

# Structure and binding energy of the H<sub>2</sub>S dimer at the CCSD(T) complete basis set limit

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This study presents results for the binding energy and geometry of the H<sub>2</sub>S dimer which have been computed using Møller-Plesset perturbation theory (MP2, MP4) and coupled cluster (CCSD, CCSD(T)) calculations with basis sets up to aug-cc-pV5Z. Estimates of  $D_e$ ,  $E_{ZPE}$ ,  $D_o$ , and dimer geometry have been obtained at each level of theory by taking advantage of the systematic convergence behavior toward the complete basis set (CBS) limit. The CBS limit binding energy values of  $D_e$  are 1.91 (MP2), 1.75 (MP4), 1.41 (CCSD), and 1.69 kcal/mol (CCSD(T)). The most accurate values for the equilibrium S-S distance  $r_{SS}$  (without counterpoise correction) are 4.080 (MP2/aug-cc-pV5Z), 4.131 (MP4/aug-cc-pVQZ), 4.225 (CCSD/aug-cc-pVQZ), and 4.146 Å (CCSD(T)/aug-cc-pVQZ). This study also evaluates the effect of counterpoise correction on the H<sub>2</sub>S dimer geometry and binding energy. As regards the structure of (H<sub>2</sub>S)<sub>2</sub>, MP $n$ , CCSD, and CCSD(T) level values of  $r_{SS}$ , obtained by performing geometry optimizations on the counterpoise-corrected potential energy surface, converge systematically to CBS limit values of 4.099 (MP2), 4.146 (MP4), 4.233 (CCSD), and 4.167 Å (CCSD(T)). The corresponding CBS limit values of the equilibrium binding energy  $D_e$  are 1.88 (MP2), 1.76 (MP4), 1.41 (CCSD), and 1.69 kcal/mol (CCSD(T)), the latter in excellent agreement with the measured binding energy value of  $1.68 \pm 0.02$  kcal/mol reported by Ciaffoni *et al.* [Appl. Phys. B **92**, 627 (2008)]. Combining CBS electronic binding energies  $D_e$  with  $E_{ZPE}$  predicted by CCSD(T) vibrational second-order perturbation theory calculations yields  $D_o = 1.08$  kcal/mol, which is around 0.6 kcal/mol smaller than the measured value of  $1.7 \pm 0.3$  kcal/mol. Overall, the results presented here demonstrate that the application of high level calculations, in particular CCSD(T), in combination with augmented correlation consistent basis sets provides valuable insight into the structure and energetics of the hydrogen sulfide dimer. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4985094>]

## I. INTRODUCTION

Non-covalent interactions involving sulfur are crucial in controlling the supramolecular structure and function, as manifested in a wide range of sulfur-centered H-bonds in peptides and proteins.<sup>1</sup> The hydrogen sulfide dimer (H<sub>2</sub>S)<sub>2</sub> is a particularly interesting case of sulfur-driven H-bonding and serves as a prototype for SH...S bonding in metal-sulfide complexes<sup>2</sup> and metalloproteins.<sup>3</sup> For example, SH...S interactions stabilize the orientation of cysteine residues at the surface of the [4Fe-4S] core of ferredoxin, and by doing so, fine-tune the reduction potential of the ferredoxin core with important implications for the flow of electrons in electron transport chains. SH...S interactions also play a key role in the domain of physical chemistry and the Earth sciences. For instance, knowledge of the structure and binding energy of (H<sub>2</sub>S)<sub>2</sub> is essential in interpreting results from IR studies of H<sub>2</sub>S clusters<sup>4</sup> and the gas phase studies of metal-H<sub>2</sub>S solvation.<sup>5</sup> From a geochemical perspective, SH...S interactions are at the heart of understanding the molecular structure and composition of supercritical H<sub>2</sub>S and thus the role that H<sub>2</sub>S-rich fluids play in transport of metals in Earth's crust.<sup>6</sup> Consequently, there is a critical need

to apply high level theoretical calculations, i.e., CCSD(T)/CBS (complete basis set), in order to provide accurate estimates of the structure and stability of the hydrogen sulfide dimer.

Only two experimental measurements exist for the binding energy of (H<sub>2</sub>S)<sub>2</sub>: a  $D_o$  value of  $1.7 \pm 0.3$  kcal/mol<sup>7</sup> reported over forty years ago, and a more recent binding energy value of  $D_e = 1.68 \pm 0.02$  obtained using cavity enhanced absorption spectroscopy (CEAS);<sup>8</sup> both values are rather close to each other, and thus, there are obvious uncertainties in at least one of these determinations. The value of  $D_o$  quoted for (H<sub>2</sub>S)<sub>2</sub> falls not very far short of the measured dissociation energy for (H<sub>2</sub>O)<sub>2</sub> ( $D_o = 3.16 \pm 0.03$  kcal/mol),<sup>9</sup> thus, (H<sub>2</sub>S)<sub>2</sub> appears moderately strongly bound, albeit more loosely than (H<sub>2</sub>O)<sub>2</sub>. A more recent study reported (H<sub>2</sub>S)<sub>2</sub> in supersonic jets of H<sub>2</sub>S/He using vacuum-ultraviolet-ionization detected-infrared predissociation (VUV-ID-IRPD) spectroscopy<sup>4</sup> and revealed strong redshifts in the donor SH stretching frequency, consistent with the results from IR measurements in N<sub>2</sub><sup>10</sup> and Ar<sup>11</sup> matrices. These authors also compared measured SH stretching frequencies against MP2/aVTZ results and included CCSD(T)/aVTZ binding energies. As expected, there have been several theoretical calculations of the structure and energies of (H<sub>2</sub>S)<sub>2</sub> using DFT, MP2 theory, and CCSD(T) theory. Early examples of MP $n$  and coupled cluster works on (H<sub>2</sub>S)<sub>2</sub> include MP4,<sup>12</sup> MBPT(E3),<sup>13</sup> MP2,<sup>14,15</sup> and more recently, MP2/CBS,<sup>16</sup> and

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CCSD(T) calculations.<sup>14,16</sup> The impact of electron correlation and basis set convergence was not explored in these studies; however, these effects have been discussed in detail for other dimers such as  $(\text{H}_2\text{O})_2$ ,<sup>17-19</sup>  $(\text{HF})_2$ ,<sup>20,21</sup> and  $\text{HF-N}_2$ ,<sup>22</sup> demonstrating that an understanding of both effects is essential, if accurate estimates of structures and binding energies are to be obtained.

The results presented here include MP2, MP4, and coupled cluster CCSD and CCSD(T) calculations for  $(\text{H}_2\text{S})_2$ , in which the basis set convergence of structure parameters, spectroscopic constants, and binding energies are examined employing basis sets up to aug-cc-pV5Z quality. This approach builds closely on recent theoretical studies that have predicted CBS limit molecular properties for weakly bound complexes using MP2, MP3, MP4, CCSD, and CCSD(T) levels of theory in combination with correlation consistent basis sets.<sup>17-22</sup> These studies have demonstrated that when effects of correlation and basis set are treated systematically, correlated methods can yield results of remarkable detail and accuracy and provide insight into weakly bound systems that are either difficult or impossible to explore by experiment. The primary purpose of the current work, therefore, is to assess the importance of both the level of correlation treatment and basis set completeness for  $(\text{H}_2\text{S})_2$ . Another major theme in this study is the effect of basis set superposition error (BSSE) on the calculated dimer binding energy and geometry; this study takes into account counterpoise (CP) corrections for BSSE both on the binding energies and molecular structure using the CP method of Boys and Bernardi.<sup>23</sup> Effects of BSSE on the structure of  $(\text{H}_2\text{S})_2$  were estimated by carrying out full geometry optimizations on the CP-corrected potential energy surface (PES). As these calculations impose considerable computational demands, especially in the case of MP4, CCSD, and CCSD(T), CP-corrected geometry optimizations were undertaken at the MP2 level with basis sets up to aug-cc-pV5Z quality and at the MP4, CCSD, and CCSD(T) levels of theory with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets.

## II. COMPUTATIONAL METHODS

Structure and binding energies of  $(\text{H}_2\text{S})_2$  were examined using MP2 and MP4 level Møller-Plesset perturbation theory and the coupled cluster methods CCSD and CCSD(T) as implemented in the GAUSSIAN 09 (version D01) suite of electronic structure codes.<sup>24</sup> All calculations employ the augmented correlation consistent basis sets aug-cc-pVnZ of Dunning and co-workers<sup>25,26</sup> with  $n = \text{D, T, Q, 5}$  (abbreviated as aVDZ, aVTZ, aVQZ, aV5Z, respectively), as these exhibit a well-known asymptotic convergence behavior with respect to the basis set size. This behavior will be utilized to estimate the CBS limit of structure parameters and energies for  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$  at each level of theory ranging from MP2 to CCSD(T). In brief,  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$  geometries were fully optimized at the MP2 level of theory with basis sets up to aV5Z quality, and in the case of MP4, CCSD, and CCSD(T), with aVDZ, aVTZ, and aVQZ basis sets, respectively. The CBS limit values for the structure parameters of  $(\text{H}_2\text{S})_2$ , binding energy ( $D_e$ ), zero point energy ( $E_{\text{ZPE}}$ ), and zero-point energy

(ZPE)-corrected binding energy ( $D_0$ ) were obtained using the CBS limit extrapolation method proposed by Peterson and co-workers.<sup>27</sup> For instance, the four MP2 dimer binding energies (aVDZ-aV5Z) were extrapolated to their CBS limit value using a mixed Gaussian exponential expression according to

$$D_e(n) = D_e(\infty) + Ae^{-(n-1)} + Be^{-(n-1)^2}, \quad (1)$$

where  $n$  is the basis set cardinal number ( $n = 2, 3, 4, 5$  for aVDZ, aVTZ, aVQZ, aV5Z, respectively),  $A$  and  $B$  are constants obtained by least square fitting the respective aVDZ, aVTZ, aVQZ, and aV5Z values of  $D_e$  to Eq. (1), and  $D_e(\infty)$  is the corresponding complete basis set limit binding energy.

Basis set superposition errors on the binding energies and structures of  $(\text{H}_2\text{S})_2$  were estimated by conducting full geometry optimizations on the uncorrected and counterpoise (CP)-corrected PES. Previous studies of small dimer complexes<sup>20,22</sup> have shown that CBS limit binding energies and structures obtained on the CP-corrected PES are almost identical to those where *post hoc* BSSE corrections were applied, the only caveat being that CP optimization using CCSD and CCSD(T) is computationally demanding and often impractical in combination with basis sets larger than aVTZ. All geometry optimizations on the CP-corrected PES were undertaken using internal coordinates [Fig. 1], and in the case of MP2,  $(\text{H}_2\text{S})_2$  geometries were fully optimized using the basis set range aVDZ, aVTZ, and aVQZ, while for the higher methods, i.e., MP4, CCSD, and CCSD(T), only aVDZ and aVTZ level full geometry optimizations were carried out; for larger aVQZ basis set calculations with MP4, CCSD, and CCSD(T), only intermolecular parameters were optimized, and intramolecular parameters were held constant at their estimated aVQZ values.

Anharmonic CCSD(T)/aVQZ level frequencies and zero-point energies (ZPE's) of  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$  have been calculated by combining CCSD(T)/aVQZ level harmonic vibrational frequencies ( $\omega_i$ ) with MP2/aVQZ anharmonicities using vibrational second-order perturbation theory (VPT2). Anharmonic vibrational frequencies ( $\nu_i$ ) at the CCSD(T)/aVQZ level of theory have been estimated according to

$$\nu_i[\text{CCSD(T)/aVQZ}] = \omega_i[\text{CCSD(T)/aVQZ}] + \{\nu_i[\text{MP2/aVQZ}] - \omega_i[\text{MP2/aVQZ}]\}. \quad (2)$$

Building on CCSD(T)/aVQZ fundamental and harmonic frequencies of  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$ , VPT2 ZPE estimates for both molecules,  $\Delta E_{\text{ZPE}}$ , and  $D_0$  were obtained using the following expressions:<sup>28</sup>

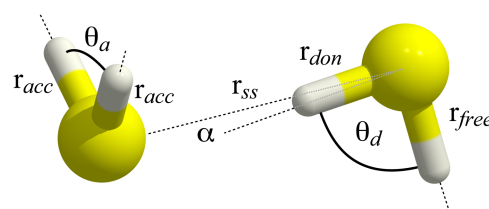


FIG. 1. Configuration of the hydrogen sulfide dimer studied in this work.

$$ZPE_{VPT2} = 1/2(ZPE_H + ZPE_F) + \chi_0 - 1/4 \sum \chi_{ii}, \quad (3)$$

$$ZPE_H = 1/2 \sum \omega_i [\text{CCSD(T)/aVQZ}], \quad (4)$$

$$ZPE_F = 1/2 \sum \nu_i [\text{CCSD(T)/aVQZ}], \quad (5)$$

$$D_0 = D_e - 2ZPE_{VPT2}(\text{H}_2\text{S}) + ZPE_{VPT2}(\text{H}_2\text{S})_2, \quad (6)$$

where  $ZPE_H$  and  $ZPE_F$  are the harmonic and fundamental zero-point energies,  $\chi_0$  and  $\chi_{ii}$  are anharmonic constants obtained from VPT2 calculations, respectively; this approach has been used successfully to predict accurate vibrational frequencies, ZPE's, and binding energies for a wide range of dimer complexes with low frequency ( $<200 \text{ cm}^{-1}$ ) anharmonic vibrations.<sup>29</sup> All VPT2 level anharmonicities were calculated at the MP2/aVQZ level using GAUSSIAN 09.<sup>24</sup>

### III. RESULTS AND DISCUSSION

#### A. Monomer data

Table I compares experimental and calculated equilibrium geometries ( $r_{\text{SH}}$ ,  $\phi$ ), dissociation energies, harmonic vibrational frequencies ( $\omega_n$ ), dipole moments ( $\mu$ ), and polarizability components ( $\alpha_{xx}$ ,  $\alpha_{yy}$ ,  $\alpha_{zz}$ ) of the  $\text{H}_2\text{S}$  molecule at the MP2, MP4, CCSD, and CCSD(T) levels of theory as a function of basis set; all geometries were fully optimized with basis sets ranging from aVDZ to aV5Z and include harmonic

vibrational frequency calculations. As expected, MP4, CCSD, and CCSD(T) provide the highest level of accuracy for the  $\text{H}_2\text{S}$  molecule among all four correlated methods. The results for the equilibrium geometry of  $\text{H}_2\text{S}$  show that the calculated values of  $r_{\text{SH}}$  and  $\phi$  are accurately reproduced at the CCSD and CCSD(T) levels of theory with aVQZ basis sets to within  $0.001 \text{ \AA}$  and  $0.1^\circ$ , respectively. As shown in Table I, the values for the  $\text{H}_2\text{S}$  dissociation energy calculated by CCSD(T) vary smoothly from 81.3, 88.3, 89.5 to 90.1 kcal/mol as the basis set is expanded from aVDZ, aVTZ, aVQZ to aV5Z, respectively; the CCSD(T) dissociation energy with aV5Z is less than 0.2 kcal/mol above the reported experimental value of 89.9 kcal/mol,<sup>28</sup> while the corresponding MP4 dissociation energy is slightly smaller, by around 0.8 kcal/mol, than the experimental value.

Table I also lists two types of CBS limit extrapolations of  $E_e$ ,  $D_0$ ,  $r_{\text{SH}}$ , and  $\phi$ , which have been derived by fitting energies and geometric parameters to Eq. (1): the first value, abbreviated as CBS[D,T,Q], was derived by fitting aV(D,T,Q)Z results for  $E_e$ ,  $D_0$ ,  $r_{\text{SH}}$ , and  $\phi$  to Eq. (1) and a second CBS limit value, abbreviated as CBS[D,T,Q,5], in which the fit was performed using the full range of aV(D,T,Q,5)Z basis set. At the aV5Z level,  $r_{\text{SH}}$  varies slightly from 1.3327 (MP2), 1.3375 (MP4), 1.3356 (CCSD) to 1.3382  $\text{\AA}$  (CCSD(T)) ( $r_{\text{SH}}$  expt. = 1.3356  $\text{\AA}$ ), and as seen from Table I, differences between aVQZ and aV5Z values for MP4, CCSD, and CCSD(T) for

TABLE I. Bond dissociation energies (kcal/mol), optimal structures, dipole moments, and polarizability components of  $\text{H}_2\text{S}$ .

Methods	Basis set	Energy ( $E_h$ )	$D_0$ (kcal)	$r_{\text{S-H}}$ ( $\text{\AA}$ )	$\phi$ (deg)	$\omega_1$ ( $\text{cm}^{-1}$ )	$\omega_2$ ( $\text{cm}^{-1}$ )	$\omega_3$ ( $\text{cm}^{-1}$ )	$\mu_e$ (D)	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{\text{tr}}$
										(10 <sup>-24</sup> cm <sup>3</sup> )			
MP2	aVDZ	-398.853 218	83.09	1.3496	92.44	1193	2754	2779	1.065	3.393	3.495	3.400	3.429
	aVTZ	-398.908 795	87.59	1.3363	92.23	1211	2772	2792	1.006	3.578	3.679	3.579	3.612
	aVQZ	-398.926 526	89.00	1.3340	92.23	1213	2776	2795	1.007	3.598	3.705	3.599	3.634
	aV5Z	-398.934 043	89.69	1.3327	92.24	1216	2780	2799	1.005	3.592	3.695	3.592	3.627
	CBS[D,T,Q]	-398.936 572	89.80										
	CBS[D,T,Q,5]	-398.937 549	89.95										
MP4	aVDZ	-398.879 875	84.62	1.3543	92.43	1189	2708	2729	1.029	3.487	3.521	3.489	3.499
	aVTZ	-398.940 030	88.67	1.3410	92.24	1205	2723	2739	0.992	3.577	3.658	3.577	3.604
	aVQZ	-398.956 516	89.93	1.3392	92.32	1207	2724	2741	1.004	3.595	3.672	3.594	3.620
	aV5Z	-398.962 320	90.50	1.3375	92.30	1209	2731	2747	1.002	3.585	3.661	3.587	3.611
	CBS[D,T,Q]	-398.965 577	90.64										
	CBS[D,T,Q,5]	-398.965 639	90.74										
CCSD	aVDZ	-398.875 953	83.46	1.3535	92.63	1200	2712	2732	1.029	3.465	3.496	3.467	3.476
	aVTZ	-398.932 283	87.01	1.3396	92.56	1221	2732	2747	0.991	3.543	3.613	3.545	3.567
	aVQZ	-398.947 768	88.19	1.3372	92.61	1224	2739	2753	1.002	3.556	3.623	3.557	3.579
	aV5Z	-398.953 277	88.72	1.3356	92.61	1228	2745	2759	0.999	3.582	3.653	3.583	3.606
	CBS[D,T,Q]	-398.956 284	88.86										
	CBS[D,T,Q,5]	-398.956 388	89.07										
CCSD(T)	aVDZ	-398.880 846	81.3	1.3556	92.45	1188	2692	2713	...	3.415	3.507	3.416	3.446
	aVTZ	-398.940 832	88.3	1.3419	92.28	1205	2711	2727	...	3.575	3.652	3.576	3.601
	aVQZ	-398.957 311	89.5	1.3399	92.36	1208	2714	2730	...	3.591	3.665	3.591	3.616
	aV5Z	-398.963 190	90.1	1.3382	92.32	1211	2721	2736	...	3.582	3.652	3.583	3.606
	CBS[D,T,Q]	-398.966 372	90.1										
	CBS[D,T,Q,5]	-398.966 497	90.3										
Expt.			89.9 <sup>a</sup>	1.3356 <sup>b</sup>	92.11 <sup>b</sup>	1183	2615	2626	0.978 <sup>c</sup>	3.841 <sup>d</sup>	3.749 <sup>d</sup>	3.736 <sup>d</sup>	3.774 <sup>d</sup>

<sup>a</sup>Reference 30.

<sup>b</sup>Reference 31.

<sup>c</sup>Reference 37.

<sup>d</sup>Reference 38.

$r_{\text{SH}}$  and  $\phi$  are relatively small. Thus, at the MP4, CCSD, and CCSD(T) levels of theory, values of  $r_{\text{SH}}$  and  $\phi$  are nearly converged with the aVQZ basis set. The CCSD(T)/CBS[DTQ] and CCSD(T)/CBS[DTQ5] limit values for  $r_{\text{SH}}$  of 1.3390 and 1.3381 Å, respectively, are longer by around 0.0034 and 0.0025 Å than the recommended experimental estimate of 1.3356 Å.<sup>29</sup> Previously reported theoretical structures for H<sub>2</sub>S have been determined with comparable levels of theory,<sup>30,31</sup> and these are in excellent agreement with the results reported here. For instance, our  $r_{\text{SH}}$  value at the CCSD(T)/aV5Z level of theory is 1.3382 Å and compares favorably with a value of 1.3379 Å derived from CCSD(T)/aug-cc(5+d)Z calculations.<sup>31</sup>

Estimates for  $E_e$  and  $D_o$  for MP2, MP4, CCSD, and CCSD(T) up to the CBS limit are also summarized in Table I. The CCSD(T)/CBS[D,T,Q] value of  $E_e$  is just 0.125  $mE_h$  smaller than the corresponding CCSD(T)/CBS[D,T,Q,5] value of  $E_e$ . The difference between the CBS[D,T,Q] limit SCF total energy ( $-398.720\,777\,E_h$ ) and CCSD(T) value ( $-398.966\,372\,E_h$ ), yields a valence correlation energy for H<sub>2</sub>S of around 246  $mE_h$ , which is in excellent agreement with the CCSD(T)/CBS estimate of 247  $mE_h$ .<sup>32</sup> For MP2 and CCSD, the CBS[D,T,Q] limit correlation energies are 215 and 235  $mE_h$ , which are in good agreement with reported values of 221  $mE_h$  and 237  $mE_h$ , respectively.<sup>33</sup> CBS extrapolations of CCSD(T) total energies carried out using the full aV(D,T,Q,5)Z basis set range yield a valence correlation energy for H<sub>2</sub>S of around 245  $mE_h$ ; in other words, the correlation energy is almost fully recovered by fitting aV(D,T,Q)Z to Eq. (1). The accuracy of this method is further corroborated by comparing H<sub>2</sub>S dissociation energies at the CCSD(T)/CBS[D,T,Q] (90.1 kcal/mol) and CCSD(T)/CBS[D,T,Q,5] (90.3 kcal/mol) levels of theory along with the experimental estimate of 89.9 kcal/mol.<sup>28</sup>

Table I also lists the dipole moments and polarizabilities of H<sub>2</sub>S, and these are compared with CCSD(T) results.<sup>34</sup> With the largest basis set considered (aV5Z), the dipole moment was found to be 1.0050 (MP2), 1.0021 (MP4), and 0.9998 D (CCSD). At the experimental geometry of H<sub>2</sub>S (expt.  $r_{\text{SH}} = 1.3356$  Å,  $\phi = 92.11^\circ$ ), the calculated values of  $\mu$  are 1.0051 (MP2), 1.0009 (MP4), and 0.9986 D (CCSD), which, in the case of CCSD, is in reasonable agreement with the

experimental value of 0.9783 D.<sup>35</sup> Figure 2 shows the convergence behavior of dipole moment at the MP2, MP4, and CCSD levels of theory using the aV(D,T,Q,5)Z range of basis sets. While calculated values of  $\mu$  appear to converge toward the CBS limit, MP4 and CCSD results display an irregular convergence behavior, in particular, between the  $\mu$  values with aVTZ and aVQZ basis sets, a feature consistent with theoretical results on the convergence behavior of the dipole moment for H<sub>2</sub>O.<sup>17</sup>

The convergence of the average polarizability ( $\alpha_{\text{rr}}$ ) of H<sub>2</sub>S with the basis set size is presented graphically in Fig. 2 for MP2, MP4, CCSD, and CCSD(T) along with CBS limit values of  $\alpha_{\text{rr}}$ . In general, values of  $\alpha_{\text{rr}}$  display a weaker basis set dependence than  $\mu$  and are nearly converged at aVTZ. For MP2, MP4, CCSD, and CCSD(T) calculations,  $\alpha_{\text{rr}}$  increases by just 5% as the basis set size increases from aVTZ, aVQZ to aV5Z, and polarizabilities remain within around 0.5% of each other at the aV5Z level. At the CCSD level of theory and with the aV5Z basis set, the polarizability is slightly lower than estimates of  $\alpha_{\text{rr}}$  from MP2, MP4, and CCSD(T) calculations. Average polarizabilities at the MP2 and MP4 levels with aVQZ and aV5Z basis sets deviate by around  $0.142 \times 10^{-24}$  cm<sup>3</sup> from the measured estimate of  $3.774 \times 10^{-24}$  cm<sup>3</sup><sup>36</sup> but, on the other hand, are still closer to the measured value of  $\alpha_{\text{rr}}$  than CCSD and CCSD(T) results with the same basis sets, e.g., the difference between  $\alpha_{\text{rr}}$  for CCSD(T) with aV5Z and the experiment is  $0.169 \times 10^{-24}$  cm<sup>3</sup>. These results are consistent with previous calculations for H<sub>2</sub>S, which predicted a similar ( $\sim 0.14 \times 10^{-24}$  cm<sup>3</sup>) difference between experimental and MP2 calculated values of  $\alpha_{\text{rr}}$ .<sup>36</sup> At the highest level of theory, CCSD(T), the average polarizability  $\alpha_{\text{rr}}$  of H<sub>2</sub>S is  $3.616 \times 10^{-24}$  (aVQZ) and  $3.606 \times 10^{-24}$  cm<sup>3</sup> (aV5Z), and the CCSD(T)/CBS[D,T,Q,5] value of  $\alpha_{\text{rr}}$  for H<sub>2</sub>S ( $3.609 \times 10^{-24}$  cm<sup>3</sup>) still lies significantly outside the uncertainty range of the experimental estimate of  $3.774 \times 10^{-24}$  cm<sup>3</sup>,<sup>36</sup> these results are consistent with the reported large basis set CCSD(T) calculations ( $\alpha_{\text{rr}} = 3.69 \times 10^{-24}$  cm<sup>3</sup>).<sup>34</sup>

## B. Dimer structure and binding energy $D_e$

Results for the equilibrium intersulfur distance ( $r_{\text{SS}}$ ), dimer binding energy ( $D_e$ ), and H<sub>2</sub>S monomer geometries at

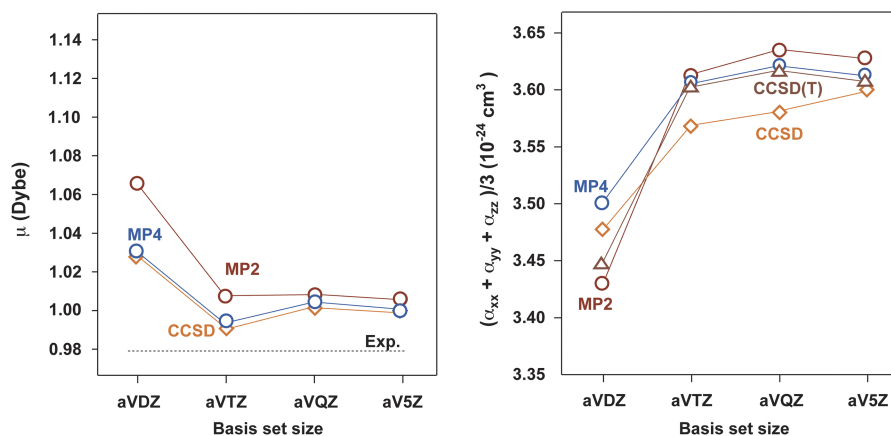


FIG. 2. Variation of the dipole moment  $\mu$  and average polarizability component  $\alpha_{\text{rr}}$  as a function of basis set size at the MP2, MP4, CCSD, and CCSD(T) levels of theory.

TABLE II. Calculated binding energies ( $D_e$ ), uncorrected and counterpoise-corrected, and optimal geometries for  $(\text{H}_2\text{S})_2$ .

Method	Basis set	Energy ( $E_h$ )	$D_e$ (kcal/mol) <sup>c</sup>	$r_{SS}$ (Å)	$\alpha$ (deg)	$r_{frer}$ (Å)	$r_{don}$ (Å)	$r_{acc}$ (Å)	$\Theta_d$ (deg)	$\Theta_a$ (deg)
MP2	aVDZ	-797.710 187	2.354 [1.542]	4.0968	4.53	1.3496	1.3532	1.3502	92.64	92.56
	aVTZ	-797.821 024	2.126 [1.750]	4.0759	4.92	1.3363	1.3405	1.3368	92.41	92.34
	aVQZ	-797.856 264	2.014 [1.833]	4.0802	5.52	1.3342	1.3384	1.3347	92.47	92.37
	aV5Z	-797.871 224	1.968 [1.857]	4.0802	5.32	1.3328	1.3370	1.3333	92.44	92.36
	CBS[D,T,Q] <sup>a</sup>	-797.876 248	1.946 [1.881]							
	CBS[D,T,Q,5] <sup>a</sup>	-797.878 196	1.943 [1.876]							
MP4	aVDZ	-797.763 250	2.195 [1.366]	4.1383	4.28	1.3543	1.3570	1.3548	92.60	92.50
	aVTZ	-797.883 155	1.942 [1.613]	4.1249	4.53	1.3411	1.3443	1.3415	92.45	92.42
	aVQZ	-797.915 944	1.826 [1.702]	4.1314	5.91	1.3391	1.3423	1.3395	92.55	92.43
	CBS[D,T,Q] <sup>a</sup>	-797.933 938	1.754 [1.749]							
	CCSD	aVDZ	-797.754 934	1.900 [1.189]	4.1940	4.54	1.3536	1.3555	1.3541	92.83
CCSD	aVTZ	-797.867 112	1.597 [1.320]	4.2086	4.59	1.3395	1.3417	1.3399	92.73	92.64
	aVQZ	-797.897 897	1.480 [1.376]	4.2253	4.64	1.3372	1.3393	1.3376	92.81	92.73
	CBS[D,T,Q] <sup>a</sup>	-797.914 820	1.411 [1.409]	4.2360						
	CCSD(T)	aVDZ	-797.765 126	2.155 [1.336]	4.1488	4.01	1.3556	1.3581	1.3561	92.60
CCSD(T)	aVTZ	-797.884 663	1.881 [1.559]	4.1373	6.37	1.3419	1.3448	1.3424	92.52	92.37
	aVQZ	-797.917 435	1.765 [1.641]	4.1461	6.07	1.3397	1.3426	1.3402	92.60	92.47
	CBS[D,T,Q] <sup>a</sup>	-797.935 446	1.696 [1.689]							
	Expt.		1.68 ± 0.02 <sup>b</sup>							

<sup>a</sup>Total energies and binding energies calculated by fitting values of  $E$  and  $D_e$  to exponential expression Eq. (1).

<sup>b</sup>Experimental value taken from Ref. 8.

<sup>c</sup>Values in square brackets are counterpoise corrected binding energies.

the MP2, MP4, CCSD, and CCSD(T) levels of theory, as a function of basis set size up to aV5Z, are presented in Table II and Fig. 3. CBS[D,T,Q] and CBS[D,T,Q,5] limit values of the total electronic energy  $E_e$ , binding energy  $D_e$ , and  $r_{SS}$  have been estimated by extrapolating values of  $E_e$ ,  $D_e$ , and  $r_{SS}$  to Eq. (1); values of  $E_e$  and  $D_e$  at the MP4, CCSD, and CCSD(T) levels of theory have been estimated by carrying out full geometry optimizations with aVDZ, aVTZ, and aVQZ basis sets.

Calculations at the MP2 level for  $(\text{H}_2\text{S})_2$  show that  $D_e$  converges from 2.35 (aVDZ) to 1.97 kcal/mol (aV5Z), and values of  $D_e$  appear well-converged with the aVQZ basis set;

the difference between MP2 values of  $D_e$  with aVQZ and aV5Z is small, around 0.04 kcal/mol. Higher-order electron correlation has a significant effect on  $D_e$ : the CP-uncorrected values of  $D_e$  with aVDZ shift from 2.19 (MP4), 1.90 kcal/mol (CCSD), and 2.16 kcal/mol for CCSD(T), and  $D_e$  decreases for all methods with increasing basis set size (see Fig. 3). The CP-uncorrected binding energies at the CCSD(T) level of theory are 1.88 (aVTZ), 1.76 (aVQZ), and 1.70 kcal/mol at the CBS limit. Figure 3 and Table II also present binding energies where BSSE corrections have been applied *post hoc*, i.e., following the

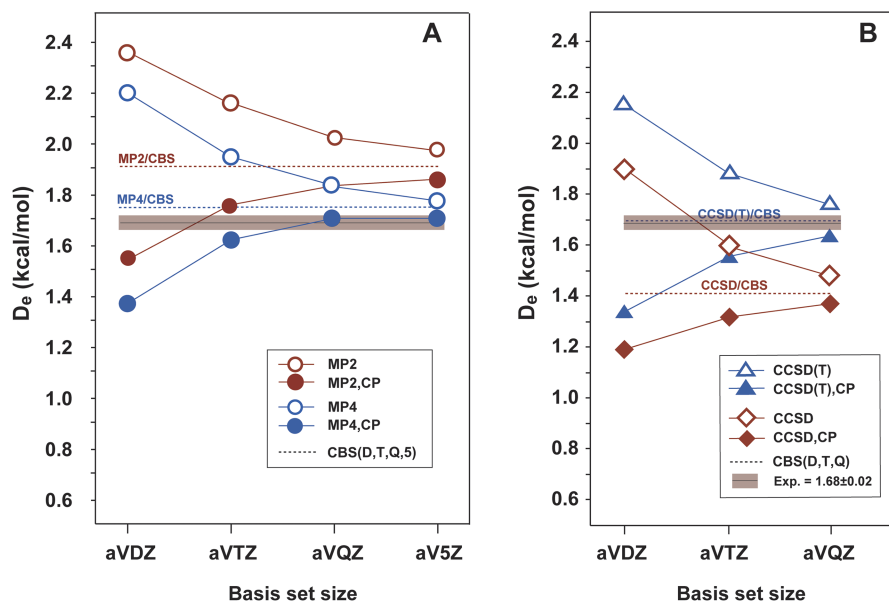


FIG. 3. Calculated MP2, MP4, CCSD, and CCSD(T) binding energies  $D_e$  for  $(\text{H}_2\text{S})_2$  as a function of basis set size up to the CBS limit; *post hoc* counterpoise-corrected values of  $D_e$  shown as full symbols.

geometry optimization; a second case where the BSSE correction is applied during the geometry optimization is discussed further below. For all methods, uncorrected values of  $D_e$  converge from above, while CP-corrected binding energies converge from below. For CCSD(T), the CP-corrected binding energies are 1.34 (aVDZ), 1.56 (aVTZ), and 1.64 kcal/mol (aVQZ), and thus, at the CCSD(T)/aVQZ level, the difference between uncorrected and CP-corrected values of  $D_e$  is just 0.12 kcal/mol. With the largest basis set (aVQZ), the uncorrected and CP-corrected CCSD(T) binding energies are close to equal with the averaged CBS[D,T,Q] limit of 1.693 kcal/mol, and as seen from Fig. 3, the averaged CCSD(T)/CBS[D,T,Q] estimate of  $D_e$  is in excellent agreement with the experimental dimer binding energy value of  $D_e = 1.68 \pm 0.02$ .<sup>8</sup> This convergence behavior allows for the uncorrected and CP-corrected values of  $D_e$  to be used as an estimate of the average CBS limit binding energy: for the aVDZ-aVQZ basis set range, the averaged CBS limit of the binding energy is 1.91 kcal/mol (MP2), 1.75 (MP4), 1.41 (CCSD), and 1.69 kcal/mol (CCSD(T)). Table III lists a breakdown of the CCSD(T) energies into interaction ( $E_{int}$ ), deformation ( $E_{def}$ ), and BSSE as a function of basis set size up to aVQZ. A key observation is the relatively small value (0.01 kcal/mol) and basis set independence of  $E_{def}$ , both for CP uncorrected and CP corrected  $(\text{H}_2\text{S})_2$  geometries, while the magnitude of the BSSE correction shifts to smaller values with increasing basis set size and causes  $D_e$  to shift upward. Interestingly, the value of  $E_{def}$  for  $(\text{H}_2\text{S})_2$  is very close to the monomer deformation energy predicted for a stacked benzene dimer ( $\sim 0.01$  kcal/mol),<sup>39</sup> but still significantly below the water monomer deformation energy ( $\sim 0.1$  kcal/mol) in the more strongly bound water dimer.

Values for the  $(\text{H}_2\text{S})_2$  equilibrium geometry, intersulfur distance  $r_{SS}$ , and monomer geometries in  $(\text{H}_2\text{S})_2$  are also shown in Table II at the MP2, MP4, CCSD, and CCSD(T) levels of theory as a function of basis set size up to the complete basis set limit. Values of  $r_{SS}$  for  $(\text{H}_2\text{S})_2$  with the aVQZ basis set are 4.080 (MP2), 4.131 (MP4), 4.225 (CCSD), and 4.146 Å (CCSD(T)). CCSD slightly overestimates  $r_{SS}$ ,

TABLE III. Breakdown of the binding energy (kcal/mol) for  $(\text{H}_2\text{S})_2$  into deformation, interaction, and counterpoise-correction terms for uncorrected and CP-corrected CCSD(T) levels with aVnZ basis sets.

Term	CP-uncorrected PES		
	aVDZ	aVTZ	aVQZ
$E_{Int}$ . <sup>a</sup>	2.139	1.887	1.761
$E_{Def}$ . <sup>b</sup>	0.016	0.004	0.004
$D_e$ . <sup>c</sup>	2.155	1.881	1.765
$\Delta E_{CP}$ . <sup>d</sup>	0.819	0.322	0.124
Term	CP-corrected PES		
	aVDZ	aVTZ	aVQZ
$E_{Int}$ .	1.412	1.567	1.639
$E_{Def}$ .	0.002	0.003	0.004
$D_e$	1.414	1.570	1.643

<sup>a</sup>Interaction energy,  $E_{Int} = D_e + E_{Def}$ .

<sup>b</sup>Deformation energy,  $E_{Def} = E_{Def,don} + E_{Def,acc}$ .

<sup>c</sup>Binding energy,  $D_e = E_{dimer} - 2E_{mono}$ .

<sup>d</sup>Counterpoise correction energy,  $\Delta E_{CP}$ .

relative to CCSD(T), whereas MP4 and MP2 do the opposite for all basis sets. In MP2 calculations with aVQZ and aV5Z basis sets,  $r_{SS}$  and  $\alpha$  are within less than a thousandth of an angstrom (0.0003 Å) and a few tenths of a degree (0.2°), respectively, and thus, the MP2/aVQZ dimer equilibrium geometry appears to be converged. CCSD values of  $r_{SS}$  shift toward longer distances, from 4.194 Å with aVDZ, 4.209 Å with aVTZ, and 4.225 Å with aVQZ. Full geometry optimization using MP4 and CCSD(T) with aVDZ and aVTZ basis sets leads to a decrease in  $r_{SS}$  by around 0.013 Å and 0.011 Å and a moderate increase, 0.006 Å and 0.009 Å, respectively, upon going to aVQZ; for MP4 and CCSD(T), values of  $r_{SS}$  first shorten as the basis set is enlarged from aVDZ to aVTZ and then slightly lengthen as the basis set is further expanded to aVQZ; thus, no clear convergence is found for  $r_{SS}$  with MP4 and CCSD(T). These trends align well with the results from MP4 and CCSD(T) calculations on the  $\text{N}_2\text{-HF}_2$  dimer,<sup>22</sup> in which the  $\text{N}\cdots\text{H}$  intermolecular bond distance displays an irregular convergence behavior, though toward similar values as obtained from CP-corrected geometry optimizations.

Theoretical results on the CP-corrected PES with MP2, MP4, CCSD, and CCSD(T) are shown in Table IV and CP-corrected values of the intersulfur distance  $r_{SS}$  are presented graphically in Fig. 4 together with the values obtained from CP-uncorrected optimizations of  $(\text{H}_2\text{S})_2$ . The calculated values of  $r_{SS}$  obtained on the CP-corrected MP2 PES are plotted for aVDZ, aVTZ, and aVQZ basis sets and exhibit in each case systematic CBS limit convergence. At the MP2/CBS limit, the CP-corrected geometries differ by less than 0.02 Å from uncorrected results, and the averaged CBS limit for  $r_{SS}$  is estimated to be 4.092 Å. At the CCSD/aVDZ, CCSD/aVTZ, and CCSD/aVQZ levels of theory, the CP corrected values of  $r_{SS}$  are 4.353, 4.268, and 4.245 Å, respectively, and at the CCSD/CBS limit,  $r_{SS}$  is just 0.003 Å shorter than the uncorrected  $r_{SS}$  value of 4.236 Å. For CCSD(T)/aVDZ and CCSD(T)/aVTZ levels of theory calculations, values of  $r_{SS}$  on the CP-corrected PES are 4.304 and 4.199 Å, respectively, and further shift to 4.178 Å for CCSD(T)/aVQZ. Table IV shows that CCSD(T) values of  $D_e$  obtained by optimizing  $(\text{H}_2\text{S})_2$  on the CP-corrected PES incrementally approach the experimental binding energy value of  $1.68 \pm 0.02$  kcal/mol<sup>8</sup> as the basis set is expanded from aVDZ (1.41 kcal/mol), aVTZ (1.57 kcal/mol) to aVQZ (1.64 kcal/mol). The CCSD(T)/CBS value of  $D_e$  obtained by fitting aVDZ, aVTZ, and aVQZ energies to Eq. (1) is 1.687 kcal/mol, and this extrapolation yields CBS energies in excellent agreement with the CBS extrapolated binding energy value of 1.689 kcal/mol that was obtained with *post hoc* CP correction.

### C. Anharmonic vibrational frequencies and $D_0$

To complement our CCSD(T)/CBS estimates of  $D_e$ , we have calculated anharmonic vibrational frequencies and values of ZPE for  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$  at the CCSD(T) level of theory using VPT2. As noted in Sec. II, anharmonic vibrational frequencies and values of ZPE and  $D_0$  have been estimated using CCSD(T)/aVQZ frequencies, and anharmonic effects were accounted for by using VPT2/MP2/aVQZ

TABLE IV. Binding energies and equilibrium structures for  $(\text{H}_2\text{S})_2$  calculated on the counterpoise (CP)-corrected potential energy surface.

Method	Basis set	Energy ( $E_h$ )	$D_e$ (kcal/mol)	$r_{SS}$ (Å)	$\alpha$ (deg)	$R_{free}$ (Å)	$R_{don}$ (Å)	$R_{acc}$ (Å)	$\Theta_d$ (deg)	$\Theta_a$ (deg)
MP2	aVDZ	-797.708 997	1.607	4.2344	5.85	1.3495	1.3524	1.3500	92.65	92.56
	aVTZ	-797.820 446	1.764	4.1369	5.82	1.3363	1.3399	1.3368	92.43	92.34
	aVQZ	-797.855 980	1.836	4.1126	5.97	1.3381	1.3342	1.3347	92.48	92.38
	CBS[D,T,Q] <sup>a</sup>	-797.876 142	1.879	4.0996						
MP4	aVDZ	-797.762 049	1.447	4.2931	5.66	1.3534	1.3563	1.3546	92.61	92.50
	aVTZ	-797.882 648	1.619	4.1773	5.54	1.3411	1.3439	1.3415	92.46	92.39
	aVQZ <sup>b</sup>	-797.915 749	1.705	4.1561	6.04	1.3392	1.3421	1.3396	92.53	92.45
	CBS[D,T,Q] <sup>a</sup>	-797.933 945	1.757	4.1458						
CCSD	aVDZ	-797.753 911	1.258	4.3529	6.07	1.3535	1.3550	1.3539	92.84	92.70
	aVTZ	-797.866 687	1.330	4.2675	5.75	1.3396	1.3414	1.3399	92.74	92.65
	aVQZ <sup>b</sup>	-797.897 734	1.379	4.2454	6.11	1.3372	1.3393	1.3376	92.85	92.74
	CBS[D,T,Q] <sup>a</sup>	-797.914 813	1.410	4.2334						
CCSD(T)	aVDZ	-797.763 945	1.414	4.3035	6.43	1.3555	1.3574	1.3559	92.62	92.54
	aVTZ	-797.884 642	1.570	4.1992	6.70	1.3419	1.3445	1.3423	92.52	92.41
	aVQZ <sup>b</sup>	-797.917 240	1.643	4.1776	5.84	1.3399	1.3427	1.3403	92.59	92.49
	CBS[D,T,Q] <sup>a</sup>	-797.935 093	1.687	4.1666						

<sup>a</sup>Total energies, counterpoise corrected binding energies, and structure parameters calculated by fitting values of  $E$ ,  $D_e$ , and  $r_{ss}$  to Eq. (1).

<sup>b</sup>MP4, CCSD, and CCSD(T) intramolecular parameters  $R_{free}$ ,  $R_{don}$ , and  $R_{acc}$  held constant at estimated aVQZ values; intermolecular distances  $r_{ss}$ , angle  $\alpha$ , and dihedral angles optimized freely.

anharmonicities. Calculated CCSD(T)/aVQZ frequencies are reported in Table V together with experimental vibrational frequencies for  $\text{H}_2\text{S}$  and measured intramolecular vibrational frequencies for  $(\text{H}_2\text{S})_2$ ;<sup>4</sup> there are no measured intermolecular vibrational frequencies for this system. It is noteworthy that MP2/aVQZ and CCSD(T)/aVQZ vibrational frequencies for  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$  do not converge monotonously to the CBS limit, and thus, the extrapolation scheme shown in Eq. (1) was not applied to generate CBS limit frequencies and values of ZPE; instead, CCSD(T)/aVQZ ZPE's with VPT2/MP2/aVQZ corrections have been added to CCSD(T)/CBS values of  $D_e$  to establish a new and accurate value for  $D_0$ . Briefly, for  $(\text{H}_2\text{S})_2$  Bhattacharjee and co-workers reported four intramolecular SH stretching frequencies at 2618 ( $\nu_9$ ), 2618 ( $\nu_1$ ), 2605 ( $\nu_2$ ), and 2618 ( $\nu_3$ )  $\text{cm}^{-1}$ . Table V shows that harmonic CCSD(T)/aVQZ frequencies overestimate all four measured values by 111  $\text{cm}^{-1}$  ( $\nu_9$ ), 108  $\text{cm}^{-1}$  ( $\nu_1$ ), 109  $\text{cm}^{-1}$  ( $\nu_2$ ), and 101  $\text{cm}^{-1}$  ( $\nu_3$ ). The results from CCSD(T)/aVQZ VPT2 calculations using Eq. (2), on the other hand, agree well with the measured

values and differ from the experiment by only 11  $\text{cm}^{-1}$  ( $\nu_9$ ), 9  $\text{cm}^{-1}$  ( $\nu_1$ ), 10  $\text{cm}^{-1}$  ( $\nu_2$ ), and 25  $\text{cm}^{-1}$  ( $\nu_3$ ), and thus, VPT2 corrected CCSD(T)/aVQZ frequencies reproduce experimental SH stretches very well. Similarly, red-shifts for the SH stretching modes in  $(\text{H}_2\text{S})_2$  are accurately reproduced using VPT2: for instance, the CCSD(T)/aVQZ red-shift in the asymmetric SH stretching frequency  $\nu_1$  is 7  $\text{cm}^{-1}$  and is in excellent agreement with the experimentally observed value of 9  $\text{cm}^{-1}$ . Table V also shows that the symmetric SH stretch in  $(\text{H}_2\text{S})_2$  is split into two bands at 2605 and 2590  $\text{cm}^{-1}$ , and these are red-shifted relative to  $\text{H}_2\text{S}$  by around 10  $\text{cm}^{-1}$  and 25  $\text{cm}^{-1}$ , respectively. CCSD(T)/aVQZ VPT2 frequencies moderately underestimate the red-shift by 5  $\text{cm}^{-1}$  and 20  $\text{cm}^{-1}$  and predict  $\nu_2$  and  $\nu_3$  at 2615  $\text{cm}^{-1}$ . Finally, if we apply Eq. (6) together with CCSD(T)/aVQZ  $\nu_i$  estimates for  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$ , we obtain  $\text{ZPE}_{VPT2}(\text{H}_2\text{S}) = 0.5(9.52 + 9.20) + 0.01 - 0.04 = 9.33$  kcal/mol and  $\text{ZPE}_{VPT2}(\text{H}_2\text{S})_2 = 0.5(19.91 + 19.09) - 0.09 - 0.14 = 19.27$  kcal/mol. Combining ZPE's with the CCSD(T)/CBS binding energy  $D_e = -1.68$  kcal/mol yields

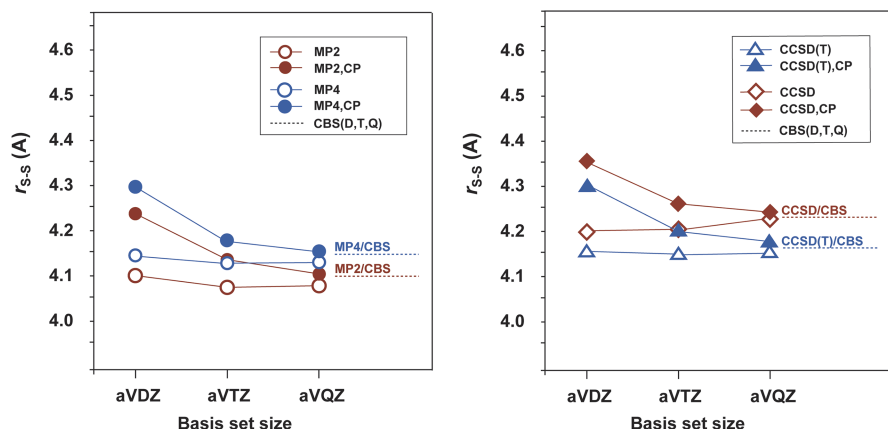


FIG. 4. Calculated MP2, MP4, CCSD, and CCSD(T) intersulfur distances  $r_{ss}$  for  $(\text{H}_2\text{S})_2$  as a function of basis set size up to the CBS limit; values of  $r_{ss}$  obtained by optimizing the geometry of  $(\text{H}_2\text{S})_2$  on the CP-corrected PES shown as full symbols.

TABLE V. MP2/aVQZ and CCSD(T)/aVQZ harmonic ( $\omega$ ,  $\text{cm}^{-1}$ ), anharmonic ( $\nu$ ,  $\text{cm}^{-1}$ ), experimental vibrational frequencies, and zero-point energies (kcal/mol) for  $\text{H}_2\text{S}$  and  $(\text{H}_2\text{S})_2$ .

Mode	Assignment	$\omega_{\text{MP2/aVQZ}}$	$\nu_{\text{MP2/aVQZ}}$	anh.	$\omega_{\text{CCSD(T)/aVQZ}}$	$\nu_{\text{CCSD(T)/aVQZ}}^{\text{a}}$	$\nu_{\text{Expt.}}^{\text{b}}$	$\Delta^{\text{c}}$
$\text{H}_2\text{S}$								
$\omega_3$	asym. S-H stretch	2796	2697	-99	2733	2634	2626	-9
$\omega_1$	sym. S-H stretch	2776	2680	-96	2717	2620	2615	-5
$\omega_2$	H-S-H bend	1214	1185	-28	1208	1180	1183	3
ZPE <sup>d</sup>		9.70	9.38		9.52	9.20	9.18	-0.02
ZPE <sub>VPT2</sub> <sup>e</sup>						9.33		
SDA			0.04					
$X_0$			0.01					
$(\text{H}_2\text{S})_2$								
$\omega_9$	ac. asym. S-H stretch	2791	2691	-100	2729	2629	2618	-11
$\omega_1$	do. asym. S-H stretch	2786	2688	-97	2726	2627	2618	-9
$\omega_2$	ac. sym. S-H stretch	2771	2674	-97	2714	2615	2605	-10
$\omega_3$	do. sym. S-H stretch	2731	2654	-77	2691	2615	2590	-25
$\omega_4$	do. H-S-H bend	1218	1186	-32	1213	1182		
$\omega_5$	ac. H-S-H bend	1212	1184	-27	1207	1180		
$\omega_{10}$	do. out-of-plane bend	283	223	-59	261	197		
$\omega_6$	In-plane donor wag	161	131	-29	148	1		
$\omega_8$	ac. bend	73	47	-26	73	47		
$\omega_7$	S-S stretch	81	63	-18	77	59		
$\omega_{11}$	ac. twist	64	55	-8	58	49		
$\omega_{12}$	do. torsion	38	33	-5	19	35		
ZPE <sup>d</sup>		20.31	19.48		19.91	19.09		
ZPE <sub>VPT2</sub> <sup>e</sup>						19.27		
SDA <sup>f</sup>			0.14					
$X_0$			-0.09					

<sup>a</sup>Calculated using Eq. (2).<sup>b</sup>Reference 37 for  $\text{H}_2\text{S}$  and Ref. 4 for  $(\text{H}_2\text{S})_2$ .<sup>c</sup> $\Delta = \nu_{\text{Expt.}} - \nu_{\text{CCSD(T)/aVQZ}}$ .<sup>d</sup>Calculated using Eqs. (4) and (5).<sup>e</sup>Calculated using Eq. (3).<sup>f</sup>SDA =  $-\frac{1}{4} \sum \chi_{ii}$ .

a CCSD(T) best estimate for  $D_0 = D_e - 2\text{ZPE}_{\text{VPT2}}(\text{H}_2\text{S}) + \text{ZPE}_{\text{VPT2}}(\text{H}_2\text{S})_2 = 1.08$  kcal/mol, which is around 0.6 kcal/mol smaller than the experimental binding energy  $D_0 = 1.7 \pm 0.3$  kcal/mol.<sup>7</sup>

#### D. Comparison with previous work

There are only two experimental measurements of the binding energy for  $(\text{H}_2\text{S})_2$ : a recent determination of  $D_e$ , which was obtained by measuring collision cross sections for  $\text{H}_2\text{S}$  transitions in the 1.58  $\mu\text{m}$  region using CEAS<sup>8</sup> and is an experimental determination of  $D_e$ ,<sup>38</sup> and the other experimental binding energy  $D_0$ , which was obtained from IR intensity measurements (4.0  $\mu\text{m}$ ) and yielded a value of  $1.7 \pm 0.3$  kcal/mol.<sup>7</sup> To our knowledge, no measurements exist covering all twelve frequencies  $\nu_1$  through  $\nu_{12}$ ; the only measured set of vibrational frequencies for  $(\text{H}_2\text{S})_2$  are those by Bhattacharjee and co-workers, and these are limited to intramolecular SH stretching modes. We have compiled into Table VI the best estimate CBS values of  $D_e$ ,  $E_{\text{ZPE}}$ ,  $D_0$ , and  $r_{\text{SS}}$  calculated in this study, and these have been derived by extrapolation of  $aVnZ$  ( $n = \text{D,T,Q}$ ) results for CP-corrected calculations, i.e., calculations that include full geometry

optimizations on the CP-corrected PES; values for  $E_{\text{ZPE}}$  and  $D_0$  are estimated using CCSD(T)/aVQZ harmonic frequencies and include VPT2 anharmonicities at the MP2/aVQZ level. From Table IV, it can be seen that our best estimate value for  $D_e = 1.69$  kcal/mol obtained at the CCSD(T)/CBS level of theory is in excellent agreement with the experimental value of  $D_e = 1.68 \pm 0.02$  kcal/mol.<sup>8</sup> The best estimate CCSD(T)/aVQZ value of  $E_{\text{ZPE}}$  listed in Table VI is 0.60 kcal/mol, and together with our CCSD(T)/CBS level value of  $D_e$ , it yields a CCSD(T) binding energy of  $D_0 = 1.08$  kcal/mol. Previously reported values of the  $E_{\text{ZPE}}$  ranged from 0.8 to 1.1 kcal/mol. For instance, de Oliveira *et al.*<sup>15</sup> reported an  $E_{\text{ZPE}}$  value of 0.89 kcal/mol using an *ab initio* based force field and this yielded  $D_0 = 0.74$  kcal/mol. A more recent estimate of  $E_{\text{ZPE}}$  of  $(\text{H}_2\text{S})_2$  is a value of 0.94 kcal/mol at the MP2/aVTZ level of theory.<sup>4</sup> The study also reported a CCSD(T)/CBS  $D_0$  binding energy of 0.97 kcal/mol, which is around 0.1 kcal/mol smaller than our best CCSD(T) value of  $D_0$  (see Table VI); this discrepancy is probably rooted in the MP2 geometries that were applied to estimate the CCSD(T)/CBS value of  $D_0$ .<sup>4</sup>

The best estimate CBS limit values for the intersulfur distances  $r_{\text{SS}}$  at the MP2, MP4, and CCSD(T) levels of theory are 4.122, 4.146, and 4.167 Å on the CP-corrected PES



TABLE VI. Comparison of present binding energies, ZPE's, and structure parameters with prior experimental and theoretical results.

Reference	Year	Method	Basis set	$D_e$ (kcal/mol)	$E_{ZPE}^*$ (kcal/mol)	$D_o$ (0 K) (kcal/mol)	$r_{S-S}$ (Å)	$r_{don.}$ (Å)	$\alpha$ (deg)
Frisch <i>et al.</i> <sup>a</sup>	1985	MP4SDQ	6-31G(d,p)	1.40	0.8	0.6	4.524	1.327	1.4
Fernandez <i>et al.</i> <sup>b</sup>	1985	MP2	6-31G* + d	0.99			4.620	1.326	...
Jorgensen <sup>c</sup>	1986	MM/LJ		2.48			3.61		
Woodbridge <i>et al.</i> <sup>d</sup>	1986	MP2	6-31G(2d)	2.3	1.1	1.2	4.161	1.361	3.2
Woon <i>et al.</i> <sup>e</sup>	1990	HF	...	1.59			4.316		
de Oliveira <i>et al.</i> <sup>f</sup>	1995	MP2	[9s6p/3s]	2.01			4.11		5.6
de Oliveira <i>et al.</i> <sup>g</sup>	1996	MM/LJ	...	1.63	0.89	0.74	4.186		
Tsujii <i>et al.</i> <sup>h</sup>	2002	B3LYP	6-311(3d,3p)				4.210		2.3
Hermida-Ramon <i>et al.</i> <sup>i</sup>	2005	MP2	VDZ	1.54			4.094	1.343	7.6
Bhattacharjee <i>et al.</i> <sup>j</sup>	2013	MP2	aVDZ	1.75	0.94	0.81	4.07	1.35	6.7
		MP2	aVTZ	1.75	0.94	0.81	4.08	1.33	6.7
		CCSD	aVTZ	...	...	0.28			
		CCSD(T)	aVTZ			0.59			
		CCSD(T)	CBS			0.97			
Orabi <i>et al.</i> <sup>k</sup>	2014	MP2	CBS[D,T,Q]	1.861					
Alberti <i>et al.</i> <sup>l</sup>	2016	MM/LJ		1.525			3.989	1.269	4.0
		MP2	aVDZ				4.079	1.334	6.7
		CCSD(T)	aVTZ	1.527					
This study		MP2	CBS[D,T,Q]	1.879			4.122	1.3307	5.97
		MP4	CBS[D,T,Q]	1.757			4.146	1.3413	6.04
		CCSD	CBS[D,T,Q]	1.410			4.233	1.3383	6.11
		CCSD(T)	CBS[D,T,Q]	1.687	0.60	1.08	4.167	1.3419	5.84
Lowder <i>et al.</i> <sup>m</sup>	1970	Expt.							1.70 ± 0.31
Ciaffoni <i>et al.</i> <sup>n</sup>	2008	Expt.		1.68 ± 0.02					

<sup>a</sup>Reference 12.<sup>b</sup>Reference 44.<sup>c</sup>Reference 48.<sup>d</sup>Reference 45.<sup>e</sup>Reference 13.<sup>f</sup>Reference 14.<sup>g</sup>Reference 15.<sup>h</sup>Reference 49.<sup>i</sup>Reference 46.<sup>j</sup>Reference 4.<sup>k</sup>Reference 16.<sup>l</sup>Reference 47.<sup>m</sup>Reference 7 (IR).<sup>n</sup>Reference 8 (CEAS/IR).

and 4.080, 4.131, and 4.146 Å in the case of CP-uncorrected results, respectively. Our best estimate CCSD(T)/CBS value for  $r_{SS}$  (4.167 Å) is in relatively poor agreement with the measured value of  $r_{SS}$  for the trimer complex  $(H_2S)_2$ -Ar by Mandal *et al.* (4.053 Å).<sup>41</sup> Argon tagging induces a similar decrease in the interoxygen distance  $r_{OO}$  in the water dimer:  $(H_2O)_2$ -Ar (2.945 Å)<sup>42</sup> vs  $(H_2O)_2$  (2.976 Å),<sup>43</sup> and thus, much of the discrepancy between our CCSD(T) results and those of Mandal *et al.* is likely due the presence of an Ar atom in the experimentally recorded  $(H_2S)_2$  microwave spectrum.

As seen from Table VI, the majority of previous MP2 calculations have produced somewhat scattered results for the intersulfur distance,<sup>39-41</sup> and this is in part due to the relatively small basis sets used in the work by these authors. The most accurate values to date of  $r_{SS}$  for  $(H_2S)_2$  are 4.07 Å (MP2/aVDZ) and 4.08 Å (MP2/aVTZ),<sup>4</sup> and these are in excellent agreement with our MP2 results with maximum deviations on the order of around 0.003 Å; corresponding MP2/aVDZ and MP2/aVTZ SH donor distances  $r_{don.}$  in  $(H_2S)_2$  are 1.35 and 1.33 Å, respectively, and these values are in good agreement

with our MP2 estimates of 1.349 and 1.336 Å. The structure of  $(H_2S)_2$  has also been simulated using Lennard-Jones (LJ) type force fields: for instance,  $(H_2S)_2$  interacting by a LJ(6,12) potential yields a binding energy value of 1.53 kcal/mol and an equilibrium separation  $r_{SS}$  of 3.989 Å,<sup>16</sup> which is considerably shorter than our CCSD(T)/CBS estimate. In contrast, the results from Coulomb-Lennard Jones CLJ(6,12) potential calculations yield a larger binding energy  $D_e$  (1.63 kcal/mol) and extended intersulfur distance  $r_{SS} = 4.186$  Å,<sup>15</sup> values that align more closely with our best CCSD(T)/CBS estimate for  $D_e$  (1.687 kcal/mol) and  $r_{SS}$  (4.167 Å); the error bar listed for the CLJ(6,12) potential calculations is estimated to be around 0.03 kcal/mol; thus, our CCSD(T)/CBS value for  $D_e$  falls just within the small error bracket of the CLJ(6,12) number. Given the good agreement between our CCSD(T)/CBS values of  $D_e$ ,  $r_{SS}$ , and those generated with CLJ(6,12) potentials,<sup>15</sup> it would be interesting to examine if CCSD(T) theory could be applied to calculate geometries and binding energies for larger hydrogen sulfide clusters. For example, the reported MP2/cc-pVDZ binding energies for  $(H_2S)_3$  and  $(H_2S)_4$  are

4.80 and 7.59 kcal/mol, respectively, or 1.60 and 1.89 kcal/mol per hydrogen bond.<sup>46</sup> These values probably represent an overestimation of the true binding energy, and thus, additional MP $n$ /CBS and CCSD(T) level calculations are needed to determine accurate geometries and values of  $D_e$  for (H<sub>2</sub>S)<sub>3</sub>, (H<sub>2</sub>S)<sub>4</sub>, and even larger clusters.

#### IV. CONCLUSIONS

We have examined the structure and binding energies of the hydrogen sulfide dimer with the electron correlation methods MP $n$ , CCSD, and CCSD(T). Using a systematic sequence of a  $VnT$  basis sets with  $n = 2-5$ , (H<sub>2</sub>S)<sub>2</sub> structures and energies have been determined at the CBS limit, without and with CP correction. The results from CBS limit extrapolations of MP $n$ , CCSD, and CCSD(T) reported here are the first accurate set of estimates of the intersulfur distance  $r_{SS}$ , equilibrium dimer binding energies  $D_e$  and  $D_0$  for (H<sub>2</sub>S)<sub>2</sub>. This study finds that MP4 and, in particular, CCSD(T) are the most reliable methods for predicting values of  $r_{SS}$  and  $D_e$  for (H<sub>2</sub>S)<sub>2</sub>. Using a complete basis set extrapolation scheme based on CP-corrected full geometry optimizations and energies for (H<sub>2</sub>S)<sub>2</sub>, we arrive at CBS estimates of  $D_e = 1.687$  kcal/mol and  $r_{SS} = 4.167$  Å with CCSD(T) and  $D_e = 1.757$  kcal/mol and  $r_{SS} = 4.146$  Å with the MP4 method. MP2/CBS calculations yield values of  $D_e$  of 1.879 kcal/mol and a CP-corrected intersulfur distance of 4.099 Å; therefore, MP2 theory moderately overestimates the binding energy, by ~10%, while providing only a marginally shorter (0.07 Å) value of  $r_{SS}$  compared to CCSD(T). Combining our best estimate CCSD(T)/CBS electronic binding energies  $D_e$  with E<sub>ZPE</sub> predicted by CCSD(T) VPT2 calculations yields  $D_0 = 1.08$  kcal/mol, which is around 0.6 kcal/mol smaller than the measured value of  $1.7 \pm 0.3$  kcal/mol. Several important points emerge from the results presented here. First, the MP4, CCSD, and CCSD(T) level binding energies, obtained with and without the use of the CP-corrected PES, converge systematically to the same CBS limit values of  $D_e$ . For example, the CCSD(T)/CBS limit binding energy of  $D_e = 1.689$  kcal/mol is just 0.002 kcal/mol larger than the corresponding CCSD(T)/CBS value that was calculated on the CP-corrected PES ( $D_e = 1.687$  kcal/mol). The same is true at the MP2 level of theory. From Tables II and IV, we see that binding energies calculated at MP2/CBS closely match those obtained on the CP-corrected potential energy surface (1.881 vs 1.879 kcal/mol). As regards the structure of (H<sub>2</sub>S)<sub>2</sub>, MP $n$  and CCSD(T) results all display an irregular convergence behavior, the only exception being the regular convergence behavior of the intersulfur distance  $r_{SS}$  obtained with CCSD. CCSD/CBS values of  $r_{SS}$  obtained on the CP-corrected PES (4.2360 Å) and on the CP-uncorrected CCSD/CBS PES (4.2334 Å) converge to within a few thousandths of an angstrom. Finally, the CCSD(T) binding energy  $D_e$  calculated at the CBS limit on the CP-corrected PES agrees very well with the measured binding energy value of  $1.68 \pm 0.02$  kcal/mol<sup>8</sup> and lies exactly within the error range of the experimental value. These results clearly highlight the level of accuracy that can be obtained provided that high level CCSD(T) calculations with large basis sets are undertaken with the use of the CP-corrected PES.

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