Higher-order relativistic corrections to the vibration-rotation levels of H_2S

Paolo Barletta
Department of Physics and Astronomy,
University College London,
Gower St, London WC1E 6BT, U.K.

Attila G. Császár,
Department of Theoretical Chemistry, Eötvös University,
H-1518 Budapest 112, P.O. Box 32, Hungary

Harry M. Quiney,
School of Chemistry, University of Melbourne,
Victoria 3010, Australia

Jonathan Tennyson
Department of Physics and Astronomy,
University College London,
Gower St, London WC1E 6BT, U.K.

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Abstract

Relativistic corrections beyond the simple one-electron mass-velocity–Darwin (MVD1) approximation to the ground-state electronic energy of H_2S are determined at over 250 geometries. The corrections considered include the two-electron Darwin, the Gaunt and Breit corrections, and the one-electron Lamb-shift. Fitted correction surfaces are constructed and used with an accurate *ab initio* nonrelativistic Born–Oppenheimer potential, determined previously (J. Chem. Phys. 115 (2001) 1229), to calculate vibrational and rotational levels for $H_2{}^{32}S$. The calculations suggest that one- and two-electron relativistic corrections have a noticable influence on the levels of H_2S. As for water, the effects considered have markedly different characteristics for the stretching and bending states.

1 Introduction

The major factor determining the accuracy of variationally computed rovibrational energy levels is the potential energy hypersurface (PES) employed for such calculations. State-of-the-art *ab initio* electronic structure techniques are now capable,[1–6] perhaps after well-defined and systematic adjustments including extrapolations,[3,7,8] to predict vibrational band origins (VBOs) and other spectroscopic properties with an accuracy of better than 0.1%. To achieve this accuracy in the case of the ground-state PES of H_2O it was necessary to consider not only core-valence electron correlation[1] and coupling between electronic and nuclear motion,[9,10] but also effects originating from special relativity.[11–14] It became clear from these concerted studies on water that the relativistic effects are sizeable both for the stretching and bending degrees of freedom (Table 3, *vide infra*). Since previously it was not expected that geometry dependence of relativistic effects can be so large for light molecules, more experience is needed to understand the chemical significance of such small corrections on rovibrational spectra of small light molecules. In this letter we extend our investigation of electronic relativistic effects[4] to the ground-state PES and the rovibrational levels of H_2S.

Starting from the most sophisticated molecular theory, quantum electrodynamics (QED), the effects not considered in simple non-relativistic electronic structure theory can be separated into three distinct contributions: (a) one-body effects, arising directly and indirectly from the high velocity of (some of) the electrons; (b) two-body effects, arising through the exchange of virtual photons between electrons; and (c) radiative corrections, involving emission of virtual photons by an electron and subsequent reabsorption of the photon by the same particle (the leading terms are the so-called one- and two-electron Lamb-shifts).[11,13–18] All these effects have been investigated for the ground-state PES of H_2O, but not for other molecules, with the result that their importance decreases in the order given above. Although almost all of the one-electron relativistic energy correction is associated with the fast-moving core electrons, the differential (geometry-dependent) one-electron relativistic energy corrections are clearly[19] associated with changes in the valence shell; namely, it seems[18–20] that rehybridization in the valence shell results in significant changes in the relativistic energies.

One-electron relativistic corrections have been considered for the ground-state PES of H_2S[4,18] and the resulting shifts in the rovibrational states proved to be rather sizeable, of the same order as the corrections found for water. After the dominant one-electron mass-velocity (MV) and Darwin (D1) corrections are covered, one needs to consider the two-electron Darwin (D2) term. It is important for several reasons: (a) it appears to be the most important two-electron relativistic correction; (b) the sum MVD2 = MVD1 + D2 defines the Coulomb–Pauli approximation as spin-orbit interactions can be neglected for light closed-shell molecules[18] and it is generally assumed that the Coulomb–Pauli Hamiltonian[15] yields good approximations to results obtained from variational four-component solutions of the many-electron relativistic Dirac–Coulomb equation;[15,18] (c) it is closely related to the spin–spin interaction term; and (d) it allows[13] an estimation of the two-electron Lamb-shift effect. In order to go one step beyond MVD2, the Dirac–Coulomb–Gaunt/Breit Hamiltonian includes magnetic interactions between pairs of electronic currents, neglecting certain $O((Z\alpha)^2)$ contributions.[11,17,21] We have already probed the Gaunt and Breit energy corrections for water.[11,14]

The relativistic studies mentioned above and simple physical arguments suggest that the inclusion of the geometry dependence of one-body relativistic effects in the ground-state PES of H_2S has a noticable effect on the calculated VBOs and rotational term values. On the other hand, two-body effects are expected to be rather insensitive to changes in the geometry not affecting the volume of the molecule; this is especially the case for changes in bond angle. The third and possibly the smallest correction is due to the leading QED effect requiring renormalization of divergences, the one-electron Lamb-shift effect (self-energy and vacuum polarization[21]). The effect of Lamb-shift correction energies on the ground-state PES of water and on the related rovibrational states has been investigated by some of us,[13] yielding significant corrections up to 1 cm^{-1} in magnitude for higher-lying vibrational states of water. In that paper it was proposed that for molecular calculations the one-electron Lamb shift can be estimated from the standard D1 term(s) by using simple atomic scale factors. Inclusion of the two-electron Lamb-shift effect in the PES has had, on the other hand, negligible influence on the rovibrational states of water;[13] therefore, it is not considered further in this study. Similarly, a recent calculation has shown that higher-order corrections such as spin-orbit interactions make a negligible contribution to the shape of the water ground state potential energy surface.[18]

2 Computational Techniques

The energy corrections due to the two-electron Darwin term, D2, have been computed with aug-cc-pCVTZ CCSD(T)[22,23] wave functions, at the same level as the previous calculations of MVD1 correction energies.[4]

Relativistic energy corrections due to the Gaunt and Breit interactions were obtained in first order of perturbation theory using the four-component Dirac–Hartree–

Fock (DHF) wave function,[17] the recommended exponent factors for the Gaussian nuclear charge distribution,[24] and the following [S, H] basis set: [11*s*6*p*3*d*, 6*s*3*p*] for the large component. The restricted kinetic balance prescription[17] was used to generate the small-component basis functions from the large component set in a one-to-one mapping. The calculations have been repeated at over 250 structures comprising the data set $1.1 \leq$ distance/Å ≤ 1.7 and $41 \leq$ angle/deg ≤ 172.

The computer codes DIRCCR12[25] and BERTHA[17,26] have been employed for the electronic structure calculations involving the D2, and the Gaunt and Breit terms, respectively. One-electron Lamb shift corrections were estimated at each geometry using the prescription of Pyykkö *et al.*[13] and the one-electron Darwin (D1) terms calculated previously.[4] Values for each energy correction have been placed on the web, see below.

The absolute values of the (Gaunt,Breit) energy corrections on the PES of H_2S are about (94.5,87.7) mE_h, while the maximum difference within the region covered by our grid is (54.6,44.2) cm^{-1}. The D2 effect is smaller in an absolute sense, being -32.9 mE_h and 10.2 cm^{-1}, respectively. The magnitude of the Lamb shift is 0.062 mE_h, whereas its variation with the geometry achieves a maximum of 17 cm^{-1}. Figure 1 shows how the two-electron Darwin, the Lamb, and the Breit corrections vary as a function of bond angle and the symmetric stretching coordinate.

In order to use the calculated relativistic corrections in nuclear motion calculations we have fitted them to an analytic functional form

$$V(S_1, S_2, S_3) = \sum c_{ijk}\, S_1^i\, S_2^j\, S_3^k \tag{1}$$

where the symmetrized displacement coordinates S_1, S_2, S_3 are defined as follows:

$$\begin{aligned} S_1 &= \frac{R_1 + R_2}{2\,R_\mathrm{e}} + 1 \\ S_2 &= \frac{R_1 - R_2}{R_e} \\ S_3 &= \cos\Theta - \cos\Theta_\mathrm{e} \end{aligned} \tag{2}$$

and R_1,R_2 and Θ are respectively the bondlenghts and bondangle, of which R_e and Θ_e are the equilibrium values (R_e =1.3374 Åand Θ_e =1.6111 rad). In expansion 1 54 terms have been included. The computer algebra package *Mathematica*[27,28] was used for the fitting and for the automatic generation of the PES subroutines in FORTRAN. The 54 coefficients obtained from a least-squares fit to our data points can be downloaded from the web site ftp://ftp.tampa.phys.ucl.ac.uk/pub/vr/potentials/H2S.rel, and are incorporated within FORTRAN routines representing the PESs. The fit gives an accurate representation of the data and has a standard deviation of 0.05 cm^{-1} or better.

Nuclear motion calculations were performed using the DVR3D program suite[29] and previously optimized basis sets.[4] Calculations were only performed for the $H_2{}^{32}S$ isotopomer, using atomic masses.

3 Discussion

Tables 1 and 2 summarize calculations for selected vibrational and rotational term values of H_2S, respectively. These calculations were all performed with PESs being a sum of non-relativistic and relativistic correction surfaces, where the nonrelativistic surface is the CBS FCI + C *ab initio* Born–Oppenheimer (BO) surface of Tarczay, Császár, Polyansky, and Tennyson.[4] Table 3 compares relativistic energy corrections on the stretching and bending VBOs of H_2S to those of water.

The MVD1 relativistic correction[4] for the pure bending levels grows about linearly, a good approximate formula for it is $+0.7n_2$, where n_2 is the bending quantum number. There is a rapid linear increase in the MVD1 stretching correction, which is well approximated by $-4.2(n_1 + n_3)$, where n_1 and n_3 are stretching quantum numbers. Additivity of the stretch and bend corrections seems to hold to better than 95%.

The effect of inclusion of the two-electron Darwin (D2) correction terms in the PES on the VBOs of H_2S is as follows: (a) it is almost two orders of magnitude smaller than the effect arising from the inclusion of the MVD1 term; (b) it is significantly smaller than the effect observed in the case of water; and (c) it raises the bending bend origins as $+0.038n_2$ and lowers the stretching bend origins as -0.045 $(n_1 + n_3)$; and (d) for stretch-bend combination levels the stretching and bending corrections seem to be additive to a good approximation; for example, the corrections for (100), (020), and (120) are -0.05, $+0.08$, and $+0.03$ cm^{-1}, respectively.

As expected, the Gaunt correction is considerably larger for both the bending and stretching levels than the D2 correction. It grows almost linearly with excitation, and is well approximated as $-0.52(n_1 + n_3)$ and -0.12 n_2 cm^{-1}, respectively. As for the D2 correction, there seems to be an additivity of stretching and bending Gaunt correction for the stretch-bend combination levels.

The Breit corrections are always smaller than the Gaunt corrections, in most cases by some 20%. The Breit correction is well approximated for the stretching and bending levels as $-0.40(n_1 + n_3)$ and -0.10 n_2 cm^{-1}, respectively.

For the region of the spectrum covered in our treatment the Lamb-shift effect can also be approximated with linear forms; for the stretching levels it is $0.24(n_1 + n_3)$. It is essentially independent of bending excitation.

To understand the observed relativistic shifts in the bending band origins of H_2S it is worth recalling how relativity affects the barrier to linearity of H_2S. Our previous studies[3,18,30] indicate that the one-electron kinetic relativistic effect (MVD1) and the D2 term raise the barrier by about 233 and 5.36 cm^{-1}, respectively. Both the MVD1 and the D2 bending curves show monotonic behavior (see Figure 1). The Gaunt correction raises the barrier by 0.43 cm^{-1}, the correction to it in the Breit operator compensates this effect by 0.07 cm^{-1}, and consequently the Breit correction raises the barrier by 0.37 cm^{-1}. The approximation to the Lamb-shift correction lowers the barrier by almost 12 cm^{-1}. As seen in Table 1, these changes in the PES mostly translate directly into shifts of the computed bending band origins.

The relative smallness of the two-electron corrections is connected with the fact that these effects are strongly localized near the nuclei.

Table 2 shows the $J = 17$ rotational term values for the vibrational ground state calculated using the same models analysed above for the VBOs. Interestingly, the effect of the inclusion of two-electron relativistic corrections on the rotational term values is relatively small. The D2 shift is approximately constant and negligible. The Lamb shift effect is also rather small: it increases with K_a and at its maximum for $J = 17$ it contributes a mere 0.2 cm^{-1}. The Breit and Gaunt terms have a much stronger influence on the rotational levels, up to 1 cm^{-1}.

4 Conclusions

We have calculated *ab initio* the contribution of various two-electron relativistic correction terms and the one-electron Lamb shift to the potential energy surface of H_2S and investigated their consequence on the vibration–rotation energy levels. Using this information it is possible to quantify the contributions of various terms which are neglected in a standard non-relativistic Born–Oppenheimer Schrödinger treatment of the electronic structure problem. For H_2S the largest relativistic contribution to any vibrational band origin for which there is experimental data that have been assigned arises from the scalar one-electron correction, given by the one-electron mass-velocity plus Darwin (MVD1) terms, and it is -15.8 cm^{-1}. The two-electron Darwin term (D2) contributes only $+0.82$ cm^{-1}, the Gaunt term contributes -4.48 cm^{-1}, and the Breit (= Gaunt + retardation) term contributes -3.71 cm^{-1}. These can be compared with Lamb shift effects which contribute a maximum of $+1.3$ cm^{-1} , and the adiabatic correction (or BODC) which contributes –2.5 cm^{-1} . The non-adiabatic Born–Oppenheimer corrections remains unquantified but our experience with water suggests that they should be of the same order of magnitude as the BODC. In considering these numbers it should be remembered that lack of convergence of the best non-relativistic Born–Oppenheimer electronic structure calculations[4] give an error of up to 30 cm^{-1} in the vibrational band origins.

Some important points should be noted about the above contributions. First, the maximum contribution does not distinguish between the behaviour of the bending and stretching modes, although for nearly all cases the magnitude and the sign of the contribution is mode dependent (Table 3). For example, the error in the electronic structure calculation is predominantly in the bending mode.[4] Second, the corresponding contributions to the pure rotational energies are rather small so that the net effect is that two-electron relativistic effects contribute little. Finally, the differing signs of the various contributions may lead to a fortuitous cancellation of errors, and results whose agreement with the observations is superficial, and possibly misleading with respect to the accuracy of the individual contributions.

In comparison with our previous study on water,[14] two-electron relativistic corrections have a minor but still spectroscopically relevant contribution to the rovibrational levels of H_2S. The absolute value of the relativistic correction is one order of magnitude larger in H_2S than in water but its geometry dependence is almost the same. This can be easily understood as H_2S has core orbitals of very low energy which contribute to the absolute value of the relativistic energy correction but the geometry dependence is given by the valence orbitals whose structure is approximately the same for the two molecules. In other words, it can be recalled that the magnitude of the effective relativistic effects scales as $(Z/n)^2$ where Z is the nuclear charge and n is the principle quantum number. Although the valence electrons of sulphur are more efficiently shielded from the nuclear charge than they are in oxygen, the combination of the nuclear charge and principal quantum number effects (with an enhanced effectiveness of shielding in sulphur) all conspire to make the atomic relativistic effect in the valence electrons similar in the two molecules ($Z/n \approx 5$ for H_2S, 4 for H_2O). The chemical bonding in H_2O and H_2S is similar in character, so it is reasonable to expect some common features for the relativistic corrections in the two molecules.

In fact, as it can be seen in Table 3, the individual corrections to vibrational band origins are all similar in magnitude. However, there can be differences of signs or behaviour between $H_2{}^{16}O$ and $H_2{}^{32}S$. It is not easy to generalise from these results to a simple model capable of making quantitative predictions of corrections for rovibrational levels of other small molecules.

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References

[1] H. Partridge, D. W. Schwenke, J. Chem. Phys. 106 (1997) 4618.

[2] A. G. Császár, W. D. Allen, Y. Yamaguchi, H. F. Schaefer III, in: P. Jensen, P. R. Bunker (Eds.), Computational Molecular Spectroscopy, Wiley, Chichester, 2000.

[3] A. G. Császár, G. Tarczay, M. L. Leininger, O. L. Polyansky, J. Tennyson, W. D. Allen, in: J. Demaison, K. Sarka, E. Cohen (Eds.), Spectroscopy from Space, NATO ASI Series C, Kluwer, Dordrecht, 2001.

[4] G. Tarczay, A. G. Császár, O. L. Polyansky, and J. Tennyson, J. Chem. Phys. 115 (2001) 1229.

[5] T. van Mourik, G. J. Harris, O. L. Polyansky, J. Tennyson, A. G. Császár, and P. J. Knowles, J. Chem. Phys. 115 (2001) 3706.

[6] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke and P.J. Knowles, unpublished results.

[7] A. G. Császár, M. L. Leininger, J. Chem. Phys. 114 (2001) 5491.

[8] T. Helgaker, W. Klopper, H. Koch, J. Noga, J. Chem. Phys. 106 (1997) 9639.

[9] N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, J. Tennyson, Chem. Phys. Lett. 260 (1996) 381.

[10] D. W. Schwenke, J. Phys. Chem. A 105 (2001) 2352.

[11] H. M. Quiney, H. Skaane, I. P. Grant, Chem. Phys. Lett. 290 (1998) 473.

[12] A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, J. Tennyson, Chem. Phys. Lett. 293 (1998) 317; 312 (1999) 613 (E).

[13] P. Pyykkö, K. Dyall, A. G. Császár, G. Tarczay, O. L. Polyansky, J. Tennyson, Phys. Rev. A 63 (2001) 024502.

[14] H. M. Quiney, P. Barletta, G. Tarczay, A. G. Császár, O. L. Polyansky, J. Tennyson, Chem. Phys. Lett. 344 (2001) 413.

[15] K. Balasubramanian, Relativistic effects in Chemistry, Part A: Theory and techniques and Part B: Applications, Wiley, New York, 1997.

[16] P. Pyykkö, Chem. Rev. 88 (1988) 563 and the electronic bibliography *http://www.csc.fi/lul/rtam*.

[17] H. M. Quiney, H. Skaane, I. P. Grant, Adv. Quant. Chem. 32 (1999) 1.

[18] G. Tarczay, A. G. Császár, W. Klopper, H. M. Quiney, Mol. Phys. 99 (2001) 1769 and references cited therein.

[19] J. Katriel, D. Feller, E. R. Davidson, Int. J. Quant. Chem. 26 (1984) 489.

[20] A. G. Császár, W. D. Allen, H. F. Schaefer III, J. Chem. Phys. 108 (1998) 9751.

[21] H. A. Bethe, E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms, Springer-Verlag, Berlin, 1957.

[22] T. H. Dunning, Jr., J. Chem. Phys. 90 (1989) 1007.

[23] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.

[24] Relativistic Effects in Heavy Element Chemistry (REHE, A program of the European Science Foundation) Newsletter No. 13, *http://www.chemie.uni-erlangen.de/hess/html/esf/nl.html*, 1995.

[25] DIRCCR12-95, an integral-direct explicitly correlated coupled-cluster program written by J. Noga and W. Klopper.

[26] I. P. Grant, H. M. Quiney, Int. J. Quantum Chem. 80 (2000) 283.

[27] Mathematica, Version 2.2, Wolfram Research, Inc. (1993).

[28] S. Wolfram, Mathematica: A System for Doing Mathematics by Computers, 2nd ed., Addison-Wesley, Redwood City, CA, 1991.

[29] J. Tennyson, J. R. Henderson, N. G. Fulton, Comp. Phys. Comms. 86 (1995) 175.

[30] G. Tarczay, A. G. Császár, M. L. Leininger, W. Klopper, Chem. Phys. Lett. 322 (2000) 119.

[31] I. Kozin, P. Jensen, J. Mol. Spectrosc. **163** 483 (1994).

[32] J.-M. Flaud, O. Vaittinen, A. Campargue, J. Mol. Spectrosc., **190** 262 1998.

[33] A. D. Bykov, O. V. Naumenko, M. A. Smirnov, L. N. Sinitsa, L. R. Brown, J. Crisp, D. Crisp, Can. J. Phys., **72** 989 (1994).

[34] O. L. Polyansky (unpublished results), based on work reported in S. P. Nelkov, K. M. T. Yamada, G. Winnewisser, L. Poteau, R. Bocquet, J. Demaison, O. L. Polyansky, M. Y. Tretyakov, J. Mol. Spectrosc., **173** 380 (1995).

Table 1

Vibrational band origins, in cm^{-1}, for $H_2{}^{32}S$. Absolute values are given for the observed (Obs) VBOs and for the *ab initio* PES corresponding to the CBS FCI + C Born–Oppenheimer (BO) + Born–Oppenheimer Diagonal Correction ($\Delta V_{\rm ad}$) surface, and increments are given for the relativistic one-electron mass-velocity and Darwin (MVD1, $+\Delta V_{\rm rel}$), the two-electron Darwin (+D2), the Gaunt (+Gaunt), the Breit (+Breit) and the one-electron Lamb-shift (Lamb) surface corrections. Increments are given as individual contributions. Note that retardation is given as Breit − Gaunt.

	Obs[a]	BO+$\Delta V_{\rm ad}$	+ $\Delta V_{\rm rel}$	+D2	+Gaunt	+Breit	+Lamb
(010)	1182.57	1181.96	0.68	0.03	−0.16	−0.13	0.01
(020)	2353.96	2358.40	1.48	0.08	−0.26	−0.23	0.00
(100)	2614.14	2620.77	−4.34	−0.05	−0.53	−0.40	0.24
(030)	3513.79	3523.50	2.17	0.12	−0.36	−0.32	0.00
(110)	3779.17	3785.49	−3.76	−0.01	−0.68	−0.53	0.26
(040)	4661.68	4673.79	2.58	0.15	−0.47	−0.42	0.00
(120)	4932.70	4945.18	−3.09	0.03	−0.79	−0.63	0.25
(200)	5144.99	5159.22	−8.42	−0.09	−1.06	−0.81	0.48
(002)	5243.10	5256.55	−8.37	−0.09	−1.09	−0.83	0.48
(050)	5797.24	5807.64	2.68	0.18	−0.61	−0.53	0.01
(130)	6074.58	6092.58	−2.60	0.07	−0.89	−0.72	0.25
(210)	6288.15	6303.08	−7.89	−0.05	−1.20	−0.93	0.49
(012)	6388.10	6399.27	−7.85	−0.05	−1.23	−0.95	0.49
(102)	7576.38	7598.99	−12.44	−0.13	−1.57	−1.20	0.70
(300)	7752.26	7773.58	−12.80	−0.13	−1.58	−1.20	0.72
(112)	8697.14	8721.30	−12.01	−0.10	−1.71	−1.32	0.71
(202)	9911.02	9942.54	−16.42	−0.17	−2.07	−1.57	0.93
(400)	10188.30	10218.33	−16.83	−0.18	−2.09	−1.59	0.95
(212)	11008.68	11042.65	−16.09	−0.14	−2.20	−1.69	0.94
(302)	12149.46	12190.18	−20.31	−0.21	−2.55	−1.94	1.14
(024)	12481.88	12521.13	−16.04	−0.11	−2.37	−1.83	0.97
(104)	12524.63	12563.63	−20.72	−0.22	−2.59	−1.97	1.17
(000)	14285.07	14335.34	−20.39	−0.17	−2.84	−2.18	1.20
(000)	14290.75	14343.55	−23.67	−0.23	−2.98	−2.27	1.31

Table 1, continued

	Obs[a]	BO+$\Delta V_{\rm ad}$	+ $\Delta V_{\rm rel}$	+D2	+Gaunt	+Breit	+Lamb
(001)	2628.46	2635.05	−4.08	−0.04	−0.55	−0.43	0.23
(011)	3789.27	3795.77	−3.45	−0.01	−0.70	−0.55	0.24
(021)	4939.10	4951.15	−2.77	0.03	−0.81	−0.65	0.24
(101)	5147.22	5161.25	−8.35	−0.09	−1.06	−0.81	0.47
(031)	6077.60	6095.11	−2.27	0.07	−0.91	−0.74	0.24
(111)	6289.17	6303.89	−7.83	−0.05	−1.21	−0.94	0.48
(121)	7420.09	7441.30	−7.29	−0.02	−1.32	−1.03	0.49
(201)	7576.55	7599.08	−12.43	−0.13	−1.57	−1.20	0.70
(003)	7779.32	7800.75	−12.34	−0.12	−1.63	−1.25	0.70
(211)	8697.16	8721.24	−12.01	−0.10	−1.71	−1.32	0.71
(301)	9911.02	9942.54	−16.42	−0.17	−2.07	−1.57	0.93
(103)	10194.45	10224.30	−16.64	−0.17	−2.11	−1.61	0.94
(311)	11008.68	11042.65	−16.09	−0.14	−2.20	−1.69	0.94
(203)	12149.46	12190.18	−20.31	−0.21	−2.55	−1.94	1.14
(401)	12525.20	12564.12	−20.69	−0.22	−2.59	−1.97	1.17
(000)	14285.07	14335.33	−20.39	−0.17	−2.84	−2.17	1.20
(000)	14290.75	14343.80	−12.97	0.01	−2.45	−1.92	0.87

[a] Observed fundamentals are taken from ref.[31–33] All two-electron corrections are referenced to the Born–Oppenheimer (BO) + Born–Oppenheimer Diagonal Correction ($\Delta V_{\rm ad}$) + relativistic MVD1 ($\Delta V_{\rm rel}$) surface result.

Table 2

Rotational term values (J=17), in cm^{-1}, for the vibrational ground state of $H_2{}^{32}S$.

	Obs[a]	BO+$\Delta V_{\rm ad}$	+ $\Delta V_{\rm rel}$	+D2	+Gaunt	+Breit	+Lamb
$17_{0,17}$	1524.49	1524.74	−0.03	−0.044	−0.572	−0.482	−0.015
$17_{1,16}$	1683.75	1684.02	−0.03	−0.040	−0.623	−0.523	−0.008
$17_{2,15}$	1831.34	1831.62	−0.03	−0.036	−0.670	−0.561	−0.001
$17_{3,14}$	1967.71	1967.98	−0.01	−0.032	−0.712	−0.596	0.004
$17_{4,13}$	2093.24	2093.46	0.01	−0.028	−0.750	−0.627	0.008
$17_{5,12}$	2208.13	2208.32	0.05	−0.025	−0.784	−0.655	0.011
$17_{6,11}$	2312.61	2312.72	0.10	−0.021	−0.813	−0.679	0.013
$17_{7,10}$	2406.69	2406.69	0.18	−0.017	−0.838	−0.700	0.013
$17_{8,9}$	2490.12	2489.94	0.33	−0.012	−0.857	−0.716	0.009
$17_{9,8}$	2561.68	2561.00	0.65	−0.003	−0.864	−0.724	−0.004
$17_{10,7}$	2617.72	2616.09	1.27	0.011	−0.853	−0.719	−0.033
$17_{11,6}$	2658.75	2656.77	1.50	0.018	−0.855	−0.721	−0.043
$17_{12,5}$	2699.41	2698.60	0.72	0.003	−0.902	−0.755	−0.003
$17_{13,4}$	2751.57	2752.42	−0.36	−0.019	−0.967	−0.802	0.054
$17_{14,3}$	2811.86	2814.02	−1.23	−0.036	−1.023	−0.842	0.101
$17_{15,2}$	2874.31	2877.66	−2.02	−0.051	−1.076	−0.880	0.144
$17_{16,1}$	2934.84	2939.39	−2.84	−0.067	−1.126	−0.915	0.188
$17_{17,0}$	2985.79	2992.06	−3.91	−0.089	−1.178	−0.951	0.244

[a] Observed rotational term values are taken from ref.[34] For explanation of column headings see Table 1.

Table 3

Relativistic corrections to vibrational band origins of $H_2{}^{16}O$ and $H_2{}^{32}S$.

Correction surface	$H_2{}^{16}O$ stretch	$H_2{}^{16}O$ bend	$H_2{}^{32}S$ stretch	$H_2{}^{32}S$ bend
MVD1	$-2.8(n_1+n_3)$	$+1.4n_2$	$-4.15(n_1+n_3)$	$+0.7n_2$
D2	$-0.04(n_1+n_3)$	$-0.07+0.12n_2$	$-0.045(n_1+n_3)$	$+0.04n_2$
Gaunt	$-0.8(n_1+n_3)$	uneven	$-0.52(n_1+n_3)$	$-0.12n_2$
Retardation	$+0.15(n_1+n_3)$	$-0.02n_2$	$+0.12(n_1+n_3)$	$+0.02n_2$
Lamb-shift	$+0.18(n_1+n_3)$	$-0.11n_2$	$-0.40(n_1+n_3)$	$0.00n_2$

[a] All values are given in cm^{-1}, n_1 and n_3 are stretching quantum numbers, and n_2 is the bending quantum number. Stretch–bend additivity holds better than 95 %.

Figure captions

Figure 1

Contour plot of two-electron relativistic correction surfaces as a function of the bond angle (in degrees) and the symmetric stretching (in Å) coordinates. (a) Two-electron Darwin (D2) surface. The contour lines are separated by 1 cm^{-1} with a maximum at the top of the figure. (b) Lamb shift surface. The contour lines are separated by 1 cm^{-1}, increasing from the top-left corner towards the right/down. (c) Breit – Gaunt interaction surface. The contour lines are separated by 1 cm^{-1}, increasing from left to right. (d) Breit interaction surface. The contour lines are separated by 5 cm^{-1}, decreasing from left to right.