# *Ab initio* intermolecular potential energy surface and thermophysical properties of hydrogen sulfide†

Robert Hellmann,*[a] Eckard Bich,[a] Eckhard Vogel[a] and Velisa Vesovic[b]

A six-dimensional potential energy hypersurface (PES) for two interacting rigid hydrogen sulfide molecules was determined from high-level quantum-mechanical *ab initio* computations. A total of 4016 points for 405 different angular orientations of two molecules were calculated utilizing the counterpoise-corrected supermolecular approach at the CCSD(T) level of theory and extrapolating the calculated interaction energies to the complete basis set limit. An analytical site–site potential function with eleven sites per hydrogen sulfide molecule was fitted to the interaction energies. The PES has been validated by computing the second pressure virial coefficient, shear viscosity, thermal conductivity and comparing with the available experimental data. The calculated values of volume viscosity were not used to validate the potential as the low accuracy of the available data precluded such an approach. The second pressure virial coefficient was evaluated by means of the Takahashi and Imada approach, while the transport properties, in the dilute limit, were evaluated by utilizing the classical trajectory method. In general, the agreement with the primary experimental data is within the experimental error for temperatures higher than 300 K. For lower temperatures the lack of reliable data indicates that the values of the second pressure virial coefficient and of the transport properties calculated in this work are currently the most accurate estimates for the thermophysical properties of hydrogen sulfide.

## 1 Introduction

The understanding of the relationship between the macroscopic thermophysical properties of fluids and the interactions among individual molecules is the ultimate goal of statistical mechanics. Last decade has witnessed great advances in our ability to calculate the thermophysical properties of fluids directly from intermolecular forces.[1–3] Provided that the intermolecular forces are realistic the accuracy of calculations, at least for the dilute gas, is commensurate with the uncertainty of the available experimental data. Such calculations do not only improve our insight into the dominant microscopic processes, but also allow us to supplement the available experimental data. This is especially useful for fluids and conditions where experimental data are of high uncertainty or nonexistent.

Hydrogen sulfide is a highly toxic and flammable gas that is also corrosive in the presence of water. Its handling requires special care and, not surprisingly, the experimental thermophysical property data are rather scarce.[4,5] The recent worldwide trends towards using cleaner energy have re-focused the attention to the lack of hydrogen sulfide data. This is especially true for the processes that involve natural gas, where $H_2S$ can be a major constituent. The industrial sweetening of natural gas leads to streams of pure $H_2S$ or of mixtures with $CO_2$. Nowadays, there is a tendency to inject such mixtures back into the reservoirs as part of the Carbon-Capture and Storage campaign. To optimally design such processes there is a need for accurate and reliable thermophysical property data. As performing the measurements on hydrogen sulfide is fraught with difficulties, computational means become a viable and readily available alternative to obtain the required data.

The present work serves a dual purpose. One is to answer the need for accurate data on thermophysical properties of hydrogen sulfide in the dilute-gas limit. In order to do this we first determined an accurate, *ab initio* intermolecular potential energy hypersurface (PES) for hydrogen sulfide based on high-level quantum-mechanical computations. The other is to provide a unique and stringent test of the accuracy of the proposed intermolecular pair potential, by comparing the calculated thermophysical properties to experimental data.

[a] *Institut für Chemie, Universität Rostock, D-18059 Rostock, Germany. E-mail: robert.hellmann@uni-rostock.de; Fax: +49 381 498 6502; Tel: +49 381 498 6509*
[b] *Department of Earth Science and Engineering, Imperial College, London, SW7 2AZ, UK*
† Electronic supplementary information (ESI) available: Details of Euler angles and rotation matrices used; parameters and equilibrium structures of the analytical potential function; details of multipole moment analysis; results of the *ab initio* calculations for all 4016 points used for the fit of the analytical potential function. See DOI: 10.1039/c1cp20873j

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To date no high-quality *ab initio* PES for the $H_2S$–$H_2S$ interaction has become available. Previous *ab initio* studies were in most cases limited to very few selected configurations, like equilibrium structures and transition states.[6–10] Only Woon and Beck[11] developed two analytical site–site potentials based on fits to about 30 *ab initio* points each, using different basis sets at the MP2 level of theory. In molecular simulations involving hydrogen sulfide simple empirical effective pair-potentials were utilized (see for example ref. 1,12–19).

The new *ab initio* PES presented in this paper is based on counterpoise-corrected supermolecular calculations for more than 4000 mutual configurations of two rigid hydrogen sulfide molecules. Highly accurate Coupled-Cluster methods are applied utilizing large basis sets of up to quadruple-zeta quality with bond-functions. In addition, corrections for relativistic effects as well as core–core and core–valance correlations were determined. A 11-centre site–site potential function with isotropic site–site interactions was fitted to the calculated interaction energies in which not only the site–site interaction parameters but also the positions of the sites were fully optimized. The site–site potential model was chosen because of its simplicity, which makes it easy to use when calculating macroscopic properties by means of molecular simulations.

In order to validate the determined intermolecular potential we computed the second pressure virial coefficient, the viscosity, the thermal conductivity and the volume viscosity of gaseous hydrogen sulfide over a wide temperature range. The choice of the thermophysical properties was governed by the availability of experimental data. In the dilute-gas limit molecules interact through binary collisions and the knowledge of the molecule–molecule pair potential energy is sufficient to characterize the interaction. The second virial coefficient can be calculated from the intermolecular PES by utilizing statistical mechanics. In order to calculate the transport and relaxation properties one utilizes the kinetic theory of molecular gases which expresses those properties in terms of generalized cross-sections.[20] These cross sections are determined by the dynamics of the binary collisions that in turn are governed by the intermolecular PES.

The second virial coefficient was determined classically including quantum corrections. For transport and relaxation properties a quantum-mechanical approach is not computationally feasible and we performed the computations by means of the classical-trajectory approach. The evaluation of transport and relaxation properties of hydrogen sulfide in this manner is a continuation of our previous studies on $CO_2$, $CH_4$ and $H_2O$ that demonstrated the accuracy and usefulness of the classical-trajectory approach.[2,21–25] The calculations were performed on the assumption that both hydrogen sulfide molecules behave as rigid rotors. This assumption was dictated by the nature of the available intermolecular potential, which was developed using the zero-point vibrationally averaged configuration. In order to include the effects of vibrationally active modes we employed the approximation described in our previous work to correct,[21–23] where necessary, the generalized cross sections obtained from the classical-trajectory calculations based on the rigid-rotor assumption.

In the next section we present the new *ab initio* potential energy surface for $H_2S$ focusing the discussion on monomer geometry, calculation of the interaction energies and providing

an accurate analytical representation of the new PES. In Section 3 we summarize how the second pressure virial coefficients are obtained from the PES and compare with the available experimental data. In the following section we extend the validation of the PES by comparing the calculated values of shear viscosity and thermal conductivity with the experimental data. Finally we present and discuss the calculation of the volume viscosity of $H_2S$.

## 2 Intermolecular potential

### 2.1 Monomer geometry

The intermolecular potential between two $H_2S$ molecules is a 12-dimensional hypersurface, if all intramolecular degrees of freedom are considered explicitly. This high dimensionality would require a very large number of *ab initio* calculations to adequately sample the entire PES. However, if the monomers are approximated as rigid rotors, the PES is only six-dimensional. Past experience with different small molecules shows that a highly accurate intermolecular PES can be constructed if the zero-point vibrationally averaged geometry is used for the rigid monomers, see for example ref. 26–29.

We calculated fully *ab initio* the zero-point vibrationally averaged geometry for $H_2S$ in several steps utilizing the CCSD(T)[30] method with all electrons correlated. In a first step the geometry was optimized with the cc-pwCV5Z basis set[31] to obtain the best possible equilibrium geometry. This resulted in a SH bond length of 1.3349 Å and an HSH bond angle of 92.314°. In the next step the equilibrium geometry was also determined with the cc-pwCVQZ basis set[31] leading to a bond length of 1.3348 Å and a bond angle of 92.306°. Then a cubic force-field calculation was performed with the cc-pwCVQZ basis set in the cc-pwCVQZ equilibrium geometry to obtain the corresponding zero-point vibrationally averaged geometry which resulted in an averaged bond length of 1.3505 Å and an averaged bond angle of 92.211°. Finally the differences in the bond length and bond angle between the vibrationally averaged and the equilibrium geometries at the cc-pwCVQZ level were added to the corresponding values of the cc-pwCV5Z equilibrium geometry to approximate the vibrationally averaged geometry at the cc-pwCV5Z level. This resulted in a bond length of 1.3506 Å and a bond angle of 92.219°. These values are consistent with results from rovibrational spectroscopy of 1.3518 Å and 92.13°, respectively.[32] The small differences could be due to uncertainties in the spectroscopic values or due to relativistic effects which were not considered in the *ab initio* computations. The *ab initio* values were used for all further calculations.

### 2.2 *Ab initio* calculation of interaction energies

Each configuration of two rigid $H_2S$ molecules can be expressed as a function of the distance $R$ between the centres of mass of the monomers and the five Euler angles $\theta_1$, $\theta_2$, $\psi_1$, $\psi_2$ and $\phi$, see the ESI† for details concerning the Euler angles and rotation matrices. Angular configurations were generated by varying all five angles between 0° and 180° (higher values for the angles are not needed due to symmetry) in steps of 45°, which resulted in 405 symmetry-distinct angular configurations.

Ten centre of mass separations between 2.5 Å and 9.0 Å were considered leading to a total of 4050 $H_2S$–$H_2S$ configurations, 34 of which at small distances had to be discarded, because either two hydrogen atoms were too close to each other in these configurations or the quantum-mechanical computations failed due to near linear dependencies in the basis sets used.

For all configurations the interaction energies $V(R,\theta_1,\theta_2,\psi_1,\psi_2,\phi)$ were calculated using the supermolecular approach including the full counterpoise correction[33] at the frozen-core CCSD(T) level of theory with the aug-cc-pV(X + d)Z basis sets[34] for X = 3,4 (i.e. aug-cc-pV(T + d)Z and aug-cc-pV(Q + d)Z). Both basis sets were augmented by a small 3s3p2d1f set of bond functions located in the centre of mass of the two molecules. The exponents of the bond functions are 0.1, 0.3 and 0.9 for both s and p, 0.25 and 0.75 for d and 0.45 for f. The correlation parts of the interaction energies, $V_{CCSD(T)corr}$, computed with these two basis sets, were extrapolated to the complete basis set (CBS) limit with the two-point extrapolation scheme proposed by Halkier et al.,[35]

$$V_{CCSD(T)corr}(X) = V_{CCSD(T)corr}^{CBS} + \alpha X^{-3}. \qquad (1)$$

No extrapolation was necessary for the SCF interaction energies, because the differences between the results for the two basis sets are already very small. Thus the SCF interaction energies obtained from the aug-cc-pV(Q + d)Z calculations were used to approximate the CBS limit. It should be noted that, compared to the CCSD(T) interaction energies in the CBS limit, the corresponding MP2 interaction energies are significantly too negative.

The neglect of core–core and core–valence correlations and relativistic effects in the CCSD(T) calculations of the interaction energies introduces non-negligible errors. Hence, for all configurations we computed corrections for these effects which were added to the non-relativistic frozen-core CCSD(T) interaction energies in the CBS limit:

$$V = V_{CCSD(T)}^{CBS} + \Delta V_{core} + \Delta V_{rel}. \qquad (2)$$

The corrections for core–core and core–valence correlations were determined by calculating the differences between the CCSD(T) interaction energies obtained with all electrons correlated (except for the 1s electrons of sulfur) and the CCSD(T) interaction energies obtained with the frozen-core approximation. The aug-cc-pwCVTZ basis set[31] was used for these computations. Although there are several options for core–valence sets, our analysis indicates that using higher basis sets than aug-cc-pwCVTZ would not be justifiable, as the small increase in accuracy would be offset by a very high computational cost. The corrections are very small at intermediate and large distances but more important in the repulsive region. At the MP2 level of theory they are on average overestimated by about a factor of two at small intermolecular separations compared with the CCSD(T) level.

The relativistic corrections were calculated by means of the Cowan–Griffin approximation.[36] The frozen-core MP2 level was found to be sufficiently accurate for these computations. We also found that basis sets with tight correlation functions were needed for fast convergence of the relativistic corrections to the CBS limit. Thus the aug-cc-pwCVTZ basis set was

again used. The resulting relativistic corrections are similar in magnitude to the corrections for core–core and core–valence correlations. It should be emphasized again that the monomer geometry used in all calculations of interaction energies was determined at a non-relativistic level of theory so that the influence of the relativistic deformation of the monomer geometry on the interaction energies is not accounted for.

The results of the ab initio calculations for all 4016 mutual configurations of the two $H_2S$ molecules can be found in the ESI.† The Mainz-Austin-Budapest version of ACESII[37] and the CFOUR program[38] were used for all ab initio computations.

### 2.3 Analytical potential function

A site–site potential function with 11 sites per molecule was fitted to the calculated interaction energies. The sites are arranged within each molecule, in accordance with the $C_{2v}$ symmetry of $H_2S$, as follows. Three sites are located along the $C_2$ symmetry axis, three pairs of sites were placed in the molecular plane and one pair of sites is located out of plane. This corresponds to seven different types of sites and 28 different types of site–site combinations. The functional form used for each site–site interaction potential is

$$V_{ij}(R_{ij}) = A_{ij}\exp(-\alpha_{ij}R_{ij}) - f_6(R_{ij},b_{ij})\frac{C_{6ij}}{R_{ij}^6}$$
$$- f_8(R_{ij},b_{ij})\frac{C_{8ij}}{R_{ij}^8} + \frac{q_iq_j}{R_{ij}}, \qquad (3)$$

where $R_{ij}$ is the distance between site $i$ in molecule 1 and site $j$ in molecule 2. The damping functions $f_6$ and $f_8$ are given[39] as follows

$$f_n(R_{ij},b_{ij}) = 1 - \exp(-b_{ij}R_{ij})\sum_{k=0}^{n}\frac{(b_{ij}R_{ij})^k}{k!}. \qquad (4)$$

The total interaction potential is the sum over all 121 site–site interactions:

$$V(R,\theta_1,\theta_2,\psi_1,\psi_2,\phi) = \sum_{i=1}^{11}\sum_{j=1}^{11}V_{ij}[R_{ij}(R,\theta_1,\theta_2,\psi_1,\psi_2,\phi)].$$
$$(5)$$

The site–site interaction parameters $A_{ij}$, $\alpha_{ij}$, $b_{ij}$, $C_{6ij}$ and $C_{8ij}$ for all 28 types of site–site combinations, the site charges $q_i$ for all seven types of sites and the positions of the sites within the molecule (constraint to the symmetry conditions outlined above) were fully optimized in a non-linear least-squares fit to the 4016 ab initio interaction energies. Two further constraints were imposed: (i) the total charge of the monomers must be zero; (ii) the isotropic average of the $C_6$ dispersion coefficient, $C_{6iso} = \sum_{i=1}^{11}\sum_{j=1}^{11}C_{6ij}$, must be equal to the accurate value of 216.8 a.u. as obtained by Pazur et al.[40] from dipole oscillator strength distributions (DOSDs). The latter constraint is the only non-ab initio information used in the construction of the PES.

The dipole moment of the $H_2S$ monomer corresponding to the fitted site charges, 0.979 D, is in excellent agreement with the experimental value of 0.974 ± 0.005 D[41] and with a value of 0.988 D, which we computed ab initio for an isolated monomer at the CCSD(T)/aug-cc-pwCV5Z level with all
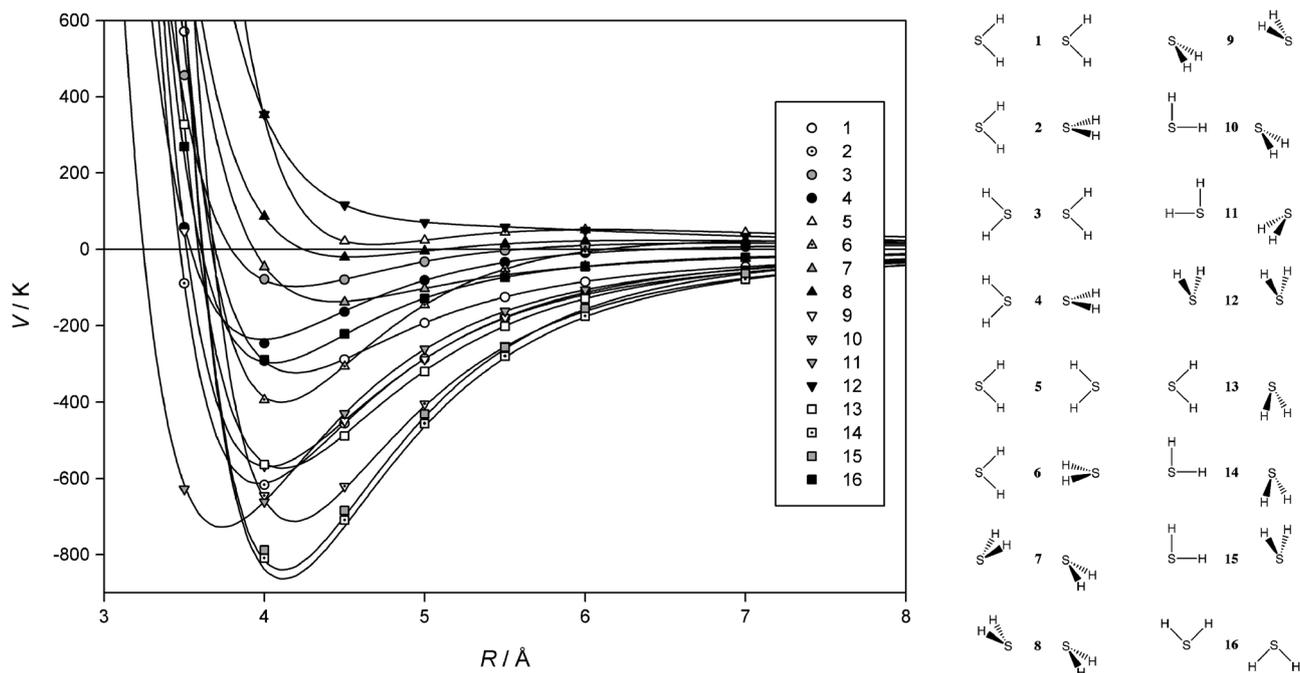
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**Fig. 1** The $H_2S$–$H_2S$ interaction potential $V$ as a function of the distance $R$ for 16 of the 405 considered angular configurations. The *ab initio* calculated values are represented by symbols and the fitted analytical potential function by solid lines.

electrons correlated, but without taking into account relativistic effects. The components of the quadrupole and octupole tensors that result from the site charges agree also within a few percent with the corresponding values from the *ab initio* calculation for the isolated monomer.

The developed potential is highly anisotropic as can be seen in Fig. 1, which illustrates the distance dependence of the fitted analytical potential function and of the *ab initio* calculated interaction energies for 16 of the 405 considered angular configurations. The interaction energies $V$ are given in Kelvin, *i.e.* they have been divided by Boltzmann's constant $k_B$. Fig. 2 shows the comparison between the interaction energies computed with the analytical potential function and the *ab initio* values for energies smaller than 3000 K. The figure illustrates that the deviations from a straight line are rather small, demonstrating the high quality of the fit. Towards the highly repulsive region the quality of the fit deteriorates considerably.
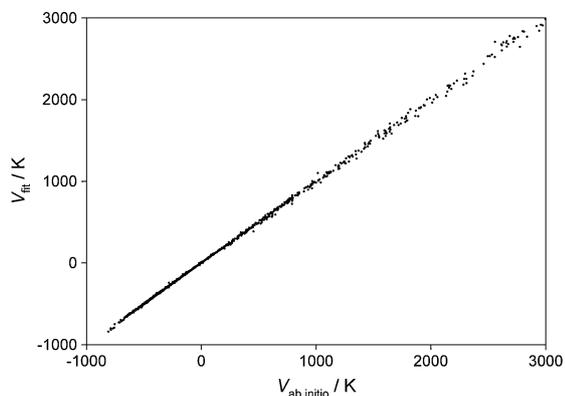


**Fig. 2** Interaction energies from the analytical fit *versus ab initio* calculated ones.

However, the values of the PES at such short separations have negligible influence on the calculation of thermophysical properties of $H_2S$ for temperatures below 2000 K.

The analytical potential function features three symmetry-distinct equilibrium structures with interaction energies of −826.9 K, −848.0 K and −888.5 K. The latter two correspond closely to the minima of the angular configurations 15 and 14, respectively, in Fig. 1.

The potential parameters and further details of the multipole analysis and of the equilibrium structures are also given in the ESI.†

## 3 Second pressure virial coefficient

The classical statistical mechanical expression for the second pressure virial coefficient of a pure gas consisting of rigid asymmetric top molecules is given by

$$
B_{cl}(T) = -\frac{N_A}{16\pi^2} \int\limits_0^{2\pi} \int\limits_0^{2\pi} \int\limits_0^{2\pi} \int\limits_0^{\pi} \int\limits_0^{\pi} \int\limits_0^{\infty}
$$
$$
\times \left[ \exp\left( -\frac{V(R, \theta_1, \theta_2, \psi_1, \psi_2, \phi)}{k_B T} \right) - 1 \right] \tag{6}
$$
$$
\times R^2 dR \sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d\psi_1 d\psi_2 d\phi.
$$

At low and intermediate temperatures quantum effects are not negligible. We considered quantum effects in an approximate manner by replacing the potential $V$ in eqn (6) by a temperature-dependent effective potential, $V_{eff}^{TI}(T)$, developed by Takahashi and Imada[42] and recommended by Schenter.[43] By using this effective potential, the classical virial coefficient including the full first-order quantum correction is recovered, whereas higher-order corrections are approximated. Explicit expressions for

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the effective potential between two rigid asymmetric tops can be found in our previous paper.[29]

Measurements of the volumetric behavior of pure hydrogen sulfide were carried out by Reamer *et al.*,[44] by Lewis and Fredericks,[45] and by Liu.[46] Reamer *et al.* reported only the primary experimental $pVT$ data. Subsequently, Dymond and Smith[47] published values for the second pressure virial coefficient of hydrogen sulfide inferred by Pesuit using the data from Reamer *et al.* In addition, Khoury and Robinson[48] reported $B$ values for $H_2S$ obtained on the basis of the Reamer *et al.* data, but at temperatures which do not correspond to the isotherms measured by Reamer *et al.* Unlike Reamer *et al.*, Lewis and Fredericks[45] analyzed their data to derive second and higher pressure virial coefficients. In 2002, Dymond *et al.*[49] developed a correlation for the second pressure virial coefficient of hydrogen sulfide based on some of the values reported by Khoury and Robinson[48] and on the values of $B$ derived by Liu[46] from his $pVT$ measurements made with a Burnett apparatus. Finally, Lemmon and Span[4] generated a so-called short reduced Helmholtz energy equation of state (EOS) for hydrogen sulfide. Although a number of coefficients were fitted to substance specific data sets, the fundamental form of the equation was determined using a simultaneous optimization to a primary data set consisting of thermophysical properties of a larger number of fluids. The short reduced Helmholtz energy EOS, intended for typical nonpolar and weakly polar fluids, is currently being used by NIST as reference in the REFPROP program.[50] The $B$ values resulting from this equation of state should be characterized by a reasonably low uncertainty.

The comparison of the experimental and experimentally based second pressure virial coefficients with the values calculated from the new *ab initio* interaction potential of hydrogen sulfide is illustrated in Fig. 3. Where necessary, temperatures reported on IPTS-68, IPTS-48 and ITS-27 were converted to the International Temperature Scale of 1990 (ITS-90).
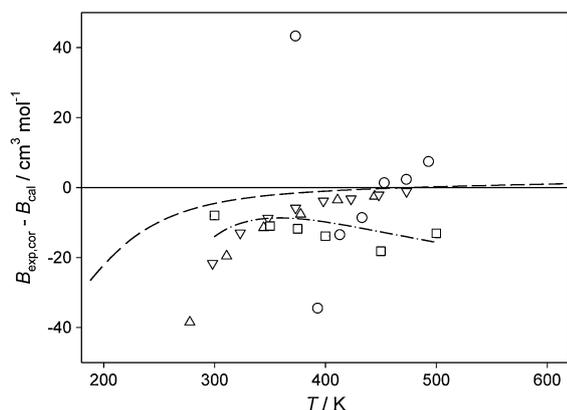


**Fig. 3** Differences $(B_{\text{exp,cor}} - B_{\text{cal}})$ of experimental $(B_{\text{exp}})$ and of correlated $(B_{\text{cor}})$ second pressure virial coefficients from values $(B_{\text{cal}})$ calculated with the new *ab initio* potential for $H_2S$ as a function of temperature. Experimental data: △, Reamer *et al.* (1950)[44] (volumetric data evaluated by Pesuit according to Dymond and Smith);[47] ▽, Reamer *et al.* (1950)[44] (volumetric data evaluated by Khoury and Robinson);[48] ○, Lewis and Fredericks (1968);[45] □, Liu (1985).[46] Correlated values: ---, Dymond *et al.* (2002);[49] ---, Lemmon and Span (2006)[4] and REFPROP (NIST 23, version 9.0).[50]

The figure shows an excellent agreement with the REFPROP values, within $\pm 1$ cm$^3$ mol$^{-1}$, at temperatures $T > 400$ K, where the values of the second pressure virial coefficient become larger than $B > -100$ cm$^3$ mol$^{-1}$. The differences increase with decreasing temperature to about $-(5$ to $25)$ cm$^3$ mol$^{-1}$ in the range 300 K $> T > 200$ K, where the second pressure virial coefficient varies approximately between $-180$ and $-450$ cm$^3$ mol$^{-1}$. This is an excellent agreement between the calculated values and those obtained from the currently most reliable correlation. As can be observed from Fig. 3, the experimental values of different workers exhibit a larger mutual uncertainty. In summary, at temperatures $T > 300$ K the experimental data, as well as the correlation by Dymond *et al.*,[49] are less reliable than the REFPROP values[4,50] and the values obtained in this work. Below 300 K having the calculated $B$ values is significant as there are no experimental data.

## 4 Transport properties

The shear viscosity $\eta$, the thermal conductivity $\lambda$, and the volume viscosity $\eta_V$ of a polyatomic gas in the limit of zero density can be expressed as:[20,51]

$$\eta = \frac{k_B T}{\langle v \rangle_0} \frac{f_\eta^{(n)}}{\mathfrak{S}(2000)}, \qquad (7)$$

$$\lambda = \frac{5 k_B^2 T}{2 m \langle v \rangle_0} \frac{\mathfrak{S}(1001) - 2r\mathfrak{S}\begin{pmatrix} 1001 \\ 1010 \end{pmatrix} + r^2\mathfrak{S}(1010)}{\mathfrak{S}(1010)\mathfrak{S}(1001) - \mathfrak{S}\begin{pmatrix} 1001 \\ 1010 \end{pmatrix}^2} f_\lambda^{(n)}, \quad (8)$$

$$\eta_V = \frac{k_B c_{\text{int}}}{c_V^2} \frac{k_B T}{\langle v \rangle_0 \mathfrak{S}(0001)} f_{\eta_V}^{(n)}, \qquad (9)$$

where $\langle v \rangle_0 = 4(k_B T/\pi m)^{1/2}$ is the average relative thermal speed, $m$ is the molecular mass, and $c_V$ is the isochoric heat capacity. The parameter $r$ is given by

$$r = \left(\frac{2}{5}\frac{c_{\text{int}}}{k_B}\right)^{1/2}, \quad c_{\text{int}} = c_{\text{rot}} + c_{\text{vib}}. \qquad (10)$$

Here $c_{\text{int}}$ is the contribution of both the rotational, $c_{\text{rot}}$, and the vibrational, $c_{\text{vib}}$, degrees of freedom to $c_V$. The quantities $f_\eta^{(n)}$, $f_\lambda^{(n)}$ and $f_{\eta_V}^{(n)}$ are $n$th-order correction factors that can be expressed in terms of generalized cross sections.[20,52–54] They account for the effects of higher basis-function terms in the perturbation-series expansion of the solution of the Boltzmann equation.[20] The quantities $\mathfrak{S}(2000)$, $\mathfrak{S}(1010)$, $\mathfrak{S}(1001)$, $\mathfrak{S}\begin{pmatrix} 1001 \\ 1010 \end{pmatrix}$ and $\mathfrak{S}(0001)$ are generalized cross sections, and the notation and conventions employed are fully described elsewhere.[20,24] The evaluation of viscosity, thermal conductivity and volume viscosity from a given intermolecular potential basically amounts to the computation of the relevant generalized cross sections. We computed them by means of classical trajectories and used for this purpose the modified TRAJECT software code,[55,56] employed also in our previous studies to determine the generalized cross sections for pure water and methane.[2,24,25]

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The hydrogen sulfide molecule was represented in the trajectory calculations as a rigid asymmetric top. For a given total energy, translational plus rotational, classical trajectories describing the collision of two molecules were obtained by integrating Hamilton's equations from pre- to post-collisional values (initial and final separation: 400 Å). The total-energy-dependent generalized cross sections were evaluated for 25 values of total energy by means of a Monte Carlo procedure in line with our previous work,[2,21–25] whereby the initial values of thirteen integration variables were chosen using a pseudo-random number generator. The final energy integration was performed by means of the Chebyshev quadrature. At each energy up to 160 000 classical trajectories were evaluated. The number of trajectories had to be reduced significantly for low energies, because the computational demand to achieve a sufficient accuracy for a given trajectory is increasing as the energy decreases. Nevertheless, the number of trajectories was sufficient to compute the most important transport, $\mathfrak{S}(p0st)$,

relaxation, $\mathfrak{S}(0qst)$, and production, $\mathfrak{S}\begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}$,

cross sections to the accuracy of about $\pm 0.3\%$, $\pm 1\%$ and $\pm 5\%$, respectively.

## 4.1 Shear viscosity

The viscosity of hydrogen sulfide was calculated by means of eqn (7), whereas the higher-order correction factor, $f_\eta^{(n)}$, was evaluated to the third order ($n = 3$) employing expressions, in terms of generalized cross sections, given in our previous work.[24] The contributions of the higher-order corrections amount to at most $+0.2\%$ in the temperature range of the experiments, and the contribution of the third-order correction itself is always smaller than $+0.01\%$. The calculated transport cross section $\mathfrak{S}(2000)$, which governs the viscosity, is characterized by the customary monotonic decrease with temperature. Based on the precision with which the $\mathfrak{S}(2000)$ cross section was evaluated, we estimate the precision of the computed viscosity values to be of the order of $\pm 0.3\%$ over the whole range of the experimental temperatures.

In principle, a stringent validation test for the intermolecular potential requires us to choose only primary viscosity data, namely data obtained in high-precision instruments for which a full working equation is available and necessary corrections can be applied. Such data should be characterized by a low defined uncertainty and a proven compatibility with data obtained from other methods or at least in other instruments. A critical review of the literature revealed only eight data sets of measurements on the viscosity of hydrogen sulfide at low pressures, confirming that viscosity data for hydrogen sulfide are indeed scarce. Due to data scarcity comparison is also made with correlated[5,50,57] hydrogen sulfide viscosity values.

The early viscosity measurements were performed by Graham,[58] Rankine and Smith[59] and Jung and Schmick[60] with capillary viscometers. Recent analysis[5] indicated that their uncertainty is of the order of $\pm 3$–5%. In the late sixties and early seventies, Pal, Bhattacharyya and co-workers[61–64] reported in four papers several series of measurements on hydrogen sulfide as part of their study of the viscosities of polar gases and their mixtures. The measurements, for which

an uncertainty of $\pm(0.6$ to $1.0)\%$ was claimed, were carried out with oscillating-disk viscometers and covered an extended temperature range of 221 K to 483 K. Since the series of measurements on the mixtures were performed at almost the same but fewer temperatures and the results are nearly identical, only the viscosity data for pure hydrogen sulfide vapor of Pal and Barua[61] and of Bhattacharyya et al.[63] are considered in this paper.

Very recently, Vogel[65] has performed two series of measurements with an all-quartz oscillating-disk viscometer, resulting in 33 final viscosity data points in the temperature range from 292 K to 682 K. The uncertainty of these measurements is estimated to be $\pm 0.2\%$ based on previous work to determine reference viscosity values of argon in the same temperature range and with the same instrument.[66]

It is important to note that the theoretical calculations are valid for the limit of zero density, however measurements in this limit are not feasible. Whereas the older experiments[58–60] were performed at atmospheric pressure, Pal, Bhattacharyya and co-workers[61–64] carried out their experiments at pressures of about 0.01 MPa. Vogel[65] performed his measurements at a constant density of 0.74 kg m$^{-3}$, which equates to pressures of about 0.05 MPa to 0.1 MPa in the measured temperature range. For the comparison with the theoretical values of this paper, Vogel corrected his experimental data to the limit of zero density by taking into account the effect of the initial density dependence.[67] The correction was of the order of $+0.20\%$ at ambient temperature, decreasing to $-0.04\%$ at the highest temperature. The corresponding correction for the data of ref. 58–64 was also carried out based on the information given in those papers, although these data suffer from a high uncertainty. In addition, the experimental temperature values were corrected to the temperature scale ITS-90.

Fig. 4 illustrates the comparison between experimental and correlated viscosity coefficients and the values computed
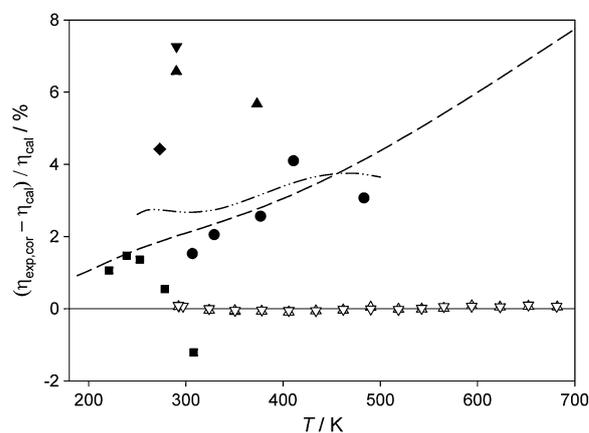


**Fig. 4** Deviations of experimental ($\eta_{exp}$) and of correlated ($\eta_{cor}$) viscosity coefficients from values ($\eta_{cal}$) calculated with the new ab initio potential for H$_2$S as a function of temperature. Experimental data: ◆, Graham (1846);[58] ▲, Rankine and Smith (1921);[59] ▼, Jung and Schmick (1930);[60] ●, Pal and Barua (1967);[61] ■, Bhattacharyya et al. (1970);[63] △, Vogel (2011), first series of measurements;[65] ▽, Vogel (2011), second series of measurements.[65] Correlated values: ⎯·⎯·⎯, Liley et al. (1988);[57] ---, Schmidt et al. (2008)[5] and REFPROP (NIST 23, version 9.0).[50]

in this work. The agreement with the data of Vogel[65] is excellent, all experimental values are reproduced within ±0.1%. Even though this nearly exact match is most likely fortuitous, the main focus should be directed to the identical temperature dependence of the experimental and theoretical viscosity values. The experimental data of Bhattacharyya et al.,[63] which extend to the lowest temperature of 221 K, are reproduced within ±1.5%, somewhat outside the joint claimed uncertainty. Furthermore, the data of Pal and Barua[61] measured to 483 K, the highest temperature of earlier papers, lie 2 to 4% above our computed values. In addition, both data sets are characterized by a different temperature function compared with that of the theoretically calculated values. Finally, the correlated values by Liley et al.[57] as well as the REFPROP values by Schmidt et al.[5] and Lemmon et al.[50] overestimate the theoretically calculated values and the experimental data by Vogel, the difference increasing with increasing temperature. This is not surprising since both correlations are based on the experimental data of Pal, Bhattacharyya and co-workers.[61–64]

## 4.2 Thermal conductivity

The thermal conductivity of hydrogen sulfide was calculated by means of eqn (8). The higher-order correction factor, $f_\lambda^{(n)}$, was evaluated up to the second order, as the expressions for higher orders, in terms of generalized cross sections, are not yet available. Since both velocity coupling[20,52] and angular-momentum coupling[68] were taken into account, knowledge of 18 generalized cross sections was required to calculate $f_\lambda^{(2)}$ using the expressions given by Maitland et al.,[69] Viehland et al.[54] or Bich et al.[70] The evaluated correction factor $f_\lambda^{(2)}$ is a weak function of temperature with values ranging from 1.003 to 1.007. The two transport cross sections $\mathfrak{S}(1010)$ and $\mathfrak{S}(1001)$, which govern the thermal conductivity, are of similar magnitude, while the production cross section $\mathfrak{S}\begin{pmatrix} 1001 \\ 1010 \end{pmatrix}$ is an order of magnitude smaller, which is in agreement with the behavior of other gases. The values of internal contributions to the isochoric heat capacity, which enter eqn (10), were obtained from the equation of state by Lemmon and Span.[4] Based on the precision with which the cross sections were evaluated, we estimate that the precision of the calculated thermal conductivity is of the order of ±0.5% over the whole range of temperatures.

A review of the literature resulted in only five data sets of measurements on the thermal conductivity of hydrogen sulfide at low density, revealing not only an absence of primary data but also a general shortage of data. The common hot-wire technique was used in all these measurements, whereas the authors estimated the uncertainty of their data to be ±1%. The earliest thermal conductivity measurement was carried out by Eucken.[71] In the late sixties Correia et al.[72] as well as Barua, Manna, Mukhopadhyay and Srivastava[73–75] performed a series of measurements on hydrogen sulfide as part of their studies of the thermal conductivities of polar gases and of their mixtures with other gases. In analogy to viscosity, the thermal conductivity data for the vapor mixtures with hydrogen sulfide[74,75] were excluded from the comparison
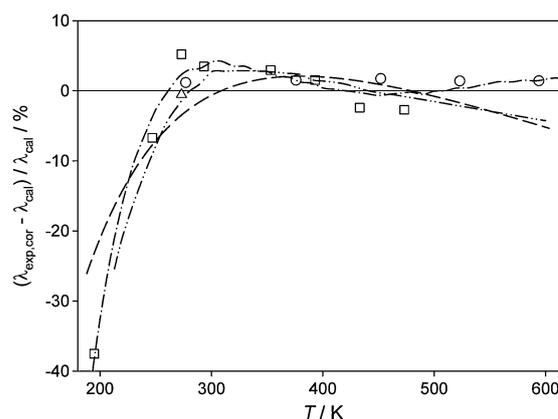


**Fig. 5** Deviations of experimental ($\lambda_{exp}$) and of correlated ($\lambda_{cor}$) thermal conductivity coefficients from values ($\lambda_{cal}$) calculated with the new *ab initio* potential for $H_2S$ as a function of temperature. Experimental data: △, Eucken (1913);[71] ○, Correia et al. (1968);[72] □, Barua et al. (1968).[73] Correlated values: ---, Vargaftik et al. (1978);[76] —·—·—·, Liley et al. (1988);[57] ---, REFPROP (NIST 23, version 9.0).[50]

with the theoretically calculated values. Corrections for the initial density dependence of the thermal conductivity as well as of the experimental temperatures to the temperature scale ITS-90 were made, although their effect on the comparison is small. Due to the scarcity of experimental data, comparison is also made with correlated[50,57,76] hydrogen sulfide thermal conductivity values.

Fig. 5 illustrates the comparison between experimental and correlated thermal conductivity coefficients and the values computed in this work. The agreement with the datum of Eucken is excellent, but certainly only by chance. The agreement with the experimental data of Correia et al.[72] is also very good. These experimental data are about 1–2% higher than the theoretical values and somewhat outside the joint claimed uncertainty, however both sets are characterized by the same temperature function. The agreement with the data of Barua et al.[73] above room temperature is better than 5%. However, at lower temperatures, extending to 195 K, the difference is rather large. It is obvious that the experimental datum at 195 K suffers from lower accuracy than the rest of the data. It unduly influences the temperature trend of the correlations by Vargaftik et al.,[76] by Liley et al.[57] and the REFPROP values.[50]

## 4.3 Volume viscosity

The volume or bulk viscosity of hydrogen sulfide was calculated by means of eqn (9). The higher-order correction factor, $f_{\eta V}^{(n)}$, was evaluated up to the third order. For this purpose we have employed the second-order kinetic theory expression given by Maitland et al.[69] and the recently derived third-order kinetic theory expression.[2,25] The contribution of the second-order correction to the bulk viscosity increases with temperature reaching 2% at room temperature and a maximum of 8% at the highest temperature, 2000 K, considered in this work. The third-order result differs from the second-order result by less than 0.13% over the whole temperature range investigated. The second-order correction is larger than that observed for water and carbon dioxide, but smaller than that for methane and nitrogen.

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The experimental data for volume viscosity are scarce. Only four sets of measurements are available, comprising of seven data points in total. Geide[77] and Bauer *et al.*[78] performed measurements of the sound absorption around room temperature, while Winter and Bass[79] covered the temperature range from 298 K to 683 K. Geide interpreted the resulting spectra in terms of rotational relaxation, but Bauer *et al.* and Winter and Bass considered both rotational relaxation and vibrational relaxation. The analysis of the measurements is fraught with uncertainty, as the relatively small absorption due to internal relaxation is obtained as a difference between measured absorption spectra and estimated contribution of the classical absorption. Only Winter and Bass gave some estimates of uncertainty ranging from $\pm 10\%$ at room temperature to $\pm 20\%$ at 683 K. The inappropriateness of such low uncertainty bounds can be best seen if one compares the results of the three sets of measurements at room temperature in terms of the rotational relaxation number. Geide quoted $Z_{rot} = 31$, Winter and Bass gave $Z_{rot} = 8$, and Bauer *et al.* quoted $Z_{rot} = 5$. Such large discrepancies between measurements, which have been observed for other gases as well, indicate that the data sets cannot be used to validate the PES of hydrogen sulfide, but rather that the present calculation can help distinguish between different values proposed for the bulk viscosity and rotational relaxation process in hydrogen sulfide.

Recently Meijer *et al.*[80] used coherent Rayleigh–Brillouin spectroscopy to infer the bulk viscosity of gases from measured spectra at gigahertz frequencies. A measurement of hydrogen sulfide spectra was performed at 293 K and 4 bar giving a value for bulk viscosity to which the authors ascribed $\pm 7\%$ uncertainty.

Fig. 6 shows the comparison between our theoretical results and the measurements. The comparison has been performed in terms of bulk viscosity as this is the primary quantity extracted from the measured spectra. For this purpose we have converted the quoted rotational relaxation time values of Geide[77]
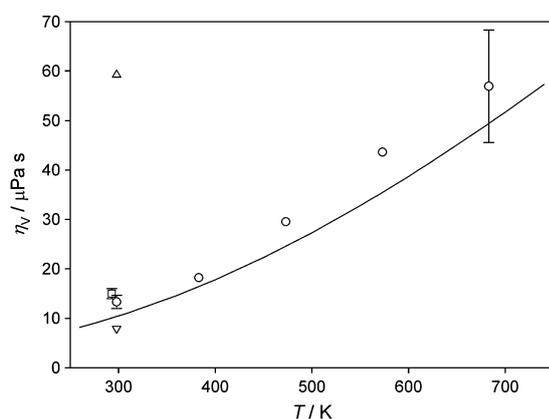
and Winter and Bass[79] and the quoted rotational relaxation number of Bauer *et al.*[78] to volume viscosity values using the expressions described in our previous papers.[2,25]

The current calculations underestimate the bulk viscosity measured by Winter and Bass[79] by on average 20%. Although at the highest temperature this is within the claimed uncertainty of the experimental data, at room temperature the agreement is outside the mutual uncertainty. However, the temperature dependence of these experimental data is reproduced by the current calculations. Considering that the Winter and Bass data indicated the presence of a constant impurity of 2% $N_2$ in most of their measurements, the agreement between the measured/inferred and calculated values is satisfactory.

The comparison at room temperature indicates a large spread of the values. Although the Meijer *et al.*[80] and the Winter and Bass[79] data agree within their claimed mutual uncertainty, their values are 20–30% higher than our calculated ones. The observed deviations also need to be examined in the context of results for other gases. For instance, the Meijer *et al.* value for the volume viscosity of methane at room temperature is 30% higher than that measured by Hill and Winter[81] and roughly 80% higher than our calculated value, which itself is in agreement with the measured values of Prangsma *et al.*[82] The datum of Bauer *et al.*[78] is approximately 30% below the calculated value, while the volume viscosity measured by Geide[77] is nearly six times larger than the calculated one. As a number of workers[78,83] have argued already, the current calculations support the supposition that the data point of Geide is most likely erroneous.

## 5   Summary and conclusions

A new six-dimensional potential energy hypersurface for two rigid hydrogen sulfide molecules was determined from quantum-mechanical *ab initio* calculations. In total 4016 interaction energies were determined utilizing the CCSD(T) level of theory, basis sets up to aug-cc-pV(Q + d)Z with bond functions, and extrapolating the computed interaction energies to the complete basis set. The PES was represented by an accurate site–site potential function, which was fitted to the calculated interaction energies.

To validate the accuracy of the proposed *ab initio* potential surface we have calculated the second pressure virial coefficient and compared with the available data. The computed values are in excellent agreement with the recommended REFPROP values above 400 K. Below 400 K the differences between the two increase with decreasing temperature, reaching 5.5% at 200 K. Our results support the conclusion that the REFPROP values are more reliable than a simple correlation of the available data.

To further validate the PES and also to provide values of transport properties in the dilute-gas limit, we have calculated the shear viscosity, thermal conductivity and volume viscosity of hydrogen sulfide over the temperature range of 180 K to 2000 K. The required generalized cross sections were computed by means of the classical trajectory method, employing our intermolecular potential energy hypersurface.

For the viscosity an excellent agreement with the data of Vogel[65] was obtained; they were reproduced within 0.1% over

**Fig. 6** Comparison of experimental or experimentally based values ($\eta_{V,exp}$) for the volume viscosity with values ($\eta_{V,cal}$) calculated according to the third-order theory with the new *ab initio* potential for $H_2S$ as a function of temperature. Experimentally based data (inferred from rotational relaxation times or rotational collision numbers): △, Geide (1963);[77] ▽, Bauer *et al.* (1970);[78] ○, Winter and Bass (1970).[79] Experimental data: □, Meijer *et al.* (2010).[80] The error bars shown correspond to the estimated experimental uncertainties (see the text). Calculated values: —.

the entire temperature range of the experiments. The agreement with the data of Bhattacharyya *et al.*,[63] which extend to 221 K, is also very good, although it is somewhat outside the joint claimed uncertainty. The currently accepted REFPROP values,[50] based on the correlation of Schmidt *et al.*,[5] overestimate the computed values, and consequently overestimate the latest Vogel data, with the differences increasing with increasing temperature. Hence there is a need to reassess the current correlation for the viscosity of hydrogen sulfide in the light of the current results and the availability of new data.

For the thermal conductivity there is a satisfactory agreement with the available experimental data above room temperature; most of the data are reproduced within 5%. However, at the lowest temperature of 195 K the calculated value is nearly twice the experimental datum. It seems unlikely that the calculated values for the thermal conductivity at low temperatures are characterized by such large uncertainties.

The available volume viscosity data for hydrogen sulfide are of generally low accuracy and not suitable for validating the potential surface. Although the volume viscosity is much more sensitive to the anisotropy of the potential surface than other properties, it is argued that the current computed values make an important addition to our knowledge of the rotational relaxation process in hydrogen sulfide, especially in view of the scarcity and low accuracy of the experimental data.

In conclusion the proposed potential surface for hydrogen sulfide has been validated against the best available thermophysical data. The data are generally reproduced rather well and the computed values provide a reliable and accurate estimate of the second pressure virial coefficient, shear viscosity, thermal conductivity and volume viscosity of hydrogen sulfide over the temperature range 180 K to 2000 K. The theoretically calculated values will be published separately in order to provide accurate data for thermophysical properties of hydrogen sulfide.

## Acknowledgements

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