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Production of singlet oxygen atoms by photodissociation of oxywater

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Quantum chemical calculations are reported for the energies of the few lowest electronic singlet states of oxywater along dissociation of the oxygen-oxygen bond into water and singlet oxygen using multistate multireference second-order Møller–Plesset perturbation theory. We compute an energy of 21 kcal/mol to remove one oxygen atom in the lowest singlet state. The two lowest excited singlet states have vertical excitation energies of 2.64 and 2.96 eV (470 and 419 nm) and are leading to the dissociation of the molecule. The two charge transfer states are accessible at vertical excitation of 4.91 and 5.22 eV (253 and 238 nm). © *2009 American Institute of Physics*.
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I. INTRODUCTION

The hydroxyl radical is mainly responsible for the oxidation efficiency of the troposphere due to its ability to oxidize many atmospheric trace gases. Due to oxidation many trace gases are made harmless before entering the more sensitive ozone layer. Therefore the hydroxyl radical acts as a natural cleansing agent in the troposphere and protects the ozone layer from highly reactive trace gases. An understanding of these processes is necessary in order to explain the natural recovery of the ozone layer.[1] Recently Rohrer and Berresheim[2] showed a strong correlation between the abundance of hydroxyl radicals and solar ultraviolet radiation. The main process initiated by ultraviolet radiation in the stratosphere is the dissociation of ozone into singlet oxygen atoms and oxygen molecules,

$$O_3 \rightarrow O_2(A^1\Delta_g) + O(^1D).$$

The intensity of solar ultraviolet radiation is directly related to the concentration of singlet oxygen atoms in the stratosphere. Singlet oxygen atoms can react with water molecules to form hydroxyl radicals,

$$O(^1D) + H_2O \rightarrow 2OH.$$

In this paper we want to discuss the production of singlet oxygen atoms by photodissociation of singlet oxywater,

$$O \cdot OH_2 + h\nu \rightarrow O(^1D) + H_2O.$$

Singlet oxywater might be produced by the photolysis of ozone molecules attached to ice clusters,[3,4]

$$O_3 + nH_2O + h\nu \rightarrow O_2 + O \cdot OH_2 + (n-1)H_2O.$$

Ignatov and co-workers[3,4] studied the photolysis of ozone on ice clusters at 80 K. They observed a significant peak in the experimental infrared (IR) spectra at 2860 cm^{-1}. In their study they have performed calculations of the IR spectra of several reactive oxygen containing molecules attached to small ice clusters with density functional theory. The calculations suggest that the peak originates from either a combination band of hydrogen peroxide (HOOH) solvated in ice or from an OH-stretch vibration of oxywater (OOH_2) solvated in ice. Furthermore their calculations have shown that the ice surface is stabilizing the oxywater against the reaction into hydrogen peroxide by the formation of four hydrogen bonds. The rearrangement of oxywater into hydrogen peroxide by assistance of water molecules has also been studied by Okajima.[5,6] Whereas Ignatov *et al.*[3] fixed the oxygen atoms to their positions in ice crystals, Okajima[5,6] relaxed all coordinates. His calculations show that the inclusion of the additional water molecules lowers the energy difference between the two species significantly but also decreases the reaction barrier when compared to the gas phase reaction because oxywater is stabilized by its large dipole moment.

The majority of theoretical studies of oxywater are focused on the geometrical structure of oxywater and the rearrangement into hydrogen peroxide,[7–13]

$$O \cdot OH_2 \rightarrow HOOH.$$

To the best of our knowledge the work of Filatov *et al.*[8] is the only study that considers the formation of oxywater by the reaction of oxygen atoms with water molecules,

$$O(^1D) + H_2O \rightarrow O \cdot OH_2.$$

They have used *ab initio* multireference methods that are important for this reaction because of the open-shell character of the singlet oxygen atoms. They have found the structure at equilibrium and of the transition states by using the complete active space self-consistent field (CASSCF) method. They have computed the energy to remove the oxygen atom to be 24.2 and 25.6 kcal/mol at the CASSCF and multireference configuration interaction (MRDCI)[14,15] level of theory, respectively. The latter numbers have been computed at the CASSCF-optimized geometries.

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The study of Filatov *et al.*[8] was restricted to the lowest electronic singlet state. In this paper we calculate the six lowest electronic singlet states of oxywater along the potential energy curve resulting in water and singlet oxygen atoms in the ^{1}S and ^{1}D states. We are using the multistate multireference second-order Møller–Plesset perturbation theory (MSMRMP2) (Ref. 16) in order to take care of the multiconfigurational character of the states considered.

In Sec. II we give details of our calculation and in Sec. III we present and discuss our results. The paper ends with a summary of our conclusions.

II. COMPUTATIONAL DETAILS

The geometry of oxywater has been taken from Huang *et al.*[7] (r_{OO}=1.578 Å, r_{OH}=0.974 Å, $\angle_{HOH}$ =105.8°, $\angle_{oop}$=73.4°). We have explored the potential energy curve originating from the elongation of the oxygen-oxygen bond up to a bond distance of 10 bohr. The molecular complex has C_s symmetry at all positions of the potential energy curve. We are using the triple zeta valence polarization (TZVP) basis set of Schäfer *et al.*[17] to describe the atomic orbitals. This basis set is augmented by three diffuse *s*-type Gaussians (α=0.059,0.032,0.0066) and one diffuse *p*-type Gaussian (α=0.059 74) located on each of the oxygen atoms. The molecular orbitals are produced with the restricted open-shell Hartree–Fock method for the lowest triplet state using the TURBOMOLE program package.[18] In the correlated calculations described below, the two-electron integrals were computed using the density-fitting method.[19] For the density fitting we have used the optimized TZVP auxiliary basis set of Weigend *et al.*[20] augmented with the diffuse functions mentioned above.

The energies of the all electronic states are calculated with the MSMRMP2 (Ref. 16) using the DIESEL program package.[21] The two energetically lowest occupied molecular orbitals corresponding to the two oxygen 1*s* orbitals are kept doubly occupied in the correlated calculations, and the two energetically highest virtual molecular orbitals are deleted. The reference space is constructed in the following way. From all six configurations which correspond to the five ^{1}D and the ^{1}S states of the oxygen atom in the oxygen-water system we have produced all single and double excitations from the six highest occupied (the oxygen *p*-shell) into the six lowest virtual orbitals. This procedure generates reference spaces with 625 configurations [1128 configuration states functions (CSFs)] of A′ symmetry and 556 configurations (1078 CSFs) of A″ symmetry. The multireference singles-doubles space spanning the first-order interaction space consists of about 5×10^6 configurations (about 32 $\times10^6$ CSFs) in each symmetry.

The MSMRMP2 method is based on multipartitioning of the electronic Hamiltonian using the multireference Møller–Plesset partitioning.[22] With this partitioning the zeroth-order Hamiltonian is not diagonal. Therefore the contributions to the second-order energies have to be computed by matrix inversion. In order to reduce the computational bottleneck resulting in heavy use of computer resources necessary for the matrix inversion, we are using a configuration-selection procedure. The selection procedure divides the configurations of the first-order interaction space into two sets based on the strength of the interaction with the reference space.[14,15,23] In the weaker interacting set only the projected diagonal part of the zeroth-order Hamiltonian is taken into account, which is trivial to invert. Here we are using T_{sel} $=10^{-5}$ hartree as selection threshold.

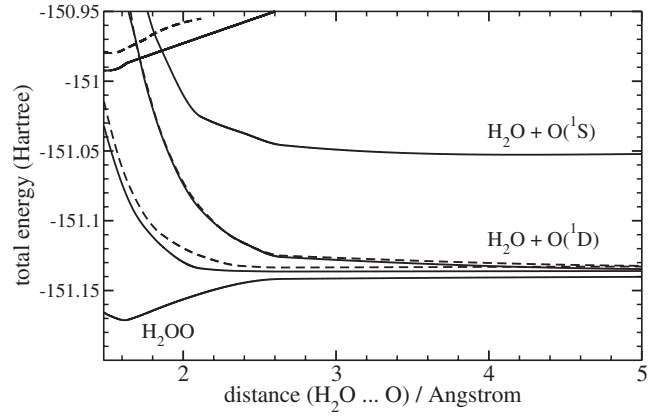

FIG. 1. Potential energy curves for OOH_2 along the oxygen-oxygen coordinate. Solid lines are used for the *A′* states and dashed lines for the *A″* states. Note that the fourth and fifth curves are closely adjacent to each other. The curves partly shown in the upper left part are corresponding to charge-transfer states with a positive charge on the water molecule and negative charge on the oxygen atom.

III. RESULTS AND DISCUSSION

The potential energy curves for the dissociation of oxywater along the oxygen-oxygen bond are given in Fig. 1. The few lowest lying singlet states are shown. These are corresponding to the dissociation into water and oxygen atoms in its ^{1}D and ^{1}S states.

In Table I we present the vertical excitation energies together with oscillator strengths for electronic transitions from the lowest singlet state of oxywater at its equilibrium geometry. Furthermore the dipole moments of the states are given. The equilibrium geometry is taken from Filatov *et al.*[8]

The lowest of the five curves correlating with dissociation into water and oxygen (^{1}D) states has a minimum at an oxygen-oxygen bond distance of 1.64 Å. The binding energy is 21.3 kcal/mol. This is 4 kcal/mol lower than the value of 25.6 kcal/mol calculated by Filatov *et al.*[8] at the MRDCI level of theory.

The remaining four curves of this dissociation channel are of repulsive character. They occur in two pairs, each one consisting of an A′ and A″ states. The two lowest excited states have vertical excitation energies of 2.64 and 2.96 eV (470 and 419 nm) and will dissociate into singlet oxygen (^{1}D) atoms and water.

Close to the equilibrium geometry, two states corresponding to charge-transfer states between water and atomic oxygen are accessible at vertical energies of 4.91 and 5.22 eV (253 and 238 nm). Both charge-transfer states have local minima at oxygen-oxygen bond lengths of about 1.50 and 1.53 Å, respectively. The second pair of repulsive curves corresponding to dissociation into water and (^{1}D) oxygen atoms is intersecting at oxygen-oxygen bond lengths of

TABLE I. Some parameters of the few lowest states calculated at the equilibrium geometry of oxywater. The geometric parameters are taken from Filatov *et al.* (Ref. 8). The energies ΔE for vertical excitation from the lowest singlet state are given in eV and nanometers. μ_x and μ_y are the nonzero components of the dipole moment in atomic units. f denotes the oscillator strength for excitation from the lowest singlet state. Note that at equilibrium geometry the states $3^1A'$ and $2^1A''$ are the charge-transfer states discussed in Fig. 1.

State	$\frac{\Delta E}{\text{eV}}$	$\frac{\Delta E}{\text{nm}}$	$\frac{\mu_x}{\text{a.u.}}$	$\frac{\mu_y}{\text{a.u.}}$	f
$1^1A'$	0.00	⋯	−1.39	0.87	⋯
$2^1A'$	2.64	470	−0.83	0.80	0.1×10^{-3}
$1^1A''$	2.96	419	−0.76	0.80	0.1×10^{-3}
$3^1A'$	4.91	253	0.73	−0.39	5.0×10^{-3}
$2^1A''$	5.22	238	0.76	−0.36	17.5×10^{-3}

about 1.71 and 1.69 Å. It is difficult to draw conclusions with respect to the photochemistry from this limited view of the intersection. In order to study the photochemistry of the two pairs of states it is necessary to do much more detailed studies including more dimensional regions of the potential energy surface. The two charge-transfer states are listed in Table I as states $3^1A'$ and $2^1A''$, reflecting the energetic ordering at equilibrium geometry. The corresponding dipole moments are nearly opposite in direction to the dipole moment of the ground state, indicating the charge-transfer character. In environments containing water molecules the charge transfer could trigger a proton transfer from the solvent, resulting in the production of OH radicals. The proton transfer could in return lower the energy for this reaction. The importance of water as a catalyst in radical reactions has been discussed in a recent study by Vöhringer-Martinez *et al.*[24] The oscillator strength for the electronic excitation from the ground state into the two charge-transfer states is 5.0×10^{-3} and 17.5×10^{-3}, respectively. This is a significantly higher than the value 0.1×10^{-3} calculated for the excitation into the two lowest lying repulsive states $2^1A'$ and $1^1A''$. The photochemistry at excitation energies above 4.9 eV will be controlled by the charge-transfer states and the intersecting pair of repulsive states. The large oscillator strengths of the two states might help to identify oxywater by spectroscopic methods and to distinguish it from spectra of hydrogen peroxide.

Another repulsive curve crosses the two charge states at 1.86 and 1.81 Å. This curve will lead to dissociation into water and electronically excited oxygen atoms in the ^{1}S state.

IV. CONCLUSIONS

We have calculated the energies of the few lowest electronic singlet states of oxywater along dissociation of the oxygen-oxygen bond into water and singlet oxygen atoms with the MSMRMP2. The curve of the lowest electronic state has a minimum with a binding energy of about 21 kcal/mol. Two repulsive states dissociating into water and singlet (^{1}D) oxygen atoms can be reached at vertical excitation energies of 2.64 and 2.96 eV (470 and 419 nm).

Two charge-transfer states are found at vertical energies of 4.91 and 5.22 eV (253 and 238 nm) above the ground states. Two repulsive states are intersecting the charge-transfer states close to the equilibrium geometry of the ground state, leading to dissociation into water and singlet (^{1}D) oxygen atoms.

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