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The dipole moment surface for hydrogen sulfide H_2S

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ABSTRACT

In this work we perform a systematic *ab initio* study of the dipole moment surface (DMS) of H_2S at various levels of theory and of its effect on the intensities of vibration–rotation transitions; H_2S intensities are known from the experiment to display anomalies which have so far been difficult to reproduce by theoretical calculations. We use the transition intensities from the HITRAN database of 14 vibrational bands for our comparisons. The intensities of all fundamental bands show strong sensitivity to the *ab initio* method used for constructing the DMS while hot, overtone and combination bands up to 4000 cm^{-1} do not. The core-correlation and relativistic effects are found to be important for computed line intensities, for instance affecting the most intense fundamental band (ν_2) by about 20%. Our recommended DMS, called ALYT2, is based on the CCSD(T)/aug-cc-pV(6+d)Z level of theory supplemented by a core-correlation/relativistic corrective surface obtained at the CCSD[T]/aug-cc-pCV5Z-DK level. The corresponding computed intensities agree significantly better (to within 10%) with experimental data taken directly from original papers. Worse agreement (differences of about 25%) is found for those HITRAN intensities obtained from fitted effective dipole models, suggesting the presence of underlying problems in those fits.

1. Introduction

Hydrogen sulfide (H_2S) is a light, nonrigid asymmetric rotor molecule. Microwave and infrared spectra of H_2S display unusual band intensities for a number of vibrational states. For example, the ν_1, ν_2 and ν_3 fundamental bands of H_2S are two-to-three orders of magnitude weaker than those in similar triatomics such as H_2O and H_2Se and are much weaker than those of combination bands ($\nu_1+\nu_2$, $\nu_2+\nu_3$ and $\nu_1+\nu_3$) [1]. In this respect the asymmetric stretch fundamental band ν_3 is particularly weak and even weaker than the $2\nu_2$ bending overtone. Furthermore all fundamental bands show intensity anomalies in their rotational distributions. The *P*-branch transitions of the ν_1, ν_2 and ν_3 bands are much less intense than the *R*-branch [1–3]. For the ν_3 band, some 'forbidden' $\Delta K_a = \pm 2$ transitions are actually more intense than the corresponding 'allowed' $\Delta K_a = 0$ transitions [1]. Reproducing these intensity features using an *ab initio* electric dipole moment surface (DMS) represents a challenge for theoretical spectroscopy and H_2S is therefore an important benchmark system [4–6].

Ab initio DMSs have been calculated for H_2S by Senekowitsch et al. [7] and by Cours, Tyuterev and co-workers [6,8,9]. Senekowitsch et al.'s DMS was used as the basis for extensive studies of both H_2S [7] and HDS [10]. Although this work qualitatively reproduced some of the anomalies in the H_2S spectrum, there were large discrepancies

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between the calculated and the experimental intensities of the fundamental bands. These discrepancies were attributed to the very small first derivatives of the dipole moment function along the symmetric and asymmetric stretch displacement coordinates [7] (see also the review by Yurchenko [11]).

Cours et al. [6,8] presented a significantly improved H_2S DMS. They actually computed three different *ab initio* DMS's [6]; their recommended surface was based on the (frozen-core, non-relativistic) coupled-cluster singles, doubles and perturbative triples (CCSD [T]) method and a basis set derived from Dunning's cc-pV5Z [12] (but similar in size to aug-cc-pVQZ). Note that for their recommended surface Cours et al. used for the perturbative triples correction the 'square brackets' variant due to Urban et al. [13] rather than the much more popular (and generally more accurate) 'round brackets' one of Raghavachari et al. [14], although they also explored the other variant. Our calculations show that Cours et al's [6] best DMS overestimates the most intense transitions of both the ν_1 and ν_2 fundamental bands by about 30% and 40%, respectively, as well as the $\nu_1+\nu_2-\nu_2$ hot band by about 30%. These bands, as well as the ν_3 fundamental band, are especially sensitive to the DMS used; other bands lying below 4000 cm^{-1} show reduced sensitivity.

The aim of the present study is to produce a systematically improved DMS for H_2S building on the experience gained from our recent studies on the water molecule [15–17], see Lodi and Tennyson [18] for a general discussion. These studies have resulted in a DMS surface, LTP2011 [17], which has been shown in a number of studies of being capable of predicting transition intensities with an uncertainty close to 1% for the majority of lines [17,19,20]. This has resulted in transition intensities computed using this DMS being extensively used to replace measured data in standard line lists [21,22].

As a result of a systematic study analysing a large set of electronic structure approaches we present a new *ab initio* DMS (referred to as ALYT2) based on the CCSD(T)/aug-cc-pV(6+d)Z level of theory supplemented by a core-correlation/relativistic corrective surface obtained at the CCSD[T]/aug-cc-pCV5Z-DK level. This DMS is based on a very dense grid of 10 000 geometries covering energies up to about 20 000 cm^{-1}. We use the program DVR3D [23] to solve the ro-vibrational Schrödinger equation in conjunction with a new, empirical potential energy surface (PES). This PES is a further refinement of the empirical PES by Tyuterev [24] based on newly available experimental energy levels and will be reported elsewhere [25].

The computed ALYT2 DMS was evaluated both with respect to the stability and consistency of the *ab initio* treatment employed and by comparison with transitions from the HITRAN 2008 database [26]. We note that the 2012 release of HITRAN [22] has been substantially extended for H_2S at both long [27] and short wavelengths [28,29] but contains the same data in the mid-infrared which is what concerns us here. As discussed below, it transpires that our best *ab initio* results are in much better agreement with directly-measured line intensities in HITRAN than with those line intensities calculated from effective dipole moment models.

2. Dipole moment calculations

The electronic structure computations reported here were performed with the quantum chemistry package MOLPRO [30], while the ro-vibrational lines intensities were calculated using the DVR3D nuclear motion program suite [23]. Calculations were performed in Radau coordinates and used the bisector embedding [31]. The following (atomic) masses were used: $m(\text{H}) = 1.007825$ Da, $m(^{32}\text{S}) = 31.972071$ Da. The discrete variable representation (DVR) grids comprised 40 Morse-like oscillators defined using the parameters $r_e = 3.8$, $\omega = 0.005$ and $D_e = 0.4$ all in a.u., and 48 associated-Legendre polyonomials for the angular coordinate. The vibrational Hamiltonian matrices used in the DVR3DRJZ program had dimension 6000 and 2000 solution for each k were selected for the solution of the full rotational-vibrational problem in the program ROTLEV3B; the final vibrational–rotational basis used in ROTLEV3B was truncated to $1400 \times (J+1)$. These parameters are sufficient to converge levels to better than 0.1 cm^{-1} and, in almost all cases, much better than this. Calculations were performed for all rotational states, J, up to 40, but unless otherwise stated, comparisons are presented for states with rotational quantum number up to $J=5$. Transitions involving $J \le 5$ encompass the majority of the strong lines. Our final comparisons are performed are for J up to 27 for pure rotational lines and up to $J=20$ for other transitions, which corresponds to the range of values found in HITRAN.

In our calculations we used a system of axes pq with the S atom at the origin and where q is the axis which bisects the $\widehat{\text{HSH}}$ bond angle and p is the in-plane axis perpendicular to it [32,33]. Dipole components μ_α $(\alpha = p, q)$ were computed as numerical energy derivatives by $\mu_\alpha = (E_{+\lambda_\alpha} - E_{-\lambda_\alpha})/(2\lambda_\alpha)$, where $\lambda_\alpha = 7.5 \times 10^{-4}$ a.u. is an external, weak, static and uniform electric field along the α direction. This method is thought to be more accurate than computing dipoles as an expectation value [18] and has the further advantage of allowing one to take into account corrections to the dipoles due to terms in the Hamiltonian treated by first-order perturbation theory to the energy, such as relativistic corrections. The approach we adopt mirrors the composite focal point analysis scheme used for high-accuracy *ab initio* energy studies [34].

2.1. Core correlation and relativistic corrections

Core-correlation and relativistic corrections are known to be essential for the calculation of accurate *ab initio* potential energy surfaces [35,36]. Their effect on DMSs was shown to be small but relevant for the water molecule [16,17]. We investigated the magnitudes of these effects for the H_2S DMS for the first time.

In a preliminary test dipole moments were computed using the CCSD[T] method on a grid of 200 geometries using four, increasingly-sophisticated levels of theory: (1) frozen-core, non-relativistic; (2) frozen-core, relativistic; (3) all-electron, non-relativistic; (4) all-electron, relativistic. The basis set used for the various levels of calculations are, respectively, aug-cc-pV5Z basis set [12], aug-cc-pV5Z-DK [37], aug-cc-pCV5Z [38] and aug-cc-pCV5Z-DK [37].

The relativistic calculations were carried out using the second-order Douglas–Kroll–Hess Hamiltonian as implemented in Molpro and in the all-electron calculations the 1*s* orbital of the sulfur atom was kept frozen.

Indicative plots of these corrections are shown in Fig. 1. Relativistic effects reduce the magnitude of dipoles by about 0.017 Debyes (D); core-correlation gives a smaller contribution of less than 0.005 D for energies up to 13 000 cm^{-1} and up to 0.010 D for energies up to 25 000 cm^{-1}, generally leading to a reduction of the dipole magnitude. Dipoles computed by the combined relativistic/core-correlation calculations (point 4 above) give an overall correction identical (within 0.0005 D) to the sum of the corrections calculated individually; in other words the relativistic and core-correlation corrections can be processed independently.

For the water molecule it was found [16,39] that core-correlation and relativistic corrections, which both have an absolute magnitude of about 0.0008 D, cancel each other out almost entirely, so that their sum only contributes by about 0.0001 D. The situation for H_2S is different as in this case both relativity and core-correlation tend to reduce the magnitude of dipoles, so that mutual cancellation between the two contributions does not generally happen. An exception to this behavior occurs for energies up to 5000 cm^{-1} for the small component of the dipole moment (perpendicular to the bond-angle bisector); in this particular case the two corrections have similar magnitude (about 0.001 D) and opposite signs, so that they do largely cancel. However, no cancellation occurs for the correction to the large component of the dipole (along the bond-angle bisector).

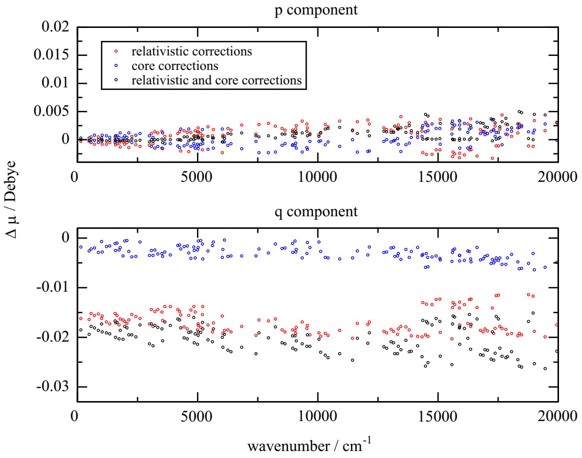

Fig. 1. Effect of relativity and core correlation on the dipole moment components for 200 selected geometries using CCSD[T] using aug-cc-pCV5Z (core correction), aug-cc-pV5Z-DK (relativistic correction) and aug-cc-pCV5Z-DK (relativistic and core correction basis sets. The quantity plotted, $\Delta\boldsymbol{\mu}$, is the difference between dipoles computed allowing for corrections due to the relativity or core-electron correlation or both and dipoles computed at the non-relativistic, frozen-core level.

It is not possible to directly infer the effect of the corrections on computed ro-vibrational line intensities, as these depend in a complicated way on the derivatives of the DMS, rather than on its absolute value. In fact, as discussed below, even though these two corrections affect the value of dipoles by only about 2% their effect on line intensities can be as large as an order of magnitude (see below). Both relativistic and core-correlations corrections were included in our final ALYT2 surface.

2.2. Equilibrium dipole

The effects of different levels of the *ab initio* theory on the dipole moment of H_2S were analysed at the empirical equilibrium geometry $r_e = 1.3356$ Å, $\theta_e = 92.11^\circ$ [40] and compared to the accurately-known experimental value $\mu_e = 0.978325(10)$ D [41]. The three coupled cluster variants considered, CCSD-T [42], CCSD(T) and CCSD[T], give dipoles which differ by 0.0003–0.0014 D depending on the basis set and type of calculation (frozen core, all electron, relativistic) used.

Table 1 gives a summary of dipole moments computed at the equilibrium geometry. Lines 2–3 of Table 1 correspond to calculation with or without core-correlation and relativistic corrections. Finally, a vibrational-averaging correction was added by performing nuclear motion calculations using the DVR3D program suite [23] and the ALYT2 DMS presented below. Our final value for the permanent dipole moment of H_2S is 0.0081 D (0.8%) smaller than the experimental value. If the relativistic and core-correlation effects were discarded the discrepancy with experiment would slightly increase to 1.0%.

2.3. Construction of the dipole moment surface

The DMS was computed using a very dense grid of 10 000 symmetry-independent geometries. These geometries cover bond lengths from 2.00 to 3.40 a_0 and bond angles from 55° to 140°. The grid was designed to be

Table 1
Permanent dipole at the equilibrium geometry $r = 1.3356$ Å and $\theta = 92.11^\circ$ using different levels of theory.

Row	Method	μ_e (D)
1	CCSD(T)/aug-cc-pV(6+d)Z	0.9884
2	CCSD[T]/aug-cc-pCV5Z-DK with corrections	0.9696
3	CCSD[T]/aug-cc-pCV5Z-DK without corrections	0.9876
4	Core and relat. corrections = row 2 - row 3	−0.0180
5	Row 1 plus row 4	0.9704
6	Vibrational averaging	−0.0002
7	Calculated permanent dipole moment	0.9702
	Experimental value [41]	0.978325(10)

denser in the vicinity of the equilibrium geometry and to cover energies up to 20 000 cm^{-1}. Several coupled-cluster methods were used to construct dipole moment surfaces: CCSD(T), CCSD[T], CCSD(T)-F12b and CCSD(T)-F12c [43] in conjunction with the following basis sets: cc-pVQZ, aug-cc-pV5Z, aug-cc-pCV5Z-DK, aug-cc-pV(Q+d)Z and aug-cc-pV(6+d)Z [12,38,44]. The explicitly correlated F12 [43] calculations used the OptRI basis set [45] for the resolution of the identity approximation.

In order to fit the computed *ab initio* points we represented the two q and p dipole moment components $\mu^{(q)}$ and $\mu^{(p)}$ by a MORBID-like expansion [33], also used by Cours et al. [6]. In this representation $\mu^{(q)}$ and $\mu^{(p)}$ are given by the following expansions in terms of the coordinate displacements $\Delta r_1 = r_1 - r_e$, $\Delta r_2 = r_2 - r_e$, and $\cos\rho_e - \cos\bar{\rho}$, where $\bar{\rho} = \pi - \theta$, θ is the bond angle and r_1 and r_2 are the bond lengths:

$$\mu^{(q)}(\Delta r_1, \Delta r_2, \Delta\bar{\rho}) = \sin\bar{\rho}\left[\mu_0^{(q)}(\bar{\rho}) + \sum_j \mu_j^{(q)}(\bar{\rho})\Delta r_j + \sum_{j\le k}\mu_{jk}^{(q)}(\bar{\rho})\Delta r_j\Delta r_k \right.$$
$$\left. + \sum_{j\le k\le m}\mu_{jkm}^{(q)}(\bar{\rho})\Delta r_j\Delta r_k\Delta r_m + \sum_{j\le k\le m\le n}\mu_{jkmn}^{(q)}(\bar{\rho})\Delta r_j\Delta r_k\Delta r_m\Delta r_n + \cdots\right], \qquad (1)$$

$$\mu^{(p)}(\Delta r_1, \Delta r_2, \Delta\bar{\rho}) = \mu_0^{(p)}(\bar{\rho}) + \sum_j^{(p)} \mu_j^{(p)}(\bar{\rho})\Delta r_j + \sum_{j\le k}\mu_{jk}^{(p)}(\bar{\rho})\Delta r_j\Delta r_k$$
$$+ \sum_{j\le k\le m}\mu_{jkm}^{(p)}(\bar{\rho})\Delta r_j\Delta r_k\Delta r_m + \sum_{j\le k\le m\le n}\mu_{jkmn}^{(p)}(\bar{\rho})\Delta r_j\Delta r_k\Delta r_m\Delta r_n + \cdots, \qquad (2)$$

where all indices j, k, m, and n assume the values 1 or 2,

$$\mu_{jk\ldots}^{(q)}(\bar{\rho}) = \sum_{i=0}^{N} Q_{jk\ldots}^{(i)}(\cos\rho_e - \cos\bar{\rho})^i, \qquad (3)$$

$$\mu_{jk\ldots}^{(p)}(\bar{\rho}) = \sum_{i=0}^{N} P_{jk\ldots}^{(i)}(\cos\rho_e - \cos\bar{\rho})^i, \qquad (4)$$

and the $Q_{jk\ldots}^{(i)}$ and $P_{jk\ldots}^{(i)}$ are molecular dipole parameters. The expansion coefficients in Eqs. (3) and (4) are subject to the conditions that the functions $\mu^{(q)}$ are unchanged under the interchange of the identical protons, whereas the function $\mu^{(p)}$ is antisymmetric under this operation. Typically 48 terms were used for the q component and 33 for p components. For all the electronic-structure methods investigated the fitted surfaces reproduced the *ab initio* data with a root-mean-square deviation of less than 2×10^{-4} D.

Our best DMS, called ALYT2, corresponds to the CCSD(T)/aug-cc-pV(6+d)Z level of theory supplemented by a core-correlation/relativistic correction surface obtained at the CCSD[T]/aug-cc-pCV5Z-DK level. It was constructed as follows:

$$\mu_{\text{final}}(r_1, r_2, \theta) = \mu_{\text{aug-cc-pV(6+d)Z}}^{\text{uncorrected}}(r_1, r_2, \theta)$$
$$+ \mu_{\text{aug-cc-pCV5Z-DK}}^{\text{corrected}}(r_1, r_2, \theta) - \mu_{\text{aug-cc-pCV5Z-DK}}^{\text{uncorrected}}(r_1, r_2, \theta). \qquad (5)$$

The coefficients $Q_{ij\ldots}^{(i)}$ and $P_{ij\ldots}^{(i)}$ for the fit to ALYT2 are provided as supplementary material. The corresponding *ab initio* values of the q and p components are presented graphically in Fig. 2. All resulting surfaces were then used to compute intensities for transitions involving states with $J \le 5$. Detailed discussion of the results is given in the following section.

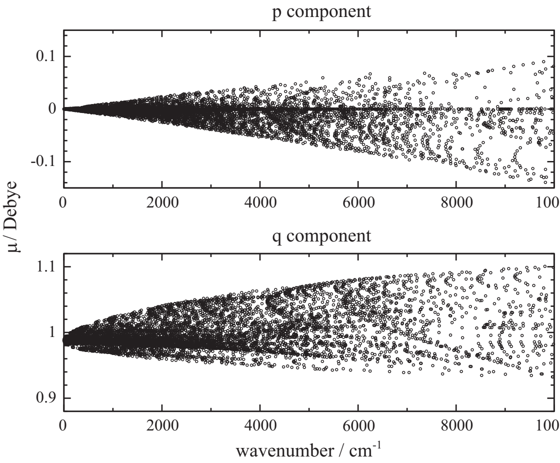

Fig. 2. The *ab initio* points for the two components of the dipole moment surface using CCSD[T]/aug-cc-pCV5Z-DK.

Comparing our ALYT2 DMS with that of Cours et al. [6] we found that the $\mu^{(q)}$ component shows significant differences of about 0.03 D between the two surfaces already within 0.3 Å of the equilibrium geometry, while the $\mu^{(p)}$ component agrees to within about 10^{-3} D. The asymmetric $\mu^{(p)}$ component was found to change very slowly with geometry.

3. Transition intensity calculations

As discussed above, we considered the four electronic structure methods CCSD(T), CCSD[T], CCSD(T)-F12b and CCSD(T)-F12c in conjunction with the five basis sets cc-pVQZ, aug-cc-pV5Z, aug-cc-pCV5Z-DK, aug-cc-pV(Q+d)Z and aug-cc-pV(6+d)Z. This led to 13 different DMSs, which were all used to produce and analyse line intensities. More details on these tests are given in the supplementary material and a discussion can be found in Azzam's PhD thesis [46]. Here we mostly concentrate on the results for our best dipole moment surface, ALYT2.

In order to test the DMS we evaluate the intensity ratios between our calculated intensities ($I_{\text{Calc.}}$) and the line intensities from HITRAN 2008 (I_{HITRAN}) for selected, intense lines in the rotational band and in 13 vibrational bands up to 4000 cm^{-1}.

Fig. 3 and Table 2 report the intensity ratios obtained using ALYT2 as well as the DMS of Cours et al. [6]. We make here three remarks: (i) one can see that the DMS of Cours et al. describes the intensities of the ν_3 band correctly; specifically, the 140 lines considered show a standard deviation of about 13% for the intensity ratio ($I_{\text{Calc.}}/I_{\text{HITRAN}}$) with maximum and minimum differences of +55% and −0.44% respectively, thus agreeing better with HITRAN than ALYT2 for this band. It should be noted, however, that the HITRAN intensities are obtained from intensity calculations based on effective dipole moment models fitted to a rather limited number of measured lines. As will be shown

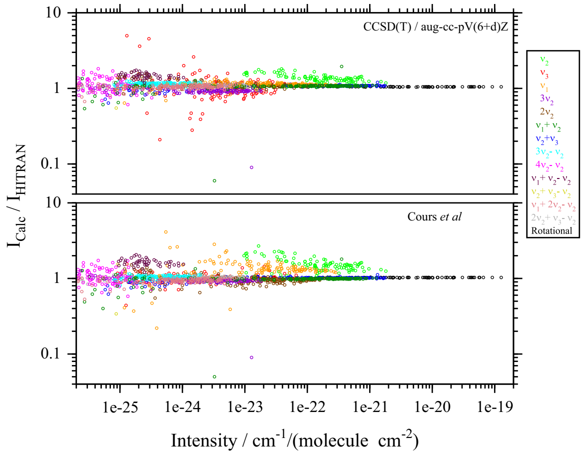

Fig. 3. Intensity ratios ($I_{Calc.}/I_{HITRAN}$) vs. HITRAN's line intensities using either our new ALYT2 DMS or the one by Cours et al. [6]. This plot contains lines with J values up to 5 for 14 vibrational bands.

below, our calculated intensities agree much better with the directly measured line intensities taken from the original sources. (ii) The DMS by Cours et al. overestimates the line intensities of the ν_1 and ν_2 fundamental and $\nu_1+\nu_2-\nu_2$ hot bands, while ALYT2 gives better results in terms of average intensity ratios for the lines in each band, see Table 2. (iii) Both our DMSs (including all our 13 surfaces, see supplementary material) and the DMS by Cours et al. [6] give very good intensity predictions for the higher vibrational bands with a standard deviation of about 11% and an average difference of +4% ($I_{Calc.}/I_{HITRAN}$) for more than 1000 transitions. In conclusion, our ALYT2 surface shows significantly improved behavior.

Table 2 also gives the vibrational band intensity for each band considered. These were obtained by summing over the intensity of all lines in a band at 296 K. This methodology has a tendency to make the calculated bands slightly stronger as calculations have complete coverage of the band and intensities for all lines, whereas compilations

Table 2
Quantitative analysis of the intensity ratios presented in Fig. 3; ($I_{Calc.}/I_{HITRAN}$) ratios were calculated for the rotational band and 13 vibrational bands up to 4000 cm^{-1}. σ is the unweighted standard deviation. Also given is the vibrational band intensity in cm^{-1}/(molecule cm^{-2}), with powers of ten in parenthesis. The fundamental bands ν_1, ν_2 and ν_3 as well as the hot band $\nu_1+\nu_2-\nu_2$ are particularly sensitive to the DMS used.

Band	Average	σ	Max.	Min.	lines	$I_{band.}$	Reference
Rotational	1.05	0.01	1.08	1.03	87	1.10(−18)	ALYT2
	1.03	0.01	1.05	1.01		1.08(−18)	Cours et al. [6]
						1.05(−18)	HITRAN
ν_3	1.11	0.59	4.98	0.21	140	9.33(−22)	ALYT2
	1.00	0.13	1.55	0.44		9.38(−22)	Cours et al. [6]
						9.07(−22)	HITRAN
ν_2	1.35	0.18	1.81	0.94	105	3.44(−20)	ALYT2
	1.55	0.32	2.69	0.99		3.79(−20)	Cours et al. [6]
						2.65(−20)	HITRAN
ν_1	1.13	0.12	1.56	0.64	120	5.62(−21)	ALYT2
	1.35	0.20	1.95	0.41		6.54(−21)	Cours et al. [6]
						4.99(−21)	HITRAN
$\nu_1+\nu_2-\nu_2$	1.46	0.12	1.74	1.18	45	1.39(−23)	ALYT2
	1.63	0.17	2.06	1.21		2.22(−23)	Cours et al. [6]
						1.39(−23)	HITRAN
$2\nu_2$	1.12	0.12	1.64	0.84	140	5.28(−21)	ALYT2
	0.97	0.14	1.51	0.55		4.59(−21)	Cours et al. [6]
						4.83(−21)	HITRAN
$3\nu_2$	0.91	0.12	1.14	0.09	123	4.54(−22)	ALYT2
	0.93	0.13	1.26	0.09		4.59(−22)	Cours et al. [6]
						5.05(−22)	HITRAN
$\nu_1+\nu_2$	1.06	0.14	1.95	0.06	156	6.59(−20)	ALYT2
	0.97	0.14	1.80	0.05		6.06(−20)	Cours et al. [6]
						6.05(−20)	HITRAN
$\nu_2+\nu_3$	1.06	0.08	1.20	0.64	162	5.54(−20)	ALYT2
	0.99	0.07	1.12	0.62		5.18(−20)	Cours et al. [6]
						5.09(−20)	HITRAN
$4\nu_2-\nu_2$	1.15	0.05	1.25	0.96	97	4.56(−23)	ALYT2
	1.04	0.06	1.15	0.81		4.80(−23)	Cours et al. [6]
						5.30(−23)	HITRAN
$\nu_2+\nu_3-\nu_2$	0.92	0.36	1.42	0.55	4	4.41(−25)	ALYT2
	0.89	0.61	1.54	0.34		4.07(−25)	Cours et al. [6]
						4.74(−25)	HITRAN
$\nu_1+2\nu_2-\nu_2$	1.04	0.07	1.15	0.67	130	2.16(−22)	ALYT2
	0.93	0.07	1.05	0.53		1.94(−22)	Cours et al. [6]
						2.04(−22)	HITRAN
$2\nu_2+\nu_3-\nu_2$	1.10	0.04	1.20	0.87	124	3.36(−22)	ALYT2
	1.02	0.04	1.11	0.84		3.14(−22)	Cours et al. [6]
						3.05(−22)	HITRAN

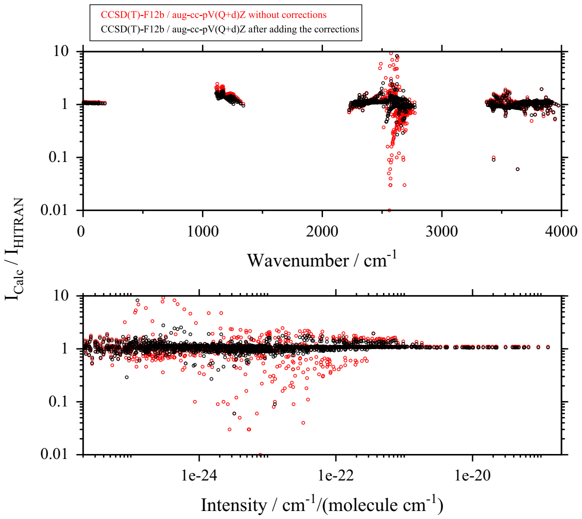

Fig. 4. Effect of adding the corrections on the intensities using CCSD(T)-F12b/aug-cc-pV(Q+d)Z.

are usually missing weak lines. With this caveat, the agreement between the HITRAN band intensities, our calculations with ALYT2 and those of Cours et al. [6], is in line with the comments made above.

In various comparisons made using the HITRAN 2008 intensity data we noticed that some lines in hot and combination bands in our calculations had intensities 50% lower than their counterparts in HITRAN, while some other lines had intensities more than 150% higher. All these lines showed the same disagreements in all calculations using both our DMSs and that by Cours et al. [6]. Further investigation showed that such disagreements could be tracked down to problems in line intensities from the HITRAN database associated with extrapolations from effective dipole moment fits; in the following discussion we will label these as "problematic lines".

We therefore decided to carry out a set of separate comparisons for actually measured intensities and for those predicted on the basis of effective dipole moment models. This required collecting the measured lines directly from the original literature [1]. New comparisons were made for the 2200–4000 cm^{-1} region. The following two bands were excluded from this analysis: (i) the rotational band, because of the very good agreement with all HITRAN data, (ii) the ν_2 band, because we could not access the data from the original reference [47]. The results of our analysis are illustrated in Fig. 5. We observed that our best DMS, ALYT2, gave significantly better agreement when compared to the actual measured data only: the error, as represented by the unweighted standard deviation σ of the intensity ratio $I_{\mathrm{Calc.}}/I_{\mathrm{HITRAN}}$, was 6.5% from an average of 1.020 for the measured lines and 25% from an average of 1.036 for the predicted lines. Interestingly, the DMS by Cours et al. [6] also reproduces the predicted lines with σ=25% and an average ratio $I_{\mathrm{Calc.}}/I_{\mathrm{HITRAN}}$ 0.990, but doubles σ to 14% (with an average of 0.996) for the measured lines. Results are summarised in Fig. 5, which suggests that the models used to extrapolate the measured H_2S data may have some problems in predicting reliable intensities. Given the unusual nature of the H_2S DMS, this would not be surprising.

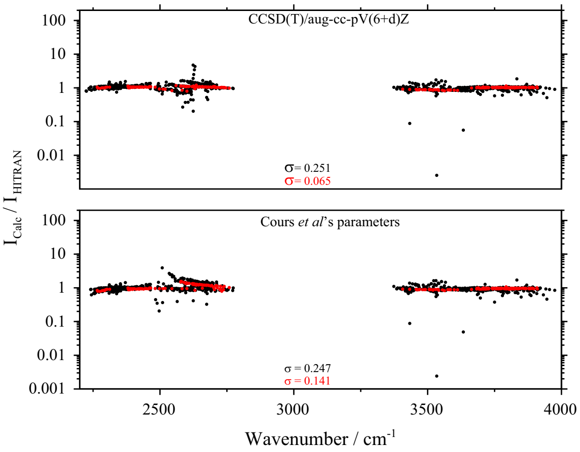

Fig. 5. Intensity ratios for lines computed using either our new ALYT2 DMS or the one by Cours et al. [6] and the HITRAN database. The standard deviation of the intensity ratios, σ, is also given; values in red are relative to lines which were directly measured, values in black to lines for which HITRAN uses intensities predicted by using fitted effective Hamiltonians. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

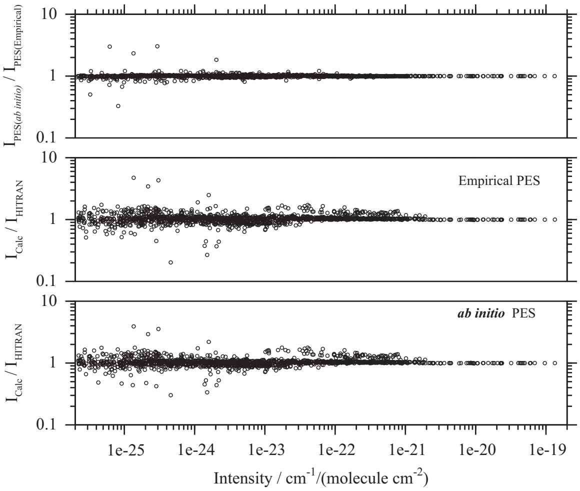

Fig. 6. Intensity ratios investigating the sensitivity of computed line intensities to the calculated nuclear wavefunctions.

A possible source of errors in our calculations is in the computed nuclear wavefunctions. It is therefore necessary to check if the disagreement in the problematic lines is due to systematic errors introduced by these wavefunctions, for example due to an incomplete treatment of resonance interactions. To test the sensitivity of the transitions intensities on the calculated wavefunctions, an *ab initio* PES was constructed using CCSD(T)/aug-cc-pV(6+d)Z with the core and relativistic corrections. New eigenvalues and wavefunctions were obtained with this PES and used with the ALYT2 DMS to compute transition intensities. Fig. 6 shows the results of the test. Apart from very weak lines, our transition intensities are not sensitive to the calculated wavefunctions.

Table 3
Sample of $H_2{}^{32}S$ lines belonging to hot and combination bands and displaying large differences in transition intensities between our calculations and HITRAN 2008 [26]. Columns give transition wavenumber, ν in cm^{-1} and intensities, I in cm^{-1}/(molecule × cm^{-2})(powers of ten in brackets); Calculation A is CCSD[T]/agu-cc-pCV5Z-DK with corrections and B is CCSD(T) /aug-cc-pV(6+d)Z after adding corrections (ALYT2).

HITRAN [26]			Transition		Calculations (this work)			I_A/I	I_B/I
ν	I	Uncertainty (%)	$\nu_1'\nu_2'\nu_3'-\nu_1''\nu_2''\nu_3''$	$J'_{K_a,K_c}-J''_{K_a,K_c}$	ν	I_A	I_B		
3750.02	5.63(−26)	2–5	1 1 0-0 0 0	$3_{3,0}-4_{2,3}$	3750.03	2.36(−26)	1.46(−26)	0.42	0.58
3945.54	2.85(−26)	2–5	1 1 0-0 0 0	$5_{4,1}-4_{1,4}$	3945.58	1.35(−26)	3.27(−26)	0.47	0.51
3531.25	1.41(−25)	5–10	0 4 0-0 1 0	$5_{0,5}-4_{1,4}$	3531.21	8.23(−26)	8.18(−26)	0.58	0.58
3531.26	4.73(−26)	5–10	0 4 0-0 1 0	$5_{1,5}-4_{0,4}$	3531.21	8.23(−26)	8.18(−26)	1.74	1.73
3551.69	8.07(−26)	5–10	0 4 0-0 1 0	$5_{1,4}-4_{2,3}$	3551.65	1.32(−25)	1.31(−25)	1.63	1.62
3552.14	2.74(−26)	5–10	0 4 0-0 1 0	$5_{2,4}-4_{1,3}$	3552.11	4.44(−26)	4.40(−26)	1.62	1.61
3566.65	3.71(−26)	5–10	0 4 0-0 1 0	$5_{2,3}-4_{3,2}$	3566.61	5.76(−26)	5.72(−26)	1.55	1.54

Table 4
Sample of $H_2{}^{32}S$ lines belonging to combination bands and displaying large differences in line positions between our calculations and HITRAN 2008 [26], possibly because of misassignements. Columns give transition wavenumber, ν in cm^{-1} and intensities, I in cm^{-1}/(molecule × cm^{-2}) (powers of ten in parenthesis); calculation are for ALYT2 and an empirical PES [25].

Band	$J'_{K_a,K_c}-J''_{K_a,K_c}$	HITRAN		Calculated		$\Delta\nu$	I_{Calc}/I_{HITRAN}
		ν	I	ν	I		
0 0 1	$4_{1,3}-5_{5,0}$	2337.94	5.58(−25)	2335.96	4.16(−25)	1.99	0.745
0 3 0	$3_{3,0}-4_{4,1}$	3433.15	1.35(−23)	3434.09	1.19(−24)	−0.95	0.088
0 3 0	$3_{0,3}-2_{1,2}$	3533.91	1.54(−23)	3532.45	3.90(−26)	1.46	0.003
1 1 0	$4_{0,4}-5_{3,3}$	3633.33	3.43(−24)	3631.54	1.91(−25)	1.79	0.056
1 1 0	$4_{3,2}-3_{2,1}$	3833.31	3.73(−22)	3832.78	6.89(−22)	0.53	1.850

We identified a total of 248 problematic lines covering wavenumbers from 2300 cm^{-1} to 4200 cm^{-1} and involving levels with J up to 17. Table 4 gives a sample set of lines; these show large differences in their positions compared to the other measured and predicted lines, see Table 3 for a comparison. A full set of problematic lines is given in the supplementary data. These lines all come originally from Brown et al. [1].

4. Discussion

Our calculations show that the intensities of transitions within the fundamental bands are very sensitive to changes in the treatment used to compute the dipole moment components. Conversely, the intensity of transitions within other bands, with the exception of the $\nu_1+\nu_2-\nu_2$ hot band, are well reproduced, with a standard deviation of about 11% and an average ratio of 1.04 for the 1023 transitions belonging to other bands we tested (see Table 2).

The H_2S DMS has a rather unusual topography. In particular, the asymmetric component $\mu^{(p)}$ changes very slowly in the vicinity of the equilibrium geometry and undergoes a sign change in this region. This causes the transition dipoles to be very small after $\mu^{(p)}$ is averaged over the vibrational wavefunctions. This behavior contrasts with that of the H_2O and H_2Se molecules, where the sign-change for the asymmetric component happens for geometries with energies above 4000 cm^{-1} for H_2Se and around 10 000 cm^{-1} for H_2O.

Our calculations show that the core and relativistic corrections to dipole moments for H_2S molecule not only alter their values significantly but also improve the calculated intensities, see Fig. 4. These corrections are particularly important for the ν_2 bending mode (the strongest band after the rotational band). For water, these corrections also found to be important for reproducing the ν_2 bending mode frequency but to essentially cancel each other out in the DMS [16].

Among all the surfaces tested, the ALYT2 DMS constructed using CCSD(T)/aug-cc-pV(6+d)Z with core and the relativistic corrections gave the best transitions intensities. One way of giving a comparison is to consider the standard deviations of $I_{Calc.}/I_{HITRAN}$ for lines involving J up to 5. For bands below 4000 cm^{-1} ALYT2 reproduces intensities in the rotational band to 1% and intensities in the ν_2 band to 18%. For the other bands ALYT2 gives an error of 22.5%, which reduces to 6.5% when only actually measured line intensities are considered in the comparison. The intensities of the predicted lines only agree with our calculations to about 25%, even after the problematic lines are removed from the comparison, suggesting that the predictions based on effective dipole moment models are considerably less reliable than direct measurements.

We believe that our results represent a significant improvement over the DMS of Cours et al. [8]; with respect to the latter our new ALYT2 DMS reproduces the rotational intensities to the same accuracy and considerably improves on it for most vibrational band intensities. Specifically, with respect to HITRAN intensities of the ν_2 band and of other directly measured lines in other bands, ALYT2 leads to differences which are about half of those produced by the DMS Cours et al. [8].

5. Conclusions

Several new *ab initio* dipole moment surfaces for H_2S molecule were calculated using a variety of theoretical procedures. The core and relativistic corrections were found to give significant contributions to line intensities and, therefore, in contrast to the case of the water molecule where they were found to approximately cancel out, cannot be neglected. Comparisons of calculated transitions intensities with those available in HITRAN for 14 vibrational bands show that while the fundamental bands are all very sensitive to the method used in the calculations, hot and combination bands below 4000 cm^{-1} are not. Our best dipole moment surface, which we call ALYT2, is constructed using CCSD(T)/aug-cc-pV(6+d) Z with core and the relativistic corrections added. Using the ALYT2 surface the ν_2 band is still 18% too strong; this is contrasted with water where the LTP2011 DMS has been shown to reproduce a variety of observed intensities to about 1% [17,20]. This consideration both bears testimony to the difficulties of accurately modelling H_2S line intensities and clearly indicates the need of further research. The ALYT2 DMS calculated in this work was used to compute a high temperature H_2S line list as part of the ExoMol project [48]. Such a line list is important for a variety of astrophysical studies and will be reported elsewhere [49].

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Appendix A. Supplementary data

Supplementary data associated with this paper can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2015.03.029.

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