained for SH and H_2S are summarized in Table IV. The equilibrium bond length in SH, r_e , at the 6Z level and the experimental value¹⁹ are 1.342 and 1.345 Å, respectively. The H_2S geometries (r_e , bond angle) for 6Z theory and experiment are (1.338 Å, 92.4°), and (1.328 Å, 92.2°),⁴¹ respectively. We can see a close accord (0.003 Å) between computed and experimental bond lengths for SH. For the H_2S geometry, the correlation is not as close, with errors of about 0.01 Å and 0.2°. This is typical for CCSD(T) theory in which the mean absolute deviations for the G2 test set of molecules obtained with the aug-cc-pVQZ basis set are 0.009 Å (for bond lengths to hydrogen) and 0.4° (for angles between bonds to hydrogen).²⁴ The small geometry errors reflect factors other than basis set truncation such as the core/valence correlation contribution. Table IV also reveals that the extra computational expense of obtaining 5Z and 6Z geometries would not usually be necessary.

Ab initio energies and their contributions to the bond strengths are shown in Table V. These energies include relativistic corrections, a correction for neglect of core/valence electron correlation, and a zero point energy vibrational correction for the D_0 values. Then the five basis set extrapolations, Eqs. (5)–(9), were performed and the results are shown in Tables I and II. Root mean square deviations of the

TABLE V. *Ab initio* energies for H₂S and its fragments.

Calculation	H (hartrees)	S (hartrees)	SH (hartrees)	H ₂ S (hartrees)	ΔE_1^a (kJ mol ⁻¹)	ΔE_2^b (kJ mol ⁻¹)
CCSD(T)/aug-cc-pVDZ	-0.499 33	-397.610 56	-398.238 01	-398.880 85	336.4	376.8
CCSD(T)/aug-cc-pVTZ	-0.499 82	-397.656 14	-398.291 34	-398.940 83	355.4	393.0
CCSD(T)/aug-cc-pVQZ	-0.499 95	-397.667 98	-398.305 72	-398.957 31	361.8	398.1
CCSD(T)/aug-cc-pV5Z	-0.500 00	-397.671 88	-398.310 66	-398.963 19	364.4	400.5
CCSD(T)/aug-cc-pV6Z	-0.500 00	-397.673 52	-398.312 57	-398.965 32	365.1	401.0
CCSD(T)/cc-pwCV5Z	-0.500 00	-397.672 13	-398.310 88	-398.963 47	364.3	400.6
CCSD(T) =FULL/cc-pwCV5Z ^c	-0.500 00	-398.077 22	-398.716 24	-399.368 99	365.0	401.0
Scalar relativistic correction ^d	...	...	...	...	-1.1	-1.0
Spin-orbit correction ^e	0	-0.000 89	-0.000 86	0	-0.1	-2.3
Zero point energy ^f	0	0	0.006 07	0.014 98	-15.9	-23.4

^a ΔE_1 is the difference between products and reactants for SH→S+H.^b ΔE_2 is the difference between products and reactants for H₂S→SH+H.^cAll electrons included in correlation treatment.^dReference 44.^eReferences 19 and 23.^fReference 46.

fits through the data points are given in Table III. While all the CBS limits are similar, we found that Eq. (7) consistently gave the best fit through our data points (see Table III). The fit through points obtained with the DZ through 6Z levels given by Eq. (5), the simple exponential extrapolation, and Eq. (9) were also very good. The combined Gaussian/exponential fit, Eq. (6), and the simpler two-parameter fit, Eq. (8), were not as accurate. Throughout this discussion the calculated value from this study that will be referred to is the extrapolation from Eq. (7), which is shown in Fig. 1. The average difference between the CBS limits obtained from Eq. (5) and (7) is 0.7 kJ mol⁻¹, and the average difference for Eqs. (7) and (9) is 0.2 kJ mol⁻¹. Therefore, we estimate the uncertainty in the empirical extrapolation to be up to around 1 kJ mol⁻¹. We note that the energies here are close to con-

vergence; the difference between the energies from the largest basis set and the infinite limit are 1 kJ mol⁻¹ for both dissociation reactions (see Fig. 1).

Table V shows that, with the cc-pwCV5Z basis set, inclusion of all electrons in the coupled cluster treatment lowers the absolute energies of the sulfur species by about 0.4 hartrees. However, core electron correlation mostly cancels for the dissociation energies: it raises $D_0(\text{S-H})$ and $D_0(\text{HS-H})$ by only 0.7 and 0.4 kJ mol⁻¹, respectively.

Relativistic effects on the atomization energies of molecules can be important for species that contain second-row atoms.⁴² The relativistic contributions can be approximately divided into a scalar term (which depends on the speed of the electrons) and a vector term (which depends on spin and orbital angular momentum).⁴³ The latter term can be derived from experimental spin-orbit splittings. Scalar relativistic terms from Kedziora *et al.*⁴⁴ are the most recently published and were employed in the present work (see Table V). Purely spin-orbit corrections derived from the measured S (³P_J) and SH (²Π_J) electronic energy levels,^{19,23} are given in Table V as well. We also examined three other sets of relativistic corrections. One, given by Martin *et al.*,⁴³ would increase our SH dissociation energy by approximately 0.3 kJ mol⁻¹, increase the HS-H dissociation energy by roughly 0.1 kJ mol⁻¹, and overall increase the atomization energy of H₂S by about 0.4 kJ mol⁻¹. Use of the results of Pisani and Clementi⁴⁵ as quoted by Kedziora *et al.*,⁴² which include a spin-orbit correction within them, would increase the S-H bond strength by 0.9 kJ mol⁻¹ and would decrease the HS-H bond strength by the same amount. Use of a scalar relativistic correction given by Feller and Dixon¹⁷ would have increased our atomization energy of H₂S by 0.8 kJ mol⁻¹. There is therefore an uncertainty of up to ±1 kJ mol⁻¹ in the magnitude of the scalar relativistic correction obtained with current methods.

We obtained the H₂S zero point energy correction [$E(0,0,0)=39.3$ kJ mol⁻¹] from the data reported by Allen⁴¹ as reanalyzed by Miller *et al.*⁴⁶ Similarly, we obtained the

FIG. 1. Points and solid lines: Calculated D_0 values from CCSD(T)/aug-cc-pV n Z theory, which include zero point energy, core-valence and relativistic contributions. Dashed lines: complete basis set limits obtained by fitting to Eq. (7) (see text).

TABLE VI. Computed and experimental geometries for OH and H₂O.

Calculation	O–H bond length (Å)	HO–H bond length (Å)	H–O–H bond angle (deg)
CCSD(T)/aug-cc-pVDZ	0.980	0.966	103.9
CCSD(T)/aug-cc-pVTZ	0.973	0.962	104.2
CCSD(T)/aug-cc-pVQZ	0.971	0.959	104.4
CCSD(T)/aug-cc-pV5Z	0.970	0.958	104.4
CCSD(T)/aug-cc-pV6Z	0.970	0.958	104.5
Experiment ^a	0.971	0.958	104.5

^aEquilibrium geometries (r_e , θ_e) from Refs. 19 and 48.

D₂S zero point energy correction [$E(0,0,0)$ = 28.3 kJ mol⁻¹] from the study by Miller *et al.*⁴⁶ These corrections allow for anharmonicity in the vibrational modes. The SH and SD anharmonic zero point energy correction values were calculated from literature data.^{19,20}

An alternative calculation of $D_0(\text{H–SH})$ is based on the exchange reaction (10). Geometry information for OH and H₂O, at up to the CCSD(T)/aug-cc-pV5Z level of theory, is summarized in Table VI, and Table VII shows the energy change ΔE for the H-atom exchange reaction between OH and SH. It may be seen that ΔE converges much more rapidly than for the bond breaking reactions (1) and (2), and all energy changes from DZ through 6Z agree to within 1.7 kJ mol⁻¹. Our best estimate is the mean of results from the 5Z and 6Z basis sets, which appear to have converged. The same kinds of correction to reflect effects of core electron correlation, scalar relativistic terms, spin–orbit terms and zero-point vibrational energy, as discussed above, were made to obtain ΔH_0 , and hence $D_0(\text{H–SH})$.

B. Atomization Enthalpy of H₂S and D₂S

We computed $\Delta_{\text{at}}H(\text{H}_2\text{S})$ as the sum of our dissociation energies, D_0 (Table I), and obtained a value of 725.7 kJ mol⁻¹. This is approximately 1 kJ mol⁻¹ higher than the values from both NIST-JANAF Thermochemical Tables¹⁹ and the thermochemical tables of Gurvich *et al.*¹⁸ The difference of 1 kJ mol⁻¹ between our computed $\Delta_{\text{at}}H$ and the ther-

mochemical tabulations^{18,19} is comparable to the uncertainty in the empirical CBS extrapolations and the relativistic corrections, which as noted above we estimate could each contribute around 1 kJ mol⁻¹ of error. This error is small, and probably represents the smallest error that can be reasonably expected with current theoretical approaches. Our $\Delta_{\text{at}}H$ value is 1.6 kJ mol⁻¹ higher than the result calculated by means of G2 theory, and is 3.0 kJ mol⁻¹ higher than the G3 result.^{11,14} Our value is 2.3 kJ mol⁻¹ above that of Feller and Dixon, $\Delta_{\text{at}}H = 723.4$ kJ mol⁻¹, who extrapolated the double, triple, and quadruple zeta energies to the CBS limit.¹⁷ The atomization enthalpy obtained as the sum of the bond strength measurements of Morley *et al.*⁵ is 1.8 kJ mol⁻¹ greater than our result, and the sum of the most precise bond strengths $\Delta_{\text{at}}H = 726.7$ kJ mol⁻¹ discussed in the Introduction is 1.0 kJ mol⁻¹ above our value. Similarly, we derive $\Delta_{\text{at}}H(\text{D}_2\text{S}) = 736.6$ kJ mol⁻¹ from the ground state, which is about 2.3 kJ mol⁻¹ lower than the value derived from measurements by Morley *et al.*⁵ and 1.3 kJ mol⁻¹ above the NIST-JANAF value,¹⁹ 735.3 ± 0.8 kJ mol⁻¹.

C. The S–H and S–D bond strengths

The ground state dissociation energy of SH has been studied extensively, and some of the literature data are displayed in Table I. Our directly computed value for $D_0(\text{S–H})$ is 349.9 kJ mol⁻¹, with a likely uncertainty of up to 2 kJ mol⁻¹. This value agrees, within the error limits, with the experimental value given by Continetti,³ the value calculated from the thermochemical tables of Gurvich *et al.*,¹⁸ the measurement by Morley *et al.*,⁵ and the value derived from the NIST-JANAF Tables.¹⁹ The corrected JANAF value (see below) agrees even more closely. Earlier theoretical approaches tended to underestimate the bond dissociation enthalpies.^{9,10,12,13} More recent calculations yielded data which are very close to experimental values. The energy calculated by means of G2 theory is just outside the lower limits of the energy derived from Gurvich *et al.*¹⁸ and the NIST-JANAF Tables,¹⁹ while the G3 value is close to our result and that of Morley *et al.*⁵ (see Table I). The G3 methodology

TABLE VII. *Ab initio* energies for OH and H₂O.

Calculation	OH (hartrees)	H ₂ O (hartrees)	ΔE_3^a (kJ mol ⁻¹)	ΔE_4^b (kJ mol ⁻¹)	$D_0(\text{H–SH})$ (kJ mol ⁻¹)	$D_0(\text{H–OH})$ (kJ mol ⁻¹)
CCSD(T)/aug-cc-pVDZ	-75.584 08	-76.273 90	-123.4	500.1	376.6	466.6
CCSD(T)/aug-cc-pVTZ	-75.645 59	-76.342 33	-124.0	517.0	375.9	483.5
CCSD(T)/aug-cc-pVQZ	-75.664 50	-76.363 59	-124.7	522.9	375.3	489.3
CCSD(T)/aug-cc-pV5Z	-75.670 62	-76.370 30	-123.8	524.3	376.2	490.7
CCSD(T)/aug-cc-pV6Z	-75.672 68	-76.372 56	-123.7	524.8	376.2	491.3
CCSD(T)/cc-pwCV5Z	-75.669 19	-76.368 63	-123.0	523.6		
CCSD(T)=FULL/cc-pwCV5Z ^c	-75.729 99	-76.429 78	-123.5	524.6		
Scalar relativistic correction ^d	...	...	-0.3	-0.7		
Spin–orbit correction ^e	-0.000 32	0	-1.4	0.8		
Zero point energy ^f	0.008 41	0.021 10	9.9	-33.3		

^a ΔE_3 is the difference between products and reactants for $\text{OH} + \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} + \text{SH}$.

^b ΔE_4 is the difference between products and reactants for $\text{H}_2\text{O} + \rightarrow \text{OH} + \text{H}$.

^cAll electrons included in correlation treatment.

^dReference 44.

^eReferences 19 and 23.

^fReference 46.

includes a core-valence correction and an atomic spin-orbit correction. If we were to use a more balanced treatment of spin-orbit coupling, that is, with a correction for SH as well as S, the calculated energy would become 352.0 kJ mol⁻¹ which lies 2.1 kJ mol⁻¹ above our estimate. Maung¹⁵ reported a theoretical value for the ground state dissociation energy derived via CBS-Q theory, an alternative complete basis set methodology, <1 kJ mol⁻¹ above our value. He made no correction for spin-orbit coupling or other relativistic effects, which fortuitously cancel for this molecule (see Table II). Feller and Peterson's D_e value¹⁶ appears to be about 3–4 kJ mol⁻¹ too high, relative to the present calculation, and the later Feller and Dixon value¹⁷ is about 2 kJ mol⁻¹ above ours.

We also calculated the dissociation energy for S–D. These values are listed in Table II. Our value of $D_0(\text{S–D}) = 354.7$ kJ mol⁻¹ falls between experimental values; it is within the ranges recommended by Morley *et al.*⁵ and Chase,¹⁹ but lies above the value quoted by Huber and Herzberg.²⁰

D. The H–SH and D–SD bond strengths

The value from this study for $D_0(\text{HS–H})$ derived via the direct dissociation reaction (2) is 375.8 kJ mol⁻¹. Consideration of the congeneric exchange reaction (10) leads to 376.2 kJ mol⁻¹. These values are only 0.4 kJ mol⁻¹ apart, in line with the likely uncertainties in basis set extrapolation and the relativistic corrections, and they lie within 0.5 kJ mol⁻¹ of the most precise measurements recently reported by Shiell *et al.*,⁷ who obtained $D_0 = 376.24 \pm 0.05$ kJ mol⁻¹. We note that analysis of the exchange reaction (10) yields consistent and accurate results even with the smallest (double zeta) basis sets considered here, and therefore is computationally far more efficient.

Our direct dissociation value is 6 kJ mol⁻¹ above the value from the NIST-JANAF Thermochemical Tables,¹⁹ and 0.6 kJ mol⁻¹ outside the error limits. It seems likely that the NIST-JANAF value is too low, because four measurements based on photoionization,⁴⁷ photodissociation,^{2,5} and reaction and equilibration with atomic Br⁴ give D_0 around 6–9 kJ mol⁻¹ greater than the NIST-JANAF Tables. In fact the tabulated values¹⁹ for SH are in error. The discussion in the NIST-JANAF tables is based on $D_0(\text{H–SH}) = 372.5 \pm 6.3$ kJ mol⁻¹ obtained via appearance potentials (as outlined in the Introduction) by Dibeler and Liston.²¹ Erroneous thermal corrections for SH, discussed below, and an apparently unjustified reduction in the error limits, yield a different D_0 from the *tabulated* data. We show the corrected value as well in Table I. This corrected value now agrees with our result to within the error limits. Theoretical calculations have given similar bond dissociation energies: G2 and G3 theories yield 377.4 and 373.0 kJ mol⁻¹, respectively,^{11,14} while Maung¹⁵ reported a larger dissociation energy of 380.3 kJ mol⁻¹, which appears to be too high (partly this reflects neglect of relativistic effects).

Based on reaction (4), our calculated $D_0(\text{DS–D})$ is 381.9 kJ mol⁻¹ which is 1.5 kJ mol⁻¹ below the result $D_0 = 383.4 \pm 0.6$ kJ mol⁻¹ obtained by Morley *et al.*,⁵ and falls within the range derived from the NIST-JANAF Tables.¹⁹

E. Experimental thermochemistry and bond strength of SH

We now comment on the thermochemistry of the SH radical. Because literature values for $D_0(\text{S–H})$ are not in complete accord with the atomization enthalpy of H₂S, as discussed in Sec. I, we combine the very precisely measured $D_0(\text{HS–H})$ (Ref. 7) with $\Delta_f H_0$ for atomic H and H₂S (Ref. 19) and derive $\Delta_f H_0(^2\Pi_{3/2} \text{SH}) = 142.6 \pm 0.8$ kJ mol⁻¹. The dominant source of uncertainty is the thermochemistry of H₂S, and had we employed $\Delta_f H_0$ from Gurvich *et al.*¹⁸ we would have obtained $\Delta_f H_0(\text{SH}) = 142.5 \pm 0.5$ kJ mol⁻¹. We select the larger uncertainty and note that this enthalpy of formation is more positive and more precise than previous evaluations: it is in accord with the selection of Gurvich *et al.*¹⁸ of 140.0 ± 3.5 kJ mol⁻¹.

The temperature dependence of $\Delta_f H(\text{SH})$ is not entirely clear. According to NIST-JANAF tabulations¹⁹ this quantity increases by 2.84 kJ mol⁻¹ from 0 to 298.15 K, but by only 0.45 kJ mol⁻¹ according to Gurvich *et al.*¹⁸ Both tabulations list the same $H_{298.15} - H_0$ values for hydrogen and sulfur in reference states, 8.47 and 4.41 kJ mol⁻¹, and only slightly different thermal corrections for SH(g) of 9.27 and 9.10 kJ mol⁻¹, respectively.^{18,19} As noted in the NIST-JANAF text, the tables do not allow for spin-orbit splitting in SH, and when this correction is made, the Gurvich *et al.* $H_{298} - H_0$ value is confirmed. This does not account for the tabulated 0 K value of $\Delta_f H(\text{SH})$ in the NIST-JANAF Tables,¹⁹ which is in error. The literature value¹⁸ of $H_{298.15} - H_0(\text{SH})$ implies $\Delta_f H_{298.15}(\text{SH}) = \Delta_f H_0(\text{SH}) + 0.45$ kJ mol⁻¹, and we use this to recommend $\Delta_f H_{298.15}(\text{SH}) = 143.1 \pm 0.8$ kJ mol⁻¹.

Combination of $\Delta_f H_0(^2\Pi_{3/2} \text{SH}) = 142.6 \pm 0.8$ kJ mol⁻¹ with data¹⁸ for atomic H and S yields $D_0(\text{S–H}) = 348.4 \pm 0.8$ kJ mol⁻¹. This value is 1.5 kJ mol⁻¹ below our calculation (Table II) and 2.3 kJ mol⁻¹ below $D_0 = 350.7 \pm 1.2$ kJ mol⁻¹ determined by Morley *et al.*⁵ A possible resolution of these discrepancies, aside from increasing the uncertainty limits, is that the enthalpy of formation of atomic S (277.18 ± 0.15 kJ mol⁻¹ at 298 K),¹⁸ which rests largely on $\Delta_f H(\text{S}_2)$ and $D_0(\text{S–S})$, might be in error by around –1 kJ mol⁻¹.

F. The H–OH bond strength

$D_0(\text{H–OH})$, and the associated heat of formation of hydroxyl radical, have been the focus of recent attention. Appearance potential measurements by Ruscic *et al.*²⁷ confirm a bond strength significantly different from that listed in standard tables, of 494.0 ± 0.2 (Ref. 18) and 493.3 ± 1.2 (Ref. 19) kJ mol⁻¹. These new results were supported by coupled-cluster calculations with basis sets up to sextuple zeta. Our own data at similar levels of theory in Table VII lead to $D_0(\text{H–OH}) = 492.6$ kJ mol⁻¹. This value lies very close to the lower experimental assignment by Ruscic *et al.*²⁷ of 491.9 ± 0.4 kJ mol⁻¹, and the spectroscopic determination of 492.28 ± 0.06 kJ mol⁻¹ by Harich *et al.*⁴⁰

IV. CONCLUSIONS

Coupled cluster theory with very large basis sets, up to sextuple zeta quality, has been applied to the first and second

bond dissociation enthalpies of H_2S . Core-valence correlation effects had little impact although relativistic factors were more important, and are accounted for only partially by spin-orbit coupling. Analysis of S-H dissociation yields a best estimate of $D_0(\text{S-H})$ in good accord with a variety of experimental measurements. Two approaches were applied to the H-SH bond strength. The first was to consider the dissociation reaction, and the second to consider H-atom exchange between SH and OH. The results were consistent and within 0.5 kJ mol^{-1} of extremely precise spectroscopic measurements by Shiell *et al.*⁷ Uncertainties in basis set extrapolation and scalar relativistic terms each contribute around 1 kJ mol^{-1} of uncertainty. Based on these recent experiments, we recommend thermochemistry for the SH radical which is more positive than in previous evaluations: $\Delta_f H_0(^2\Pi_{3/2} \text{SH}) = 142.6 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298.15}(\text{SH}) = 143.1 \pm 0.8 \text{ kJ mol}^{-1}$. These values depend on the accuracy of $\Delta_f H(\text{H}_2\text{S})$, and imply $D_0(\text{S-H}) = 348.4 \pm 0.8 \text{ kJ mol}^{-1}$, 1.5 kJ mol^{-1} below our calculation. Our data for the H-OH bond strength support a recent revision²⁷ which implies that the enthalpy of formation of OH is more negative than listed in standard tables.¹⁹

ACKNOWLEDGMENTS

We are grateful to Professor Kirk Peterson for provision of the pw-CVxZ basis sets, to Professors Mark Ashfold and Angela Wilson for helpful discussions. Financial support was provided by the National Science Foundation (Grant No. CTS-0113606), the R. A. Welch Foundation (Grant No. B-1174), and the UNT Faculty Research Fund. The calculations were performed on the National Center for Supercomputing Applications SGI/Cray Origin 2000 under Grant No. CHE000015N.

¹A. J. Hynes and P. H. Wines, in *Gas-Phase Combustion Chemistry*, edited by W. C. Gardiner, Jr. (Springer-Verlag, New York, 2000), Chap. 3.

²L. Schneider, W. Meier, K. H. Welge, M. N. R. Ashfold, and C. M. Western, *J. Chem. Phys.* **92**, 7027 (1990).

³R. E. Continetti, B. A. Balko, and Y. T. Lee, *Chem. Phys. Lett.* **182**, 400 (1991).

⁴J. M. Nicovich, K. D. Kreutter, C. A. v. Dijk, and P. H. Wine, *J. Phys. Chem.* **96**, 2518 (1992).

⁵G. P. Morley, I. R. Lambert, D. H. Mordaunt, S. H. S. Wilson, M. N. R. Ashfold, R. N. Dixon, and C. M. Western, *J. Chem. Soc., Faraday Trans.* **89**, 3865 (1993).

⁶S. H. S. Wilson, J. D. Howe, and M. N. R. Ashfold, *Mol. Phys.* **88**, 841 (1996).

⁷R. C. Shiell, X. K. Hu, Q. J. Hu, and J. W. Hepburn, *J. Phys. Chem. A* **104**, 4339 (2000).

⁸P. A. Cook, S. R. Langford, R. N. Dixon, and M. N. R. Ashfold, *J. Chem. Phys.* **114**, 1672 (2001).

⁹D. M. Hirst and M. F. Guest, *Mol. Phys.* **46**, 427 (1982).

¹⁰P. J. Bruna and G. Hirsch, *Mol. Phys.* **61**, 1359 (1987).

¹¹L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).

¹²J. K. Park and H. S. Sun, *Chem. Phys. Lett.* **194**, 485 (1992).

¹³D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **99**, 1914 (1993).

¹⁴L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).

¹⁵N. Maung, *J. Mol. Struct.* **460**, 159 (1999).

¹⁶D. Feller and K. A. Peterson, *J. Chem. Phys.* **110**, 8384 (1999).

¹⁷D. Feller and D. A. Dixon, *J. Chem. Phys.* **115**, 3484 (2001).

¹⁸*Thermodynamic Properties of Individual Substances*, edited by L. V. Gurvich, I. V. Veyts, and C. B. Alcock (Hemisphere, New York, 1989), Vol. 1.

¹⁹*NIST-JANAF Thermochemical Tables*, edited by M. W. Chase, Jr. (American Chemical Society and the American Institute of Physics, Woodbury, 1998).

²⁰K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

²¹V. H. Dibeler and S. K. Liston, *J. Chem. Phys.* **49**, 482 (1968).

²²H. F. Prest, W.-B. Tzeng, J. J. M. Brom, and C. Y. Ng, *Int. J. Mass Spectrom. Ion Phys.* **50**, 315 (1983).

²³C.-W. Hsu, D. P. Baldwin, C. L. Liao, and C. Y. Ng, *J. Chem. Phys.* **100**, 8047 (1994).

²⁴D. Feller and K. A. Peterson, *J. Chem. Phys.* **108**, 154 (1998).

²⁵K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **106**, 4119 (1997).

²⁶K. L. Bak, P. Jorgensen, J. Olsen, T. Helgaker, and W. Klopper, *J. Chem. Phys.* **112**, 9229 (2000).

²⁷B. Ruscic, D. Feller, D. A. Dixon, K. A. Peterson, L. B. Harding, R. L. Asher, and A. F. Wagner, *J. Phys. Chem. A* **105**, 1 (2001).

²⁸M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9 Gaussian, Inc., Pittsburgh, PA, 1998.

²⁹H.-J. Werner, P. J. Knowles, R. D. Amos *et al.*, MOLPRO Quantum Chemistry Package 2000.1, 2000.

³⁰T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).

³¹D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).

³²T. van Mourik and T. H. Dunning, Jr., *Int. J. Quantum Chem.* **76**, 205 (2000).

³³K. A. Peterson, cc-pwCVxZ basis sets (personal communication, 2000).

³⁴D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **101**, 8877 (1994).

³⁵K. A. Peterson, D. E. Woon, and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 7410 (1994).

³⁶J. M. L. Martin, *Chem. Phys. Lett.* **259**, 679 (1996).

³⁷J. M. L. Martin and T. J. Lee, *Chem. Phys. Lett.* **258**, 136 (1996).

³⁸A. K. Wilson and T. H. Dunning, Jr., *J. Chem. Phys.* **106**, 8718 (1997).

³⁹P. Hassanzadeh and K. K. Irikura, *J. Phys. Chem. A* **101**, 1580 (1997).

⁴⁰S. A. Harich, D. W. H. Hwang, X. Yang, J. J. Lin, X. Yang, and R. N. Dixon, *J. Chem. Phys.* **113**, 10073 (2000).

⁴¹H. C. Allen, Jr. and E. K. Plyler, *J. Chem. Phys.* **25**, 1132 (1956).

⁴²G. S. Kedziora, J. A. Pople, V. A. Rassolov, M. A. Ratner, P. C. Redfern, and L. A. Curtiss, *J. Chem. Phys.* **110**, 7123 (1999).

⁴³J. M. L. Martin, A. Sundermann, P. L. Fast, and D. G. Truhlar, *J. Chem. Phys.* **113**, 1348 (2000).

⁴⁴G. S. Kedziora, J. A. Pople, M. A. Ratner, P. C. Redfern, and L. A. Curtiss, *J. Chem. Phys.* **115**, 718 (2001).

⁴⁵L. Pisani and E. Clementi, *J. Chem. Phys.* **101**, 3079 (1994).

⁴⁶R. E. Miller, G. E. Leroy, and D. F. Eggers, Jr., *J. Chem. Phys.* **46**, 2292 (1967).

⁴⁷S. T. Gibson, J. P. Greene, and J. Berkowitz, *J. Chem. Phys.* **85**, 4815 (1986).

⁴⁸B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).