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CASSCF/CASPT2 Studies of the Lowest States of $H_5O_2^+$

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CASSCF and CASPT2 calculations have been performed on the ground and two lowest singlet and triplet excited states of the protonated dihydrate. Two subsystems can be identified in the excited states: an excited water molecule and a ground state oxonium ion. The electric properties have been computed (dipole moment and dipole polarizabilities). The dipole polarizabilities are very large in the excited states of the complex (up to 500 au for the largest component). This can be due to the presence of nearly degenerate higher excited states or to an easy proton/hydrogen transfer process. The excitation energies, around 8 eV for both states, show that the photodissociation of $H_5O_2^+$ is probably possible in the atmosphere. The stabilization energy of the excited states with respect to the isolated subsystems is about 5−6 kcal/mol, including the relaxation contribution.

1. Introduction

Proton transfer in water has been the subject of a considerable amount of theoretical and experimental investigations during these last decades.[1,2] As a matter of fact, this process plays an important role in a variety of chemical and biological reactions, such as acid−base neutralization, electrophilic addition, photosynthesis, and the catalytic activity of enzymes, etc. One prototype system commonly used to investigate proton transfer between oxygen atoms is the protonated dihydrate, $H_5O_2^+$, where the proton migrates between the two oxygen atoms.[3]

Theoretical studies on $H_5O_2^+$ are numerous. In general, they have been essentially concerned with the search for the most stable configuration of its ground state, with special attention given to tunneling processes. It comes out that the theoretically predicted structure of $H_5O_2^+$ is very sensitive to the level of theory employed: two structures, either of C_2 or C_s symmetry (see Figure 1), are very close in energy.[4] The C_s structure may be considered as a complex formed by the water molecule and the oxonium ion, whereas the C_2 structure corresponds to a central proton surrounded by two water molecules. At the Hartree−Fock level, the C_s structure is a minimum on the potential energy hypersurface and the C_2 symmetry stationary point is a transition state. At the correlated level, the C_2 structure turns out to be the global minimum and the C_s structure becomes a transition state. The size of the basis set employed also affects these potential energy hypersurfaces. One can therefore conclude that the two structures are close in energy and separated by relatively low barriers. This facilitates the low-energy proton transfer between the two H_2O moieties.

This $H_5O_2^+$ system, which results from the hydration reaction of $H_3O^+ + H_2O \rightarrow H_5O_2^+$, has been observed under various experimental conditions. Interestingly enough it has also been found in the earth's atmosphere. At the altitudes between about 40 and 80 km the protonated hydrates, $H_3O^+(H_2O)_n$, are the predominant positive ions in the earth's atmosphere, and there remain some difficulties to satisfactorily explain the high values of their observed concentration.[5,7] However, above 82 km, their concentration decreases very rapidly to zero. A number of attempts have been made to determine their photodissociation cross sections but without any success. This photodissociation is only supposed to occur for wavelengths lower than 180 nm.[8] Excited states of protonated hydrates are also likely to be of interest in femtosecond spectroscopy experiments.[9] More generally, proton transfer reactions are important in chemical and biological processes, which often involve enough energy to proceed in excited states, as exemplified in refs 10−12. In particular, ref 11 gives a review of experimental work published in the last decade, with several results obtained by using ultrafast techniques. They are concerned with a wide variety of systems. As underlined by Roszak, protonated hydrates can model many excited state processes.[13]

Our previous studies were devoted to the water molecule[14] and the oxonium ion.[15] The present work is focused on the lowest excited states of the following $H_5O_2^+$ complex, which is one of the smallest aggregates of the protonated hydrate series. We report here the first part of a more extensive study of intermolecular interactions in the lowest excited states of this complex. To our knowledge no other previous study has been devoted to the excited states of this system, except the semiempirical calculations on the photodissociation cross sections performed by Thomas et al.[8] for $H_3O^+(H_2O)_{n=1,2}$. We present here the structural, energetic, and electric properties of the two lowest excited states of the system calculated at different levels of theory. Ab initio calculations have been performed using the CASSCF/CASPT2 approach that has been successfully employed in our earlier study of electric properties of the water molecule[14] and oxonium ion.[15] Since the study of excited states in general requires large and extended basis sets (this is especially true in the case of diffuse Rydberg excited states), particular attention has been given to the choice and the determination of an adequate basis set for these calculations.

2. Methods and Computational Details

2.1. Methods. The importance of including both static and dynamic electron correlation in ab initio calculations is well-known,[16] especially when excited states are involved. Therefore,

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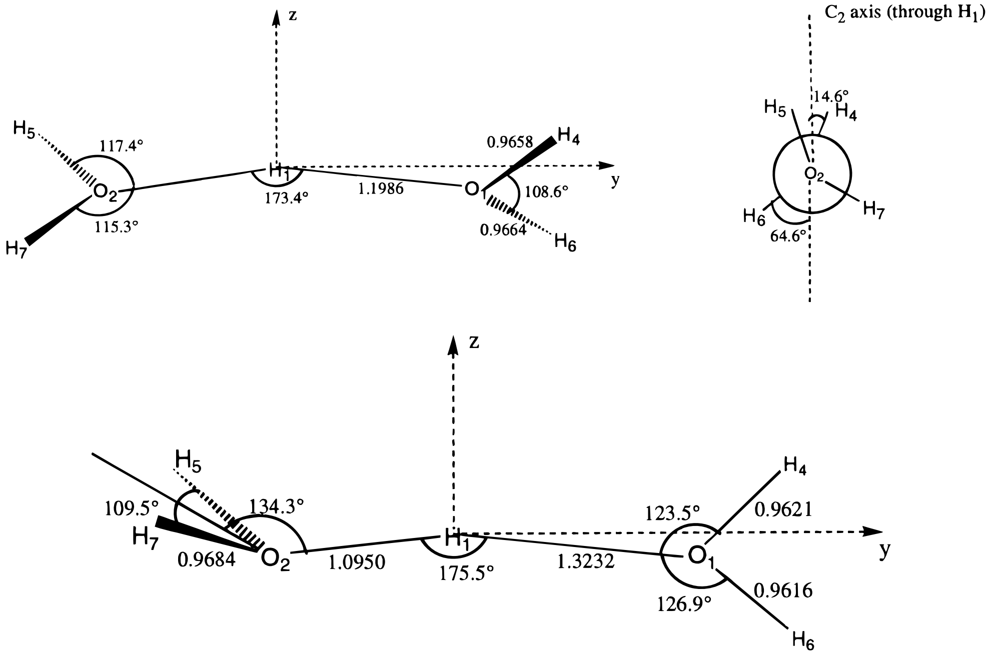

Figure 1. Geometric parameters of the minimum of the C_2 and C_s structures of the ground state of $H_5O_2^+$. Angles and bond distances (in Å) taken from ref 4.

all calculations have been performed using the CASSCF/CASPT2[17,19] approach. Our earlier studies of H_2O[14] and H_3O^+ [15] have shown that the CASSCF treatment of the electron correlation, even with large active spaces, is not able to provide quantitatively accurate results for the polarizability data of the excited states. The CASPT2 results have been found stable, even for CASSCF reference wave functions obtained with relatively small active spaces. In the case of water, it has been shown[14] that this method could be as efficient as the CCSD(T) approaches[20] and much less demanding in computer time and resources.

All calculations have been performed using the MOLCAS-3 package of quantum chemistry programs[21] and carried out on an IBM RS6000/590 workstation. The values of the electric properties reported in this paper have been calculated by using the finite perturbation scheme.[22,23] The energies calculated for different numerical values of the field strength F_μ ($\mu = x, y, z$) have been fitted to either quadratic or quartic polynomials in F_μ, depending on the magnitude of the polarizability values.

2.2. CASSCF/CASPT2 Calculations. The two core 1s(O) orbitals of $H_5O_2^+$ are inactive at the CASSCF level and frozen at the CASPT2 level. The notation (n_1,n_2) will refer to the symmetry partition of the active space. It corresponds to the distribution of the 16 valence electrons among n_1 and n_2 active orbitals belonging to the two irreducible representations of either C_2 or C_s symmetry groups.

In our earlier paper on electric properties of water,[14] a systematic study of the extension of active spaces showed that the CASPT2 method exhibits excellent performance even with medium size active space CASSCF reference functions; this feature has been confirmed in the study of the electric properties of the oxonium ion.[15] Therefore, for the excited states only one active space has been considered in this study. This active space is composed of 13 active orbitals and should lead to reliable results at the CASPT2 level of approximation. There are 16 active (valence) electrons in CASSCF calculations, and in the case of the two excited states, there are four orbitals that remain weakly occupied in the CASSCF wave function. Furthermore, these orbitals have a mixed character and can therefore be considered as used simultaneously by the two subsystems during the CASSCF optimization procedure. The active space of 13 active orbitals should therefore correspond to the spaces of respectively nine and eight active orbitals used in the calculations of the isolated excited water molecule[14] and the ground state oxonium ion,[15] respectively. According to our previous studies[14,15] and to the nature of the lowest excited states of the protonated dihydrate, active spaces of such size must be sufficient to obtain reliable values for the electric properties at the CASPT2 level. The partitioning of these 13 orbitals into the different irreducible representations of the C_s or C_2 symmetry groups will be discussed in the next sections.

2.3. Calculation of Electric Properties. For the ground state of $H_5O_2^+$, we have chosen values of ±0.005 au for the electric field strength, and the electric dipole moment and polarizabilities have been obtained by using a parabolic fit. For the excited states, the polarizabilities are 1 order of magnitude higher than those of the ground state; consequently, lower values of the external field strength have been used to avoid excessive contamination due to higher nonlinear terms. Our previous study of the water excited states[14] showed that the calculated electric properties exhibit some dependence on the magnitude of the field which disappears by fitting the energy data to quartic polynomials. Therefore, we have chosen values of ±0.001 and ±0.0025 au for the electric field strength, and the calculated electric properties of the two lowest excited states have been obtained by using a quartic fit.

The method used for the evaluation of electric properties needs a high accuracy of the CASSCF and CASPT2 energy calculations. Therefore, the CASSCF energies were converged through at least 10 decimals, and the CASSCF one-particle density matrix had a threshold of 5×10^{-7}, which should make the CASPT2 energy accurate to about eight decimals.

2.4. Basis Set. *2.4.1. Preliminary Basis Set Considerations.* It is well-known that the study of excited states requires in general large and extended basis sets like the ANO (atomic natural orbitals)[24] basis sets developed by Widmark et al.[25] and widely used in the study of excited states. For the description of Rydberg excited states or the calculation of molecular electric properties, additional polarization and diffuse functions are generally needed. As an example, three s, two p, and one d

TABLE 1: Dipole Moment, Electric Dipole Polarizabilities, and Vertical Excitation Energy of the $^1B_1$ Excited State of the Water Molecule in Basis S[a]

	$1B_1$			
	R-ANO		basis-S	
	CASSCF	CASPT2	CASSCF	CASPT2
α_{xx}	83.7	56.5	43.9	37.7
α_{yy}	90.6	68.8	59.2	53.3
α_{zz}	280	143	265	156
μ_y	0.6879	0.4601	0.5990	0.4545
ΔE	7.34	7.26	7.21	7.02

[a] C_{2v} symmetry and (5,2,2,0) active space. R(OH) = 2.0036 au, H−O−H = 103.0°,[14,26] orientation same as in Figure 2. All results in au, except for the excitation energy results in eV.

diffuse functions have been added to the original oxygen ANO basis set derived by Widmark et al.[25] in the study of the electric properties of the two lowest excited states of water.[26] Note that reliable results could be obtained with an extension of the ANO basis set limited to the oxygen atom. This basis set, which will be hereafter referred to as basis R-ANO, has been successfully used in our previous studies on the electric properties of the water molecule[14] and oxonium ion[15] lowest excited states.

In the case of the $H_5O_2^+$ system, this R-ANO basis set could not have been used, as it required too large computer resources (about 3.2 Gbytes of memory are needed for the storage of the integrals). Therefore, our purpose was to obtain a smaller basis set able to predict reliable values for the properties of this system in its ground and two lowest excited states.

In most cases, the diffuse and polarization functions added to standard Gaussian sets are chosen so as to obtain the best energies. However some molecular properties, in particular the electric polarizabilities, may depend critically on regions of the configurational space that are of relatively small importance for the total energy. Therefore, even at high correlated levels of theory, basis sets obtained in this way may not be well adapted for the calculation of such properties. To generate appropriate Gaussian sets of intermediate size, we have used as a starting point the so-called polarized GTO/CGTO sets[27] which are known for their good performance in calculations of molecular electric properties. This polarized GTO/CGTO set, based on the use of the basis set polarization approach,[28,29] will be hereafter referred to as basis S. It has been used successfully in our earlier study of the electric properties of the ground and two lowest excited states of the oxonium ion.[15] Its adequacy can be easily explained by the nature of the excited states of the oxonium ion which are the valence excited states; however in the case of H_2O, the two lowest excited states are of Rydberg character and this basis set may not be adequate. In order to check this point, we have therefore computed the electric dipole moment and polarizabilities of the two lowest excited states of the water molecule in basis S. The calculated values for the $^1B_1$ excited state are reported in Table 1; for comparison, the corresponding values obtained in the R-ANO basis set (considered as the most accurate ones for an equivalent active space) are also reported in this table.

At both levels of calculation, the excitation energies calculated with bases S and R-ANO are in good agreement. Although basis S is capable of predicting the high anisotropy of the polarizability tensor of the $^1B_1$ excited state, the values obtained for components are rather different from the R-ANO reference data. For the α_{zz} component, a rather good agreement between the two basis sets is observed, but this is no longer true for the two other components. At both levels of calculation, basis S results are largely underestimated, and they differ by 22−33% from the R-ANO reference values at the CASPT2 level. The same trend is observed for the $^3B_1$ state (not reported here).

The failure of basis S to describe correctly the polarizability components of the lowest excited states of water can be easily explained by the nature of these excited states, which are of Rydberg character. Since polarizability depends on the diffuseness of the electron cloud in the investigated excited states, it is obvious that basis S fails in the description of the outer regions and their polarization. The polarized sets[27] have been developed essentially for calculations of electric properties for electronic ground and most valence[30] excited states. Furthermore, it is well-known that the electric properties are playing an important role in the different models used for the description of intermolecular interactions. Since basis S is incapable, even at a highly correlated level, of providing accurate values for the electric polarizabilities of the water lowest excited states, this basis set will surely fail in the description of the intermolecular interactions in the excited states of the $H_5O_2^+$ system.

2.4.2. Extended Polarized Basis Set (Basis S+) for Excited Rydberg States. Our purpose is therefore to obtain, by adding diffuse and polarization functions to basis S, a basis set of moderate size capable of yielding accurate values for the electric properties of the two subsystems (i.e., H_2O and H_3O^+ lowest excited states and ground state). Since basis S already leads to accurate values for the electric properties of the oxonium ion, it is a good starting point, and we essentially focused our interest on improving the description of the lowest excited states of H_2O.

In the first step, we added the same number of s-, p-, and d-type diffuse functions to basis S as done in ref 26 in the earlier study to build the R-ANO basis set. To obtain the exponents of the diffuse functions, we simply kept constant the ratio between two consecutive diffuse function exponents of each type in basis S. Therefore we obtain an extended basis set by the addition of three diffuse s-type GTOs (exponents: 0.026 956, 0.008 071, 0.002 417), two diffuse p-type GTOs (exponents: 0.018 972, 0.005 637), and one diffuse d-type GTO (exponent: 0.0190) to the oxygen basis set.

The resulting basis set was then used for the investigation of the electric properties of the two lowest excited states of water. Since this extension has led to excellent agreement with the earlier R-ANO results, we attempted some reduction of the extended set. We found that adding only the three s-type and the first p-type diffuse GTOs to basis S was leading to essentially the same results. This is the smallest basis that we have obtained, capable of predicting reliable values for the electric properties of water lowest excited states. It will be hereafter referred to as basis S+, with, namely, [13,7,4/8,4,2] for oxygen and [6,4/3,2] for hydrogen atoms. Therefore, the total basis set for the $H_5O_2^+$ system is composed of 105 basis functions, which is much smaller than if it were built with the R-ANO set (243 basis functions). The results obtained with this basis set are reported in Table 2 and are, at the CASPT2 level, in agreement with the reference results of our earlier study.

3. Results and Discussion

3.1. Ground State of $H_5O_2^+$. *3.1.1. Geometry.* The fully optimized structures obtained by Xie et al.[4] have been used for the ground state of the hydrated oxonium ion $H_5O_2^+$. In their study, the authors examined the potential energy surfaces of the C_s and C_2 structures of the $H_5O_2^+$ system using various basis sets and different levels of theory. It appears that the potential hypersurface of the $H_5O_2^+$ system is very flat and the energy difference between the two structures is very small. Xie et al. predict that the most reliable global minimum of $H_5O_2^+$ is of C_2 symmetry and the C_s structure is energetically higher by only 0.38 kcal/mol.

TABLE 2: Dipole Moment, Electric Dipole Polarizabilities, and Excitation Energies for the Two Lowest Excited States of the Water Molecule in Basis S+[a]

	$^1B_1$				$^3B_1$			
	R-ANO		basis S+		R-ANO		basis S+	
	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2
α_{xx}	83.7	56.5	77.3	56.1	64.0	46.7	59.9	46.8
α_{yy}	90.6	68.8	82.0	67.8	60.6	48.3	56.8	48.7
α_{zz}	280	143	271	158	206	112	199	121
μ_y	0.6879	0.4601	0.6749	0.4683	0.4550	0.3053	0.4371	0.3139
ΔE_v[b]	7.58	7.22	7.55	7.18	7.15	6.98	7.17	6.92
ΔE_a[c]	7.34	7.26	7.28	7.12	6.85	6.74	6.78	6.59

[a] All results in au, except for the excitation energy results in eV. The active space is the same as in Table 1. $^1B_1$: R(OH) = 2.0036 au, H−O−H = 103.0°.[14,26] $^3B_1$: R(OH) = 2.047 au, H−O−H = 104.1°.[14,26] [b] Vertical excitation energy. [c] Adiabatic excitation energy.

TABLE 3: Dipole Moment and Electric Dipole Polarizabilities of the Ground State of the $H_5O_2^+$ System in Basis S+[a]

		α_{xx}		α_{yy}		α_{zz}		μ_y		μ_z	
symmetry	active space	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2
C_2	(6,5)	18.2	19.2	12.9	13.2	13.4	13.7			−0.5762[b]	−0.5658[b]
C_2	(6,6)	20.2	21.2	13.1	13.6	13.5	14.2			−0.5633[b]	−0.5404[b]
C_2	(7,6)	20.2	21.5	13.2	13.8	13.7	14.2			−0.5590[b]	−0.5575[b]
C_s	(8,4)	13.2	15.8	18.2	19.3	13.4	14.2	−0.4868[b]	−0.4414[b]	−0.5124[b]	−0.5234[b]
								1.8522[c]	1.8976[c]	−0.5811[c]	−0.5921[c]

[a] All results in au. [b] The dipole moment is calculated at the center of nuclear charges. [c] The dipole moment is calculated at the O_2 atom (Figure 1).

Therefore we have used, for the calculation of the electric properties of the ground state of the $H_5O_2^+$ system, the C_2 and C_s structures they have obtained at the CCSD(T) level by using the triple-ζ plus double polarization basis set of Dunning; the optimized C_2 and C_s structure parameters obtained by Xie et al.[4] are given in Figure 1. It has been checked that these structures are very close to those obtained by an optimization with basis S+ at the CASSCF level.

3.1.2. Electric Properties. For the calculation of the dipole moment and electric polarizabilities of the ground state of the $H_5O_2^+$ system (see Figure 1 for the definition of the axes), we have used three active spaces of different sizes, up to the limit of our computational resources. They are composed of either 11, 12, or 13 active orbitals. These orbitals have been partitioned into the two irreducible representations of the C_2 symmetry group, namely, A and B, leading to the following active spaces: (6,5), (6,6), and (7,6). The calculated properties are reported in Table 3.

For all three active spaces, the CASPT2 dipole moments of the ^1A ground state are quite close to each other and the ground state dipole moment as calculated by the CASSCF method with increasingly large active spaces slowly approaches the results obtained in CASPT2 calculations. Similar pattern of the active space dependence is observed for the dipole polarizability. For each of the three components of the tensor, the calculated CASSCF and CASPT2 values are quite close to each other and the CASSCF values approach slowly the CASPT2 results. The present data for the dipole moment and electric polarizabilities of the ground state of $H_5O_2^+$ show that the dynamic correlation corrections to the CASSCF results are not of primary importance.

For the dipole moment, our best value of −0.5575 au, obtained at the CASPT2 level for the largest active space CASSCF reference function, compares well with the value of −0.550 au obtained some years ago by Karlström.[31] To our knowledge, neither experimental nor theoretical data seem to be available for a comparison concerning the $H_5O_2^+$ electric polarizability results. However: (i) the calculated values of the polarizability tensor are stabilized at the CASPT2 level. (ii) In their theoretical study of the electric polarizabilities of some oxonium hydrates, $H_3O^+(H_2O)_{n=2-6}$, Waite and Papadopoulos[32] show that the polarizability of these clusters increases with the size of the system and that the polarizability tensor is always anisotropic. Our average value of 16.5 au for the polarizability of $H_5O_2^+$ is larger than that of the water molecule (9.5 au) or the oxonium ion (6.5 au). The polarizability tensor is anisotropic, the α_{xx} component (21.5 au) being larger than the other two components, which are equivalent ($\alpha_{yy} \approx \alpha_{zz} \approx 14$ au).

We have also determined the polarizabilities of the C_s structure of the $H_5O_2^+$ system; these values have been computed for an active space composed of 12 orbitals partitioned in the two A′ and A″ irreducible representations of the C_s symmetry group, respectively, leading to a (8,4) active space. The calculated values are reported in Table 3; like in the C_2 structure, the polarizability tensor is anisotropic, but in this case the dominant component is along the central $O_2H_1O_1$ pseudoaxis. Let us note that the calculated values are in agreement with an estimation from semiempirical expressions proposed by Thole for interacting isotropic systems,[33] which gives $\alpha_{\|} = 19.3$ au and $\alpha_{\perp}=14.8$ au. The average polarizability of this C_s structure is 16.4 au, very close to the value obtained for the C_2 structure (16.5 au). These two structures are also very close in energy (0.42 kcal/mol).

It is noteworthy that both structures have a similar μ_z component, but, of course, the C_s structure has a nonzero μ_y component (Table 3). In order to compare with the dipole moments of the isolated species, we give the values calculated with the operator origin chosen at the O_2 atom (Figure 1). The μ_z component (−0.59 au) is very close to that of the isolated oxonium ion given in ref 15, corrected for the origin and neglecting the small changes involved in the geometry and the orientation of H_3O^+ in the complex. The μ_y component (1.90 au) is larger than the μ_y component of isolated water (0.73 au[14]). The long range model has been used to estimate the induced dipole moment of the water molecule in the complex, $\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\alpha}\mathbf{E}$. The electric field $\mathbf{E}$ due to H_3O^+ has been replaced by that due to a positive point charge at the location of the respective oxygen atom, and the water molecule has been located at the calculated minimum energy distance (see Figure 1). Using the water polarizability computed in ref 14, namely,

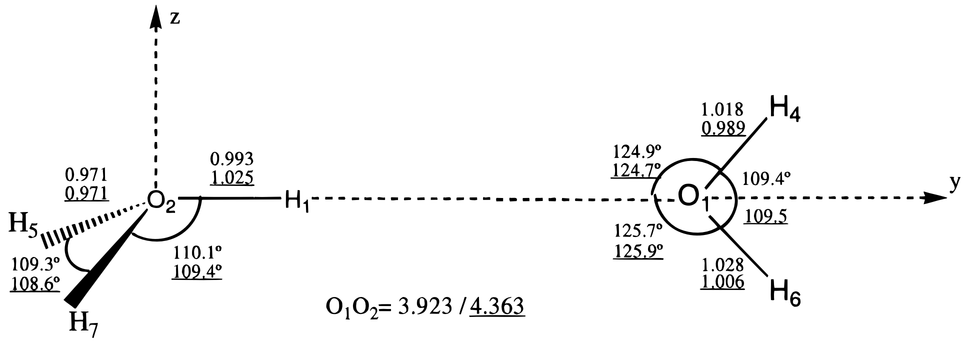

Figure 2. Geometric parameters of the minimum C_s structures of the two lowest excited states of the $H_5O_2^+$ system. The parameters that are not underlined correspond to the $^3A''$, the underlined ones to the corresponding singlet excited state. Bond distances in Å. Note that the water subsystem is not in the same coordinate system as in refs 14 and 26.

TABLE 4: Excitation Energies, Dipole Moments, and Electric Dipole Polarizabilities of the $^1A''$ and $^3A''$ Excited States of $H_5O_2^+$ in Basis S+[a]

state	method	ΔE	μ_y	μ_z	α_{xx}	α_{yy}	α_{zz}
$^1A''$	CASSCF	8.47	2.036[b]	−0.2768[b]	92	366	108
	CASPT2	8.07	2.012[b]	−0.2690[b]	128	520	98
			6.414[c]	−0.3384[c]			
$^3A''$	CASSCF	8.30	1.675[b]	−0.4157[b]	88	331	121
	CASPT2	7.75	1.567[b]	−0.3958[b]	108	443	96
			5.633[c]	−0.4822[c]			

[a] All results in au, except ΔE in eV. [b] The dipole moment is calculated at the center of nuclear charges. [c] The dipole moment is calculated at the O_2 atom (Figure 2).

α_{yy} = 9.55 au, such an approximation leads to the value of 0.46 au for the $\mu_{\text{ind},y}$ component. This gives the total y component of 1.19 au. With the reservation for all approximations involved in the lowest order induction model, this result reasonably well approximates the value of 1.90 au given in Table 3. The dipole moment components of the C_s structure of the ground state of $H_5O_2^+$ are thus rather well reproduced by the sum of the permanent moments of the two isolated species and the induced moments in the complex.

3.2. Excited States of $H_5O_2^+$. *3.2.1. Geometries and Nature of the Excited States.* The geometries of the lowest singlet and triplet excited states of the $H_5O_2^+$ system have been optimized at the CASSCF gradient level with basis S+. These calculations have been performed starting from the C_2 geometry of the ground state (Figure 1), without any symmetry constraint. For both excited states, the calculations lead to a similar structure of C_s symmetry with two species, an oxonium ion and a water molecule, well separated (Figure 2). Both excited states considered in this study result from a one-electron excitation from the 2a″ to the 9a′ orbital. These two orbitals correspond respectively to an oxygen atom lone pair and a 3s orbital of the same oxygen atom. This oxygen atom (O_1 on Figure 2) belongs to the water molecule, and both excited states correspond therefore to a system composed of an oxonium ion in its ground state and a water molecule in an excited state. These two excited states will now be referred to as $^1A''$ and $^3A''$, respectively. This corresponds to their labeling in the C_s symmetry group. The geometrical parameters of both excited states are reported in Figure 2. For both structures, the terminal OH bond lengths and HOH angle values of the H_3O^+ subsystem are in the same range as those in the oxonium ion ground state (0.978 Å and 111.59° with the R-ANO basis set in ref 15), but due to the presence of the neighboring water molecule, the central O_2H_1 bond is somewhat longer. In the water molecule subsystem, the OH bond lengths are longer than in the ground state of isolated water (0.958 Å) and shorter than the values obtained in $^1B_1$ (1.06 Å) and $^3B_1$ (1.08 Å) of isolated water. These bond distances are shorter in the singlet excited state than in the triplet excited state. For both excited states, the central O_2, H_1, and O_1 atoms are on the same alignment; in the triplet excited state, the intermolecular distance, H_1O_2, is about 2.9 Å, whereas this distance is larger by about 0.4 Å in the corresponding singlet excited state. These intermolecular distances in the excited states are considerably longer than in the ground state (1.3 Å[4]). It can be interpreted as arising from increased valence repulsion, due to the large size of the 3s Rydberg orbital.

According to the configuration composition of their wave function, the two excited states considered here are of the same nature as the two lowest excited states of the water molecule, namely, $^3B_1$ and $^1B_1$. This result is not very surprising since it is easier to excite a water molecule (excitation energies of 6.7 and 7.1 eV for the $^3B_1$ and $^1B_1$, respectively[14]) than an oxonium ion (9.04 and 9.63 eV for the $^3A_2''$ and $^1A_2''$ states, respectively[15]). However the geometry parameters show that the water molecule in excited states of $H_5O_2^+$ may significantly differ from the isolated water molecule excited states. It is thus worthwhile to look more carefully at the information which can be obtained from the excitation energies of $H_5O_2^+$.

3.2.2. Excitation Energies. The excitation energies computed for the two lowest excited states of the $H_5O_2^+$ system are reported in Table 4. In an isolated water molecule, the $^3B_1$ excited state is more stable than the corresponding singlet excited state by about 0.4 eV (see Table 2). In the $H_5O_2^+$ system, the $^3A''$ is also more stable than the $^1A''$ excited state, by about 0.33 eV. The excitation energies are higher than in the case of an isolated water molecule by about 1 eV for each excited state. The increase in excitation energies (see section 3.2.1) is accompanied by less pronounced changes in the H_2O moiety as compared to those of the isolated molecule.

The photodissociation of a molecule is a process which takes place in two steps: first, there is absorption of a photon, which results in an electronic excitation of the molecule. Once the molecule is excited, many processes may occur, including the dissociation of the molecule into two fragments, one in its ground state and the other in an excited state. In general, the spin multiplicity of a molecule in its ground state corresponds to a singlet, and the excited state involved in the process must thereby also be a singlet for spin-allowed dissociation channels.

Therefore, the excitation energy obtained here for the $^1A''$ excited state (8.07 eV) allows to predict that the photodissociation of the $H_5O_2^+$ system should take place for a wavelength of 153.6 nm, leading to an oxonium ion in its ground state and an excited water molecule. Some time ago, Thomas et al.[8] suggested that, above 82 km of altitude in the earth's atmosphere, the photodissociation of the $H_3O^+(H_2O)_n$ aggregates by sunlight could occur for wavelengths in the order of 175−193 nm (Schumann Runge absorption band) or 121.6 nm (Lyman α-line), which does not agree well with our calculated value of 153.6 nm. However, the spectral domain for wavelengths around 120 nm is very complex and cannot be restricted to these two absorption bands.[34] As an example, the region above 140 nm is dominated by an intense continuum, on which superpose the Fraunhofer absorption rays. This domain is very close to our predicted value of 153.6 nm for the photodissociation of $H_5O_2^+$.

3.2.3. Dipole Moment and Electric Properties. For the determination of the dipole moment and electric polarizabilities of the $^1A''$ and $^3A''$ excited states of $H_5O_2^+$, we have chosen to perform the calculations in only one active space, namely, (9,4), which should be large enough to provide reliable values for the calculated properties (see section 2.2). Moreover, with the lowering of symmetry in the presence of the external electric field along the x axis, the use of a larger active space would lead to a prohibitively large size of the three-particle density matrices which need to be generated in the CASPT2 scheme. Therefore, the values reported in Table 4 for the electric properties of the two lowest excited states of the $H_5O_2^+$ system are the best values we can attain with present computational resources.

The dipole moments of the two excited states of the $H_5O_2^+$ system have two distinct components: μ_y and μ_z. For both excited states, the dipole moments are dominated by the component along the y axis and the $^3A''$ excited state, like in the case of the isolated water molecule, is less polar than the corresponding singlet excited state. In the case of the isolated water molecule, the dipole moments in $^1B_1$ and $^3B_1$ excited states were found to have the opposite direction to the dipole moment in the ground state. This feature can also be observed here when the dipole moment is calculated at the center of nuclear charges: in the C_s structure of the ground state, the axial component of the dipole moment is negative, whereas in the two excited states, this component becomes positive. As for the ground state, the dipole moment is recalculated for the origin at the O_2 atom (Figure 2) and compared to the permanent moments of the isolated species and the induced moments in the complex. Again, the μ_z component essentially originates from the oxonium ion, slightly modified by the changes in the geometry and the orientation of H_3O^+. The μ_y component is respectively −0.46 and −0.30 au for the singlet and triplet excited states of isolated water.[14] The long range model gives an induced dipole μ_y component of 1.011 and 0.897 au, respectively, for the singlet and triplet excited states of the water molecule in the complex (Figure 2). This leads to a total y component of 0.55 and 0.60 au, respectively. These values are drastically different from those reported in Table 4 (6.41 and 5.63 au, respectively) and clearly show that the low-order multipole expansion approximation cannot be used to estimate the induced dipole moment in the case of the excited states. Though the distance between H_3O^+ and H_2O is much larger in the excited states than in the ground state, the excited states of H_2O bring a very sizable and diffuse charge distribution. This may cause that neither the multipole expansion nor the linear induction approximation are valid for $H_5O_2^+$. However, the disagreement with the values of Table 4 can also be due to an important reorganization of the charges in the complex. At the present stage of our work, it is difficult to propose a reliable interpretation of these results.

TABLE 5: The Three Lowest Singlet and Triplet A″ Excited States of the $H_5O_2^+$ System

state	CASSCF energy (au)	relative energies (eV)
1 $^1A''$	−152.186 622	0.0
2 $^1A''$	−152.146 302	1.10
3 $^1A''$	−151.795 153	10.7
1 $^3A''$	−152.196 200	0.0
2 $^3A''$	−152.144 117	1.42
3 $^3A''$	−151.761 861	11.8

For the isolated water molecule, in either the $^1B_1$ or $^3B_1$ excited state, the polarizability tensor is found to be highly anisotropic. The average value of the polarizability is about 95 and 75 au for the singlet and triplet excited states, respectively.[14] For the oxonium ion in its ground state, this value is 6.5 au,[15] which is considerably smaller than the high values obtained for the average polarizability of the two lowest excited states of isolated water. As seen above from the geometry, the wave function, and the excitation energies of the two excited states of $H_5O_2^+$, two subsystems can be identified, i.e., the oxonium ion in its ground state and the excited water molecule, somewhat modified with respect to the isolated systems. It is thus interesting to compare the values obtained here for the polarizability tensor components of these two excited states with the polarizabilities of the $^1B_1$ and $^3B_1$ excited states of an isolated water molecule.

For both excited states of the $H_5O_2^+$ system, the polarizability tensor is highly anisotropic, the α_{yy} component being 4−5 times larger than the other two components which are rather equivalent (Table 4). Except for this feature, no similarity can be found with the polarizabilities of the corresponding excited states of an isolated water molecule. Furthermore, the largest component determined here does not correspond to the largest component of the polarizability tensor of an isolated water molecule, in either the $^1B_1$ or $^3B_1$ excited state.

According to these considerations, and taking into account the very high value obtained for the α_{yy} component of the polarizability tensor of both excited states, we can reasonably propose the following conclusions: the polarizabilities calculated here either contain a contribution from higher excited states of the same symmetry which would be very close in energy or would indicate the possibility of a proton transfer process between the oxonium ion and the water molecule. In order to verify these two hypotheses, further calculations have been performed as follows:

(a) For both singlet and triplet excited states, an average CASSCF calculation over the first three roots, with equal weights, has been performed; the energies obtained in these calculations are reported in Table 5. For both singlet and triplet A″ excited states, the second root is very close to the first one in energy: 1.1 and 1.4 eV, respectively; therefore, for both excited states, the first two roots are nearly degenerate.

(b) To evaluate the barrier for proton transfer, the following calculation for the $^3A''$ excited state has been performed. The hydrogen atom lying between the two oxygen atoms has been kept at equal distances from these two atoms. The geometry of the resulting structure has been optimized at the CASSCF-gradient level, with the only constraint that the two central OH distances are equal and constant, the other parameters being allowed to relax. This calculation leads to a nearly C_2 symmetric structure (Figure 3) being by about 0.28 kcal/mol less stable than the C_s equilibrium geometry; a more complete

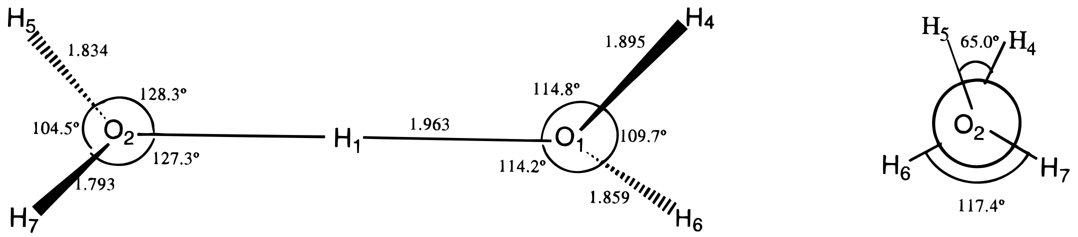

Figure 3. Geometric parameters of the equilibrium structure obtained in the $^3A''$ excited state, when the H_1 atom has been put at equal distances from the two O_1 and O_2 atoms. Bond distances in Å.

TABLE 6: Interaction Energies of the $^1A''$ and $^3A''$ Excited States of the $H_5O_2^+$ System Obtained from CASSCF and CASPT2 Calculations[a]

	E_{int}				
	CASSCF	CASPT2	E_{int}^{corr}	E_{relax}	E_{stab}
$^1A''$	−10.91	−10.26	−9.64	3.70	−5.89
$^3A''$	−10.54	−9.92	−9.11	3.75	−5.32

[a] The stabilization energy, E_{stab}, takes into account the BSSE corrections and the relaxation energy. All values in kcal mol^{-1}.

geometry optimization of such a structure would still decrease the barrier. It is thus clear that the hydrogen atom can very easily transfer between the two oxygen atoms. We can question if it is a proton or a hydrogen atom transfer. This point has been discussed by Roszak et al.[10] in the case of $(H_3N\cdots H\cdots OH_2)^+$ considering that, despite the arbitrariness and possible artifacts of any electron population, Mulliken gross atomic population (GAP) analysis could be a useful tool to study the composition of electron density. This analysis shows that proton transfer occurs in the ground state, while the hydrogen atom is transferred in excited states. It seems that our own studies exhibit similar differences between the ground and excited states. However, the Mulliken electronic populations for very diffuse basis sets are unreliable, and this feature must be taken with care till further checks can be made, using other basis sets or other kinds of population analyses. This situation being unclear, we shall use the notation “proton/hydrogen transfer”.

The present results support both of the hypotheses proposed above. On one hand, we see that the two most stable A″ excited states are nearly degenerate, both for the singlets and the triplets; the polarizabilities calculated for the $^1A''$ and $^3A''$ excited states can thus account for a contribution from the higher excited states. On the other hand, the calculation performed for the triplet excited state shows that the proton/hydrogen can easily transfer from the oxonium ion to the water molecule; both features can explain the particularly high value calculated for the “axial” component of the polarizability tensor (α_{yy}) of this excited state. For the $^1A''$ excited state, the intermolecular distance between the oxonium ion and the water molecule is somewhat larger than in the corresponding triplet excited state, but the other features are similar (C_s as the most stable geometry, a very high value calculated for the α_{yy} component, the two most stable excited states nearly degenerate). The proton/hydrogen transfer involves only very low barriers and can be easily accomplished within the usual range of thermal energies. The low values of these barriers suggest that a dynamic rather than static approach to the problem is more appropriate, including the possible breakdown of the Born−Oppenheimer approximation in the excited states of $H_5O_2^+$.

3.2.4. Interaction and Relaxation Energies. In order to analyze the origin of the stability of the excited states, the interaction energies have been computed for the two lowest excited states of the $H_5O_2^+$ system. These values are reported in Table 6. To overcome size consistency problems, the energy of the isolated subsystems in the geometry of the complex has been obtained by calculating the energy of the system with an intermolecular distance of 100 au.

The interaction energies show that both excited states are equally stabilized. Although these energies are smaller than in the ground state of the $H_5O_2^+$ system (−33.4 kcal/mol[4]), they are not negligible and motivate further studies of potential surfaces for these two excited states. The CASPT2 interaction energies, E_{int}, given in Table 6 do not account for the basis set superposition error corrections. To evaluate the BSSE, we did the following calculations. The water molecule has been considered in the geometries of the two excited states of the complex involved here. The energy of the water molecule has been calculated with two different basis sets; the first one is defined by the basis functions centered on the oxonium ion and water molecule atoms, whereas the second one is composed of the basis functions centered on the water molecule atoms only. For the oxonium ion, similar calculations have been performed; the ion has been considered in its ground state and in the geometries of the complex, and its energy has been computed with the total basis set and the basis set defined by the functions centered on the oxonium ion atoms. For each state, the difference between the two calculated energies gives an estimate of the BSSE contribution. The results of these calculations are reported in Table 7. The BSSE corrections are more important at the CASPT2 level than at the CASSCF level but remain, as expected with our rather large basis sets, relatively small. For the triplet A″ excited state, this BSSE is of about 0.8 kcal/mol at the CASPT2 level, whereas for the corresponding singlet excited state, this quantity is somewhat smaller, of about 0.7 kcal/mol at the CASPT2 level. The interaction energies corrected for the BSSE, E_{int}^{corr}, are reported in Table 6.

TABLE 7: Energies of the Water and Oxonium Ion Subsystems in the Geometries of the Singlet and Triplet Excited Complexes[a]

	geometry of the singlet excited state complex				geometry of the triplet excited state complex			
	$H_2O-{}^1A''$		$H_3O^+-{}^1A'$		$H_2O-{}^3A''$		$H_3O^+-{}^1A'$	
basis set	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2
complex	−75.852392	−75.999497	−76.375738	−76.531040	−75.869697	−76.019876	−76.375738	−76.531040
monomer	−75.852249	−75.999141	−76.375181	−76.530259	−75.869487	−76.019342	−76.375181	−76.530259
BSSE (kcal/mol)	0.09	0.22	0.35	0.49	0.15	0.34	0.35	0.49

[a] C_s symmetry. The water molecule is in a singlet or triplet A″ excited state, and the oxonium ion is in the ground state. The energies are computed at the CASSCF and CASPT2 levels with a (5,2) active space.

The relaxation energies, E_{relax}, have also been calculated for these two excited states (Table 6). Since the geometries are optimized at the CASSCF-gradient level, only the relaxation energy at the CASSCF level has been calculated. For both excited states, this contribution is about 3.7 kcal/mol. It is obtained from the energy of the subsystems computed in the geometry of the complex in their geometry when isolated. Therefore, the stabilization energies of the ${}^1A''$ and ${}^3A''$ states with respect to the isolated subsystems, E_{stab}, are respectively -5.89 and -5.32 kcal/mol (Table 6).

4. Conclusion

Our main goal was to obtain reliable results for the structural, energetic, and electric properties of the protonated dihydrate $H_5O_2^+$ in its ground and two lowest excited states, the ultimate aim being to use these results in future investigations of intermolecular interactions in various geometrical configurations of the two ${}^1A''$ and ${}^3A''$ excited states. The calculations have been performed at the CASSCF level of approximation with a medium-size active space (composed of 13 orbitals), and the remaining electron correlation contribution was obtained by using the CASPT2 approach. Since this active space was at the limit of the computational resources, these results are considered as the most accurate ones at the present stage.

The geometries of both excited states have been found mutually similar, although very different from the ground state geometry. In the ground state, the structure is composed of a central proton surrounded by two equivalent water molecules, whereas in the two excited states, two species are well separated. In the investigated excited states the $H_5O_2^+$ system appears as if it were composed of an oxonium ion in its ground state and a water molecule in an excited state. However, in both ground and excited states, these structures are nearly degenerate with either a C_s or C_2 structure, respectively, allowing an easy proton/hydrogen transfer.

The excitation energies calculated allow to predict that the photodissociation of the $H_5O_2^+$ system should occur for wavelengths of about 153 nm. This value is somewhat different from the earlier estimation of Thomas et al.[8] However, taking into account the complexity of the spectral domain above 120 nm, and particularly above 140 nm,[34] it probably supports the hypothesis of the possible photodissociation of $H_5O_2^+$ in the atmosphere.

The components of the dipole polarizability tensor in the excited states are found to be much larger than in the ground state; for the ${}^1A'$ ground state, this tensor is slightly anisotropic ($\alpha_{xx} = 21.5$ au and $\alpha_{yy} \approx \alpha_{zz} \approx 14$ au), whereas the excited states are highly anisotropic. The two excited states are found similarly polarizable, with α_{xx} and α_{zz} components close to each other and of the order of 100 au and a very large α_{yy} component, of the order of 500 au. This large axial component can be due to the presence of other excited states close in energy but also reflects the possibility of an easy proton/hydrogen transfer process. We have found that the proton/hydrogen transfer barrier is less than 0.3 kcal, comparable to the barrier in the ground state, which is about 0.4 kcal/mol.[4]

The stabilization energies of the two excited states of $H_5O_2^+$ with respect to the isolated subsystems are about -5.5 kcal/mol. This value is smaller than in the ground state of the system (about -35 kcal/mol) but is not negligible and can be compared to the interaction energy between two water molecules, which is about $-4.5/5$ kcal/mol.[35] The very low barriers involved in the proton/hydrogen transfer suggest that a dynamical approach, including the possible breakdown of the Born−Oppenheimer approximation in the excited states of $H_5O_2^+$, should be appropriate.

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