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# ***Ab initio* rovibrational spectroscopy of hydrogen sulfide**

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Potential energy hypersurfaces (PES) have been constructed for the ground electronic state of H<sub>2</sub>S utilizing results from state-of-the-art *ab initio* quantum chemical methods, most notably higher-order coupled cluster theory employing (core-polarized) correlation-consistent basis sets. Small corrections due to extrapolation to the complete basis set and full configuration interaction limits, core correlation, and relativistic corrections, as well as effects beyond the Born–Oppenheimer approximation have been investigated and incorporated into the final PES. Using the exact rovibrational kinetic energy operator rovibrational energy levels have been computed with the different PESs. The final converged *ab initio* PES of this study reproduces the available vibrational band origins of H<sub>2</sub><sup>32</sup>S, HD<sup>32</sup>S, D<sub>2</sub><sup>32</sup>S, and H<sub>2</sub><sup>34</sup>S with maximum deviations, gradually increasing for increased vibrational excitation, of 29(14 300), 10(3800), 7(4600), and 12(6400) cm<sup>−1</sup>, respectively, where the maximum energy above the zero-point energy is given in parentheses. The errors are considerably larger for the bending states than for the stretching states. Reproduction of rotational term values, given explicitly for *J* = 17 of the vibrational ground state, shows remarkable agreement between experiment and the purely *ab initio* approach of this study. © 2001 American Institute of Physics. [DOI: 10.1063/1.1379971]

## **I. INTRODUCTION**

The ground-state potential energy (hyper)surface (PES) of water has traditionally been a testing ground for the myriad theoretical approaches for computing (ro)vibrational eigenstates, resulting in a large number of papers on local (anharmonic force field), semiglobal, and global surfaces.<sup>1–13</sup> The most recent studies, based increasingly on state-of-the-art *ab initio* approaches,<sup>1,3,6,8,11,13</sup> resulted in PESs of unusually high accuracy. To achieve the desired accuracy, small physical effects, readily neglected during most *ab initio* constructions of PESs, such as relativistic phenomena<sup>3,10–12</sup> and non-Born–Oppenheimer effects<sup>1</sup> had to be considered, since they produce changes on the order of a few cm<sup>−1</sup> for the rovibrational eigenstates. This change is within the intrinsic accuracy of the best traditional *ab initio* PESs,<sup>14</sup> which can predict rovibrational eigenstates with an average error on the order of 0.1%. Nevertheless, spectroscopic accuracy for the rovibrational eigenstates is approached only with corrected/fitted semitheoretical<sup>14</sup> surfaces, which can reproduce experimental rovibrational eigenstates with an average error on the order of 0.1 cm<sup>−1</sup>. It has also been learned during these high-quality first-principles spectroscopic studies that while fitted surfaces interpolate excellently, their extrapolation characteristics are usually worse than those of the best purely *ab initio* surfaces. This means that it appears to be worth pushing *ab initio* methodologies to technical limits. As an application of highly accurate PESs we note that the best

semitheoretical surfaces have been employed to generate rovibrational line lists<sup>6,15,16</sup> up to 700 million entries for water, which has been used to model spectra of cool stars.<sup>15,16</sup>

The ground electronic state PES of hydrogen sulfide, H<sub>2</sub>S, the congener of H<sub>2</sub>O, also received considerable attention, especially during the 1990s.<sup>17–32</sup> This interest is due to drastically increased spectroscopic capabilities for detecting higher-lying stretching, bending, and rotational states of H<sub>2</sub>S and of its isotopomers,<sup>23,32</sup> to subsequent questions of normal mode versus local mode character of vibrational overtones,<sup>24</sup> to publicity over the fourfold clustering effects of high-*J* rotational lines,<sup>19</sup> to anomalies in the intensities of certain vibrational band origins (VBOs) of H<sub>2</sub>S,<sup>27,33,34</sup> to the important role the H<sub>2</sub>S molecule plays in the physics and chemistry of the interstellar medium and the atmospheres of planets and cool stars,<sup>16</sup> and last but not least to the role H<sub>2</sub>S plays as a fertile testing ground for PES constructions advanced for water.<sup>6,11,13,17</sup> The available semiglobal analytical representations of the ground-state PES of H<sub>2</sub>S contain some extrapolation into regions of no or limited experimental data, such as the region around linearity. Sizable differences, ranging from 18 792 cm<sup>−1</sup> (Ref. 17) to 22 821 cm<sup>−1</sup> (Ref. 18), between reported literature values calculated from empirical and (semi)theoretical PESs can be observed for the barrier to linearity. It is also notable that none of the available PESs, except the most recent one,<sup>27</sup> give a substantially shorter *r*(S–H) at linearity than at equilibrium, which is in contrast to expectation and results of sophisticated *ab initio* calculations.<sup>25</sup> Furthermore, as Fig. 1 of Ref. 25 demonstrates, farther away from equilibrium the different PES representations behave rather differently and the otherwise high-

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quality hypersurfaces due to Polyansky, Jensen, and Tennyson<sup>17</sup> (henceforth PJT) and Senekowitsch, Carter, Zilch, Werner, Handy, and Rosmus<sup>21</sup> (henceforth SCZWHR) show unphysical behavior at large S–H bond lengths and small HSH bond angles. These problems with the available PES representations also call for a re-examination of the ground-state PES of H<sub>2</sub>S.

The computed *ab initio* PESs determined in this study are judged through comparison of first-principles rovibrational eigenstates with their experimental counterparts. For this, representation of the ground-state PES of H<sub>2</sub>S needs to be reliable only at relatively low energies (up to about 20 000 cm<sup>−1</sup> above the minimum, which is still below the barrier to linearity,<sup>25</sup> 24 420 cm<sup>−1</sup>). This and the character of the ground electronic state of H<sub>2</sub>S mean that sophisticated and efficient single-reference techniques are suitable for the electronic structure computations. We decided to use the coupled cluster with singles, doubles, and corrected triples [CCSD(T)] approach<sup>35</sup> as our computational workhorse, which has proved to be reliable at predicting equilibrium properties and lower regions of PESs for a wide range of molecules.<sup>36</sup> This choice allows the use of extended basis sets during the calculations. Therefore, we investigated the performance of the correlation-consistent (cc) family of basis sets<sup>37</sup> for the prediction of PESs judged through the quality of the rovibrational levels predicted by them. Use of the cc basis sets allows efficient extrapolation to the complete basis set (CBS) limit<sup>38–43</sup> and thus testing of the CBS CCSD(T) PES. Extrapolation of CCSD(T) correlation energies to the full configuration interaction (FCI) limit is attempted through the scaled higher-order correlation (SHOC) approach,<sup>44</sup> resulting in a valence-only CBS FCI PES, an important result of this study. A further important goal is to investigate the effect of small energy correction terms, namely the relativistic and the Born–Oppenheimer diagonal correction (BODC) on the shape of the ground-state PES of H<sub>2</sub>S and on the accuracy of the resulting rovibrational eigenstates. Overall, this study is aimed to investigate how accurate an *a priori* (first-principles) approach (i.e., combined use of pure and converged electronic structure theory for the computation of the PES and an “exact” variational approach for prediction of rovibrational states) can be. Establishing a PES of spectroscopic quality for the ground electronic state of H<sub>2</sub>S is also kept in mind in this work, though empirical refinement of the *ab initio* PES of H<sub>2</sub>S is not attempted here.

## II. COMPUTATIONAL DETAILS

### A. *Ab initio* methods

The electronic structure computations reported in this paper have been performed with the DIRCCR12-95,<sup>45,46</sup> ACES II,<sup>47</sup> PSI,<sup>48</sup> BERTHA,<sup>49,50</sup> and DALTON<sup>51</sup> program systems.

As mentioned in the Introduction, neglect of high-energy points of the PES during this study has a particular advantage for the *ab initio* calculations: it allows the use of efficient and robust single-reference techniques. In this study most electronic structure calculations utilized the coupled cluster (CC) method including all singles and doubles

(CCSD),<sup>52,53</sup> as well as an estimate of the effect of connected triple excitations through a perturbative term [CCSD(T)]<sup>35</sup> for which reference wave functions have been determined by the single-configuration restricted Hartree–Fock (RHF) method.<sup>53,54</sup> In valence-only correlated-level calculations the 1*s*, 2*s*, and 2*p* core orbitals of S were kept doubly occupied. No virtual molecular orbitals were frozen in any of the correlation treatments.

The basis sets chosen for the calculations include the correlation-consistent (aug)-cc-pVXZ [*X*=3(T), 4(Q), 5] families of basis sets developed by Dunning and co-workers.<sup>37,55</sup> To cover the core polarization effect,<sup>56</sup> which proved to be sizable during the determination of the barrier to linearity of H<sub>2</sub>S,<sup>25</sup> the correlation-consistent basis sets aug-cc-pVXZ with *X*=T and Q on S have been augmented by a tight *d* function, whose exponent was taken to be the same as the tightest *d* function exponent in the aug-cc-pV5Z basis of S (3.203). The resulting basis sets are denoted as aug-cc-pVXZ+*d*. This choice for the core polarization function effectively means that the aug-cc-pV5Z and aug-cc-pV5Z+*d* basis sets are identical.

Extrapolation of RHF and correlation energies to the complete basis set (CBS) limit has been achieved through the relations<sup>38–41,43</sup>

$$E^X = E_{\text{CBS}} + a \exp(-bX) \quad (1)$$

and

$$E^X = E_{\text{CBS}} + cX^{-3}, \quad (2)$$

respectively, where  $E_{\text{CBS}}$  is the extrapolated energy,  $E^X$  denotes energies obtained from correlation-consistent-type basis sets with cardinal number *X*, while *a*, *b*, and *c* are fitting constants. In the study<sup>25</sup> on the barrier to linearity of H<sub>2</sub>S it became clear that extrapolation of the original aug-cc-pVXZ RHF energies is meaningless, these basis sets must be augmented with core polarization functions, i.e., with at least one tight *d* function. Therefore, for extrapolation of the RHF energies the aug-cc-pVXZ+*d* [*X*=3(T), 4(Q), 5] basis set results have been employed. The CBS CCSD and CCSD(T) correlation energies have been determined using correlation energies obtained with basis sets aug-cc-pVXZ+*d* with *X*=4 and 5.

The computational error in our *ab initio* calculations arises not only due to truncation of the atomic orbital (AO) basis set (one-electron space) but also due to truncation of the *n*-electron space of all Slater determinants that constitute the full configuration interaction (FCI) wave function. In order to obtain the best technically possible results, one must advance electronic structure calculations to both the one- and *n*-particle space limits. Therefore, using the SHOC approach<sup>44</sup> an attempt is made here to arrive at the CBS FCI limit from CBS CCSD(T) energies. A single, average scale factor of 1.004 45 was determined, based on calculations at six geometries,<sup>11</sup> for scaling cc-pVDZ CCSD(T) correlation energies to the FCI limit. A very similar value, 1.004 50 can be determined using only two points, those determining the barrier to linearity of H<sub>2</sub>S. This means that our valence-only CBS CCSD(T) energies can be scaled by adjusting the valence-only CBS CCSD(T) barrier to the valence-only CBS

FCI barrier determined in Ref. 25. A scale factor of 1.004 45 has been obtained this way and this scale factor has been used to scale the valence-only CCSD(T) correlation energies.

Three principal corrections to the valence-only electronic energies have been considered in this study: (a) core-valence effects,<sup>57–59</sup> which result in an improved estimate of the nonrelativistic PES of H<sub>2</sub>S; (b) relativistic effects,<sup>60–63</sup> which proved to be surprisingly large for water<sup>3,10–12</sup> and therefore are tested here again; and (c) a term resulting in isotope-dependent potential energy hypersurfaces, the Born–Oppenheimer diagonal correction (BODC).<sup>64</sup>

In our study<sup>25</sup> on the barrier to linearity of H<sub>2</sub>S it became clear that (a) the core correlation contribution to the barrier to linearity is smaller or comparable to the core polarization effect; and (b) the core correlation correction is rather sensitive to the level of theory applied for its calculation; in particular, only CCSD(T) corrections seem to be dependable. In order to investigate core correlation, traditional basis sets designed to describe bonding involving valence electrons must be augmented with tight (high exponent) Gaussian functions able to describe the core region adequately.<sup>58,59</sup> Such basis sets, denoted as (aug)-cc-pCVXZ for first-row atoms, are not available for sulfur from Ref. 55. To construct basis sets able to describe core–core and core–valence correlation, we completely uncontracted the (aug)-cc-pVXZ basis sets for H and S and then augmented the sulfur sets with a tight *2d 2f* set for *X*=T and a tight *3d 2f 2g* set for *X*=Q, whose exponents were obtained by even-tempered extension into the core with a geometric ratio of 3. The resulting basis sets are denoted here simply as aug-CVTZ and CVQZ+*d*. The core correlation effect has been computed at both the aug-CVTZ and CVQZ+*d* CCSD(T) levels but only the CVQZ+*d* CCSD(T) results are reported here.

Recent computational studies<sup>3,11–13</sup> on the rovibrational spectra of water indicated that nonrelativistic PESs are not sufficient to reproduce experimentally observed VBOs and rotational term values. The largest relativistic correction comes from the scalar one-electron mass-velocity and Darwin (MVD1) term.<sup>3</sup> Nevertheless, influence of the two-electron Darwin term<sup>12</sup> and effects not treated at the Dirac–Coulomb level, namely the Gaunt/Breit interaction<sup>12,49,61</sup> and the largest part of the QED correction, the radiative Lamb-shift effects,<sup>10,61</sup> can be substantial, at least at the level of precision sought in the ultimate *ab initio* PES determinations. Our study<sup>25</sup> of the barrier to linearity of H<sub>2</sub>S proved that the D2 and ΔDPT terms of the lowest order of the direct perturbation theory (DPT) approach of Kutzelnigg<sup>62,63</sup> contribute to the relative relativistic corrections by less than 2%. Therefore, to decrease the computational expense, and keeping in mind the remaining uncertainties in the nonrelativistic treatment, in the results reported here only the one-electron mass-velocity (MV) and Darwin (D1) terms, collectively termed MVD1, have been considered. These calculations utilized all-electron aug-CVTZ CCSD(T) wave functions. The relativistic energy correction determined in this study for H<sub>2</sub>S,  $-1.11 E_h$ , is almost completely attributable to the core electrons of the sulfur atom.

The Born–Oppenheimer diagonal corrections to the PES have been determined at the aug-TZ2Pf RHF level employ-

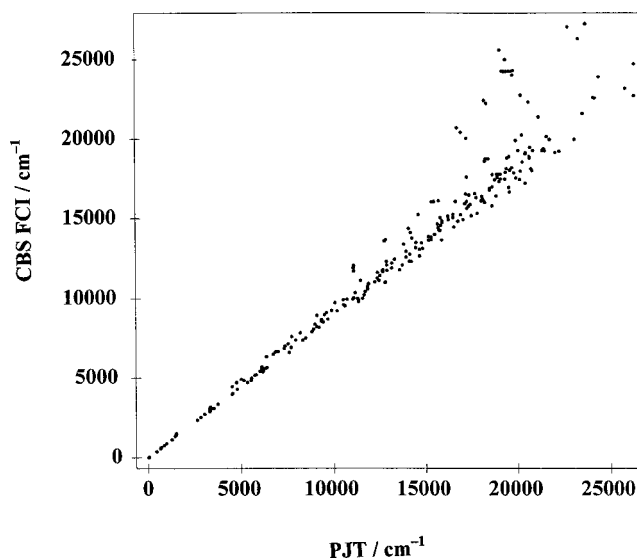


FIG. 1. Comparison of energies computed from the Polyansky–Jensen–Tennyson (PJT) potential energy hypersurface (Ref. 17) with the CBS CCSD(T) energies of this study (258 points corresponding to the grid of this study).

ing the program BORN within the PSI2.0 package.<sup>48</sup> These calculations result in mass-independent terms which can be scaled with the proper masses to obtain BODC values for any isotopomer.

## B. Selection of grid points

To reduce the number of reference (grid) points for the PES calculation, the energies corresponding to grid points around  $\{r_1/\text{\AA}, r_2/\text{\AA}, \alpha_{\text{HSH}}/\text{degree}\} = \{1.4, 1.4, 90\}$  with 0.1 Å (1 Å =  $10^{-10}$  m) and 20° increments were first calculated from the empirical analytical PJT<sup>17</sup> PES and the less important, high-energy points, those above 20 000 cm<sup>-1</sup>, have been skipped. The final points considered for the determination of the PES of H<sub>2</sub>S are contained in a grid defined by  $r_{\text{SH}} = \{0.9\text{--}2.2 \text{\AA}, \text{increment } 0.1 \text{\AA}\}$  and  $\alpha_{\text{HSH}} = \{40^\circ, 60^\circ, 80^\circ, 90^\circ, 100^\circ, 120^\circ, 140^\circ, 160^\circ, 180^\circ\}$ . Since the PJT potential values underestimate the present high-quality *ab initio* energies in a systematic way, leading to larger and larger underestimations as one moves up in energy (see Fig. 1), this choice effectively means that our *ab initio* points cover the PES up to about 25 000 cm<sup>-1</sup> for at least the bending region. This set of grid points has arbitrarily been augmented by a few points selected in the PJT energy region 20 000–25 000 cm<sup>-1</sup>, a few more around the equilibrium structure and around the linear stationary point. These latter points were included to effectively fix the structures of the nonasymptotic stationary points on the ground-state PES of H<sub>2</sub>S. Overall, this procedure resulted in 258 symmetry-unique reference structures. The selection of the grid points and all the *ab initio* data are available as supplementary material.<sup>65</sup>



### C. Analytic representation of the PES

Although feasible complementary strategies started to appear,<sup>66</sup> the most straightforward way to utilize the calculated *ab initio* energy points for rovibrational energy level calculations is to fit a suitable analytical form to them.

During the course of this study several popular analytical fitting functions have been tested, including those of Jensen,<sup>67</sup> employed by PJT,<sup>17</sup> and the form advocated by De Oliveira and Dykstra.<sup>68</sup> These studies clearly confirmed the following observations of Partridge and Schwenke (PS)<sup>6</sup> and others<sup>3,69</sup> about the Jensen form of the potential utilized by PJT: (a) it cannot describe dissociation properly (not that the PS form employed would be perfect in this sense, *vide infra*); (b) at short HH distances (small bond angles) it does not give<sup>69</sup> a reasonable representation of the potential; and (c) during the fitting we also observed an insurmountable difficulty in obtaining a smooth globally acceptable fit with a reasonable number of low-order expansion coefficients. Furthermore, while the simple form advocated by De Oliveira and Dykstra<sup>68</sup> performs well for water, it did not give an acceptable analytic representation for H<sub>2</sub>S. Finally, a slightly modified form of the PS potential,<sup>6</sup> employed for H<sub>2</sub>O, was chosen for the analytic representation of the electronic energies of H<sub>2</sub>S, as follows:

$$\begin{aligned}
 V(r_1, r_2, \theta) = & \sum_{i=1,2} D \{ \exp[-2a(r_i - r_e)] \\
 & - 2 \exp[-a(r_i - r_e)] \} + A \exp(-br_{\text{HH}}) \\
 & + \exp\{-\beta[(r_1 - r_e)^2 + (r_2 - r_e)^2]\} \\
 & \times \sum_{i,j,k} c_{ijk} [(r_1 - r_e)/r_e]^i [(r_2 - r_e)/r_e]^j \\
 & \times (\cos \theta - \cos \theta_e)^k, \quad (3)
 \end{aligned}$$

where  $r_i$  are the SH bond lengths,  $\theta$  is the HSH bond angle,  $r_{\text{HH}}$  is the HH distance (related to  $r_1$ ,  $r_2$ , and  $\theta$ ), and the indices  $i$ ,  $j$ , and  $k$  start from 0 and selectively may go up to 8 (consequently,  $V$  contains a term  $c_{000}$ ). The parameters  $A$ ,  $D$ ,  $a$ ,  $b$ ,  $\beta$ ,  $r_e$ ,  $\theta_e$ , and the symmetry-constrained  $c_{ijk}$  in Eq. (1) have been determined through nonweighted nonlinear and linear least-squares fits to the selected *ab initio* energies, taking advantage of the fact that the only nonlinear parameters in the above form of  $V$  are  $r_e$ ,  $\theta_e$ ,  $a$ ,  $b$ , and  $\beta$ . A further advantage of the above form is that in the simplified case of linear fitting well-defined standard errors can be obtained for the parameters. If these standard errors proved to be larger than the parameter itself for all *ab initio* electronic energy sets investigated, the  $c_{ijk}$  constant was eliminated from the fitting cycles. Although the fit was unweighted, the extra points about equilibrium acted to give extra weight to this region of the potential. The final form of  $V$  contains 72 parameters. The computer algebra package *Mathematica*<sup>70</sup> has extensively been employed for handling of the *ab initio* data, for refinement of the potential, for its graphical representation, and for generation of the FORTRAN code representing the potential and needed for the nuclear motion calculations. The FORTRAN codes representing the individual potentials are available as supplementary material.<sup>65</sup>

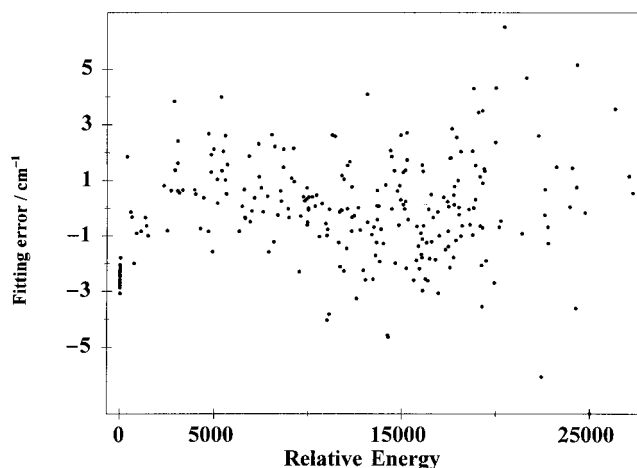


FIG. 2. Fitting error of the aug-cc-pV5Z CCSD(T) electronic energies as a function of the relative energy of the grid points (in cm<sup>-1</sup>) taking the equilibrium as the energy zero.

Analytical PESs have been fitted to electronic energy sets aug-cc-pVXZ +  $d$  CCSD(T) with  $X=3, 4$ , and  $5$ , as well as to aug-CVTZ CCSD(T). Previous studies<sup>2,6</sup> have found it preferable to fit the *ab initio* points as accurately as possible. With 72 parameters we could fit the *ab initio* energy points with an average deviation of less than 2 cm<sup>-1</sup>. In Figs. 2 and 3 we show selected aspects of the fit. Figure 2 shows the fitting error of the CBS CCSD(T) energies as a function of the relative energy of the points taking the equilibrium as the energy zero. Due to the nonweighted nature of the fit the low-energy points are deliberately not fitted much better than the high-energy points but the overall quality of the fit is reassuring. In Fig. 3 we show a contour plot of the fitted extrapolated [CBS CCSD(T)] PES for symmetric geometries, along with points showing the *ab initio* grid. At this point it is worth comparing geometries of the two station-

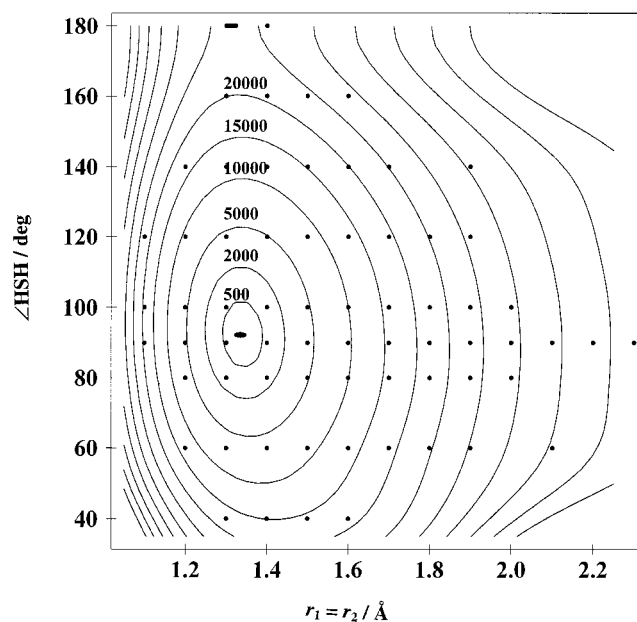


FIG. 3. Contour plot of the CBS CCSD(T) PES for symmetric geometries along with the points showing the *ab initio* grid.

any points (equilibrium,  $C_{2v}$ , and linear,  $D_{\infty h}$ ) of the fitted surfaces with results of direct *ab initio* geometry optimizations. For the equilibrium structures the (distance/Å, angle/degree) deviations are (0.000 10, 0.050) for  $X=3$ . Therefore, despite the fact that a rather coarse grid has been chosen for this study, the fitted potentials provide an excellent representation of the *ab initio* surfaces.

The analytic functional form

$$V(S_1, S_2, S_3) = \sum_{i,j,k} c_{i,j,k} S_1^i S_2^j S_3^k \quad (4)$$

has been employed to fit the core correlation (CV), relativistic (REL), and the BODC corrections to the energies, where the  $S$  symmetrized displacement coordinates are defined as  $S_1 = \frac{1}{2}(r_1 + r_2) - r_e$ ,  $S_2 = \cos(\theta) - \cos(\theta_e)$ , and  $S_3 = \frac{1}{2}(r_1 - r_2)$ , and  $(r_e, \theta_e)$  are equilibrium geometric parameters taken to be (1.3378 Å, 92.311°), close to the equilibrium values characterizing the extrapolated potential. All terms up to fifth order,  $i+j+k \leq 5$ , were retained in the expansion, while selected terms, up to  $i+j+k \leq 8$ , which proved well determined, were also retained. The only significant eighth-order terms retained were  $(ijk) = (080)$ ,  $(260)$ , and  $(062)$ . The 52 coefficients resulting from a linear least-squares fit to our data set for the CV, REL, and the BODC correction potentials can be extracted from the FORTRAN subroutines given as supplementary material.<sup>65</sup> Certain characteristics of the core–valence and relativistic correction surfaces are shown in Figs. 4(a) and 4(b), respectively.

#### D. Nuclear motion calculations

The rovibrational energy states have been determined using an exact kinetic energy (EKE) operator expressed in Radau coordinates augmented with the fitted *ab initio* PESs. The calculations utilized the discrete variable representation (DVR) technique<sup>71</sup> as implemented in the code DVR3D.<sup>72</sup> The masses employed in the calculations include atomic masses, nuclear masses, and a hydrogenic mass midway between the atomic and nuclear values, as recommended by Zobov *et al.*<sup>1</sup> for water. Optimization of the basis sets has been performed for the  $J=0$  states (vibrational band origins, VBOs). Similarly to Ref. 17, it was found optimal to use 28 symmetrized DVR grid points in each radial coordinate, 49 DVR grid points for the angular coordinate, and altogether 1000 basis functions for all  $J=0$  and  $J>0$  calculations. The Morse parameters  $D_e = 0.25 E_h$ ,  $r_e = 1.89$  bohrs, and  $\omega_e = 0.007 E_h$  have been employed for the Morse-type stretching bases. For the bending basis associated Legendre polynomials have been chosen. The  $J>0$  rovibrational states have been determined by the Tennyson–Sutcliffe two-step procedure<sup>73</sup> as implemented in the DVR3D and the ROTLEV3B codes.<sup>72</sup> The same results have been obtained using symmetrized and unsymmetrized coordinates.

#### III. RESULTS FOR ROVIBRATIONAL ENERGY LEVELS

Several valence-only potential energy hypersurfaces (PESs) have been determined at the CCSD(T) level as part of this study, those with basis sets aug-cc-pVTZ+ $d$ , aug-cc-pVQZ+ $d$ , and aug-cc-pV5Z are explicitly reported

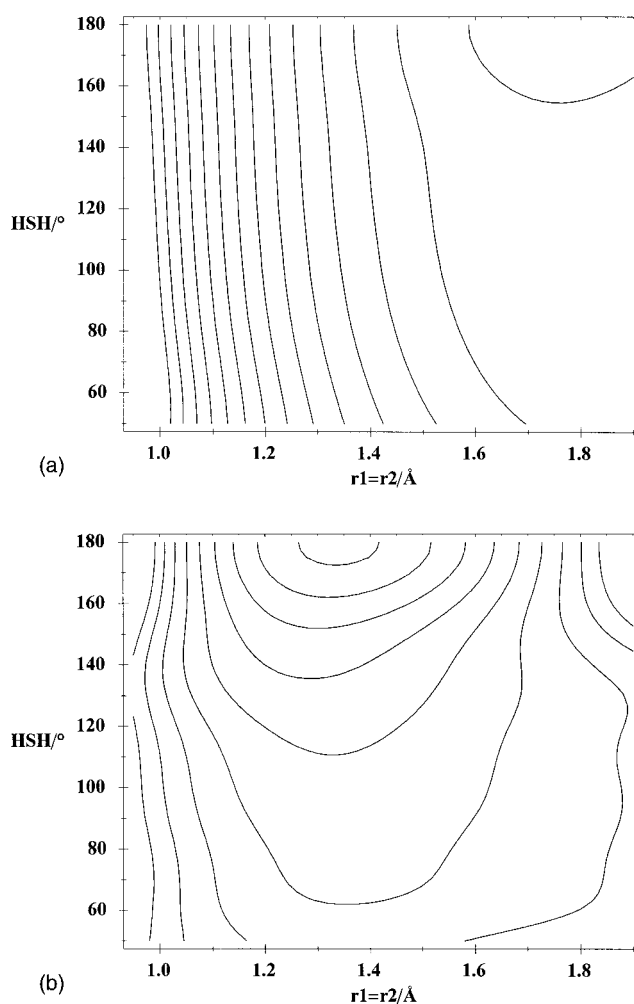


FIG. 4. Variation of the core–valence (a) and the relativistic (b) correction surfaces as a function of the symmetric stretching,  $r_1/\text{Å} = r_2/\text{Å}$ , and the bending,  $\angle\text{HSH}/\text{degree}$ , motions (contour levels every 50  $\text{cm}^{-1}$ ).

in this paper. Another surface, denoted as CBS CCSD(T), results when the electronic energies obtained with the finite basis sets are extrapolated to the complete basis set (CBS) limit. The highest quality valence-only PES is denoted as CBS FCI and is obtained when the CBS CCSD(T) correlation energies are scaled, using a single SHOC scale factor, to the FCI limit. All these surfaces can, in principle, be augmented with the core–valence (CV, C in Tables I and II), the relativistic (REL, R in Tables I and II), and the Born–Oppenheimer diagonal corrections (BODC, D in Tables I and II). Nevertheless, vibrational band origins (VBOs) and rotational energy levels obtained only with the doubly extrapolated CBS FCI PES are reported. VBOs calculated employing the above PESs are given in Table I for all levels for which experimental assignments are known to us. Data presented in Table II reveal the performance of the *ab initio* PESs for prediction of the  $J=17$  rotational levels, all observed experimentally, of the (000) vibrational state of H<sub>2</sub><sup>32</sup>S. Table III summarizes our analysis of the core–valence energy correction. Table IV contains VBOs obtained with the final *ab initio* PES (CBS FCI+CV+REL+BODC) for H<sub>2</sub><sup>32</sup>S employing atomic masses, nuclear masses, and a hydrogenic mass midway between the atomic and nuclear

TABLE I. Differences between observed (Obs.) and different computed vibrational band origins (in  $\text{cm}^{-1}$ ) for  $\text{H}_2^{32}\text{S}$ .<sup>a</sup>

Label <sup>b</sup>	Obs	CCSD(T)				FCI CBS	FCI CBS		
		T	Q	5	CBS		+C	+CR	+CRD
010/00 <sup>+</sup> 1	1182.57	+0.2	+1.7	+1.7	+2.0	+2.5	+0.3	-0.4	-0.1
020/00 <sup>+</sup> 2	2353.96	-5.3	-2.3	-2.1	-1.5	-0.5	-4.7	-6.2	-5.9
100/10 <sup>+</sup> 0	2614.14	+5.0	-0.9	-1.8	-2.6	-1.9	-6.9	-2.5	-2.1
001/10 <sup>-</sup> 0	2628.46	+6.0	-0.2	-1.3	-2.3	-1.7	-7.0	-3.0	-2.5
030/00 <sup>+</sup> 3	3513.79	-11.1	-6.5	-6.1	-5.2	-3.7	-9.8	-11.9	-11.9
110/10 <sup>+</sup> 1	3779.17	+4.6	-0.0	-0.8	-1.2	-0.0	-7.2	-3.4	-2.6
011/10 <sup>-</sup> 1	3789.27	+5.9	+0.9	-0.1	-0.9	0.2	-7.3	-3.8	-3.1
040/00 <sup>+</sup> 4	4661.68	-14.0	-7.7	-7.2	-6.0	-3.9	-11.9	-14.5	-14.7
120/10 <sup>+</sup> 2	4932.70	-1.9	-5.1	-5.7	-5.9	-4.1	-13.2	-10.1	-9.4
021/10 <sup>-</sup> 2	4939.10	+0.1	-3.5	-4.5	-5.0	-3.3	-12.8	-10.0	-9.3
200/20 <sup>+</sup> 0	5144.99	+10.2	-3.0	-4.9	-6.6	-5.1	-15.2	-6.8	-5.9
101/20 <sup>-</sup> 0	5147.22	+10.8	-2.5	-4.5	-6.3	-4.8	-15.0	-6.6	-5.7
002/11 <sup>+</sup> 0	5243.10	+10.7	-1.7	-3.6	-5.4	-4.0	-14.4	-6.0	-5.1
050/00 <sup>+</sup> 5	5797.24	-12.7	-4.8	-4.1	-2.6	0.0	-10.0	-12.7	-13.1
130/10 <sup>+</sup> 3	6074.58	-7.7	-9.6	-10.0	-9.8	-7.5	-18.5	-15.9	-15.5
031/10 <sup>-</sup> 3	6077.60	-5.5	-7.8	-8.7	-8.9	-6.6	-18.0	-15.8	-15.3
210/20 <sup>+</sup> 1	6288.15	+9.5	-2.7	-4.6	-6.0	-4.0	-16.2	-8.3	-7.1
111/20 <sup>-</sup> 1	6289.17	+10.0	-2.2	-4.2	-5.7	-3.7	-16.0	-8.1	-7.0
012/11 <sup>+</sup> 1	6388.10	+12.7	1.4	-0.4	-1.9	0.1	-12.4	-4.6	-3.4
121/20 <sup>-</sup> 2	7420.09	+3.1	-7.9	-9.8	-11.0	-8.4	-22.6	-15.3	-14.1
102/30 <sup>+</sup> 0	7576.38	+16.1	-5.5	-8.7	-11.5	-9.1	-24.0	-11.5	-10.3
201/30 <sup>-</sup> 0	7576.55	+16.3	-5.4	-8.6	-11.4	-9.0	-23.9	-11.5	-10.2
300/21 <sup>+</sup> 0	7752.26	+14.2	-5.1	-7.9	-10.2	-7.9	-22.9	-10.1	-8.6
003/21 <sup>-</sup> 0	7779.32	+16.3	-3.5	-6.6	-9.3	-7.1	-22.8	-10.4	-9.2
112/30 <sup>+</sup> 1	8697.14	+14.8	-6.0	-9.1	-11.7	-8.7	-25.8	-13.8	-12.2
211/30 <sup>-</sup> 1	8697.16	+14.8	-6.1	-9.2	-11.8	-8.8	-25.8	-13.8	-12.2
202/40 <sup>+</sup> 0	9911.02	+22.7	-8.3	-13.1	-17.2	-13.8	-33.3	-16.9	-15.2
301/40 <sup>-</sup> 0	9911.02	+22.7	-8.3	-13.1	-17.2	-13.8	-33.3	-16.9	-15.2
400/31 <sup>+</sup> 0	10 188.30	+14.6	-8.1	-12.0	-15.4	-12.2	-32.0	-15.2	-13.3
103/31 <sup>-</sup> 0	10 194.45	+6.6	-7.2	-11.3	-14.9	-11.7	-31.8	-15.1	-13.3
212/40 <sup>+</sup> 1	11 008.68	+20.8	-9.7	-14.4	-18.4	-14.4	-36.1	-20.0	-18.0
311/40 <sup>-</sup> 1	11 008.68	+20.7	-9.7	-14.5	-18.4	-14.4	-36.1	-20.0	-18.0
302/50 <sup>+</sup> 0	12 149.46	+30.4	-11.0	-17.6	-23.4	-18.9	-42.9	-22.6	-20.5
203/50 <sup>-</sup> 0	12 149.46	+30.4	-11.0	-17.6	-23.4	-18.9	-42.9	-22.6	-20.5
024/22 <sup>+</sup> 2	12 481.88	+11.0	-14.6	-18.4	-21.4	-17.2	-41.4	-25.4	-23.3
104/41 <sup>+</sup> 0	12 524.63	+26.6	-10.8	-16.3	-21.0	-16.9	-41.4	-20.7	-18.4
401/40 <sup>-</sup> 1	12 525.20	+26.9	-10.8	-16.3	-21.0	-16.8	-41.3	-20.6	-18.4
/50 <sup>+</sup> 2	14 285.07	+31.5	-17.2	-24.4	-30.3	-24.6	-52.7	-32.4	-30.0
/50 <sup>-</sup> 2	14 285.07	+31.5	-17.2	-24.4	-30.4	-24.6	-52.7	-32.4	-30.0
/60 <sup>+</sup> 0	14 290.75	+27.8	-16.4	-25.0	-32.4	-26.7	-54.3	-31.7	-29.3
/60 <sup>-</sup> 0	14 290.75	+27.8	-16.4	-25.0	-32.7	-27.0	-55.4	-31.7	-29.3

<sup>a</sup>All calculated values are reported as observed-calculated. Abbreviations employed for the PESs: T=aug-cc-pVTZ+*d*; Q=aug-cc-pVQZ+*d*; 5=aug-cc-pV5Z; CBS=complete basis set; FCI=full configuration interaction; +C=+core-valence (C) correction; +CR=+C+relativistic correction (MVD1); +CRD=+C+R+Born-Oppenheimer diagonal correction (BODC). Atomic masses are used throughout.

<sup>b</sup>Normal mode ( $v_1v_2v_3$ )/local mode [ $v_{r_1}v_{r_2}v_\theta \equiv mn^\pm v_2$ , with  $m(n)$ ,  $m \geq n$ , denoting a wave function with  $m(n)$  excited quanta in the  $r_1(r_2)$  oscillator and, consequently,  $m(n)$  nodes, and  $\pm$  denoting states of  $A_1/B_2$  symmetry of the molecular symmetry group  $C_{2v}(M)$ ] labeling.

<sup>c</sup>Observed VBOs are taken from Refs. 19, 24(b), and 32.

values. In Table V, VBOs obtained using atomic masses, for the isotopomers  $\text{D}_2^{32}\text{S}$ ,  $\text{HD}^{32}\text{S}$ , and  $\text{H}_2^{34}\text{S}$  are reported using the best mass-independent BO surface, as well as the mass-dependent BODC-corrected adiabatic surfaces.

### A. Valence-only calculations

As discussed in some detail in Ref. 25, augmentation of the original (aug)-cc-pVXZ basis sets of Dunning and co-workers<sup>37,55</sup> with tight polarization functions is necessary in order to obtain reliable RHF energies over the PES of  $\text{H}_2\text{S}$ . In this study we added one tight *d* function to the aug-

cc-pVTZ and aug-cc-pVQZ basis sets on S; these augmented basis sets are shown by the T and Q symbols under CCSD(T) of Table I. It is clear from the data presented in Table I that extension of the correlation-consistent basis set [ $X=3(\text{T})$ ,  $4(\text{Q})$ ,  $5$ , and  $\infty(\text{CBS})$ ] shifts the VBOs very systematically. As expected, the least accurate results are obtained with  $X=3$ . Unevenness of the reproduction of the experimental VBOs is also characteristic at this level of theory. It is also not surprising to find that the  $X=4$  results [aug-cc-pVQZ+*d* CCSD(T)] have the smallest mean deviation. This fact is the result of a fortuitous error cancellation (use of finite one-

TABLE II. Rotational term values (in cm<sup>−1</sup>) for the vibrational ground state of H<sub>2</sub><sup>32</sup>S.<sup>a</sup>

Label <sup>b</sup>	Obs.	CCSD(T)				FCI CBS	FCI CBS		
		T	Q	5	CBS		+C	+CR	+CRD
17 <sub>0,17</sub>	1524.49	6.83	5.71	4.96	4.44	4.58	−0.63	−0.60	−0.23
17 <sub>1,17</sub>	1524.49	6.83	5.71	4.96	4.44	4.58	−0.63	−0.60	−0.23
17 <sub>1,16</sub>	1683.75	7.54	6.31	5.48	4.90	5.06	−0.70	−0.67	−0.26
17 <sub>2,16</sub>	1683.75	7.54	6.32	5.48	4.90	5.06	−0.70	−0.67	−0.25
17 <sub>2,15</sub>	1831.34	8.21	6.88	5.98	5.35	5.52	−0.75	−0.72	−0.26
17 <sub>3,15</sub>	1831.34	8.20	6.88	5.97	5.35	5.52	−0.75	−0.72	−0.27
17 <sub>3,14</sub>	1967.71	8.80	7.40	6.43	5.76	5.94	−0.78	−0.77	−0.27
17 <sub>4,14</sub>	1967.72	8.81	7.41	6.44	5.77	5.95	−0.77	−0.76	−0.26
17 <sub>4,13</sub>	2093.24	9.37	7.91	6.89	6.18	6.37	−0.78	−0.79	−0.26
17 <sub>5,13</sub>	2093.22	9.35	7.89	6.87	6.16	6.35	−0.80	−0.81	−0.27
17 <sub>5,12</sub>	2208.13	9.86	8.36	7.29	6.56	6.75	−0.79	−0.84	−0.26
17 <sub>6,12</sub>	2208.15	9.87	8.38	7.31	6.57	6.77	−0.78	−0.82	−0.25
17 <sub>6,11</sub>	2312.61	10.32	8.81	7.71	6.95	7.15	−0.75	−0.85	−0.24
17 <sub>7,11</sub>	2312.62	10.32	8.81	7.71	6.95	7.15	−0.75	−0.85	−0.24
17 <sub>7,10</sub>	2406.69	10.73	9.26	8.13	7.35	7.55	−0.68	−0.86	−0.21
17 <sub>8,10</sub>	2406.72	10.72	9.24	8.10	7.32	7.53	−0.70	−0.88	−0.23
17 <sub>8,9</sub>	2490.12	11.10	9.74	8.59	7.81	8.01	−0.54	−0.87	−0.17
17 <sub>9,9</sub>	2490.49	11.11	9.69	8.54	7.74	7.95	−0.59	−0.87	−0.18
17 <sub>9,8</sub>	2561.68	11.51	10.46	9.34	8.57	8.75	−0.12	−0.77	0.00
17 <sub>10,8</sub>	2564.16	11.45	10.09	8.92	8.12	8.32	−0.49	−0.87	−0.14
17 <sub>10,7</sub>	2617.72	11.96	11.56	10.52	9.82	9.94	0.73	−0.55	0.32
17 <sub>11,7</sub>	2629.26	11.72	10.29	9.08	8.25	8.46	−0.55	−0.91	−0.16
17 <sub>11,6</sub>	2658.75	12.22	12.04	11.02	10.33	10.43	1.02	−0.48	0.44
17 <sub>12,6</sub>	2689.62	11.89	10.08	8.79	7.90	8.15	−0.98	−1.03	−0.32
17 <sub>12,5</sub>	2699.41	12.17	11.10	9.91	9.10	9.29	−0.05	−0.77	0.05
17 <sub>13,5</sub>	2749.71	11.95	9.46	8.05	7.06	7.38	−1.80	−1.26	−0.62
17 <sub>13,4</sub>	2751.57	12.02	9.72	8.33	7.37	7.67	−1.56	−1.20	−0.52
17 <sub>14,4</sub>	2811.62	11.93	8.63	7.07	5.97	6.38	−2.80	−1.55	−0.99
17 <sub>14,3</sub>	2811.86	11.94	8.67	7.11	6.02	6.42	−2.76	−1.54	−0.98
17 <sub>15,3</sub>	2874.29	11.87	7.70	5.99	4.79	5.29	−3.85	−1.82	−1.37
17 <sub>15,2</sub>	2874.31	11.87	7.71	6.00	4.80	5.30	−3.85	−1.82	−1.37
17 <sub>16,2</sub>	2934.84	11.74	6.69	4.83	3.52	4.13	−4.93	−2.10	−1.75
17 <sub>16,1</sub>	2934.84	11.74	6.69	4.83	3.52	4.13	−4.93	−2.10	−1.75
17 <sub>17,1</sub>	2985.79	11.14	5.00	2.97	1.54	2.30	−6.51	−2.60	−2.41
17 <sub>17,0</sub>	2985.79	11.14	5.00	2.97	1.54	2.30	−6.51	−2.60	−2.41

<sup>a</sup>All calculated values reported as observed–calculated. See footnote a to Table I for explanation of the abbreviations. Atomic masses are used throughout.  
<sup>b</sup>Observed rotational term values from Ref. 75.

TABLE III. Focal-point analysis of the core–valence correction.<sup>a</sup>

Basis	MP2		$\delta$ [CCSD]		$\delta$ [CCSD(T)]		$\delta$ [CCSDT]	
	1s	All	1s	All	1s	All	1s	All
u-pVDZ+2d(65)	251	260	+62	+64	−144	−147	+6	+4
u-aug-pVDZ+2d(82)	258	267	+65	+67	−142	−145	+7	
u-aug-pVTZ+2d2f(149)	524	539	+58	+61	−150	−154		
u-pVQZ+2d2f2g(193)	630	650	+61	+63	−152	−156		
u-pVQZ+3d2f2g(198)	648	673	+63	+66	−155	−160		
u-pVQZ+2s2p2d2f2g(256)	636	657						
u-pV5Z+2s2p2d2f2g2h(441)	693	719						

<sup>a</sup>All values are given in cm<sup>−1</sup>. The two reference structures employed are { $r_1/\text{\AA}, r_2/\text{\AA}, \angle\text{HSH}/\text{deg}$ } of {1.8,1.8,100} and {1.1,1.1,90}, corresponding to the maximum and the minimum core–valence energy correction on the ground-state PES of H<sub>2</sub>S, respectively. For each basis set the total number of contracted Gaussian functions is given in parentheses.  $\delta$  denotes correlation energy increments from the previous level of theory. “All” refers to the difference between a frozen-core (1s, 2s, and 2p on S) and an all-electron calculation, while “1s” refers to the difference between a frozen-core (1s, 2s, and 2p on S) and a frozen 1s (on S) calculation. See text for the description of the basis sets.



TABLE IV. Prediction of vibrational band origins (in  $\text{cm}^{-1}$ ) for  $\text{H}_2\text{S}$ .<sup>a</sup>

$\nu^b$	Label <sup>c</sup>	Obs. <sup>d</sup>	PJT <sup>e</sup>	CBS FCI+CRD		
				Atomic	Effective	Nuclear
1	010/00 <sup>+</sup> 1	1182.57	1182.91	1182.65	1182.81	1182.96
2	020/00 <sup>+</sup> 2	2353.96	2354.15	2359.91	2360.21	2360.51
	100/10 <sup>+</sup> 0	2614.14	2614.39	2616.47	2616.80	2617.13
	001/10 <sup>-</sup> 0	2628.46	2628.80	2630.99	2631.33	2631.66
3	030/00 <sup>+</sup> 3	3513.79	3513.84	3525.71	3526.16	3526.60
	110/10 <sup>+</sup> 1	3779.17	3779.04	3781.77	3782.25	3782.73
	011/10 <sup>-</sup> 1	3789.27	3789.18	3792.36	3792.84	3793.32
4	040/00 <sup>+</sup> 4	4661.68	4661.58	4676.43	4677.01	4677.60
	120/10 <sup>+</sup> 2	4932.70	4932.45	4942.14	4942.77	4943.39
	021/10 <sup>-</sup> 2	4939.10	4938.66	4948.43	4949.05	4949.68
	200/20 <sup>+</sup> 0	5144.99	5145.30	5150.86	5151.50	5152.14
	101/20 <sup>-</sup> 0	5147.22	5147.27	5152.97	5153.61	5154.25
	002/11 <sup>+</sup> 0	5243.10	5243.54	5248.25	5248.91	5249.57
5	050/00 <sup>+</sup> 5	5797.24	5796.63	5810.38	5811.11	5811.83
	130/10 <sup>+</sup> 3	6074.58	6074.70	6090.05	6090.82	6091.58
	031/10 <sup>-</sup> 3	6077.60	6077.27	6092.91	6093.68	6094.44
	210/20 <sup>+</sup> 1	6288.15	6287.90	6295.25	6296.04	6296.82
	111/20 <sup>-</sup> 1	6289.17	6288.70	6296.13	6296.91	6297.69
	012/11 <sup>+</sup> 1	6388.10	6384.80	6391.49	6392.30	6393.10
6	060/00 <sup>+</sup> 6		6918.05	6927.27	6928.12	6928.98
	041/10 <sup>-</sup> 4		7204.53	7222.07	7222.34	7223.24
	140/10 <sup>+</sup> 4		7205.34	7221.44	7222.96	7223.86
	220/20 <sup>+</sup> 2		7419.63	7434.24	7435.16	7436.08
	121/20 <sup>-</sup> 2	7420.09	7419.64	7434.09	7435.01	7435.93
	022/11 <sup>+</sup> 2		7515.98	7530.02	7530.96	7531.91
	102/30 <sup>+</sup> 0	7576.38	7576.42	7586.63	7587.56	7588.48
	201/30 <sup>-</sup> 0	7576.55	7576.48	7586.73	7587.66	7588.58
	300/21 <sup>+</sup> 0	7752.26	7752.65	7760.87	7761.85	7762.82
	003/21 <sup>-</sup> 0	7779.32	7779.80	7788.50	7789.47	7790.44
7	070/00 <sup>+</sup> 7		8024.70	8027.81	8028.80	8029.78
	051/10 <sup>-</sup> 5		8319.66	8334.22	8335.25	8336.28
	150/10 <sup>+</sup> 5		8323.60	8335.04	8336.07	8337.10
	131/20 <sup>-</sup> 3		8540.12	8559.26	8560.32	8561.37
	230/20 <sup>+</sup> 3		8540.57	8559.97	8561.03	8562.09
	032/11 <sup>+</sup> 3		8637.01	8656.32	8657.41	8658.49
	112/30 <sup>+</sup> 1	8697.14	8696.71	8709.38	8710.44	8711.50
	211/30 <sup>-</sup> 1	8697.16	8696.75	8709.33	8710.39	8711.44
	310/21 <sup>+</sup> 1		8877.62	8888.66	8889.77	8890.88
	013/21 <sup>-</sup> 1		8896.92	8908.77	8909.88	8910.99
8	080/00 <sup>+</sup> 8		9115.31	9113.64	9114.75	9115.86
	061/10 <sup>-</sup> 6		9421.64	9429.17	9430.33	9431.48
	160/10 <sup>+</sup> 6		9428.47	9431.21	9432.37	9433.53
	141/20 <sup>-</sup> 4		9649.64	9667.78	9668.97	9670.15
	240/20 <sup>+</sup> 4		9650.30	9668.74	9669.93	9671.11
	042/11 <sup>+</sup> 4		9747.30	9766.10	9767.31	9768.52
	221/30 <sup>-</sup> 2		9806.88	9826.20	9827.39	9828.58
	122/30 <sup>+</sup> 2		9806.96	9826.35	9827.54	9828.73
	301/40 <sup>-</sup> 0	9911.02	9910.69	9926.23	9927.41	9928.59
	202/40 <sup>+</sup> 0	9911.02	9910.70	9926.22	9927.40	9928.58
	320/21 <sup>+</sup> 2		9992.56	10 011.84	10 013.08	10 014.33
	023/21 <sup>-</sup> 2		10 004.66	10 023.56	10 024.80	10 026.04
	004/31 <sup>+</sup> 0	10 188.30	10 189.00	10 201.62	10 202.87	10 204.13
	103/31 <sup>-</sup> 0	10 194.45	10 194.16	10 207.77	10 209.02	10 210.28
	400/22 <sup>+</sup> 0		10 293.01	10 305.67	10 306.95	10 308.22
9	090/00 <sup>+</sup> 9		10 188.43	10 186.97	10 188.20	10 189.44
	071/10 <sup>-</sup> 7		10 509.30	10 507.89	10 509.16	10 510.44
	170/10 <sup>+</sup> 7		10 518.81	10 511.35	10 512.63	10 513.91
	151/20 <sup>-</sup> 5		10 747.35	10 758.69	10 760.00	10 761.31
	250/20 <sup>+</sup> 5		10 748.02	10 759.74	10 761.05	10 762.36

TABLE IV. (Continued.)

$v^b$	Label <sup>c</sup>	Obs. <sup>d</sup>	PJT <sup>c</sup>	CBS FCI+CRD		
				Atomic	Effective	Nuclear
	052/11 <sup>+</sup> 5		10 845.95	10 857.89	10 859.22	10 860.56
	231/30 <sup>-</sup> 3		10 907.01	10 929.22	10 930.54	10 931.86
	132/30 <sup>+</sup> 3		10 907.10	10 929.40	10 930.72	10 932.04
	212/40 <sup>+</sup> 1	11 008.68	11 008.85	11 026.68	11 027.99	11 029.29
	311/40 <sup>-</sup> 1	11 008.68	11 008.87	11 026.67	11 027.98	11 029.29
	330/21 <sup>+</sup> 3		11 097.44	11 120.97	11 122.34	11 123.71
	033/21 <sup>-</sup> 3		11 102.90	11 125.93	11 127.30	11 128.67
	410/31 <sup>+</sup> 1		11 291.45	11 307.87	11 309.26	11 310.64
	113/31 <sup>-</sup> 1		11 293.58	11 310.72	11 312.10	11 313.49
	014/22 <sup>+</sup> 1		11 391.14	11 407.85	11 409.26	11 410.67
10	0100/00 <sup>+</sup> 10		11 242.37	11 250.26	11 251.62	11 252.98
	081/10 <sup>-</sup> 8		11 581.33	11 572.35	11 573.75	11 575.14
	180/10 <sup>+</sup> 8		11 593.29	11 577.59	11 579.00	11 580.40
	161/20 <sup>-</sup> 6		11 832.21	11 832.60	11 834.03	11 835.46
	260/20 <sup>+</sup> 6		11 832.73	11 833.65	11 835.08	11 836.50
	062/11 <sup>+</sup> 6		11 931.86	11 932.07	11 933.52	11 934.98
	142/30 <sup>+</sup> 4		11 996.61	12 015.32	12 016.76	12 018.20
	241/30 <sup>-</sup> 4		11 996.70	12 015.13	12 016.57	12 018.01
	321/40 <sup>-</sup> 2		12 097.13	12 120.40	12 121.83	12 123.27
	222/40 <sup>+</sup> 2		12 097.14	12 120.40	12 121.84	12 123.27
	302/50 <sup>+</sup> 0	12 149.46	12 149.14	12 170.00	12 171.41	12 172.82
	203/50 <sup>-</sup> 0	12 149.46	12 149.14	12 170.00	12 171.41	12 172.82
	043/21 <sup>-</sup> 4		12 190.99	12 211.92	12 213.41	12 214.90
	340/21 <sup>+</sup> 4		12 191.68	12 211.64	12 213.14	12 214.64
	420/31 <sup>+</sup> 2		12 383.82	12 407.97	12 409.50	12 411.02
	123/31 <sup>-</sup> 2		12 383.88	12 407.99	12 409.48	12 410.99
	024/22 <sup>+</sup> 2	12 481.88	12 481.02	12 505.22	12 506.76	12 508.30
	104/41 <sup>+</sup> 0	12 524.63	12 524.60	12 543.04	12 544.56	12 546.07
	401/41 <sup>-</sup> 0	12 525.20	12 524.80	12 543.56	12 545.08	12 546.59
	500/32 <sup>+</sup> 0		12 696.83	12 713.51	12 715.07	12 716.63
	005/32 <sup>-</sup> 0		12 734.73	12 752.77	12 754.33	12 755.89

<sup>a</sup>Observed–calculated. All vibrational eigenvalues are listed up to  $v=10$ , where  $v$  is the polyad quantum number (see footnote b). The {H,S} masses employed are as follows: atomic={1.007 825,31.972 071}, effective={1.007 5505,31.972 071}, and nuclear={1.007 276 49,31.972 071}.

<sup>b</sup>Polyad quantum number  $v=v_1+2v_2+v_3$ .

<sup>c</sup>See footnote b to Table I.

<sup>d</sup>Refs. 24(a), 24(d), and 32.

<sup>e</sup>Reference 17.

and  $n$ -particle spaces) which is often utilized in quantum chemical electronic structure calculations. It should be further mentioned here that, if the goal was the exploratory determination of the rovibrational eigenstates of a molecule similar in size to H<sub>2</sub>S, the valence-only aug-cc-pVQZ+ $d$  CCSD(T) calculation of the full surface requires only a few days of CPU time on a modern personal computer. The CBS CCSD(T) results, while rather different from the  $X=3$  results, deviate more from experiment than one would like to see. This means that at the complete basis set limit computations at the CCSD(T) level will not result in a spectroscopic-quality PES even close to a deep single minimum of a principally single-reference electronic state. The simple statistics of the rms error of the predicted CCSD(T) fundamentals, 4.5, 1.0, 1.6, and 2.3 cm<sup>-1</sup> with  $X=3, 4, 5$ , and  $\infty$ , respectively, shows clearly the performance of the CCSD(T) level with different correlation-consistent basis sets.

A characteristic difference is observed between the accuracy of the CBS CCSD(T) and CBS FCI valence-only sur-

faces. The SHOC correction<sup>44</sup> of the CCSD(T) correlation energies with a single scale factor results in a basically linear VBO/cm<sup>-1</sup> correction of  $+0.3n_2$ , where  $n_2$  is the bending quantum number, for the bending states, bringing them to somewhat better agreement with experiment. The correction for the stretches is well approximated as  $-1.0-0.2(n_1+n_3)^2$ , where  $n_1$  and  $n_3$  are the stretching quantum numbers, and it moves all calculated stretching VBOs further away from experiment. For larger stretching quantum numbers this correction can become rather substantial. Additivity of the bending and stretching correction holds well for all entries of Table I. Overall it seems that even the simplified SHOC correction scheme (full SHOC correction<sup>44</sup> would require small-basis FCI calculations at each of the grid points) is useful and helps to cure at least part of the remaining discrepancies in the correlation energy prediction at the CCSD(T) level. As a result, the rms error of 2.3 cm<sup>-1</sup> of the CBS CCSD(T) fundamentals decreases to 2.0 cm<sup>-1</sup> at the valence-only CBS FCI level.

In order to check the accuracy of the determination of

TABLE V. Prediction of vibrational band origins (in cm<sup>-1</sup>) for three isotopomers of H<sub>2</sub>S.<sup>a</sup>

Label <sup>b</sup>	D <sub>2</sub> <sup>32</sup> S			HD <sup>32</sup> S			H <sub>2</sub> <sup>34</sup> S		
	Obs. <sup>c</sup>	BO	BODC	Obs. <sup>d</sup>	BO	BODC	Obs. <sup>e</sup>	BO	BODC
010/00 <sup>+</sup> 1	855.40	854.51	854.35	1032.72	1032.45	1032.21	1181.50	1181.89	1181.57
020/00 <sup>+</sup> 2		1707.15	1706.96	2056.97	2061.17	2060.92	2351.84	2358.00	2357.76
100/10 <sup>+</sup> 0	1896.43	1897.84	1897.66	1902.86	1904.52	1904.41	2612.36	2614.90	2614.42
001/10 <sup>-</sup> 0	1910.15	1911.97	1911.83	2621.46	2624.17	2623.68	2626.12	2629.07	2628.65
030/00 <sup>+</sup> 3		2555.47	2555.34	3072.49	3082.28	3082.17	3510.63	3522.55	3522.54
110/10 <sup>+</sup> 1	2742.77	2743.36	2743.02	2924.98	2926.54	2926.17	3776.09	3779.46	3778.67
011/10 <sup>-</sup> 1	2754.44	2755.60	2755.30	3634.32	3637.15	3636.47	3785.90	3789.69	3788.97
040/00 <sup>+</sup> 4		3397.65	3397.61					4672.03	4672.26
120/10 <sup>+</sup> 2		3587.39	3587.03					4938.73	4938.03
021/10 <sup>-</sup> 2		3597.44	3597.11					4944.68	4944.02
200/20 <sup>+</sup> 0		3757.31	3756.98	3756.34	3760.44	3760.22		5147.63	5146.73
101/20 <sup>-</sup> 0		3761.32	3761.00					5149.61	5148.73
002/11 <sup>+</sup> 0		3812.80	3812.49					5244.68	5243.79
050/00 <sup>+</sup> 5		4232.46	4232.52					5804.84	5805.24
130/10 <sup>+</sup> 3		4426.99	4426.69					6085.45	6084.97
031/10 <sup>-</sup> 3		4434.95	4434.67					6087.98	6087.52
210/20 <sup>+</sup> 1		4592.70	4592.21				6283.01	6291.27	6290.08
111/20 <sup>-</sup> 1	4592.32	4595.72	4595.24				6284.00	6292.06	6290.88
012/11 <sup>+</sup> 1		4646.63	4646.16				6383.36	6387.24	6386.03
060/00 <sup>+</sup> 6		5059.16	5059.30					6920.65	6921.16
041/10 <sup>-</sup> 4		5259.96	5259.75					7215.71	7215.44
140/10 <sup>+</sup> 4		5266.28	5266.08					7215.98	7215.72
220/20 <sup>+</sup> 2		5426.62	5426.11					7428.99	7427.87
121/20 <sup>-</sup> 2		5428.59	5428.09					7429.19	7428.08
022/11 <sup>+</sup> 2		5478.98	5478.48					7524.75	7523.61
102/30 <sup>+</sup> 0		5566.96	5566.48					7581.89	7580.60
201/30 <sup>-</sup> 0		5567.50	5567.03					7581.98	7580.68
300/21 <sup>+</sup> 0		5652.94	5652.42					7756.13	7754.68
003/21 <sup>-</sup> 0		5679.24	5678.79					7783.10	7781.83

<sup>a</sup>Observed–calculated. Atomic masses were used for all calculations reported here. BO=CBS FCI+CR PES; DBOC=BO augmented with the appropriate Born–Oppenheimer diagonal (BODC) correction.

<sup>b</sup>See footnote b to Table I.

<sup>c</sup>References 20 and 23(d).

<sup>d</sup>Reference 23(b).

<sup>e</sup>References 23(c) and 34.

rotational energy levels using our *ab initio* potentials we performed calculations with different *J* values. The calculations with *J* = 17 were chosen for reporting since this is the highest *J* for which complete experimental information up to *K<sub>a</sub>* = *J* is available. We report, in Table II, as “experimental” the energy levels obtained from a Padé effective Hamiltonian fit,<sup>74</sup> which reproduces all the line frequencies within experimental uncertainty.<sup>75</sup> As the results in Table II demonstrate, reproduction of experimental results by our *ab initio* potentials is very good. It should further be noted that similar conclusions hold for the rotational term values as given above for the VBOs. For example, among the CCSD(T) surfaces here again the aug-cc-pVQZ+*d* CCSD(T) surface appears to be the most accurate, due to the same fortuitous error cancellation.

B. Core–valence effects

For the grid employed in this study, the largest and the smallest core–valence energy corrections occur at {*r*<sub>1</sub>/Å,*r*<sub>2</sub>/Å,∠HSH/deg} geometries of {1.7,1.8,100} and

{1.1,1.1,90}, respectively. The difference between the largest and smallest core–valence (CV) energy correction is substantial, on the order of 400 cm<sup>-1</sup>. As can immediately be seen from Fig. 4(a), the CV correction on the PES of H<sub>2</sub>S changes drastically when stretching the molecule and is relatively insensitive to the bending motion. The latter observation is in line with results presented for the barrier to linearity of H<sub>2</sub>S, since the CV correction to the barrier was found to be only on the order of 10 cm<sup>-1</sup> at the highest levels studied. The difference between the largest and smallest CV energy correction is further investigated and the results are reported in Table III. To make these auxiliary CV calculations less expensive, the more symmetric {1.8,1.8,100} geometry was employed instead of {1.7,1.8,100}. The core–valence basis sets employed in these calculations are based on the uncontracted versions of the correlation-consistent (cc) basis sets of Dunning and co-workers.<sup>37,55</sup> In Table III this fact is emphasized by putting u, for uncontracted, in front of the cc basis sets and the augmentation on the S atom is given explicitly. Note that the CVQZ+*d* basis, described

in Sec. II A and employed during determination of the CV correction surface, is the same as the u-cc-pVQZ+3d2f2g basis of Table III. All extra exponents were obtained by an even-tempered extension of the largest related exponents of the cc basis sets into the core with a geometric ratio of 3.

As Table III reveals the CV energy correction has a very pronounced basis set dependence with the correction increasing with increased basis set size. Nevertheless, this basis set dependency is contained almost exclusively at the MP2 level. Higher-order corrections, while rather substantial, have almost no basis set dependence. This observation is rather important, especially if someone was to improve upon the *ab initio* calculations of this study. The differences between the CCSD(T) and CCSDT calculations are comfortably small. Since CCSDT calculations are expected to result in almost FCI-quality CV correlation energies, we can say with confidence that CVQZ+*d* CCSD(T) energies provide reliable estimates of the CV effect over the whole PES.

As it is clear from Tables I and II, inclusion of the core-valence (CV) effects into the *ab initio* calculation of the PES has a very large effect on the predicted VBOs and rotational term values. In fact it is the core correlation which has the largest effect on the rovibrational energies among the correction terms considered. Inclusion of the CV correction surface in the PES results in basically linear VBO/cm<sup>-1</sup> corrections both for the bends and for the stretches, which can be described as +2.0*n*<sub>2</sub> and +5.1(*n*<sub>1</sub>+*n*<sub>3</sub>), respectively. As clear from the approximate correction formula, for higher stretching excitations the CV correction becomes large. These corrections move all calculated valence-only CBS FCI VBOs further away from experiment, resulting in discrepancies, at about 12 000 cm<sup>-1</sup>, of 40 cm<sup>-1</sup> compared to 17 cm<sup>-1</sup> at the valence-only CBS FCI level. Additivity of the bending and stretching CV correction holds well for all entries of Table I. The data in Table III suggest that the large CV correction of the VBOs is a real effect and will not decrease upon improvement of the *ab initio* level employed for the determination of the CV correction surface.

As can easily be checked through explicit *ab initio* optimizations,<sup>25</sup> consideration of the CV effect changes the equilibrium geometry of the minimum on the ground-state PES of H<sub>2</sub>S. Change in the equilibrium geometry results in change in the rotational constants and subsequently in change in the rotational frequencies. These changes can easily be observed in Table II.

### C. Relativistic effects

Recently we have explored the influence of special relativity on the ground-state PES of water.<sup>10–12</sup> It turned out from these concerted studies that electronic relativistic corrections have a surprisingly large effect on the PES and consequently on the calculated rovibrational levels of water, a prototypical light molecule for which geometric variation of the relativistic energy correction, substantial in an absolute sense, was considered to be negligible. Among the theoretical treatments one can consider, kinetic relativistic effects (the Dirac–Coulomb–Pauli extension of the nonrelativistic Hamiltonian), the Breit correction, and the Lamb-shift cor-

rection alter the VBOs of water up to 11, 3, and 1 cm<sup>-1</sup>, respectively, at about 14 000 cm<sup>-1</sup> above the zero-point level.

Our calculations prove that inclusion of relativistic effects into the *ab initio* computation of the ground-state PES of H<sub>2</sub>S, similarly to water,<sup>3</sup> has a substantial, non-negligible effect. Since the precision of the underlying *ab initio* nonrelativistic PES of H<sub>2</sub>S is still not of the ultimate quality, effects smaller than that coming from the Dirac–Coulomb–Pauli (DCP) approximation are not considered in detail in this study. As mentioned in Sec. II A, in this study even the two-electron Darwin term (D2) has been neglected from the DCP Hamiltonian and only the one-electron mass-velocity and Darwin terms (MVD1) are considered here in a first-order perturbation treatment employing nonrelativistic aug-CVTZ CCSD(T) wave functions.

In the case of the rovibrational levels of H<sub>2</sub>S the relativistic shifts are almost as large as the CV corrections. Inclusion of the relativistic correction surface in the PES results in basically linear VBO/cm<sup>-1</sup> corrections for the stretching levels, which can be well approximated as -4.15(*n*<sub>1</sub>+*n*<sub>3</sub>). This correction is of the same sign but considerably larger than that obtained for water,<sup>3</sup> where it was found to be -2.8(*n*<sub>1</sub>+*n*<sub>3</sub>). As is clear from the approximate correction formula, for larger stretching excitation the relativistic correction becomes large and recorrects almost all of the substantial CV stretching shifts which grow as +5.1(*n*<sub>1</sub>+*n*<sub>3</sub>). Therefore, it is the relativistic correction which serves to re-establish the nice agreement between experiment and theory observed at the valence-only CBS FCI level and lost upon inclusion of core correlation effects. For up to *n*<sub>2</sub>=4 the correction for the bending VBOs of H<sub>2</sub>S grows almost linearly as +0.7*n*<sub>2</sub>. Additivity of the stretching and bending relativistic corrections holds better than 95%. We note that for the first few bending levels of water the MVD1 bending correction grows as +0.8*n*<sub>2</sub>.<sup>3</sup> Therefore, the dependence of the relativistic bending correction for H<sub>2</sub>S is somewhat less than that observed for water. This is in contrast to the relativistic correction to the barrier to linearity of H<sub>2</sub>O<sup>4</sup> and H<sub>2</sub>S,<sup>25</sup> which are 55 out of 11 100 cm<sup>-1</sup> and 230 out of 24 400 cm<sup>-1</sup>, respectively. This suggests that most of the relativistic correction to the bending curve of H<sub>2</sub>S occurs away from equilibrium. Figure 4(b) confirms this: the relativistic change between 70° and 120° is 54 cm<sup>-1</sup> and quasi-linear in this region, while between 140° and 180° the decidedly nonlinear change is 156 cm<sup>-1</sup>. Since the relativistic correction for the bends is of the same sign as that of the CV correction, the relativistic correction acts to worsen the agreement between *ab initio* VBOs and experiment. This result is again very similar to that observed for water.<sup>3</sup>

At this point it is worth discussing how large the effect of the neglected relativistic corrections on the relativistic correction PES of H<sub>2</sub>S is. For this purpose we selected the two points of the grid where the relativistic MVD1 energy correction exhibits its maximum and minimum values. These {*r*<sub>1</sub>/Å, *r*<sub>2</sub>/Å, ∠HSH/deg} geometries are {1.5, 1.6, 40} and {1.4, 1.4, 180}, respectively, suggesting that the relativistic correction depends most heavily on the bond angle, which can also be observed on Fig. 4(b). To save on computational



expense, the more symmetric  $\{1.6, 1.6, 40\}$  geometry was chosen as reference instead of  $\{1.5, 1.6, 40\}$ . The MVD1 relativistic energy correction difference between the two symmetric reference points is  $312\text{ cm}^{-1}$ . If the direct perturbation theory (DPT) of Kutzelnigg<sup>62,63</sup> in its lowest order is used to approximate DCP theory, the difference becomes  $329.7\text{ cm}^{-1}$  using CVQZ+*d* CCSD(T) wave functions. (Almost all of the difference between the DPT and MVD1 results is due to the D2 term.) To gauge the magnitude of the neglected Breit correction, we determined four-component u-cc-pVDZ Hartree–Fock–Dirac wave functions and treated the Breit term by first-order perturbation theory using the code BERTHA,<sup>49,50</sup> and obtained a correction of only  $11.4\text{ cm}^{-1}$ , or about 3% of the MVD1 correction. (Nevertheless, this correction might translate into VBO differences on the order of  $2\text{ cm}^{-1}$ .) We have two further remarks based on the example of water:<sup>10–12</sup> (a) the Breit and Lamb correction surfaces may show a rather different geometry dependence than the MVD1 correction surface; and (b) the cumulative effect of the neglected D2, Breit and Lamb-shift terms may be substantially less than their individual contributions. Overall it seems that no major improvement on *ab initio* rovibrational band origins of  $\text{H}_2\text{S}$  is expected from a more thorough computation of the relativistic correction surface.

#### D. BODC corrections

As the data of Table I demonstrate, the BODC correction for the bending and stretching VBOs/ $\text{cm}^{-1}$  changes almost linearly as  $0.6 - 0.2n_2$  and  $+0.4(n_1 + n_3)$ , respectively. Additivity of the stretch and bend corrections seems to hold well. Most importantly, BODC corrections to the stretching and bending VBOs are rather small, especially when compared to the substantial CV and REL corrections.

As the data of Table IV demonstrate, choosing different hydrogenic masses for the variational rovibrational calculations results in calculated VBOs which are at least as different from each other as the effect of the inclusion of the BODC correction. For example, for the  $121/20^-2$  level (see footnote b to Table I for our labeling convention) the BODC correction is  $1.2\text{ cm}^{-1}$ , while the difference between the “atomic” and “nuclear” band origins is  $1.8\text{ cm}^{-1}$ . Consequently, once the PES of  $\text{H}_2\text{S}$  will be sufficiently accurate that one has to start worrying about the BODC correction, choice of the hydrogenic mass will need to be considered. The data of Table IV allow for an interesting investigation of the intrinsic accuracy of our final *ab initio* PES.  $\text{H}_2\text{S}$  is a molecule for which the local-mode description of the VBOs is much closer to reality than that offered by normal modes. To wit, the consecutive observed unsigned differences for pure stretching VBOs with  $v = 2(100/10^+0 - 001/10^-0)$ ,  $v = 4(200/20^+0 - 111/20^-0)$ ,  $v = 6(102/30^+0 - 201/30^-0)$ ,  $v = 6(300/21^+0 - 003/21^-0)$ ,  $v = 8(301/40^-0 - 202/40^+0)$ ,  $v = 8(400/31^+0 - 103/31^-0)$ , and  $v = 10(104/41^+0 - 401/41^-0)$ , where  $v$  is the polyad quantum number  $v = v_1 + 2v_2 + v_3$ , are 14.32, 2.23, 0.17, 27.06, 0.00, 6.15, and 0.57, respectively. The empirically adjusted PJT PES<sup>17</sup> results in the following differences: 14.41, 1.97, 0.06, 27.15, 0.01, 5.16, and 0.20, respectively. Our final PES, denoted as CBS FCI+CRD, seems to be very accurate on a local scale

as it offers the following description for the local-mode splittings: 14.52, 2.11, 0.10, 27.63, 0.01, 6.15, and 0.52, respectively. It is also clear that, within each manifold, the predicted VBOs show the expected increase in the local-mode pair separations for each  $v_2$  with increasing vibrational energy. We expect that for higher vibrational excitations, where there exists substantial deviation between predictions made by the PJT<sup>17</sup> and the CBS FCI+CRD surfaces, our *ab initio* surface turns out to be more accurate.

Table V contains our predicted VBOs for the isotopomers  $\text{D}_2^{32}\text{S}$ ,  $\text{HD}^{32}\text{S}$ , and  $\text{H}_2^{34}\text{S}$ . As expected and demonstrated there, the deviations between the *ab initio* and available experimental VBOs of  $\text{D}_2^{32}\text{S}$  are considerably smaller than those for  $\text{H}_2^{32}\text{S}$ . Furthermore, our converged *ab initio* PES predicts a large number of VBOs within  $3\text{ cm}^{-1}$ . In almost all cases inclusion of the BODC correction surface of all isotopomers in the PES results in smaller deviation between theory and experiment, though the changes are only about one-quarter or less of the appropriate deviations. Nevertheless, after inclusion of all corrections considered our converged *ab initio* procedure predicts the vibrational fundamentals of  $\text{H}_2^{32}\text{S}$ ,  $\text{H}_2^{34}\text{S}$ ,  $\text{HD}^{32}\text{S}$ , and  $\text{D}_2^{32}\text{S}$ , with rms accuracies of 2.0, 1.9, 1.6, and  $1.3\text{ cm}^{-1}$ , respectively, rather close to the set goal of  $1\text{ cm}^{-1}$  of first-principles rovibrational spectroscopy.

The seemingly fast convergence of the *ab initio* rotational terms toward their experimental counterparts is remarkable, and appears to be somewhat better than that observed for the VBOs. Our final PES, where the CBS FCI PES has been corrected for core correlation, as well as relativistic, and BODC effects, reproduces the lower-lying rotational terms with an average accuracy of only  $0.02\text{ cm}^{-1}$ , truly remarkable for a purely *ab initio* PES.

The remaining discrepancy between calculated vibrational and rotational term values and their experimental counterparts, as our experience shows, can be removed by the fitting of the *ab initio* PES to experimental energy levels. Even though the discrepancy might seem significant from the effective Hamiltonian accuracy point of view, let us note that the similar amount of discrepancy will be preserved for the rotationally excited states in excited vibrational states up to very high degree of excitation, which constitutes the major advantage of variational calculations over perturbative ways of calculation.

#### IV. CONCLUSIONS

The following conclusions may be drawn from the results presented in this study about a converged *ab initio* determination of the ground electronic state PES of  $\text{H}_2\text{S}$  and about its utilization for the prediction of vibrational and rotational term values using an exact kinetic energy operator and a (nearly) variational procedure.

- During determination of a semiglobal PES of a single-reference electronic state with a single minimum, double extrapolation to the complete basis set (CBS) and full configuration interaction (FCI) asymptotes is possible and meaningful when the original CCSD(T) energy calculations utilize the hierarchical correlation-

- consistent basis sets of Dunning and co-workers<sup>37</sup> and the scaled higher-order correlation energy (SHOC) approach of Császár and Leininger,<sup>44</sup> respectively.
- (b) Our best *ab initio* PES reproduces higher-lying VBOs with an accuracy almost one order of magnitude better than the PES due to Botschwina and co-workers.<sup>18</sup> The surface is also considerably better than the best previously published *ab initio* surface due to Senekowitsch and co-workers.<sup>21</sup> It is also notable how much more systematic the deviations between theory and experiment are with the new extrapolated and corrected surfaces. This should greatly facilitate and accelerate any simple empirical adjustment of our highest-accuracy *ab initio* PES.
- (c) It is notable that the best PES of this study, CBS FCI+CRD, representing the final product of a converged *ab initio* approach including corrections due to core-valence, relativistic, and BODC effects, predicts the vibrational fundamentals of H<sub>2</sub><sup>32</sup>S, H<sub>2</sub><sup>34</sup>S, HD<sup>32</sup>S, and D<sub>2</sub><sup>32</sup>S with rms accuracies of 2.0, 1.9, 1.6, and 1.3 cm<sup>-1</sup>, respectively. An even more remarkable feature of our converged *ab initio* PES is that it reproduces the splittings between local-mode state pairs of H<sub>2</sub><sup>32</sup>S slightly better than the best empirical PES<sup>17</sup> fitted to observed rovibrational states.
- (d) Valence-only CCSD(T) calculations are capable of reproducing all vibrational energy levels below 12 500 cm<sup>-1</sup>, about half of the barrier to linearity of H<sub>2</sub><sup>32</sup>S, with a maximum unsigned difference, gradually increasing with increased vibrational excitation, of 24 cm<sup>-1</sup> at the complete basis set level. The aug-cc-pVQZ CCSD(T) PES is the best among those computed, its overall performance is better than that of the CBS CCSD(T) PES. Therefore, in common with several properties of molecular systems, such as equilibrium bond length and atomization energies, the aug-cc-pVQZ CCSD(T) treatment can be recommended for PES determinations if only a single-level calculation is affordable or appropriate.
- (e) Core-valence (CV) correlation changes the computed VBOs of H<sub>2</sub>S substantially, worsening significantly the good agreement between experiment and valence-only *ab initio* (CBS FCI) theory. For the stretching vibrations the CV correction grows as fast as +5.1(*n*<sub>1</sub>+*n*<sub>3</sub>). It is an important observation of this study that the relativistic correction seems to be almost equally large, it is -4.15(*n*<sub>1</sub>+*n*<sub>3</sub>) for the pure stretches, and corrects the core-correlated results back to close agreement with experiment for the stretching VBOs. On the other hand, since both core correlation and relativistic correction acts in the same direction, the overall effect for the pure bends is that their final predicted values are less satisfactory and are in significant disagreement with experiment. For all levels investigated the additivity of the stretching and bending corrections holds better than 95%.
- (f) As for water,<sup>1</sup> the Born-Oppenheimer diagonal correc-

tion (BODC) to the vibrational band origins (VBOs) is small, 2.5 cm<sup>-1</sup> or less up to 14 000 cm<sup>-1</sup> above the zero-point level.

- (g) We believe that the remaining error in the prediction of higher-energy bending states is due not to the incomplete treatment of the relativistic and BODC effects but to imperfections of the Born-Oppenheimer potential.
- (h) The absolute energies of the *J*=17 rotational levels of the (000) ground vibrational state are predicted with a truly remarkable accuracy. This also proves the high quality of the lower part of the converged *ab initio* PES determined in this study.

Finally, a few comments about future extensions of the work presented. In the case of water it has been shown<sup>8,13</sup> that a simple few-parameter adjustment of the bending part of the potential improves agreement between theory and experiment drastically. Similar and other refinement strategies can be attempted for the PES of H<sub>2</sub>S to achieve true spectroscopic accuracy in the prediction of VBOs and rotational term values. To predict intensities the dipole moment surface (DMS) of H<sub>2</sub>S will also be determined. Provision of a list of rovibrational levels of H<sub>2</sub>S, based on the improved PES and DMS, is left for future work.

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<sup>1</sup>N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, and J. Tennyson, *Chem. Phys. Lett.* **260**, 381 (1996).

<sup>2</sup>O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **105**, 6490 (1996).

<sup>3</sup>A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson, *Chem. Phys. Lett.* **293**, 317 (1998); **312**, 613(E) (1999).

<sup>4</sup>G. Tarczay, A. G. Császár, W. Klopper, V. Szalay, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **110**, 11971 (1999).

<sup>5</sup>E. F. Valeev, W. D. Allen, H. F. Schaefer III, and A. G. Császár, *J. Chem. Phys.* **114**, 2875 (2001).

<sup>6</sup>H. Partridge and D. W. Schwenke, *J. Chem. Phys.* **106**, 4618 (1997), and references therein.

<sup>7</sup>O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, and L. Wallace, *Science* **277**, 346 (1997).

<sup>8</sup>J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson, *Chem. Phys. Lett.* **317**, 365 (2000).

<sup>9</sup>A. G. Császár and I. M. Mills, *Spectrochim. Acta, Part A* **53**, 1101 (1997).

<sup>10</sup>P. Pykkö, K. Dyall, A. G. Császár, G. Tarczay, O. L. Polyansky, and J. Tennyson, *Phys. Rev. A* **63**, 024502 (2001).

<sup>11</sup>A. G. Császár, G. Tarczay, M. L. Leininger, O. L. Polyansky, J. Tennyson, and W. D. Allen, in *Spectroscopy from Space*, NATO ASI Series C, edited by J. Demaison and K. Sarka (Kluwer, Dordrecht, 2001).

- <sup>12</sup>H. M. Quiney, P. Barletta, G. Tarczay, A. G. Császár, O. L. Polyansky, and J. Tennyson (unpublished).
- <sup>13</sup>J. S. Kain, O. L. Polyansky, and J. Tennyson (unpublished).
- <sup>14</sup>A. G. Császár, W. D. Allen, Y. Yamaguchi, and H. F. Schaefer III, in *Computational Molecular Spectroscopy*, edited by P. Jensen and P. R. Bunker (Wiley, Chichester, 2000).
- <sup>15</sup>F. Allard, P. H. Hauschildt, S. Miller, and J. Tennyson, *Astrophys. J.* **426**, L39 (1994).
- <sup>16</sup>F. Allard, P. H. Hauschildt, D. R. Alexander, and S. Starrfield, *Annu. Rev. Astron. Astrophys.* **35**, 137 (1997).
- <sup>17</sup>O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Mol. Spectrosc.* **178**, 184 (1996).
- <sup>18</sup>P. Botschwina, A. Zilch, H.-J. Werner, P. Rosmus, and E. A. Reinsch, *J. Chem. Phys.* **85**, 5107 (1986).
- <sup>19</sup>I. Kozin and P. Jensen, *J. Mol. Spectrosc.* **163**, 483 (1994).
- <sup>20</sup>L. Halonen and T. Carrington, *J. Chem. Phys.* **88**, 4171 (1988); E. Kauppi and L. Halonen, *J. Phys. Chem.* **94**, 5779 (1990).
- <sup>21</sup>J. Senekowitsch, S. Carter, A. Zilch, H.-J. Werner, N. C. Handy, and P. Rosmus, *J. Chem. Phys.* **90**, 783 (1989).
- <sup>22</sup>T. H. Edwards, N. K. Moneur, and L. E. Snyder, *J. Chem. Phys.* **46**, 2139 (1967); R. L. Cook, F. C. DeLucia, and P. J. Helminger, *J. Mol. Struct.* **28**, 237 (1975).
- <sup>23</sup>(a) O. N. Ulenikov, E. A. Ditenberg, I. M. Olekhovitsch, S. Alanko, M. Koivusaari, and R. Anttila, *J. Mol. Spectrosc.* **191**, 239 (1998), and references therein. (b) O. N. Ulenikov, G. A. Onopenko, I. M. Olekhovitsch, S. Alanko, V.-M. Horneman, M. Koivusaari, and R. Anttila, *ibid.* **189**, 74 (1998). (c) O. N. Ulenikov, A. B. Malikova, M. Koivusaari, S. Alanko, and R. Anttila, *ibid.* **176**, 229 (1996). (d) O. N. Ulenikov, R. N. Tolchenov, E. N. Melekhina, M. Koivusaari, S. Alanko, and R. Anttila, *ibid.* **170**, 397 (1995).
- <sup>24</sup>(a) O. Vahtinen, L. Biennier, A. Campargue, J.-M. Flaud, and L. Halonen, *J. Mol. Spectrosc.* **184**, 288 (1997). (b) J.-M. Flaud, O. Vahtinen, and A. Campargue, *ibid.* **190**, 262 (1998). (c) A. Campargue and J.-M. Flaud, *ibid.* **194**, 43 (1999). (d) J.-M. Flaud, R. Grosskloss, S. Rai, R. Stuber, W. Demtröder, D. A. Tate, L.-G. Wang, and Th. F. Gallagher, *ibid.* **172**, 275 (1995).
- <sup>25</sup>G. Tarczay, A. G. Császár, M. Leininger, and W. Klopper, *Chem. Phys. Lett.* **322**, 119 (2000).
- <sup>26</sup>J. M. L. Martin, J.-P. Francois, and R. Gijbels, *J. Mol. Spectrosc.* **169**, 445 (1995).
- <sup>27</sup>T. Cours, P. Rosmus, and V. G. Tyuterev, *Chem. Phys. Lett.* **331**, 317 (2000).
- <sup>28</sup>S. Miller, J. Tennyson, P. Rosmus, J. Senekowitsch, and I. M. Mills, *J. Mol. Spectrosc.* **143**, 61 (1990).
- <sup>29</sup>D. Simah, B. Hardtke, and H.-J. Werner, *J. Chem. Phys.* **111**, 4523 (1999).
- <sup>30</sup>M. D. Prasad, *Indian J. Chem.* **39A**, 196 (2000).
- <sup>31</sup>Y. Zheng and S. Ding, *J. Mol. Spectrosc.* **201**, 109 (2000).
- <sup>32</sup>A. D. Bykov, O. V. Naumenko, M. A. Smirnov, L. N. Sinitsa, L. R. Brown, J. Crisp, and D. Crisp, *Can. J. Phys.* **72**, 989 (1994).
- <sup>33</sup>M. T. Emerson and D. F. Eggers, *J. Chem. Phys.* **37**, 251 (1962).
- <sup>34</sup>L. R. Brown, J. A. Crisp, D. Crisp, O. V. Naumenko, M. A. Smirnov, L. N. Sinitsa, and A. Perrin, *J. Mol. Spectrosc.* **188**, 148 (1998).
- <sup>35</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- <sup>36</sup>T. J. Lee and G. E. Scuseria, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer, Dordrecht, 1995), pp. 47–108; T. D. Crawford and H. F. Schaefer III, *Rev. Comput. Chem.* **14**, 33 (2000); A. G. Császár, “Anharmonic molecular force fields,” in *The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998), Vol. 1, pp. 13–30.
- <sup>37</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- <sup>38</sup>D. Feller, *J. Chem. Phys.* **96**, 6104 (1992).
- <sup>39</sup>D. Feller, *J. Chem. Phys.* **98**, 7059 (1993).
- <sup>40</sup>A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).
- <sup>41</sup>A. G. Császár, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **108**, 9751 (1998).
- <sup>42</sup>A. Halkier, T. Helgaker, W. Klopper, P. Jørgensen, and A. G. Császár, *Chem. Phys. Lett.* **310**, 385 (1999).
- <sup>43</sup>W. Klopper, K. L. Bak, P. Jørgensen, J. Olsen, and T. Helgaker, *J. Phys. B* **32**, 103 (1999).
- <sup>44</sup>A. G. Császár and M. L. Leininger, *J. Chem. Phys.* **114**, 5491 (2001).
- <sup>45</sup>DIRCCR12-95 is a set of *ab initio* programs written by J. Noga and W. Klopper, Bratislava and Zürich, 1995.
- <sup>46</sup>W. Klopper and J. Noga, *J. Chem. Phys.* **103**, 6127 (1995).
- <sup>47</sup>J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, *Int. J. Quantum Chem., Quantum Chem. Symp.* **26**, 897 (1992).
- <sup>48</sup>C. L. Janssen, E. T. Seidl, G. E. Scuseria *et al.*, PSI 2.0.8, PSITECH Inc., Watkinsville, GA, 1994.
- <sup>49</sup>H. M. Quiney, H. Skaane, and I. P. Grant, *Adv. Quantum Chem.* **32**, 1 (1999).
- <sup>50</sup>I. P. Grant and H. M. Quiney, *Int. J. Quantum Chem.* **80**, 283 (2000).
- <sup>51</sup>DALTON, an *ab initio* electronic structure program, Release 1.0, 1997, written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen *et al.*
- <sup>52</sup>G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- <sup>53</sup>W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley-Interscience, New York, 1986).
- <sup>54</sup>D. R. Hartree, *Proc. Cambridge Philos. Soc.* **24**, 89 (1928).
- <sup>55</sup>The (aug)-cc-pVXZ basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830.
- <sup>56</sup>J. M. L. Martin, *J. Chem. Phys.* **108**, 2791 (1998), and references therein.
- <sup>57</sup>W. Meyer and P. Rosmus, *J. Chem. Phys.* **63**, 2356 (1975).
- <sup>58</sup>H. Partridge, “Core-valence correlation effects,” in *The Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998), Vol. 1, pp. 581–591.
- <sup>59</sup>A. G. Császár and W. D. Allen, *J. Chem. Phys.* **104**, 2746 (1996).
- <sup>60</sup>P. Pyrkko, *Chem. Rev.* **88**, 563 (1988) and the electronic bibliography <http://www.csc.fi/lul/rtam>
- <sup>61</sup>K. Balasubramanian, *Relativistic Effects in Chemistry, Parts A and B* (Wiley, New York, 1997).
- <sup>62</sup>W. Kutzelnigg, E. Ottoschowski, and R. Franke, *J. Chem. Phys.* **102**, 1740 (1995).
- <sup>63</sup>E. Ottoschowski and W. Kutzelnigg, *J. Chem. Phys.* **102**, 1752 (1995).
- <sup>64</sup>N. C. Handy, Y. Yamaguchi, and H. F. Schaefer III, *J. Chem. Phys.* **84**, 4481 (1986).
- <sup>65</sup>See EPAPS Document No. E-JCPSA6-115-314127 containing the following files: (a) geometry parameters and absolute energies of all *ab initio* electronic structure calculations corresponding to the grid of this study (258 symmetry-unique points); and (b) FORTRAN codes representing the PESs obtained in this study. This document may be retrieved via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for more information.
- <sup>66</sup>V. Szalay, *J. Chem. Phys.* **111**, 8804 (1999).
- <sup>67</sup>P. Jensen, *J. Mol. Spectrosc.* **128**, 478 (1988).
- <sup>68</sup>G. De Oliveira and C. E. Dykstra, *Theor. Chim. Acta* **101**, 435 (1999).
- <sup>69</sup>S. E. Choi and J. C. Light, *J. Chem. Phys.* **97**, 7031 (1992).
- <sup>70</sup>S. Wolfram, *Mathematica: A System for Doing Mathematics by Computer*, 2nd ed. (Addison-Wesley, Redwood City, CA, 1991). Mathematica, Version 2.2, Wolfram Research Inc., 1993.
- <sup>71</sup>J. Tennyson and B. T. Sutcliffe, *Int. J. Quantum Chem.* **42**, 941 (1992).
- <sup>72</sup>J. Tennyson, J. R. Henderson, and N. G. Fulton, *Comput. Phys. Commun.* **86**, 175 (1995).
- <sup>73</sup>J. Tennyson and B. T. Sutcliffe, *Mol. Phys.* **58**, 1067 (1986).
- <sup>74</sup>O. L. Polyansky, *J. Mol. Spectrosc.* **112**, 79 (1985).
- <sup>75</sup>O. L. Polyansky (unpublished results), based on work reported in S. P. Belov, K. M. T. Yamada, G. Winniewisser, L. Poteau, R. Bocquet, J. Demaison, O. Polyansky, and M. Y. Tretyakov, *J. Mol. Spectrosc.* **173**, 380 (1995).