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## RESEARCH ARTICLE

Theoretical study of molecular properties of low-lying electronic excited states of  
H<sub>2</sub>O and H<sub>2</sub>S

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Geometries, excitation energies, dipole moments and dipole polarizability tensor components of the ground and four lowest excited states  ${}^3B_1$ ,  ${}^1B_1$ ,  ${}^3A_2$ ,  ${}^1A_2$  of the H<sub>2</sub>O and H<sub>2</sub>S molecules were calculated at the CASSCF, CASPT2, CCSD and CCSD(T) level of approximation. Vertical excitation and equilibrium transition energies of these states, having the Rydberg character, are reported too. Properties of both molecules in the ground and in low lying excited states are compared and discussed from the point of view of their molecular electronic structure. Upon excitation we observe dramatic changes of dipole moments and polarizabilities with respect to the ground state. We stress the change of the polarity of H<sub>2</sub>O in all excited states accompanied by the enhancement of the dipole polarizability by an order of magnitude. Large, even if less pronounced, are changes of electric properties of H<sub>2</sub>S in its excited states. Dipole moments and dipole polarizabilities of  ${}^3B_1$ ,  ${}^1B_1$  states of H<sub>2</sub>S and H<sub>2</sub>O behave quite analogously in comparison to their respective ground state. General pattern of properties of both molecules in their  ${}^3A_2$  and  ${}^1A_2$  excited states is more different due to pronounced participation of the sulphur *d*-orbitals in these states of the H<sub>2</sub>S molecule.

**Keywords:** excited states; Rydberg states; H<sub>2</sub>O; H<sub>2</sub>S; excitation energies; dipole moment; dipole polarizability; CASPT2; CCSD(T)

## 1 Introduction

Electric properties like dipole moments and dipole polarizabilities of molecules in their excited electronic states represent very important information about the character of these states. Nowadays, there are essentially two experimental techniques which provide us dipole moments and dipole polarizabilities of molecules in excited states. In the gas phase it is mainly Stark spectroscopy [1] and for the bulk it is time-resolved microwave-conductivity (TRMC) [2]. Accurate calculations of dipole moments and dipole

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polarizabilities of small molecules in their ground electronic states represent for the present quantum chemical machinery tasks which are in many cases fulfilled at very high level. In this area theoretical data certainly can compete with experimental ones. Determination of these data for molecules in excited electronic states is a more complex task, both for theory and experiment.

The aim of this study is to compare behaviour of electric properties, namely dipole moments and dipole polarizabilities of two formally similar molecules  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  with an analogous electronic structure in the ground electronic state  $X^1A_1$ . We studied four lowest excited states of the Rydberg character. These are the  $^3B_1$  and  $^1B_1$  states created by **electron excitation from the  $b_1$  orbital of dominantly  $p_x$  character to the  $a_1$  orbital of dominantly  $s$  character,  $b_1 \rightarrow a_1$ , and  $^3A_2$  and  $^1A_2$  states resulting from the electron excitation from the  $b_1$  orbital of dominantly  $p_x$  character to the  $b_2$  orbital which is a combination of the  $p_y$  orbital of oxygen (sulphur) and  $s$  orbitals of hydrogens,  $b_1 \rightarrow b_2$** . We believe that our calculations will extend the knowledge about properties of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  in low-lying excited states which are important in numerous photophysical and photochemical processes [3].

The ground and excited electronic states of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  have been extensively studied both theoretically and experimentally [3–41]. However, most of these papers studied excitation energies only. In fact, information about non-energetic quantities, such as electric properties of excited states of these molecules [3, 9, 11–15, 19] are rather scarce. This applies particularly to  $\text{H}_2\text{S}$ .

The  $^1B_1$  state of water is bent at spectroscopically accessible geometries and directly dissociative to  $\text{H}(^2S)$  and  $\text{OH}(X^2\Pi)$  [4]. The next singlet electronic state of water  $^1A_2$  is also bent dissociative [4]. This state is dipole forbidden (although quadrupole or vibronically allowed) and so far unobserved in VUV (vacuum ultraviolet) spectra [3]. While for water a single electronic state  $^1B_1$  is involved, the dissociation of  $\text{H}_2\text{S}$  entails two strongly coupled electronic states, bound  $^1B_1$  state and a dissociative  $^1A_2$  state. They have two conical intersections [30, 35, 36]. The drastic differences between the photodissociations of  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$  arise from participation of the  $3d$  orbitals of the sulphur atom.

$\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  molecules have many similarities, however, there are many differences as well. The bonding of sulphur in  $\text{H}_2\text{S}$  is different from oxygen in  $\text{H}_2\text{O}$ . Sulphur has  $d$ -orbitals in the valence shell, which are unoccupied in the ground state. This is the reason of **larger** number of lower Rydberg states of the  $\text{H}_2\text{S}$  molecule in comparison to the  $\text{H}_2\text{O}$  molecule. The energy differences between Rydberg states of  $\text{H}_2\text{S}$  are considerably smaller than for  $\text{H}_2\text{O}$ , which is linked to differences between excited states of atomic oxygen and sulphur [42]. Therefore, we expect that our calculations using the same techniques for both  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  will contribute to the knowledge and better understanding of similarities and differences of molecular properties of these molecules in their low-lying excited states.

## 2 Computational methods

Effects of the electron correlation were accounted for by CASSCF [43] and CASPT2 methods [44], and by coupled cluster methods CCSD, CCSD(T) [45, 46]. The open-shell singlets which cannot be described by a single-determinant reference wave function were in the coupled cluster approach treated by the two-determinant CCSD method [47]. All calculations were performed using the MOLCAS suit of programs [48].

**In present calculations, both molecules  $H_2O$  and  $H_2S$  lie in the  $yz$ -plane with the  $z$ -axis as the principal axes.** Orbitals of the representation  $B_1$  transform as  $x$ . We have correlated 8 electrons in both molecules  $H_2O$  and  $H_2S$ , which means the K-shell of oxygen and the K-, and L-shells of sulphur were left frozen. We employed the  $C_{2v}$  point group except calculations of perpendicular polarizabilities where we have been forced to use the  $C_s$  one.

Relativistic effects were neglected in this study. Tarczay *et al.* [49] reported the **scalar** relativistic effect on the inversion barrier of  $H_2S$  to be less than  $250\text{ cm}^{-1}$ , which is about 0.03 eV. **However, neglecting the spin-orbit (SO) contribution is not so obvious, particularly in the case of  $H_2S$ , where all four lowest excited states are rather close lying. Therefore, both SO and vibronic coupling cannot be excluded so safely as scalar relativistic effects.**

The choice of the active space plays a crucial role in the CASSCF method. Based on a detailed analysis of effect of using different active spaces on dipole moment and dipole polarizability of water by Klein *et al.* [12] we decided to use in our study their largest (7341) active space (note that a different orientation of the molecular plane is in Ref. [12]). This notation means that there are 7 active orbitals in the first irreducible representation  $A_1$ , 3 in the second one  $B_1$ , 4 in the third one  $B_2$ , and 1 in the fourth one  $A_2$ . Inner shell orbitals (1000) for  $H_2O$  and (3110) for  $H_2S$  were inactive. In order to ensure the same number of correlated orbitals in different electronic states, which is important in calculation of excitation energies the corresponding active space for  $B_1$  states resulting from the  $b_1 \rightarrow a_1$  excitation was (8341).  $A_2$  states arising from the  $b_1 \rightarrow b_2$  excitation were calculated by the (7351) active space.

Using basis sets with diffuse exponents in calculation of Rydberg states of  $H_2O$  or  $H_2S$  is inevitable [3, 15]. The smallest basis set which we used in our pilot calculations was aug-cc-pVQZ [50]. All calculations reported in this paper are carried out with the d-aug-cc-pVQZ basis set [51]. Adding the second set of "aug" functions affected vertical excitation energies up to 0.01 eV. Further extension to the t-aug-cc-pVQZ basis set [51] affected excitation energies very little. Dipole polarizabilities were affected by less than by 5%.

The evaluation of dipole moments and components of the dipole polarizability tensor was accomplished by using a numerical finite-field perturbation technique [52]. **Numerical derivatives were obtained**

1 using the Romberg scheme [53]. The external electric field strengths were set to 0.002, 0.004  
2 and 0.008 au. In cases when we could not reach sufficiently converged energies needed for applied weaker  
3 external fields we were forced to use values 0.004, 0.008, and 0.016 au.  
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### 9 3 Results and discussion

#### 10 3.1 Geometries

11 We carried out geometry optimization for the ground states and four lowest excited states of H<sub>2</sub>O and  
12 H<sub>2</sub>S. We restricted the optimization by enforcing the  $C_{2v}$  symmetry considering equal O–H or S–H bond  
13 lengths. Since the considered excited electronic states are of the dissociative character, these optimized  
14  $C_{2v}$  geometries can at most characterize an appropriate saddle points on the energy hypersurface [3]. The  
15 geometry optimization was performed at the CASPT2 level using the active space (7341) for the  $X^1A_1$   
16 state, (8341) for  $B_1$  states and (7351) for  $A_2$  states. These data together with reference theoretical [3,20,25]  
17 and experimental [54] data for the ground states are collected in Table 1. A significant change of geometry  
18 is found for excited states, particularly  $B_1$  states of H<sub>2</sub>S which are almost linear. In the case of water  
19 we got similar geometries as Li and Paldus [3] by the GMS SU CCSD method. There is agreement also  
20 between our and Cai *et al.* [20] EOM CCSD and CCSD(T) data except the  $^1A_2$  state of water. Their  
21 bond angle for this state is by 10 deg larger than ours. The literature data for geometries of the lowest  
22 excited states of H<sub>2</sub>S are rather seldom. There are published figures [22,23,26,30] with bond distance and  
23 angle dependence for the  $^1B_1$  and  $^1A_2$  states. They indicate an angle about 80 deg for the  $^1A_2$  state and  
24 provide very flat curve with almost linear geometry for the  $^1B_1$  state. The bond lengths are larger than  
25 for the ground state. Simah *et al.* [25] published geometries for H<sub>2</sub>S excited singlets with angles fixed to  
26 the ground state value. Our calculations confirm their results. Our CASPT2 ground state geometries for  
27 both studied molecules coincide with experimental ones [54].  
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44 [Insert Table 1 about here]

#### 45 3.2 Excitation energies

46 Calculated vertical excitation energies are presented in Table 2. We carried out CASSCF with 8 correlated  
47 electrons for both molecules in the (7341) active space for the  $X^1A_1$ . In the case of the H<sub>2</sub>O molecule  
48 we got vertical excitation energies in the same sequence of electronic states namely  $^3B_1$ ,  $^1B_1$ ,  $^3A_2$ ,  $^1A_2$   
49 by all methods which we used. There are numerous papers in the literature dealing with calculations of  
50 excitation energies of water [3,9,11–20]. In Table 2 we presented just most recent ones [3,15–18]. All of these  
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1 cited calculations have the same sequence of vertical excitation energies as is provided by our results. Our  
2 CASPT2 vertical excitation energies are consistently **higher** by 0.25–0.31 eV than our CASSCF values,  
3 **indicating the importance of the dynamic electron correlation.** The CCSD(T) values of triplet  
4 states differ from CASPT2 ones just by 0.01 eV. **This clearly supports the credibility of obtained**  
5 **results.** Our present coupled cluster program [48] can not calculate triple excitations for excited singlet  
6 states, however, we assume that effect of triple excitations will be for singlet states similar to triplet ones.  
7 The EOM CCSD data of Musial *et al.* [16] differ from our CASPT2 and CCSD(T) data by 0.01 eV. Li  
8 and Paldus GMS SU CCSD values [3] are by 0.09–0.12 eV **lower** than our CASPT2 ones. Their values  
9 utilizing the most sophisticated multi reference CC method are closer to experiment than our results.  
10 The cited CCSDR(3) [15] and CC3 [18] data were calculated in the same d–aug–cc–pVQZ basis set and  
11 are identical to our CASPT2 values. Very recent MS–CASPT2 [17] calculations in smaller basis set than  
12 ours gave excitation energies by 0.15–0.16 eV **lower** than our CASPT2 ones. **It is interesting that the**  
13 **best agreement with the experiment [5] resulted from our CASSCF calculations. We note,**  
14 **that we did not consider the zero point vibrational energy which would lower the calculated**  
15 **excitation energies. What follows from the experimental data is the so-called 0–0 transition**  
16 **energy.**

17 The sequence of vertical excitation energies for the  $H_2S$  molecule obtained from our CASPT2 and CCSD  
18 calculations is  $^3A_2$ ,  $^3B_1$ ,  $^1A_2$ ,  $^1B_1$  and differs from the  $H_2O$  sequence. A striking contrast between excited  
19 states of  $H_2O$  and  $H_2S$  is that both triplet and singlet  $A_2$  states of  $H_2O$  are lying much higher than the  
20  $B_1$  states, while excitation energies for both  $A_2$  and  $B_1$  states of  $H_2S$  differ very little, with the  $A_2$  states  
21 lying slightly lower. The effect of triple excitations in CCSD(T) was for  $H_2S$  even smaller than for  $H_2O$ .  
22 CCSD(T) and CASPT2 values agree within 0.01 eV, similarly as for  $H_2O$ . There are only few papers  
23 in the literature dealing with excitation energies of the  $H_2S$  molecule [6, 7, 22–30]. We present few most  
24 recent relevant data [23, 26–28] in Table 2. The valence shell Hamiltonian calculations of Stevens *et al.* [26]  
25 correlate very well with our CASPT2 and CCSD data. The DFT QR excitation energies for triplets by  
26 Minaev *et al.* [28] and  $(SC)^2$ –MR–SDCI (the size-consistent self-consistent dressing method [55]) values for  
27 singlets by Pitarch–Riuz *et al.* [27] fairly correlate with our data as well. MR–DCI results of Petsalakis and  
28 Theodorakopoulos [23] for the  $^1B_1$  state agree with our results reasonably well while their excitation energy  
29 for the  $^1A_2$  state is by 0.7 eV higher than are our CCSD and CASPT2 results in Table 2. We found no  
30 experimental data for the triplet  $^3A_2$  and  $^3B_1$  states of  $H_2S$ . **Experimental value for the  $^1A_2$  is rather**  
31 **uncertain [56]. Our vertical excitation energy for the  $^1B_1$  state agrees with experimental**  
32 **value reasonably well, differing by less than 0.08 eV. Since spin–orbit and vibronic effects**  
33 **were neglected, comparison with experiment should be taken with some caution.**



Equilibrium transition energies ( $T_e$ ) which we define as differences between energy of the given excited state and the ground electronic state calculated in their respective optimized geometries are presented in Table 3. The discussion presented in the previous paragraph for vertical excitation energies of the H<sub>2</sub>O molecule can be repeated here as well. The order of  $T_e$  is the same as it was for vertical excitation energies, however, they are consistently lower by about 0.5 eV. The CASPT2 values are by 0.22–0.23 eV **higher** than CASSCF ones. There is a very good agreement between CCSD and CASPT2 data and the effect of triples is rather small. In Table 3 are presented other theoretical data [3, 12–14, 20]. The H<sub>2</sub>O data cited in Table 3 retain our order of  $T_e$ . The EOM CCSD values of Cai *et al.* [20] differ by 0.01–0.04 eV and GMS SU CCSD of Li and Paldus [3] by 0.1 eV from our data.

In the case of equilibrium transition energies of the H<sub>2</sub>S molecule, the  $T_e$  sequence is  $^3B_1$ ,  $^1B_1$ ,  $^3A_2$ ,  $^1A_2$  and, in contrast to excitation energies in H<sub>2</sub>O, this sequence differs from vertical excitation energies. This change is due to much larger differences in optimized geometries than we observe for H<sub>2</sub>O, particularly for  $B_1$  states. This leads to large differences between  $T_e$  and vertical excitation energies, up to 1.5 eV and 0.6 eV for  $B_1$  and  $A_2$  states, respectively. We also note that the  $T_e$  sequence is the same for both H<sub>2</sub>O and H<sub>2</sub>S molecules (with vertical excitation energies it was different). Theoretical excitation energies are quite stable with our highly correlated methods. The calculated CCSD  $T_e$  values of H<sub>2</sub>S differ marginally from CASPT2 ones, similarly as it was for the H<sub>2</sub>O molecule. The same holds for vertical excitation energies as well. In the literature we did not find any relevant H<sub>2</sub>S data, which can be pointed out in this context.

[Insert Table 2 about here]

[Insert Table 3 about here]

### 3.3 Dipole moments

Dipole moments of H<sub>2</sub>O and H<sub>2</sub>S for the five lowest electronic states are collected in Table 4. Dipole moments of excited states calculated in the experimental geometry of the ground state  $X^1A_1$  will be called 'vertical' dipole moments. Those calculated in optimized geometries of individual excited states, as specified in Table 1 will be named 'adiabatic' dipole moments.

Let us discuss firstly 'vertical' dipole moments. In the case of the water molecule, our CASPT2 data for all excited states have opposite polarity with respect to the polarity of the ground state. Absolute values are smaller by about 4% for  $^1B_1$  up to 23% for the  $^3B_1$  state. The hydrogen sulphide, due to **lower** electronegativity of sulphur than oxygen, has the ground state dipole moment by about 50% smaller than that of water in the ground state. Our CASPT2 'vertical' dipole moments of H<sub>2</sub>S have opposite sign for both  $B_1$  states, like it is for H<sub>2</sub>O, with absolute values larger by 20% for triplet and 75% for singlet when

1 compared to the ground state. The water molecule in its singlet and triplet  $A_2$  states also have reversed  
2 sign of the dipole moment with respect to the ground state (like it was for  $^3B_1$  and  $^1B_1$  states) and similar  
3 absolute values. Note that  $A_2$  states of  $H_2S$  behave rather differently. Their absolute values are smaller  
4 by 48% for triplet and 35% for the singlet state than is the dipole moment in the ground  $X^1A_1$  state,  
5 however, the sign remains the same.  
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10 Large change of the dipole moment upon the excitation leading to  $B_1$  states of  $H_2O$  has been at-  
11 tributed [9] to the reorganization of the electron distribution resulting from the  $1b_1 \rightarrow 4a_1$  excitation. Main  
12 change undergoes the oxygen  $b_1(p_x)$  lone pair orbital, localized almost exclusively on the oxygen atom,  
13 perpendicularly to the molecular plane. **Upon excitation increases the importance of the diffuse**  
14  **$a_1(s)$  orbital, which is essentially the Rydberg  $3s$  orbital. A slight contribution to the  $4a_1$**   
15 **orbital comes also from the diffuse oxygen atomic  $p_z$  function.** Due to its diffuseness the change  
16 of the orbital picture affects not only dipole moments of  $B_1$  states of  $H_2O$ , but it also contributes to  
17 large increase of their dipole polarizability, as it will be seen in the next chapter (see also Ref. [9]). When  
18 discussing dipole moments for the ground and the excited states we should perhaps stress that all char-  
19 acteristics of the dipole moments are well represented by the CASSCF wave function. Actually even HF  
20 dipole moments of  $H_2O$  and  $H_2S$ , as presented in Table 3 for optimized geometries, agree qualitatively  
21 with final CASPT2 or CC results.  
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31 The  $^3A_2$  and  $^1A_2$  states of  $H_2O$  and  $H_2S$  are characterized by the  $b_1 \rightarrow b_2$  electron excitation. Singly  
32 occupied  $2b_2$  orbital of  $H_2O$  has the character of the diffuse oxygen Rydberg  $3p_y$  orbital lying in the  
33 molecular plane and oriented perpendicularly to the main  $C_{2v}$  axis of the molecule. We were initially  
34 puzzled by the observation that for the  $A_2$  states the dipole moment undergoes similar changes as  $B_1$   
35 states with respect to the ground state, including the reversed sign. The analysis of CASSCF orbitals  
36 shows that upon the  $b_1 \rightarrow b_2$  electron excitation the participation of not only the  $s$  hydrogen orbitals but  
37 also participation of their  $p_y$  orbitals in the singly occupied  $2b_2$  orbital is significantly enhanced. The  
38 participation of the oxygen  $d$  orbitals is negligible in the  $^3A_2$  state. This is reflected in the Mulliken  
39 population analysis, which shows **higher** electron  $H(s)$  density for  $A_2$  states than for the ground state and  
40 for  $B_1$  excited states and also quite significant electron population corresponding to  $H(p_y)$  orbitals (*e.g.*,  
41 0.18 electrons for the  $^3A_2$  state). For the ground state is such population by an order of magnitude smaller.  
42 Therefore, the change of the dipole moment in  $A_2$  states can be interpreted by moving the electron density  
43 toward the hydrogen side of the molecule upon the  $b_1 \rightarrow b_2$  electron excitation.  
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54 General features of changes which undergo molecular orbitals of  $H_2S$  upon excitation to the  $^3B_1$  and  
55  $^1B_1$  excited states are similar as were found for  $H_2O$ . Accordingly, also the change of the dipole moment  
56 in  $B_1$  excited states in the geometry of the ground state are similar for both molecules, as is clearly seen  
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in Table 4. More complicated is the discussion of dipole moments of  $^3A_2$  and  $^1A_2$  states of  $H_2S$ . The singly occupied  $3b_2$  orbital of  $H_2S$  in, e.g. the  $^3A_2$  state, is characterized not only by a significant contribution of the sulphur  $4p_y$  orbital along with  $s$  and  $p_y$  hydrogen orbitals, like it was for  $H_2O$ . This time, there is also a quite large contribution from the diffuse  $d_{yz}$  orbitals (larger  $d$ -coefficients belong to basis functions with smaller exponents) which are located in the molecular plane. The CASSCF electron population due to the sulphur  $d$ -orbitals in the  $^3A_2$  state is as large as 0.42 electrons while it is negligible in the analogous excited state of the water molecule. The hydrogen  $s$ - and  $p$ - populations are much **lower** than they were for  $H_2O$ . Under these circumstances the charge transfer toward the hydrogen side is less effective for  $H_2S$  than it was for  $H_2O$ . Finally, we note that the  $1^1A_2$  state of  $H_2S$  has been characterized by Petsalakis and Theodorakopoulos [23] as  $2b_1 \rightarrow Vp + Rd$  (valence  $p$  and Rydberg  $d$ ). This is in line with our interpretation.

All our CASPT2 'vertical' dipole moment absolute values are slightly smaller than CASSCF data. We do not present coupled cluster data for 'vertical' dipole moments because of relatively large amplitudes of the single excitation operator  $T_1$  which we got in calculations of excited states when the ground state geometry was used. In literature we found 'vertical' dipole moment calculations just for water by Vaval and Pal [13] and by Christiansen *et al.* [15]. These results more or less correlate with our data. We did not find any literature dipole moment data for  $H_2S$  excited states.

In Table 4 we present 'adiabatic' dipole moments obtained with CASSCF, CASPT2, CCSD and CCSD(T) methods. For  $H_2O$  and  $H_2S$  is the agreement between CASPT2 and CCSD(T) 'adiabatic' dipole moment values uniformly very good. This corresponds to good agreement of excitation energies obtained by the two methods. Influence of triple excitations is rather small, up to 5% of the total dipole moment values. In Table 4 we also present 'adiabatic' theoretical dipole moments from the literature [9–12, 14]. Only data for the ground state of both molecules and the  $^3B_1$  and  $^1B_1$  excited states of  $H_2O$  are available for comparison. Our results provide a similar picture of the dipole moment of  $H_2O$  excited states as the cited reference data. For both molecules in the ground states our CASPT2 and CCSD(T) dipole moments are in very good agreement with experiment [57, 58].

Calculations in optimized geometries of a specific excited state instead of the  $X^1A_1$  geometry obviously lead to dipole moment values which are significantly different. Let us base our analysis on CASPT2 data. 'Adiabatic' dipole moments of water are by 0.3 and 0.4 au less negative than 'vertical' ones for the  $B_1$  and  $A_2$  states respectively. **The valence angle plays a dominant role in affecting the dipole moment of  $H_2O$  and  $H_2S$ . However, in present calculations the bond length varies significantly as well (see Table 1) and therefore the  $z$ -coordinate of hydrogen atoms appears to be a better indicator of the geometry change.** These  $z$ -coordinates for water are larger by 10% and 40% for  $B_1$  and  $A_2$  states, respectively than are the  $z$ -coordinates of the  $X^1A_1$  state. This qualitatively agrees with

1 observed shifts in dipole moment values.

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3 With the hydrogen sulphide is the discussion more complicated. 'Adiabatic' dipole moment values of  
4  $H_2S$  are close to zero for all excited states studied in this paper. Shifts from 'vertical' to 'adiabatic'  
5 dipole moments are +0.5 au and +0.8 au for the  $^3B_1$  and  $^1B_1$  state and -0.2 au for  $^3A_2$  and  $^1A_2$  states,  
6 respectively. The  $z$ -coordinates of the  $B_1$  states are by 70% smaller than the ground  $X^1A_1$  state ones, so  
7 that the molecule is almost linear. The non-polar character of the  $^3B_1$  and  $^1B_1$  excited states is in line  
8 with their quasi-linear geometries. However, dipole moments of both triplet and singlet  $A_2$  states are close  
9 to zero as well. Clearly, this can not be attributed to the molecular geometry. The bond angle is close to 80  
10 deg, *i.e.* smaller than for the ground state and the bond length is longer, see Table 1. The  $z$ -coordinates of  
11  $A_2$  states are by 30% larger than  $X^1A_1$  ones. The reduced magnitude of the 'adiabatic' dipole moments of  
12 the  $^3A_2$  and  $^1A_2$  states with respect to the ground state can be partly discussed in similar lines as we did for  
13 the 'vertical' dipole moment. The general features of the participation of the sulphur and hydrogen differ  
14 from the situation commented for the experimental ground state  $X^1A_1$  geometries.  $4p_y$  sulphur orbitals  
15 contribute similarly in the two geometries but the role of hydrogen  $p_y$  orbitals is diminished. Mulliken  
16 population analysis of the CASSCF wave function shows little contribution of these orbitals. Similarly,  
17 the role of the sulphur  $d_{yz}$  orbitals is suppressed. To use these findings in a reasonable rationalization of  
18 behaviour of dipole moments in the  $^3A_2$  and  $^1A_2$  states of  $H_2S$  would be too speculative.  
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32 [Insert Table 4 about here]

### 33 3.4 Polarizabilities

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39 Dipole polarizability data of the five lowest electronic states of  $H_2O$  and  $H_2S$  are collected in Table 5. As  
40 dipole moments, also dipole polarizabilities were calculated in the experimental geometry of the ground  
41 state  $X^1A_1$ , ('vertical' ones), and also in optimized geometries of individual excited states, Table 1, which  
42 are specified in as 'adiabatic'.  
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46 Finite field calculations of perpendicular polarizability components have to be carried out in the  $C_s$   
47 symmetry. This has an unpleasant computational consequence for the  $\alpha_{xx}$  component of the  $B_1$  states and  
48  $\alpha_{yy}$  component of the  $A_2$  states, namely, they are second derivatives of energies represented by the second  
49 root in CASSCF. We were unable to converge properly the energy of the second root, especially for both  
50 triplet and singlet  $A_2$  states and thus some data are missing in Table 5. Similarly, the  $\alpha_{yy}$  component of  
51 the  $^1A_2$  state of water in the paper by Jonsson *et al.* [19] is also missing.  
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57 Dipole polarizabilities of both molecules in their ground electronic  $X^1A_1$  states are almost isotropic.  
58 Similarly to excitation and transition energies and dipole moments, CASPT2 and CCSD(T) provide very  
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1 similar polarizability values. As expected, differences between individual dipole polarizability components  
2 for the ground state obtained at the experimental  $X^1A_1$  geometry and at the theoretically optimized  
3 geometries are marginal. The electron correlation contributions to polarizabilities arising from the triple  
4 excitations in CCSD(T) are rather small, 0.2–0.3 au. We present in Table 5 also representative literature  
5 data (along with experimental polarizability for the ground state only correlated theoretical data are  
6 presented). We can see good agreement between our ground state CCSD(T) values and recent CCSD(T)  
7 calculations by Avila [41] for H<sub>2</sub>O and SOPPA calculation of Nielsen *et al.* [39] for H<sub>2</sub>S. Our CCSD(T)  
8 polarizability components for water differ by less than 0.1 au from experiment [57]. For H<sub>2</sub>S we found only  
9 experimental average polarizability  $\bar{\alpha}$  which differs from our CCSD(T) average polarizability 24.4 au, by  
10 0.3 au.

11 Upon the excitation of one of the lone pair electrons to the antibonding orbital  $b_1 \rightarrow a_1$  (leading to  
12  $B_1$  states) or  $b_1 \rightarrow b_2$  (leading to  $A_2$  states) the polarizability tensor becomes highly anisotropic with  
13 components by more than order of magnitude larger than in the ground state. Particularly large are the  
14  $\alpha_{yy}$  polarizability components of the  $^3B_1$  and  $^1B_1$  states for both H<sub>2</sub>O and H<sub>2</sub>S. For H<sub>2</sub>S in the ground state  
15 geometry are  $\alpha_{yy}$  from CASPT2 larger by a factor of 36 and 47 for the  $^3B_1$  and  $^1B_1$  states, respectively,  
16 than  $\alpha_{zz}$  for the ground state. For H<sub>2</sub>O are analogous factors 17 and 22, respectively. For both  $^3A_2$  and  $^1A_2$   
17 states of H<sub>2</sub>O at the experimental ground state geometry  $\alpha_{xx}$  and  $\alpha_{zz}$  components, which are available, are  
18 much **larger** than are these components for the ground state. In fact these components are even **larger**  
19 than those calculated for both  $^3B_1$  and  $^1B_1$  states. Completely different situation is for H<sub>2</sub>S. The  $\alpha_{zz}$   
20 component remains significantly **larger** than it is for the ground state, but the enhancement is not as  
21 large as it was for  $B_1$  states. We remind that  $A_2$  states of H<sub>2</sub>S are characterized by significant contribution  
22 of the sulphur  $4p_y$  orbital along with  $s$  and  $p_y$  hydrogen orbitals, and also by quite large contribution from  
23 the diffuse  $d_{yz}$  orbitals. Large enhancement of the polarizability due to the excitation to  $A_2$  states could  
24 be expected for the  $\alpha_{yy}$  component, which, unfortunately, is not available.

25 It is obvious that due to large differences in geometries there are also large differences between 'vertical'  
26 and 'adiabatic' polarizabilities. The most striking difference is that polarizabilities in optimized geometries  
27 (see Table 1) are much smaller than those for the experimental ground state geometry. Polarizability  
28 components for  $^3B_1$  and  $^1B_1$  states of H<sub>2</sub>O still remain relatively high and polarizability remains highly  
29 anisotropic. The two  $\alpha_{xx}$  and  $\alpha_{zz}$  components available for  $^3A_2$  and  $^1A_2$  states are similar, being still  
30 **larger** than corresponding components for the ground state, but increase only by a factor 2 - 3.

31 Very different situation is observed for H<sub>2</sub>S. For all four  $^3B_1$ ,  $^1B_1$ ,  $^3A_2$  and  $^1A_2$  excited states  $\alpha_{xx}$   
32 components, calculated at the optimized geometry, are very similar to the ground state values. Anisotropy  
33 remains high for both  $B_1$  states thanks to large  $\alpha_{yy}$  component. This is clearly related to the geometry

of these states which are nearly linear and oriented in the direction of the  $y$  axis (see Table 1). The  $\alpha_{zz}$  component is much smaller, which can be attributed, again, to the geometry of the  $^3B_1$  and  $^1B_1$  states. The  $C_{2v}$  geometry of  $H_2S$  in  $^3A_2$  and  $^1A_2$  excited states is bent, like for the ground state. The  $\alpha_{zz}$  component is larger than for the ground state by a factor 1.7–1.8. Like with dipole moments, any detailed discussion of polarizabilities at optimized geometries and their comparison to the values in the ground state, based on the analysis of the orbital participation, appears to be too speculative.

There are few reference dipole polarizability data for  $H_2O$  in excited states [9, 11, 12] which generally agree with our results. Jonsson *et al.* [19] published CASSCF and linear response calculations of the dipole polarizability of the six lowest singlets of  $H_2O$ . Their results for  $^1B_1$  and  $^1A_2$  states dramatically differ from our results. The reason of this discrepancy is insufficiency of their basis set, namely the lack of very diffuse exponents, which are vital in description of Rydberg states, particularly for polarizabilities. We carried out test calculations with our basis set chopped to match exponents of their set and we got similar results. As with the dipole moment, we did not find any dipole polarizability data for excited states of  $H_2S$ .

[Insert Table 5 about here]

#### 4 Conclusions

Results in Tables 2–5 clearly show that CASPT2 and CC calculations lead to very similar excitation energies as well as dipole moments and dipole polarizabilities, when the state under consideration is tractable by both types of methods. CASSCF with our large active space gives us qualitatively reasonable dipole moments and dipole polarizabilities, although for accurate properties more sophisticated treatment of the dynamic correlation at the level of CASPT2 or CCSD(T) is inevitable. Good agreement of CASPT2 and CCSD(T) results indicates that using our large active space in CASPT2 we are considering sufficient amount of the dynamic electron correlation. This is important since CASPT2 can treat cases which show significant amount of quasidegeneracy when the single determinant reference CCSD(T) method is not applicable. We note, however, that when the wave function of the state under consideration can be well represented by a single determinant reference, obtaining highly accurate results by CCSD(T) method is more straightforward than by the CASPT2 method for the same number of explicitly correlated electrons. The accuracy of CCSD(T) can be kept under control by inspecting the largest amplitudes arising from the CCSD treatment [60]. From the CASSCF/CASPT2 side a good indicator for the applicability of a single determinant reference approach is the weight of the dominant configuration in the CAS wave function. Considering good agreement of highly sophisticated CASPT2 and CCSD(T) results and using large diffuse



basis sets we expect that our results for the properties of H<sub>2</sub>O and H<sub>2</sub>S belong among the most accurate data published so far.

After examining the basis set convergence and a systematic consideration of the selection of the active space in CASPT2 our results may serve as benchmark data for selected geometries of H<sub>2</sub>O and H<sub>2</sub>S. This, however, was not primary goal of our study. It was rather the comparison of molecular properties, particularly dipole moments and dipole polarizabilities for the same electronic states of both molecules. Most significant are large changes of dipole moments and dipole polarizabilities in all <sup>3</sup>B<sub>1</sub>, <sup>1</sup>B<sub>1</sub>, <sup>3</sup>A<sub>2</sub> and <sup>1</sup>A<sub>2</sub> excited states with respect to the ground state properties. Considering properties of the <sup>3</sup>B<sub>1</sub> and <sup>1</sup>B<sub>1</sub> excited states, the dipole moment of both H<sub>2</sub>O and H<sub>2</sub>S in the ground state geometry change the polarity. When the geometry is optimized for a specific electronic state, the polarity is changed for H<sub>2</sub>O, while for H<sub>2</sub>S the polarity is approximately zero. This is mainly related to almost linear geometry of H<sub>2</sub>S in the triplet and singlet B<sub>1</sub> excited states. Polarizabilities of both molecules calculated in their ground state geometries increase by more than order of magnitude in B<sub>1</sub> states. In contrast to very low anisotropy in the ground state of H<sub>2</sub>O and H<sub>2</sub>S, the anisotropy in <sup>3</sup>B<sub>1</sub> and <sup>1</sup>B<sub>1</sub> excited states is very high. The enhancement of polarizabilities is much smaller when both molecules are calculated in their ground state geometries. Both molecules, particularly H<sub>2</sub>O, are highly anisotropic in geometries optimized for <sup>3</sup>B<sub>1</sub> and <sup>1</sup>B<sub>1</sub> excited states. While we observe quite similar pattern for properties of H<sub>2</sub>O and H<sub>2</sub>S in <sup>3</sup>B<sub>1</sub> and <sup>1</sup>B<sub>1</sub> excited states and their changes with respect to the ground state properties, similarities of both molecules in their <sup>3</sup>A<sub>2</sub> and <sup>1</sup>A<sub>2</sub> excited states are much less obvious. The dipole moment of H<sub>2</sub>S calculated in the ground state geometry is just reduced, but the sign remains the same as it is for the ground state. For the water molecule the direction of the dipole moment is reversed for <sup>3</sup>A<sub>2</sub> and <sup>1</sup>A<sub>2</sub> states, like it was for the triplet and singlet B<sub>1</sub> states. Only the α<sub>zz</sub> component of H<sub>2</sub>S in A<sub>2</sub> states increases in comparison with the ground state polarizability, while both α<sub>xx</sub> and α<sub>yy</sub> components are enhanced for H<sub>2</sub>O.

Our attempt for rationalizing these changes is based on the change of the orbital picture in the CASSCF wave function which H<sub>2</sub>O and H<sub>2</sub>S molecules undergo upon excitation. Large change of the dipole moment upon the excitation leading to B<sub>1</sub> states of H<sub>2</sub>O has been attributed [9] to the reorganization of the electron distribution resulting from the 1b<sub>1</sub>→4a<sub>1</sub> excitation. **The 4a<sub>1</sub> orbital of H<sub>2</sub>O, being essentially the Rydberg 3s orbital, is very diffuse. Due to its diffuseness the change of the orbital picture affects dipole moments and contributes to large increase of the dipole polarizabilities of B<sub>1</sub> states of H<sub>2</sub>O. The diffuseness of the singly occupied 6a<sub>1</sub> orbital of H<sub>2</sub>S is less manifested than in H<sub>2</sub>O, but the character remains the same.**

Differences in the behaviour of dipole moments and dipole polarizabilities of H<sub>2</sub>O and H<sub>2</sub>S in their <sup>3</sup>A<sub>2</sub> and <sup>1</sup>A<sub>2</sub> excited states are assigned to a significant contribution of the sulphur 4p<sub>y</sub> orbital along with s

1 and  $p_y$  hydrogen orbitals. In H<sub>2</sub>S there is also quite large contribution from the diffuse  $d_{yz}$  orbitals which  
2 are located in the molecular plane. Discussion of dipole moments and dipole polarizabilities in geometries  
3 optimized for any specific excited state is more difficult than is discussion and comparison of properties  
4 calculated in the geometry of the ground state of H<sub>2</sub>O and H<sub>2</sub>S. The effect of the geometry change combined  
5 with the change of the orbital picture for any specific excited state makes the pattern of properties for the  
6 two molecules less transparent.  
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Table 1. Geometries ( $\text{\AA}$ , deg) of the  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  molecule, imposing the  $C_{2v}$  symmetry.<sup>a</sup>

| State<br>Method       | $X^1A_1$ |          | $^3B_1$ |          | $^1B_1$ |          | $^3A_2$ |          | $^1A_2$ |          |
|-----------------------|----------|----------|---------|----------|---------|----------|---------|----------|---------|----------|
|                       | r        | $\theta$ | r       | $\theta$ | r       | $\theta$ | r       | $\theta$ | r       | $\theta$ |
| H <sub>2</sub> O      |          |          |         |          |         |          |         |          |         |          |
| CASPT2                | 0.959    | 104.3    | 1.107   | 108.5    | 1.083   | 105.6    | 1.234   | 94.4     | 1.222   | 92.6     |
| others                |          |          |         |          |         |          |         |          |         |          |
| SUCC <sup>b</sup>     |          |          | 1.091   | 106.7    | 1.077   | 105.5    | 1.153   | 96.6     | 1.127   | 94.4     |
| EOM CCSD <sup>c</sup> |          |          | 1.090   | 106.3    | 1.068   | 104.3    | 1.167   | 97.2     | 1.094   | 102.1    |
| CCSD(T) <sup>c</sup>  | 0.962    | 104.2    | 1.109   | 108.2    |         |          | 1.230   | 94.5     |         |          |
| exp. <sup>d</sup>     | 0.958    | 104.5    |         |          |         |          |         |          |         |          |
| H <sub>2</sub> S      |          |          |         |          |         |          |         |          |         |          |
| CASPT2                | 1.340    | 92.2     | 1.521   | 157.5    | 1.589   | 162.4    | 1.511   | 79.5     | 1.519   | 78.3     |
| others                |          |          |         |          |         |          |         |          |         |          |
| MRCI+Q <sup>e</sup>   |          |          |         |          | 1.529   | 92.2     |         |          | 1.504   | 92.2     |
| exp. <sup>d</sup>     | 1.336    | 92.1     |         |          |         |          |         |          |         |          |

<sup>a</sup> If not specified differently, geometry optimized with the d-aug-cc-pVQZ basis set at the CASPT2 level. The (1000) frozen and (1000) inactive space for  $\text{H}_2\text{O}$ , (3110) frozen and (3110) inactive space for  $\text{H}_2\text{S}$ . 8 correlated electrons for both molecules in the (7341) active space for the  $X^1A_1$  state, (8341) for  $B_1$  states and (7351) for  $A_2$  states.

<sup>b</sup> GMS SU CCSD cc-pVTZ+diff results from [3].

<sup>c</sup> aug-cc-pVTZ results from [20].

<sup>d</sup> Experiment [54].

<sup>e</sup> Angle is kept at the value of the ground state, bond length optimized by the MRCI+Q method [25].

Table 2. Vertical excitation energies (in eV) of the  $H_2O$  and  $H_2S$  molecule.<sup>a</sup>

| Excitation State                        | $b_1 \rightarrow a_1$<br>${}^3B_1$ | $b_1 \rightarrow a_1$<br>${}^1B_1$ | $b_1 \rightarrow b_2$<br>${}^3A_2$ | $b_1 \rightarrow b_2$<br>${}^1A_2$ |
|---|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| H <sub>2</sub> O                        |                                    |                                    |                                    |                                    |
| CASSCF                                  | 7.04                               | 7.40                               | 8.96                               | 9.09                               |
| CASPT2                                  | 7.29                               | 7.66                               | 9.27                               | 9.42                               |
| CCSD                                    | 7.24                               | 7.59                               | 9.20                               | 9.35                               |
| CCSD(T)                                 | 7.30                               |                                    | 9.28                               |                                    |
| others                                  |                                    |                                    |                                    |                                    |
| EOM CCSD <sup>b</sup>                   | 7.29                               | 7.68                               | 9.27                               | 9.44                               |
| GMS SU CCSD <sup>c</sup>                | 7.20                               | 7.54                               | 9.18                               | 9.32                               |
| CCSDR(3) <sup>d</sup>                   |                                    | 7.66                               |                                    | 9.42                               |
| CC3 <sup>e</sup>                        |                                    | 7.66                               |                                    | 9.42                               |
| MS-CASPT2 <sup>f</sup>                  | 7.13                               | 7.50                               | 9.12                               | 9.27                               |
| expt. <sup>g</sup>                      | 7.0                                | 7.4                                | 8.9                                | 9.1                                |
| H <sub>2</sub> S                        |                                    |                                    |                                    |                                    |
| CASSCF                                  | 5.75                               | 6.09                               | 5.79                               | 6.11                               |
| CASPT2                                  | 5.92                               | 6.27                               | 5.78                               | 6.12                               |
| CCSD                                    | 5.92                               | 6.25                               | 5.76                               | 6.10                               |
| CCSD(T)                                 | 5.93                               |                                    | 5.79                               |                                    |
| others                                  |                                    |                                    |                                    |                                    |
| $H^V$ <sup>h</sup>                      | 5.90                               | 6.35                               | 5.50                               | 5.89                               |
| MR-DCI <sup>i</sup>                     |                                    | 6.16                               |                                    | 6.80                               |
| (SC) <sup>2</sup> -MR-SDCI <sup>j</sup> |                                    | 6.47                               |                                    | 6.33                               |
| DFT QR <sup>k</sup>                     | 5.73                               |                                    | 5.36                               |                                    |
| expt. <sup>l</sup>                      |                                    | 6.33                               |                                    | 4.6–7.5                            |

<sup>a</sup> If not specified differently, calculations performed in the d-aug-cc-pVQZ basis. The CASSCF active space of the ground state is (7341), the corresponding  $B_1$  space is (8341) and  $A_2$  is (7351).

<sup>b</sup> aug-cc-pVQZ results from [16].

<sup>c</sup> aug-cc-pVTZ results from [3].

<sup>d</sup> d-aug-cc-pVQZ results from [15].

<sup>e</sup> d-aug-cc-pVQZ results from [18].

<sup>f</sup> The ANO-L type basis set  $O[5s4p2d1f]/H[3s2p1d] + (2s2p2d)$  results from [17].

<sup>g</sup> From [5].

<sup>h</sup> Effective valence shell Hamiltonian  $H^V$  calculations from [26].

<sup>i</sup> The basis set  $S[8s6p2d]/H[3s1p]$  results from [23].

<sup>j</sup> The ANO-L type basis set  $S[4s3p2d1f]/H[2s1p] + (4s4p4d2f)$  results from [27].

<sup>k</sup> DFT QR results from [28].

<sup>l</sup> From [56].

Table 3. Equilibrium ( $T_e$ ) transition energies (in eV) of the H<sub>2</sub>O and H<sub>2</sub>S molecule.<sup>a</sup>

| Excitation State         | $b_1 \rightarrow a_1$<br>${}^3B_1$ | $b_1 \rightarrow a_1$<br>${}^1B_1$ | $b_1 \rightarrow b_2$<br>${}^3A_2$ | $b_1 \rightarrow b_2$<br>${}^1A_2$ |
|--------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| H <sub>2</sub> O         |                                    |                                    |                                    |                                    |
| CASSCF                   | 6.59                               | 7.06                               | 8.37                               | 8.74                               |
| CASPT2                   | 6.81                               | 7.29                               | 8.59                               | 8.97                               |
| CCSD                     | 6.81                               | 7.26                               | 8.66                               | 9.00                               |
| CCSD(T)                  | 6.83                               |                                    | 8.63                               |                                    |
| others                   |                                    |                                    |                                    |                                    |
| CASPT2 <sup>b</sup>      | 6.80                               | 7.25                               |                                    |                                    |
| FSMRCC <sup>c</sup>      | 7.21                               | 7.52                               | 9.32                               | 9.42                               |
| FSMRCC <sup>d</sup>      | 6.88                               | 7.29                               |                                    |                                    |
| EOM CCSD <sup>e</sup>    | 6.77                               | 7.27                               | 8.68                               | 9.04                               |
| CCSD(T) <sup>e</sup>     | 6.76                               |                                    | 8.56                               |                                    |
| GMS SU CCSD <sup>f</sup> | 6.71                               | 7.15                               | 8.62                               | 8.89                               |
| H <sub>2</sub> S         |                                    |                                    |                                    |                                    |
| CASSCF                   | 4.33                               | 4.87                               | 5.15                               | 5.45                               |
| CASPT2                   | 4.42                               | 5.00                               | 5.18                               | 5.52                               |
| CCSD                     | 4.45                               | 5.07                               | 5.21                               | 5.54                               |
| CCSD(T)                  | 4.45                               |                                    | 5.21                               |                                    |

<sup>a</sup> If not specified differently, calculations performed in the d-aug-cc-pVQZ basis. The CASSCF active space of the ground state is (7341), the corresponding  $B_1$  space is (8341) and  $A_2$  is (7351).

<sup>b</sup> R-ANO basis set O[9s7p4d2f]/H[4s3p2d], the active space (7341) for the ground state and (8341) for the  $B_1$  state [12].

<sup>c</sup> Sadlej's POL basis set results from [13].

<sup>d</sup> R-ANO basis set O[9s7p4d2f]/H[4s3p2d] results from [14].

<sup>e</sup> aug-cc-pVTZ results from [20].

<sup>f</sup> aug-cc-pVTZ results from [3].

Table 4. Dipole moments of  $H_2O$  and  $H_2S$  (in au) calculated in the experimental  $X^1A_1$  geometry and in optimized  $C_{2v}$  geometries of the specific state<sup>a</sup>.

| Method                            | $X^1A_1$ | $^3B_1$ | $^1B_1$ | $^3A_2$ | $^1A_2$ |
|-----------------------------------|----------|---------|---------|---------|---------|
| $H_2O$                            |          |         |         |         |         |
| experimental $X^1A_1$ geometry    |          |         |         |         |         |
| CASSCF                            | 0.740    | -0.651  | -0.823  | -0.646  | -0.667  |
| CASPT2                            | 0.729    | -0.563  | -0.703  | -0.631  | -0.662  |
| FSMRCC <sup>b</sup>               |          |         |         |         |         |
| CCSD <sup>c</sup>                 | 0.728    | -0.567  | -0.670  | -0.437  | -0.754  |
|                                   |          |         | -0.725  |         | -0.668  |
| optimized specific state geometry |          |         |         |         |         |
| HF                                | 0.781    | -0.339  | -0.625  | -0.199  | -0.296  |
| CASSCF                            | 0.741    | -0.297  | -0.488  | -0.236  | -0.308  |
| CASPT2                            | 0.730    | -0.245  | -0.414  | -0.214  | -0.269  |
| CCSD                              | 0.737    | -0.247  | -0.429  | -0.203  | -0.265  |
| CCSD(T)                           | 0.728    | -0.238  |         | -0.214  |         |
| CASSCF <sup>d</sup>               | 0.725    | -0.416  | -0.640  |         |         |
| CC <sup>e</sup>                   | 0.724    | -0.275  | -0.448  |         |         |
| CASPT2 <sup>f</sup>               | 0.726    | -0.325  | -0.488  |         |         |
| FSMRCC <sup>g</sup>               |          | -0.520  | -0.636  |         |         |
| expt. <sup>h</sup>                | 0.7296   |         |         |         |         |
| $H_2S$                            |          |         |         |         |         |
| experimental $X^1A_1$ geometry    |          |         |         |         |         |
| CASSCF                            | 0.404    | -0.567  | -0.832  | 0.216   | 0.303   |
| CASPT2                            | 0.389    | -0.467  | -0.682  | 0.204   | 0.257   |
| optimized specific state geometry |          |         |         |         |         |
| HF                                | 0.424    | 0.098   | 0.079   | -0.014  | 0.034   |
| CASSCF                            | 0.404    | 0.086   | 0.071   | -0.001  | 0.075   |
| CASPT2                            | 0.389    | 0.084   | 0.071   | -0.016  | 0.041   |
| CCSD                              | 0.394    | 0.086   | 0.070   | -0.015  | 0.052   |
| CCSD(T)                           | 0.390    | 0.086   |         | -0.020  |         |
| MP4 <sup>i</sup>                  | 0.390    |         |         |         |         |
| MP2 <sup>j</sup>                  | 0.392    |         |         |         |         |
| CASPT2 <sup>k</sup>               | 0.382    |         |         |         |         |
| expt. <sup>l</sup>                | 0.383    |         |         |         |         |

<sup>a</sup> If not specified differently, calculations performed in the d-aug-cc-pVQZ basis. The CASSCF active space of the ground state is (7341), the corresponding  $B_1$  space is (8341) and  $A_2$  is (7351).

<sup>b</sup> Sadlej's POL basis set results from [13].

<sup>c</sup> d-aug-cc-pVQZ results from [15].

<sup>d</sup> R-ANO basis set O[9s7p4d2f]/H[4s3p2d] in the 6330 active space results from [9].

<sup>e</sup> CCSD(T) calculation for the  $^1A_1$  and  $^3B_1$  states and CCSD for  $^1B_1$  state in optimized geometries, slightly different from ours [11].

<sup>f</sup> CASPT2 (7341) calculation in optimized geometry, slightly different from ours [12].

<sup>g</sup> R-ANO basis set O[9s7p4d2f]/H[4s3p2d] results from [14].

<sup>h</sup> From [57].

<sup>i</sup> Sadlej's POL basis set results from [10].

<sup>j</sup> TZP1 basis set S[7s6p2d1f]/H[4s3p] results from [37].

<sup>k</sup> ANO-L basis set S[7s7p5d4f]/H[6s4p3d] results from [40].

<sup>l</sup> From [58].

Table 5. Dipole polarizabilities of H<sub>2</sub>O and H<sub>2</sub>S (in au) calculated in the experimental  $X^1A_1$  geometry and in optimized  $C_{2v}$  geometries of the specific state<sup>a</sup>.

| State<br>Method                   | H <sub>2</sub> O |               |               | H <sub>2</sub> S |                        |               |
|-----------------------------------|------------------|---------------|---------------|------------------|------------------------|---------------|
|                                   | $\alpha_{xx}$    | $\alpha_{yy}$ | $\alpha_{zz}$ | $\alpha_{xx}$    | $\alpha_{yy}$          | $\alpha_{zz}$ |
| $X^1A_1$                          |                  |               |               |                  |                        |               |
| experimental $X^1A_1$ geometry    |                  |               |               |                  |                        |               |
| CASSCF                            | 9.0              | 9.7           | 9.3           | 25.1             | 24.3                   | 24.2          |
| CASPT2                            | 9.2              | 9.8           | 9.5           | 24.5             | 24.2                   | 24.1          |
| CASSCF <sup>b</sup>               | 9.4              | 10.0          | 9.6           |                  |                        |               |
| CASSCF <sup>c</sup>               | 8.9              | 9.6           | 9.2           |                  |                        |               |
| CCSD(T) <sup>d</sup>              | 9.2              | 9.9           | 9.5           |                  |                        |               |
| MP4 <sup>e</sup>                  |                  |               |               | 25.1             | 24.2                   | 24.2          |
| CC-LRT <sup>f</sup>               |                  |               |               | 25.2             | 24.4                   | 24.5          |
| MP2 <sup>g</sup>                  |                  |               |               | 25.0             | 24.3                   | 24.3          |
| SOPPA <sup>h</sup>                |                  |               |               | 24.9             | 24.3                   | 24.2          |
| expt. <sup>i</sup>                | 9.3              | 10.0          | 9.6           |                  | $\bar{\alpha} = 24.71$ |               |
| optimized specific state geometry |                  |               |               |                  |                        |               |
| CASSCF                            | 9.0              | 9.7           | 9.3           | 25.1             | 24.4                   | 24.3          |
| CASPT2                            | 9.2              | 9.9           | 9.5           | 24.5             | 24.3                   | 24.2          |
| CCSD                              | 9.0              | 9.8           | 9.3           | 24.5             | 24.2                   | 24.0          |
| CCSD(T)                           | 9.3              | 9.9           | 9.6           | 24.7             | 24.3                   | 24.2          |
| $^3B_1$                           |                  |               |               |                  |                        |               |
| experimental $X^1A_1$ geometry    |                  |               |               |                  |                        |               |
| CASSCF                            | 106.5            | 202.4         | 93.2          | 157.5            | 572.8                  | 217.1         |
| CASPT2                            | 90.5             | 167.9         | 81.9          | 112.0            | 1132.1                 | 168.3         |
| optimized specific state geometry |                  |               |               |                  |                        |               |
| CASSCF                            | 50.9             | 149.7         | 51.2          | 21.8             | 53.0                   | 25.4          |
| CASPT2                            | 45.4             | 129.1         | 46.5          | 23.1             | 50.1                   | 26.2          |
| CCSD                              | 46.7             | 138.6         | 47.6          | 21.5             | 51.9                   | 24.9          |
| CCSD(T)                           | 45.9             | 128.7         | 47.0          | 21.6             | 52.0                   | 25.2          |
| CASSCF <sup>b</sup>               | 64.3             | 188.8         | 62.4          |                  |                        |               |
| CASPT2 <sup>j</sup>               | 48.7             | 132           | 50.3          |                  |                        |               |
| CCSD(T) <sup>k</sup>              | 46.8             | 132.1         | 48.4          |                  |                        |               |
| $^1B_1$                           |                  |               |               |                  |                        |               |
| experimental $X^1A_1$ geometry    |                  |               |               |                  |                        |               |
| CASSCF                            | 116.6            | 261.5         | 120.1         | 215.3            | 630.0                  | 315.2         |
| CASPT2                            | 99.1             | 212.7         | 103.9         | 155.8            | 884.7                  | 236.3         |
| CASSCF <sup>c</sup>               | 61.6             | 205.3         | 65.0          |                  |                        |               |
| optimized specific state geometry |                  |               |               |                  |                        |               |
| CASSCF                            | 66.5             | 198.4         | 76.2          | 22.9             | 54.8                   | 26.2          |
| CASPT2                            | 58.6             | 167.7         | 67.4          | 25.9             | 49.1                   | 29.8          |
| CCSD                              | 60.2             | 184.5         | 70.6          |                  | 47.7                   | 25.6          |
| CASSCF <sup>b</sup>               | 83.4             | 253.5         | 91.7          |                  |                        |               |
| CASPT2 <sup>j</sup>               | 59.4             | 165           | 70.2          |                  |                        |               |
| CCSD <sup>k</sup>                 | 55.6             | 174.0         | 68.0          |                  |                        |               |
| $^3A_2$                           |                  |               |               |                  |                        |               |
| experimental $X^1A_1$ geometry    |                  |               |               |                  |                        |               |
| CASSCF                            | 181.5            |               | 159.6         | 24.9             |                        | 64.5          |
| CASPT2                            | 141.0            |               | 121.3         | 24.4             |                        | 56.0          |
| optimized specific state geometry |                  |               |               |                  |                        |               |
| CASSCF                            | 22.7             |               | 23.4          | 22.7             |                        | 42.9          |
| CASPT2                            | 21.2             |               | 21.9          | 22.4             |                        | 43.2          |
| CCSD                              | 21.6             |               | 22.2          | 22.1             |                        | 41.3          |
| CCSD(T)                           | 21.5             |               | 22.3          | 22.2             |                        | 41.6          |
| $^1A_2$                           |                  |               |               |                  |                        |               |
| experimental $X^1A_1$ geometry    |                  |               |               |                  |                        |               |
| CASSCF                            | 222.4            |               | 202.1         | 26.7             |                        | 80.4          |
| CASPT2                            | 176.5            |               | 157.3         | 23.6             |                        | 68.6          |
| CASSCF <sup>c</sup>               | 30.2             |               | 47.7          |                  |                        |               |
| optimized specific state geometry |                  |               |               |                  |                        |               |
| CASSCF                            | 26.7             |               | 27.8          | 22.9             |                        | 45.5          |
| CASPT2                            | 24.6             |               | 22.2          | 22.8             |                        | 44.4          |
| CCSD                              | 25.1             |               | 26.0          | 22.7             |                        | 44.4          |

<sup>a</sup> If not specified differently, calculations performed in the d-aug-cc-pVQZ basis. The CASSCF active space of the ground state is (7341), the corresponding  $B_1$  space is (8341) and  $A_2$  is (7351).

<sup>b</sup> R-ANO basis set O[9s7p4d2f]/H[4s3p2d] in the 6330 active space results from [9].

<sup>c</sup> ANO basis set O[6s5p3d2f]/H[4s3p2d] results in the 6331 active space, from [19].

<sup>d</sup> d-aug-cc-pV5Z results from [41]; <sup>e</sup> Sadlej's POL basis set results from [10].

<sup>f</sup> Coupled-cluster linear response theory with basis set S[7s5p2d]/H[3s2p], results from [33].

<sup>g</sup> From [37]; <sup>h</sup> aug-cc-pVTZ results from [39].

<sup>i</sup> H<sub>2</sub>O taken from [57], H<sub>2</sub>S static DOSD estimate from [59].

<sup>j</sup> CASPT2 (7341) calculation in optimized geometry, slightly different from ours [12].

<sup>k</sup> CC calculation in optimized geometry, slightly different from ours [11].