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**Theoretical study of molecular properties of low-lying
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RESEARCH ARTICLE

Theoretical study of molecular properties of low-lying electronic excited states of
 H_2O and H_2S

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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_2O and H_2S 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_2O 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_2S in its excited states. Dipole moments and dipole polarizabilities of 3B_1 , 1B_1 states of H_2S and H_2O 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_2S molecule.

Keywords: excited states; Rydberg states; H_2O ; H_2S ; 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 H_2O and H_2S 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 H_2O and H_2S in low-lying excited states which are important in numerous photophysical and photochemical processes [3].

The ground and excited electronic states of H_2O and H_2S 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 H_2S .

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 H_2S 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 H_2S and H_2O arise from participation of the $3d$ orbitals of the sulphur atom.

H_2O and H_2S molecules have many similarities, however, there are many differences as well. The bonding of sulphur in H_2S is different from oxygen in H_2O . 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 H_2S molecule in comparison to the H_2O molecule. The energy differences between Rydberg states of H_2S are considerably smaller than for H_2O , 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 H_2O and H_2S 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 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

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12 We carried out geometry optimization for the ground states and four lowest excited states of H₂O and
13 H₂S. We restricted the optimization by enforcing the C_{2v} symmetry considering equal O–H or S–H bond
14 lengths. Since the considered excited electronic states are of the dissociative character, these optimized
15 C_{2v} geometries can at most characterize an appropriate saddle points on the energy hypersurface [3]. The
16 geometry optimization was performed at the CASPT2 level using the active space (7341) for the X^1A_1
17 state, (8341) for B_1 states and (7351) for A_2 states. These data together with reference theoretical [3,20,25]
18 and experimental [54] data for the ground states are collected in Table 1. A significant change of geometry
19 is found for excited states, particularly B_1 states of H₂S which are almost linear. In the case of water
20 we got similar geometries as Li and Paldus [3] by the GMS SU CCSD method. There is agreement also
21 between our and Cai *et al.* [20] EOM CCSD and CCSD(T) data except the 1A_2 state of water. Their
22 bond angle for this state is by 10 deg larger than ours. The literature data for geometries of the lowest
23 excited states of H₂S are rather seldom. There are published figures [22,23,26,30] with bond distance and
24 angle dependence for the 1B_1 and 1A_2 states. They indicate an angle about 80 deg for the 1A_2 state and
25 provide very flat curve with almost linear geometry for the 1B_1 state. The bond lengths are larger than
26 for the ground state. Simah *et al.* [25] published geometries for H₂S excited singlets with angles fixed to
27 the ground state value. Our calculations confirm their results. Our CASPT2 ground state geometries for
28 both studied molecules coincide with experimental ones [54].
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49 3.2 Excitation energies

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51 Calculated vertical excitation energies are presented in Table 2. We carried out CASSCF with 8 correlated
52 electrons for both molecules in the (7341) active space for the X^1A_1 . In the case of the H₂O molecule
53 we got vertical excitation energies in the same sequence of electronic states namely 3B_1 , 1B_1 , 3A_2 , 1A_2
54 by all methods which we used. There are numerous papers in the literature dealing with calculations of
55 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 H₂O 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 H₂O 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 H₂S molecule, the T_e sequence is 3B_1 , 1B_1 , 3A_2 , 1A_2 and, in contrast to excitation energies in H₂O, this sequence differs from vertical excitation energies. This change is due to much larger differences in optimized geometries than we observe for H₂O, 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 H₂O and H₂S 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 H₂S differ marginally from CASPT2 ones, similarly as it was for the H₂O molecule. The same holds for vertical excitation energies as well. In the literature we did not find any relevant H₂S 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 H₂O and H₂S 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 H₂S have opposite sign for both B_1 states, like it is for H₂O, 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 H₂S 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 H₂O 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 H₂O, 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 H₂O and H₂S, 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 H₂O and H₂S are characterized by the $b_1 \rightarrow b_2$ electron excitation. Singly
32 occupied $2b_2$ orbital of H₂O 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 H₂S upon excitation to the 3B_1 and
55 1B_1 excited states are similar as were found for H₂O. 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 α_{xx} component of the B_1 states and
48 α_{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 α_{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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similar polarizability values. As expected, differences between individual dipole polarizability components for the ground state obtained at the experimental X^1A_1 geometry and at the theoretically optimized geometries are marginal. The electron correlation contributions to polarizabilities arising from the triple excitations in CCSD(T) are rather small, 0.2–0.3 au. We present in Table 5 also representative literature data (along with experimental polarizability for the ground state only correlated theoretical data are presented). We can see good agreement between our ground state CCSD(T) values and recent CCSD(T) calculations by Avila [41] for H₂O and SOPPA calculation of Nielsen *et al.* [39] for H₂S. Our CCSD(T) polarizability components for water differ by less than 0.1 au from experiment [57]. For H₂S we found only experimental average polarizability $\bar{\alpha}$ which differs from our CCSD(T) average polarizability 24.4 au, by 0.3 au.

Upon the excitation of one of the lone pair electrons to the antibonding orbital $b_1 \rightarrow a_1$ (leading to B_1 states) or $b_1 \rightarrow b_2$ (leading to A_2 states) the polarizability tensor becomes highly anisotropic with components by more than order of magnitude larger than in the ground state. Particularly large are the α_{yy} polarizability components of the 3B_1 and 1B_1 states for both H₂O and H₂S. For H₂S in the ground state geometry are α_{yy} from CASPT2 larger by a factor of 36 and 47 for the 3B_1 and 1B_1 states, respectively, than α_{zz} for the ground state. For H₂O are analogous factors 17 and 22, respectively. For both 3A_2 and 1A_2 states of H₂O at the experimental ground state geometry α_{xx} and α_{zz} components, which are available, are much **larger** than are these components for the ground state. In fact these components are even **larger** than those calculated for both 3B_1 and 1B_1 states. Completely different situation is for H₂S. The α_{zz} component remains significantly **larger** than it is for the ground state, but the enhancement is not as large as it was for B_1 states. We remind that A_2 states of H₂S are characterized by significant contribution of the sulphur $4p_y$ orbital along with s and p_y hydrogen orbitals, and also by quite large contribution from the diffuse d_{yz} orbitals. Large enhancement of the polarizability due to the excitation to A_2 states could be expected for the α_{yy} component, which, unfortunately, is not available.

It is obvious that due to large differences in geometries there are also large differences between 'vertical' and 'adiabatic' polarizabilities. The most striking difference is that polarizabilities in optimized geometries (see Table 1) are much smaller than those for the experimental ground state geometry. Polarizability components for 3B_1 and 1B_1 states of H₂O still remain relatively high and polarizability remains highly anisotropic. The two α_{xx} and α_{zz} components available for 3A_2 and 1A_2 states are similar, being still **larger** than corresponding components for the ground state, but increase only by a factor 2 - 3.

Very different situation is observed for H₂S. For all four 3B_1 , 1B_1 , 3A_2 and 1A_2 excited states α_{xx} components, calculated at the optimized geometry, are very similar to the ground state values. Anisotropy remains high for both B_1 states thanks to large α_{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 α_{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 α_{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 H₂O and H₂S 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 H₂O and H₂S. 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 ³B₁, ¹B₁, ³A₂ and ¹A₂ excited states with respect to the ground state properties. Considering properties of the ³B₁ and ¹B₁ excited states, the dipole moment of both H₂O and H₂S in the ground state geometry change the polarity. When the geometry is optimized for a specific electronic state, the polarity is changed for H₂O, while for H₂S the polarity is approximately zero. This is mainly related to almost linear geometry of H₂S in the triplet and singlet B₁ excited states. Polarizabilities of both molecules calculated in their ground state geometries increase by more than order of magnitude in B₁ states. In contrast to very low anisotropy in the ground state of H₂O and H₂S, the anisotropy in ³B₁ and ¹B₁ 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 H₂O, are highly anisotropic in geometries optimized for ³B₁ and ¹B₁ excited states. While we observe quite similar pattern for properties of H₂O and H₂S in ³B₁ and ¹B₁ excited states and their changes with respect to the ground state properties, similarities of both molecules in their ³A₂ and ¹A₂ excited states are much less obvious. The dipole moment of H₂S 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 ³A₂ and ¹A₂ states, like it was for the triplet and singlet B₁ states. Only the α_{zz} component of H₂S in A₂ states increases in comparison with the ground state polarizability, while both α_{xx} and α_{yy} components are enhanced for H₂O.

Our attempt for rationalizing these changes is based on the change of the orbital picture in the CASSCF wave function which H₂O and H₂S molecules undergo upon excitation. Large change of the dipole moment upon the excitation leading to B₁ states of H₂O has been attributed [9] to the reorganization of the electron distribution resulting from the 1b₁→4a₁ excitation. **The 4a₁ orbital of H₂O, 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 B₁ states of H₂O. The diffuseness of the singly occupied 6a₁ orbital of H₂S is less manifested than in H₂O, but the character remains the same.**

Differences in the behaviour of dipole moments and dipole polarizabilities of H₂O and H₂S in their ³A₂ and ¹A₂ excited states are assigned to a significant contribution of the sulphur 4p_y orbital along with s

1 and p_y hydrogen orbitals. In H₂S 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 H₂O and H₂S. 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 (\AA , deg) of the H_2O and H_2S molecule, imposing the C_{2v} symmetry.^a

State Method	X^1A_1		3B_1		1B_1		3A_2		1A_2	
	r	θ	r	θ	r	θ	r	θ	r	θ
H ₂ O										
CASPT2	0.959	104.3	1.107	108.5	1.083	105.6	1.234	94.4	1.222	92.6
others										
SUCC ^b			1.091	106.7	1.077	105.5	1.153	96.6	1.127	94.4
EOM CCSD ^c			1.090	106.3	1.068	104.3	1.167	97.2	1.094	102.1
CCSD(T) ^c	0.962	104.2	1.109	108.2			1.230	94.5		
exp. ^d	0.958	104.5								
H ₂ 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 ^e					1.529	92.2			1.504	92.2
exp. ^d	1.336	92.1								

^a 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 H_2O , (3110) frozen and (3110) inactive space for H_2S . 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.

^b GMS SU CCSD cc-pVTZ+diff results from [3].

^c aug-cc-pVTZ results from [20].

^d Experiment [54].

^e 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.^a

Excitation State	$b_1 \rightarrow a_1$ 3B_1	$b_1 \rightarrow a_1$ 1B_1	$b_1 \rightarrow b_2$ 3A_2	$b_1 \rightarrow b_2$ 1A_2
H ₂ 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 ^b	7.29	7.68	9.27	9.44
GMS SU CCSD ^c	7.20	7.54	9.18	9.32
CCSDR(3) ^d		7.66		9.42
CC3 ^e		7.66		9.42
MS-CASPT2 ^f	7.13	7.50	9.12	9.27
expt. ^g	7.0	7.4	8.9	9.1
H ₂ 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 ^h	5.90	6.35	5.50	5.89
MR-DCI ⁱ		6.16		6.80
(SC) ² -MR-SDCI ^j		6.47		6.33
DFT QR ^k	5.73		5.36	
expt. ^l		6.33		4.6–7.5

^a 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).

^b aug-cc-pVQZ results from [16].

^c aug-cc-pVTZ results from [3].

^d d-aug-cc-pVQZ results from [15].

^e d-aug-cc-pVQZ results from [18].

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

^g From [5].

^h Effective valence shell Hamiltonian H^V calculations from [26].

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

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

^k DFT QR results from [28].

^l From [56].

Table 3. Equilibrium (T_e) transition energies (in eV) of the H₂O and H₂S molecule.^a

Excitation State	$b_1 \rightarrow a_1$ 3B_1	$b_1 \rightarrow a_1$ 1B_1	$b_1 \rightarrow b_2$ 3A_2	$b_1 \rightarrow b_2$ 1A_2
H ₂ 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 ^b	6.80	7.25		
FSMRCC ^c	7.21	7.52	9.32	9.42
FSMRCC ^d	6.88	7.29		
EOM CCSD ^e	6.77	7.27	8.68	9.04
CCSD(T) ^e	6.76		8.56	
GMS SU CCSD ^f	6.71	7.15	8.62	8.89
H ₂ 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	

^a 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).

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

^c Sadlej's POL basis set results from [13].

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

^e aug-cc-pVTZ results from [20].

^f 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^a.

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 ^b					
CCSD ^c	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 ^d	0.725	-0.416	-0.640		
CC ^e	0.724	-0.275	-0.448		
CASPT2 ^f	0.726	-0.325	-0.488		
FSMRCC ^g		-0.520	-0.636		
expt. ^h	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 ⁱ	0.390				
MP2 ^j	0.392				
CASPT2 ^k	0.382				
expt. ^l	0.383				

^a 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).

^b Sadlej's POL basis set results from [13].

^c d-aug-cc-pVQZ results from [15].

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

^e 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].

^f CASPT2 (7341) calculation in optimized geometry, slightly different from ours [12].

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

^h From [57].

ⁱ Sadlej's POL basis set results from [10].

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

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

^l From [58].

Table 5. Dipole polarizabilities of H₂O and H₂S (in au) calculated in the experimental X^1A_1 geometry and in optimized C_{2v} geometries of the specific state^a.

State Method	H ₂ O			H ₂ S		
	α_{xx}	α_{yy}	α_{zz}	α_{xx}	α_{yy}	α_{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 ^b	9.4	10.0	9.6			
CASSCF ^c	8.9	9.6	9.2			
CCSD(T) ^d	9.2	9.9	9.5			
MP4 ^e				25.1	24.2	24.2
CC-LRT ^f				25.2	24.4	24.5
MP2 ^g				25.0	24.3	24.3
SOPPA ^h				24.9	24.3	24.2
expt. ⁱ	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 ^b	64.3	188.8	62.4			
CASPT2 ^j	48.7	132	50.3			
CCSD(T) ^k	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 ^c	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 ^b	83.4	253.5	91.7			
CASPT2 ^j	59.4	165	70.2			
CCSD ^k	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 ^c	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

^a 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).

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

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

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

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

^g From [37]; ^h aug-cc-pVTZ results from [39].

ⁱ H₂O taken from [57], H₂S static DOSD estimate from [59].

^j CASPT2 (7341) calculation in optimized geometry, slightly different from ours [12].

^k CC calculation in optimized geometry, slightly different from ours [11].