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Molecular electric properties in electronic excited states: multipole moments and polarizabilities of H_2O in the lowest $^1B_1$ and $^3B_1$ excited states

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Summary. The dipole and quadrupole moments and the dipole polarizability tensor components are calculated for the $^1B_1$ and $^3B_1$ excited states of the water molecule by using the complete active space (CAS) SCF method and an extended basis set of atomic natural orbitals. The dipole moment in the lowest $^1B_1$ (0.640 a.u.) and $^3B_1$ (0.416 a.u.) states is found to be antiparallel to that in the ground electronic state of H_2O. The shape of the quadrupole moment ellipsoid is significantly modified by the electronic excitation to both states investigated in this paper. All components of the excited state dipole polarizability tensor increase by about an order of magnitude compared to their values in the ground electronic state. The present results are used to discuss some aspects of intermolecular interactions involving molecules in their excited electronic states.

Key words: Electric properties of electronically excited states – CAS SCF calculations for excited states – Excited states of the water molecule–Geometry of excited states of the water molecule – Properties of excited states of the water molecule – Intermolecular interactions in excited states

1. Introduction

Wide interest in electric properties of atoms and molecules follows primarily from the importance of those quantities in different models of interacting systems [1–3]. For a long time this was the principal motivation for extensive experimental and theoretical investigations of atomic and molecular electric properties. As a result, a considerable amount of reliable data has been accumulated for multipole moments and polarizabilities of atoms and molecules. However, in comparison with the abundant information concerning different electric properties of atoms and molecules in the ground electronic state, the respective data for electronic excited states are rather scarce.

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The majority of available experimental data for electric properties of molecular excited states are of a rather low accuracy. Most of them arise from the study of molecular spectra in solutions and their evaluation heavily depends on the assumed model of solvent-solute interactions [4, 5]. Direct gas-phase investigations of the Stark effect in molecular spectra are difficult and rare [6].

In comparison with the progress in experimental investigations of electric properties in molecular excited states the corresponding theoretical studies are rather limited. Accurate theoretical calculations of electric properties in electronic excited states of molecules are quite uncommon and usually limited to the lowest multipole moments of the given excited state [7, 8]. Although the theoretical evaluation of higher-order electric properties in electronic excited states is nowadays feasible, this area appears to have been at least partly neglected. On the other hand, the progress in spectroscopic techniques for the investigation of excited electronic states makes the evaluation of the excited state molecular electric properties timely and desirable.

In order to give a more general motivation for our studies of electric properties in molecular excited states let us mention that a considerable part of the excited state intermolecular relaxation processes can be understood in terms of simple models of intermolecular interactions; the excited state electric properties enter those models as their empirical parameters. A similar approach is used to discuss the environmental effects on molecular excited states [4, 5]. The same mechanism also determines the initial steps of different reactive processes involving the electronic excited states.

It is known [4, 5] that the excited-state electric properties of molecules are usually quite different from those in their ground states. Hence, the interactions involving electronically excited molecules should be considerably different from those in the ground electronic state. Obviously, the conclusions which follow from simple models of long-range interactions [1] are to some extent limited by the possibility of the excitation and/or charge transfer processes which are likely to occur for electronically excited species. Nevertheless, the electric property data for molecular excited states should be as important as they are for molecules in the ground electronic state. The corresponding data may also reveal certain interesting aspects of the electronic structure of molecular excited states.

For non-degenerate molecular excited states the basic theory underlying the concept and calculations of electric properties remains virtually the same as that for the ground electronic state [1, 9]. However, the evaluation of the excited-state electric properties is usually more difficult than for the majority of molecules in the ground electronic state. The explicit open-shell structure of the excited-state wave function requires a departure from the single determinant reference assumption which is commonly used for the evaluation of molecular electric properties in the closed-shell ground state [9–11]. Additionally, the near-degeneracy effects are generally more important in excited states than in the ground electronic state and the single-configuration methods must be replaced by the appropriate multiconfiguration techniques.

The accuracy of the calculated ground state electric properties is known to be affected by two major factors: the basis set flexibility and the electron correlation effects [9]. The diffuseness of the electron density distribution in molecular excited states requires a careful consideration of the basis set selection. The selected basis set must be evidently more flexible (diffuse) than the majority of standardized sets employed in calculations of the ground-state electric properties. One can anticipate that the diffuseness of the electron density distribution in electronically excited states is the major factor which determines the system response to electric field perturbations. This feature of molecular excited states is also likely to diminish the importance of the dynamic electron correlation contribution to the excited-state electric properties.

The dynamic correlation effects are known [9–11] to be of vital importance for accurate predictions of the ground-state electric properties in closed-shell systems. In the case of molecular excited states the dominant part of the electron correlation contribution to the calculated properties is expected to follow from a relatively small number of closely lying configurations. Thus, a very limited expansion of the excited-state wave function might be sufficient to deal with the expected near-degeneracy effects. Those effects can be efficiently accounted for by a relatively simple multiconfiguration form of the excited-state wave function and as a consequence the multiconfiguration SCF methods become a suitable tool for accurate calculations of molecular properties in electronically excited states.

In the present paper we report on our calculations of the dipole and quadrupole moments and dipole polarizabilities in the lowest ($^1B_1$ and $^3B_1$) excited states of the water molecule. All calculations have been carried out by using the complete active space (CAS) SCF method [12] with several different choices of the active orbital subspace. To satisfy the requirements concerning the basis set flexibility in calculations of electric properties in those two excited (Rydberg) states of H_2O we have employed an extended set of Gaussian functions derived from the atomic natural orbital (ANO) basis set [13] of Widmark et al. [14]. The results of the present study are used to address the problem of long-range interactions involving electronically excited molecules.

2. Methods and computational details

2.1. Calculations of the excited-state wave functions

The open-shell character of the investigated excited electronic states of the water molecule and the closeness of other excited-state configurations of the same symmetry make the validity of the single-configuration (e.g. open-shell restricted Hartree–Fock) approximation rather doubtful. On the other hand, the use of the single-configuration spin-unrestricted schemes would bring about the uncertainty of the spin contamination effect on the calculated molecular properties. Both the near-degeneracy effects and the spin-symmetry requirements are conveniently accounted for in multiconfiguration SCF approaches. The CAS CSF method [12] appears to be particularly suitable in this respect.

Given the spin and space symmetry ($^{2S+1}\Gamma$) of the total many-electron wave function resulting from CAS SCF calculations, the number of inactive (i_k) and active (a_k) orbitals in each k-th representation of the molecular symmetry group, and the number of electrons ($\mathrm{N_a}$) in the active orbital subspace [12], the structure of the CAS SCF configuration interaction (CI) wave function is uniquely determined by the following symbol:

$$^{2S+1}\Gamma(\mathrm{N_a}) \quad (i_1 i_2 \ldots / a_1 a_2 \ldots).$$

In all calculations reported in this paper the $1a_1$ orbital of H_2O, which is virtually the $1s$ orbital of the oxygen atom, is considered to be inactive, i.e. $i_1 = 1$, $i_2 = i_3 = i_4 = 0$ for the assumed C_{2v} symmetry of the molecule. In order to study

Table 1. The number of configuration state functions in CAS SCF CI expansions for different electronic states of the water molecule. C_{2v} symmetry group

Number of active orbitals per symmetry				State symmetry		
a_1	b_1	b_2	a_2	$^1A_1$	$^1B_1$	$^3B_1$
4	2	2	0	492	432	592
5	2	2	0	1436	1308	1900
6	3	3	0	18153	17640	28344

the convergence of the calculated properties with respect to the size of the CI wave function, several different choices of the active orbital subspace have been investigated. Their specification and the resulting number of configuration state functions for eight electrons in the active subspace are given in Table 1 for both the ground electronic state ($^1A_1$) and the two excited states ($^1B_1$ and $^3B_1$). Since there are several accurate calculations of electric properties of the $^1A_1$ ground electronic state of H_2O [15–17], this state has been investigated in the present paper for comparative purposes. Our CAS SCF results for the $^1A_1$ state are used to support the discussion of the accuracy and convergence of the calculated excited state properties.

Upon extending the active orbital subspace the CAS SCF wave function and the resulting properties of the given state should approach the full CI limit for the given basis set. A comparison of calculations performed with different active orbital subspaces helps to estimate the accuracy of the CAS SCF data and gives some idea about the remaining electron correlation contribution to the computed properties. This strategy has been followed in the present study. First, a suitable form of the active orbital subspace has been guessed from a series of CAS SCF calculations performed with a relatively small basis set of Gaussian functions (see Sect. 2.3). It has been found that including the a_2 symmetry orbitals in the active subspace leads to a negligible effect on the calculated electric properties while several active orbitals are needed in the other three symmetries. The final CAS SCF calculations of electric properties have been carried out with a rather large active orbital subspace comprising $a_1 = 6$, $a_2 = 3$, $a_3 = 3$, and $a_4 = 0$ orbitals [hereafter referred to as the (6330) active subspace] and an extended basis set.

2.2. *Calculations of electric properties*

It is of great advantage that the CAS SCF method satisfies the Hellmann–Feynman theorem [18]. Hence, the first-order electric properties of any CAS SCF state are calculated directly as the expectation values of the corresponding operators [19, 20]. The evaluation of higher-order properties can be accomplished by using either an analytic approach [21, 22] or a numerical finite-field perturbation technique [23]. The latter method has been employed in the present study to obtain the dipole polarizability tensors as the numerical derivatives of induced dipole moments. The accuracy of the finite-field perturbation method in calculations of the excited state polarizabilities has been carefully examined, i.a. by a comparison of the first-order derivatives of induced dipole moments with the second-order derivatives of the electric-field-dependent CAS SCF energies. Some additional numerical details are given in Sect. 2.4.

The set of electric properties of the water molecule investigated in this paper comprises the dipole and quadrupole moments and the dipole polarizability tensors for different electronic states. These are the basic molecular electric properties which determine the major part of the long-range interaction energies. The calculation of higher multipole moments and polarizabilities, though of some interest, would require a further extension of basis sets and has not been attempted in this study.

2.3. Basis sets

The present investigations have profited from the recent progress in the standardization of high-quality basis sets for molecular calculations at the correlated level [13, 14]. The ANO basis sets of Widmark et al. [14] have been carefully examined by these authors with respect to both the electron correlation energies and dipole polarizabilities of atoms. Their use in accurate calculations of molecular ground-state properties is highly recommended. However, to properly account for the electric properties of excited states the standardized ANO basis sets may require a further extension.

Most of our exploratory calculations for electric properties of different electronic states of the water molecule have been carried out with original ANO basis sets of Widmark et al. [14]. The corresponding molecular basis set has been obtained from the [14.9.4.3/6.5.3.2] oxygen basis set and the [8.4.3/4.3.2] hydrogen basis set [14] and is hereafter referred to as the ANO set.

The two excited states of the water molecule investigated in this paper arise primarily due to the oxygen Rydberg transition $1b_1(2p_y) \rightarrow 4a_1(3s)$. The ANO basis sets of Widmark et al. [14] have been devised for high-level correlated calculations on molecular electronic ground and valence-excited states. Hence, they may not be diffuse enough to account for the appropriate representation of the $3s$ Rydberg orbital and its polarization in the external electric field. For these reasons our final CAS SCF calculations of molecular properties have been carried out with an extended ANO basis set for the oxygen atom. The extended basis set, hereafter referred to as the R-ANO set, has been derived from the initial ANO set by adding three diffuse s-type GTOs (exponents: 0.023479, 0.008218, 0.002876), two diffuse p-type GTOs (exponents: 0.015789, 0.005526), and one diffuse d-type GTO (exponent 0.056273). This extension results in the R-ANO basis set of the form [17.11.5.3/9.7.4.2].

In all calculations reported in this paper the s components of d functions and the p components of f functions have been deleted. This leads to molecular basis sets comprising either 96 (ANO) or 110 (R-ANO) basis functions. Both basis sets seem to be quite suitable for the total energy calculations, while the extended R-ANO basis set is certainly more appropriate for the accurate determination of molecular properties in Rydberg excited states.

2.4. Details of numerical calculations

The coordinate system used in present calculations assumes that the water molecule lies in the xz plane with the z axis being the symmetry axis and the

Table 2. Molecular geometry data for excited electronic states of the water molecule

State	Basis set	Active space	R_{OH} (in a.u.)	∢HOH (degrees)
$^1B_1$	ANO	(4220)[a]	2.004	100.95
	ANO	(5220)[a]	2.002	102.7
	ANO	(6330)[b]	2.002	102.7
	R-ANO	(6330)[a]	2.0036	103.0
$^3B_1$	ANO	(4220)[a]	2.045	102.16
	ANO	(5220)[a]	2.043	103.6
	ANO	(6330)[b]	2.043	103.6
	R-ANO	(6330)[a]	2.047	104.1
Reference data				
$^1B_1$	[24][c]		2.00	107.5
	[25][d]		2.006	116.2
	[26][e]		2.04	105.
	[27][f]		2.04	99.2
$^3B_1$	[25][d]		2.092	120.5
	[27][f]		2.36	113.4

[a] Optimized geometry

[b] Assumed geometry

[c] Multireference CI calculations with an (*spd*) basis set for oxygen and (*sp*) basis set for hydrogen

[d] Small basis set SCF calculations

[e] CEPA calculations with an (*spd*) basis set for oxygen and (*sp*) basis set for hydrogen

[f] CI calculations with an (*spd*) basis set for oxygen and (*sp*) basis set for hydrogen

hydrogen atoms pointing to its negative direction. The $^1A_1$ ground state CAS SCF calculations have been carried out at the experimental molecular geometry ($R_{OH} = 1.81117$ a.u., ∢HOH = 104.44°) while the optimized CAS SCF equilibrium geometries have been used for excited states. A survey of the excited-state geometry data is given in Table 2. The present geometry data for the $^1B_1$ and $^3B_1$ excited states of H_2O calculated with the R-ANO basis set and the (6330) active orbital subspace seem to be clearly superior to the results of earlier calculations [24–27]. The evaluation of the excited-state electric properties has been carried out at the nuclear geometries as given in Table 2. For all choices of the active orbital subspace studied in the present paper, the resulting equilibrium geometries of H_2O are very close to each other and the small differences between them are rather insignificant for the calculated property data.

All numerical calculations reported in this paper have been performed by using the newly developed MOLCAS package of quantum chemistry programs [28]. Because of the numerical evaluation of polarizabilities a rather tight convergence threshold was used in all CAS SCF calculations, leading to the CAS SCF energies converged to at least 10^{-8} a.u. This corresponds to the density matrix threshold of about 2×10^{-5}. The external electric field strength used in calculations of induced dipole moments and polarizabilities was chosen depending on the size of the resulting quantity. Its values in our calculations for the $^1A_1$ ground state were equal to 0.005 a.u., while for the excited states the field strengths between 0.0005 a.u. and 0.001 a.u. were used. Cross-examination of the polarizability data from the dipole moment and energy derivatives was used to limit the number of decimals saved in the final results to those which were mutually consistent.

3. Results and discussion

3.1. *The convergence study*

The accuracy of molecular electric properties resulting from CAS SCF calculations depends considerably on the choice of the active orbital subspace. If the CAS SCF level of approximation is meant to give reliable results and is not to be followed by some multireference CI calculations, the determination of a suitable active orbital subspace becomes one of the main issues [9, 20]. For this reason we have performed a series of calculations of multipole moments and polarizabilities with the ANO basis set and several different choices of the active orbital subspace. Some of the representative results of those exploratory calculations are shown in Table 3.

It has already been mentioned that including the a_2 symmetry orbitals does not lead to any significant change of the electric properties in any of the three electronic states considered in Table 3. Hence, the major effort was put into establishing the largest and computationally acceptable active orbital subspace involving only a_1, b_1, and b_2 orbitals. According to the data presented in Table 3 the (6330) active space can be expected to give reliable values for the electric properties under consideration while the length of the corresponding CI expansions (Table 1) is still manageable. The ground-state property values obtained

Table 3. Convergence of CAS SCF calculations for selected electric properties of H_sO in different electronic states. Results of calculations with the ANO basis set. All values in a.u.

State	Active orbital subspace			Reference results [16]
	(4220)	(5220)	(6330)	
Dipole moment (μ_z)[a]				
$^1A_1$	−0.7506	−0.7373	−0.7218	−0.7170
$^1B_1$	0.7323	0.7124	0.6993	—
$^3B_1$	0.4818	0.4783	0.4612	—
Quadrupole moment, *yy*-component (θ_{yy})[b]				
$^1A_1$	−1.853	−1.848	−1.848	−1.8278
$^1B_1$	1.814	1.846	1.851	—
$^3B_1$	1.432	1.478	1.480	—
Dipole polarizability, *xx*-component (α_{xx})				
$^1A_1$	9.75	9.93	10.02	10.09
$^1B_1$	275.1	276.6	276.8	—
$^3B_1$	200.1	204.1	204.2	—

[a] The positive value of the dipole moment corresponds to its $O^- \rightarrow (H_2)^+$ orientation

[b] Calculated with respect to the nuclear center of mass for molecular geometries of Table 2

with the ANO basis set and the (6330) active space compare well with the results of other calculations. With respect to the accuracy of the excited state properties the conclusions are obviously not that certain. However, the possible effect of a further extension of the active subspace in CAS SCF calculations for excited states should not considerably affect the calculated property values. The major electric properties of the lowest excited states of H_2O investigated in this paper are predominantly determined by the flexibility of the open-shell orbitals on the oxygen atom. Thus, increasing the basis set flexibility appears to be more important than going beyond the (6330) active orbital subspace. In our final calculations we have used the (6330) active subspace while extending considerably the initial ANO basis set. This extension has a rather negligible effect on the electric properties of the $^1A_1$ ground electronic state of H_2O.

3.2. Electric properties of H_2O in the lowest $^1B_1$ and $^3B_1$ excited states

The results presented in this section and summarized in Table 4 correspond to CAS SCF calculations with the (6330) active orbital subspace and the extended R-ANO basis set of Sect. 2.3. All of the excited state data have been obtained at the optimized CAS SCF molecular geometries as shown in Table 2. The ground state results included also in Table 4 correspond to the experimental equilibrium geometry of H_2O. In addition to the results for the dipole and quadrupole moments and the dipole polarizability tensor we have also presented the calculated values of second moments of the electron density distribution with respect to the nuclear center of mass.

Table 4. Electric properties of H_2O in the lowest $^1B_1$ and $^3B_1$ excited states as compared to their values in the $^1A_1$ ground state. CAS SCF calculations with the (6330) active orbital subspace and the R-ANO basis set. All values in a.u.

Property	$^1B_1$	$^3B_1$	$^1A_1$
Dipole moment[a]			
μ_z	0.640	0.416	−0.725
Quadrupole moment[b]			
θ_{xx}	0.306	0.138	1.937
θ_{yy}	1.850	1.473	−1.853
θ_{zz}	−2.156	−1.611	−0.084
Dipole polarizability			
α_{xx}	253.5	188.8	10.03
α_{yy}	83.4	64.3	9.41
α_{zz}	91.7	62.4	9.64
Second moments[b]			
$\langle xx \rangle$	14.443	13.662	7.357
$\langle yy \rangle$	8.500	7.561	5.786
$\langle zz \rangle$	13.776	12.275	6.672

[a] See Footnote a to Table 3

[b] See Footnote b to Table 3. The $^1A_1$ state results correspond to the experimental equilibrium geometry

One of the characteristic features of the two excited states of the water molecule is the change of the orientation of the dipole moment with respect to its direction in the ground electronic state. However, this result is not fully accounted for by the Mulliken population analysis data. For both the $^1A_1$ and the two excited states the Mulliken population analysis predicts the negative net charge to be at the oxygen atom ($^1A_1$: -0.83, $^1B_1$: -0.25, $^3B_1$: -0.77). The change of the dipole moment upon the electronic excitation of H_2O follows predominantly from the changes of the oxygen lone pair $1b_1(2p_y)$ contribution. The hybrid orbital $(3s + \lambda p_z)$ which becomes strongly occupied in both excited states gives a large negative contribution to the dipole moment. A similar effect can also be seen from the increase of the zz-component of second moments.

The changes in the molecular quadrupole moment which occur under the electronic excitation of H_2O follow the corresponding changes in the second moments of the electron density distribution. The zz-component, which is close to zero (see Table 4) in the $^1A_1$ ground electronic state, becomes the largest one in the two excited states. The excited-state quadrupole moment ellipsoids extend in the y and z directions.

A comparison of the data of Tables 3 and 4 shows that the basis set extension is of considerable importance for the excited-state dipole moment and polarizability. The quadrupole moment components are much less affected by this extension, indicating a uniform modification of all three components of the second moment tensor.

Both the dipole moment and quadrupole moment data indicate that the long-range interactions between the water molecule in either of the two of its excited states and some polar species will be considerably different from those for the ground state of H_2O. Though the relative interaction energies at the chosen distance may remain similar, the geometries maximizing the interaction energy will be different. A similar conclusion follows from the excited-state polarizability data. The polarizability tensor of the $^1A_1$ state of H_2O is almost spherically symmetric ($\alpha_{xx} = 10.09$ a.u., $\alpha_{yy} = 9.57$ a.u., $\alpha_{zz} = 9.81$ a.u. [16], see also Table 4) while its xx-component becomes dominant in both $^1B_1$ and $^3B_1$ excited states.

The large values of the dipole polarizability in the two excited states of H_2O follow principally from the contribution of the diffuse and easily polarizable Rydberg orbital. Its diffuseness appears to be more pronounced in the $^1B_1$ state. For both excited states the polarizability data predict much stronger long-range induction interactions than for the ground electronic state. Moreover, those interactions will have a considerable orientational dependence which is almost absent in the ground state.

The large polarizability of molecules in excited electronic states is usually considered to be one of their characteristic features [4, 5]. It originates either from the diffuseness of the excited-state density distribution or from the presence of closely lying electronic states of proper symmetry, or from both these factors simultaneously. The first of them is responsible for the large values of the polarizability tensor in $^1B_1$ and $^3B_1$ excited states of H_2O. The second factor is likely to be dominant in the case of electronic excited states resulting mostly from valence excitations. While the increasing diffuseness of the density distribution will lead to the increase of polarizabilities, the presence of lower electronic states of the appropriate symmetry may eventually produce negative polarizabilities of molecular excited states. Though generally possible [4], this has not been so far predicted by accurate and reliable calculations at the *ab initio* level. In the present case the energy gap between the $^1B_1$ and $^1A_1$ states, which could in principle lead to a negative value of α_{yy} in the ${}^1B_1$ state, is much too large in comparison with excitation energies to higher ${}^1A_1$ states. A similar reasoning leads to the conclusion that both α_{xx} and α_{zz} of the first excited ${}^1B_1$ state and all components of the polarizability tensor in the lowest ${}^3B_1$ state must be positive.

3.3. Excitation energies

Although the calculation of the electronic excitation energies was not the main objective of the present study, some of the data obtained as a by-product of calculations of electric properties seem to be worth of presentation. The calculated vertical and adiabatic excitation energies are presented in Table 5 and compared with some selected data of other authors. A more comprehensive survey of related calculations and experimental transition energies can be found in [27, 29].

One of the major problems occurring in CAS SCF calculations of electronic excitation energies [8, 30] is the choice of small enough and still compatible active orbital subspaces for different electronic states. The (6330) active subspace which has been employed in our calculations for electric properties of excited states comprises both the strongly occupied and correlating orbitals appropriate for those states. If the same active orbital subspace is used for the ground electronic state, one of the previous strongly (singly) occupied orbitals becomes a correlating orbital and as a result the ground electronic state receives a better description than it should. For this reason the (5330) active orbital subspace might be more suitable for the ground-state energy calculations. The corresponding data generated with the (5330) active subspace for the ground electronic state and the (6330) subspace for the two excited states are given in Table 5.

Table 5. Electronic excitation energies (in eV) of the water molecule. A comparison of the CAS SCF results with other data

Active orbital subspace[a]				
Ground state	Excited states		${}^1A_1 \leftarrow {}^1B_1$	${}^1A_1 \leftarrow {}^3B_1$
(6330)	(6330)	Vertical[b]	7.76	7.38
		Adiabatic[c]	7.46	6.98
(5330)	(6330)	Vertical[b]	7.31	6.94
		Adiabatic[c]	7.02	6.54
Reference results				
Experimental		Vertical	7.49 [31]	7.20 [32]
			7.42 [33]	7.00 [34]
Calculated		Vertical	7.49 [29]	7.10 [29]
			7.50 [27]	7.10 [27]
		Adiabatic	7.14 [26]	
			7.03 [24]	

[a] All CAS SCF results correspond to the R-ANO basis set. See Sect. 2.3.

[b] Experimental ground state geometry of the water molecule used for each electronic state

[c] Experimental geometry for the ${}^1A_1$ ground state and the CAS SCF optimized geometry for excited states. See Table 2

The results obtained with different active orbital subspaces for the ground and excited states of H_2O appear to be closer to the experimental data than those which follow from the use of the same active subspace for all electronic states under consideration. In principle, however, the CAS SCF calculations of excitation energies should be followed by a multiconfiguration CI treatment of each excited state. This would restore the balance between the correlation contributions to different electronic states. However, as indicated by our convergence study of Sect. 3.1, a post-CAS SCF treatment of the electron correlation contribution to electric properties of molecular excited states is likely to be much less important than for accurate predictions of excitation energies.

4. Summary and conclusions

We have carried out a series of CAS SCF calculations of basic electric properties of the water molecule in its lowest singlet and triplet excited states. For the two excited states investigated in this paper the dipole moment has been found to be antiparallel to that of the ground electronic state. The form of the quadrupole moment tensor in $^1B_1$ and $^3B_1$ states also differs considerably from that in the $^1A_1$ ground state of H_2O. Numerically, the most significant changes occur for the dipole polarizability tensor whose components increase by about an order of magnitude as compared with their values in the ground electronic state. Moreover, the polarizability ellipsoid is found to considerably modify its shape upon the electronic excitation of the water molecule. According to the present study, the basic electric properties of the two excited states of the water molecule are very similar.

The dominant part of the electron correlation contribution, as indicated by our study of different active orbital subspaces, appears to be well accounted for at the level of the CAS SCF approximation with a relatively small active orbital subspace. The diffuseness of the basis set employed in calculations of electric properties in molecular excited states becomes the most important factor which determines the accuracy of the calculated data. This basis set effect is well illustrated by a comparison of our (6330) CAS SCF results for ANO (Table 3) and R-ANO (Table 4) basis sets.

The open-shell character of molecular excited states and the diffuseness of the charge density distribution in those states shift to some extent the relative importance of different computational aspects of accurate calculations of the excited state properties. In calculations for closed-shell ground electronic states of molecules both the basis set diffuseness and an extensive treatment of the electron correlation effects [9–11] seem to be almost equally important. In the case of molecular excited states the accuracy of the calculated electric property data is mostly determined by the basis set flexibility and a limited treatment of the electron correlation contribution.

The present study of electric properties in excited states of the water molecule has originated from our interest in intermolecular interactions involving electronically excited species. The present data shed some light upon the differences in intermolecular interactions which may arise from the electronic excitation of the water molecule in some medium. If a water molecule is surrounded by a dipolar medium, its electronic excitation to either $^1B_1$ or $^3B_1$ state must be followed by a reorientation effect which can be predicted on the basis of the dipole-dipole long-range interaction term [1]. In a non-polar medium the dispersion contribution to the interaction energy is expected to increase by at least an order of magnitude.

The long-range considerations of the interaction effects for molecules in their excited electronic states may have, however, even more limited range of validity than for the ground electronic state. The diffuseness of the charge density distribution in excited electronic states is expected to make the exchange-overlap [1] contributions non-negligible even at relatively large intermolecular distances. This aspect of intermoleculer forces appears to be completely neglected in the majority of models [4, 5] underlying the determination of the excited-state electric properties from different spectroscopic data. Moreover, the diffuseness of the charge density distribution in molecular excited states is likely to facilitate, through the exchange-overlap mechanism, the charge-transfer processes.

We have carried out some pilot investigations of the influence of the electronic excitation of the water molecule in the $H_2O\cdots Li^+$ system on the interaction energy surface. It turns out that the electronic state of the system which corresponds to (H_2O, $^1B_1$) interacting with $Li^+(^1S)$ is almost degenerate with the state corresponding to (H_2O^+, $^2B_1$) interacting with $Li(^2S)$. The crossing between the two potential energy surfaces for those complexes determines the rate of the charge transfer process which follows the electronic excitation of the water molecule. One may speculate about the implications of this near-degeneracy for the non-radiative relaxation processes in aqueous solutions of electrolytes and the radiation-induced charge transfer process.

The generalization of the results obtained in this study requires a comprehensive investigation of other molecules and other excited states. Some of the present data, e.g., the large polarizability values for the two lowest excited states of the water molecule, may to a certain extent originate from the Rydberg nature of the corresponding electronic transitions. For the valence excited states of small molecules, the diffuseness of the charge distribution is rather expected to resemble that in the ground state. Then, however, the vicinity of other electronic states of the appropriate symmetry might be the main factor which leads to a considerable increase of polarizabilities upon the electronic excitation. This factor may also bring about the negative values for the excited state polarizabilities [4]. Further investigations in the area of electric properties in molecular excited states and intermolecular interactions involving electronically excited molecules are in progress.

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