Theoretical study of the homolytic photolysis of hydrogen peroxide at the state-of-the-art level

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A B S T R A C T

A thorough investigation on the homolytic photolysis of hydrogen peroxide (H_2O_2) is helpful for understanding many reactions in biochemistry and environmental chemistry. There is still debate regarding this reaction's mechanism, although many types of experimental and theoretical studies have been performed. High quality potential-energy curves (PECs) are necessary to deduce the dissociation mechanism. In the current study, the PECs of H_2O_2 with respect to the O—O bond distance for the ground state and the low-lying excited states are calculated using multistate second order multiconfigurational perturbation theory. The vertical excitation energies and the dissociation energy of H_2O_2 are predicted at a high computational level. The current study is able to assign homolytic photolysis pathways of H_2O_2 observed experimentally at three regions of incident wavelength. The solvent effect is also considered in this study.

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1. Introduction

The peroxide bond plays a critical role in the vast majority of biochemical processes. As an example, many chemiluminescence reactions involve the dissociation of high energy peroxides. The peroxide bond is also important in oxidative degeneration, combustion, atmospheric and stratospheric chemistry, as well as in smog reactions [1–3]. Hydrogen peroxide (H_2O_2) is the simplest peroxide with one dihedral angle and thus is an ideal model for a high-accuracy *ab initio* calculation. The current knowledge regarding H_2O_2 provides an excellent basis to understand the peroxide bond, as well as reaction mechanisms involving the peroxide bond.

Considerable effort has been made on studying the properties and the photolytic reactions of H_2O_2 [4–6]. This photolysis has been investigated at several different wavelengths, but the mechanism is still not fully understood [7–11]. Distinguished by-products and eight possible pathways in the UV photolysis of H_2O_2 give rise to a complicated photolytic mechanism. Among the eight dissociation pathways, homolytic photolysis is the most important because it produces OH radicals that often induce other

reactions [12]. OH radicals play vital roles in biochemical and life processes as reactive oxygen species [13]. In particular, OH radicals are the most significant oxidants in the troposphere [2,3]. The homolytic photolysis itself is complicated in that it involves different excited states at different incident wavelengths. At 193 nm, photolysis involves both [1]A and [1]B states [7], while at 266 nm [9] and 280–290 nm [14], it involves only the [1]A state. At the longer wavelengths between 308 and 465 nm, it involves both the [1]A and [1]B states again [10]. In order to explain the dissociation pathways at the above 3 wavelength regions, we previously performed energy calculations in the gas phase using multistate second order multiconfigurational perturbation theory (MS-CASPT2) [15] based on geometries optimized via the complete active space multiconfiguration SCF (CASSCF) method. This theoretical study was able to explain the homolytic photolysis of H_2O_2 at 193, 266 and 280–290 nm but not at 308–465 nm [16]. In order to clear up previous ambiguities and to provide a whole picture of the homolytic photolysis of H_2O_2, calculations are performed in this paper at the highest computational level to date. The potential energy curves (PECs) are calculated via the MS-CASPT2 method at the CASPT2 optimized geometries. Furthermore, the solvent effect is considered in this study, and the dissociation energy of H_2O_2 is accurately predicted.

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2. Computational methods

The geometry optimization and the harmonic vibrational frequency analysis of the ground state were performed using the CASPT2 method [17–19]. The vertical excitation energies (T_v) and the oscillator strengths (f) were calculated using the MS-CASPT2 method. Ground and excited states PECs were also obtained using the MS-CASPT2 method. In the CASPT2 calculations of H_2O_2, the active space includes the full valence active orbital space, i.e., 14 electrons in 10 orbitals (14-in-10). The atomic natural orbital (ANO) basis sets (5s4p3d2f for oxygen and 3s2p1d for hydrogen) were used for the CASPT2 optimization, and the MS-CASPT2 energy calculations [20]. Natural bond orbital (NBO) analysis for ground and excited states were also performed. The calculations above were performed in both the gas phase and in an aqueous solution. The solvent effects of water were examined using the conductor-like polarizable continuum model (CPCM) [21,22]. All calculations were performed with the MOLCAS 8.0 quantum chemistry software [23].

3. Results and discussion

3.1. Ground state structure

The ground-state structure of H_2O_2 was previously measured from several experiments [26,28–30] as well as calculated theoretically by Koput et al. [24,31], Liu et al. [16] and Watts and Francisco [25]. The parameters of the current CASPT2 optimized geometry along with the previously determined experimental and theoretical values are listed in Table 1. The frequency analysis at the same computational level listed in Table S1 indicates that the presently optimized S_0 geometry is a real minimum. The zero-point vibrational energy of the current CASPT2 calculation is 16.4 kcal mol^{-1}, which is slightly lower than the previous CASSCF result (18.3 kcal mol^{-1}) [16].

3.2. Vertical excited energy

The T_v and f values of the six lowest-lying singlet (S_0-A, S_1-A, S_2-B, S_3-B, S_4-A and S_5-A) and six low-lying triplet states (T_1-A, T_2-B, T_3-B, T_4-A, T_5-B and T_6-B) of irreducible representations A and B were calculated with the MS-CASPT2//CASPT2 method. The current method involving dynamic correlation to calculate both the excitation energies and the geometric optimization. Thus, as shown in Table 2 and Table S2, the calculated T_v values are lower than the results of CI [32], CASSCF [33], and CIS [34] and are similar to our previous MS-CASPT2//CASSCF results [16]. The most recent investigation of H_2O_2 at the EOM-CCSD//MP2 theoretical level showed that the first and second singlet excited states are 6.08 and 6.92 eV above the ground state, respectively, and that the first and second triplet excited states are 4.99 and 6.06 eV above the ground state, respectively [35].

Table 2
The T_v (in eV), f values, and the transition characteristics of the excited states for H_2O_2.

State	T_v	f	Transition	State	T_v	Transition
S_0-A	0.00			T_1-A	4.55	(n,σ^*)
S_1-A	5.53	2.80×10^{-5}	(n,σ^*)	T_2-B	5.56	(n,σ^*)
S_2-B	6.64	6.49×10^{-3}	(n,σ^*)	T_3-B	6.27	(n,σ^*)
S_3-B	6.71	1.88×10^{-4}	(n,σ^*)	T_4-A	7.42	(n,σ^*)
S_4-A	7.65	4.03×10^{-3}	(n,σ^*)	T_5-A	7.97	(n,σ^*)
S_5-A	8.31	1.29×10^{-2}	(n,σ^*)	T_6-B	8.17	(σ,σ^*)

3.3. MS-CASPT2 calculated PECs of the ground and excited states

The CASPT2 method was used to optimize the geometry of the ground state at each fixed O—O bond length ($R_{O—O}$) in the range of 1.1 to 5.5 Å (in steps of 0.2 Å). The O—H bond ($R_{O—H}$) becomes shorter (from 0.982 to 0.967 Å) as $R_{O—O}$ stretches from 1.1 to 1.5 Å, which later becomes longer (from 0.967 Å to 0.974 Å) as $R_{O—O}$ stretches past 1.5 Å. Furthermore, ∠HOO decreases from 111.8° to 65.2° and ∠HOOH increases from 94.2° to almost 180° as the O—O bond stretches. Thus, after photolysis, the two OH fragments are in a line, which was verified experimentally using polarized laser beams [9].

The MS-CASPT2//CASPT2 method was used to calculate the energies of the seven singlet and six triplet states. Fig. 1 shows their diabatic PECs against the O—O bond distance, where the curves are labeled based on their energy order at the Franck–Condon point as shown in Table 2. The corresponding transition character of each state is also listed in Table 2. As shown in Fig. 1, the adiabatic MS-CASPT2 PECs are drawn diabatically such that they follow a particular electronic configuration through avoided crossings between two states of the same symmetry (termed diabatization) [36]. The same labels are used for the states on both sides of the crossing. The PECs in the $R_{O—O}$ range from 1.3 to 1.6 Å are enlarged
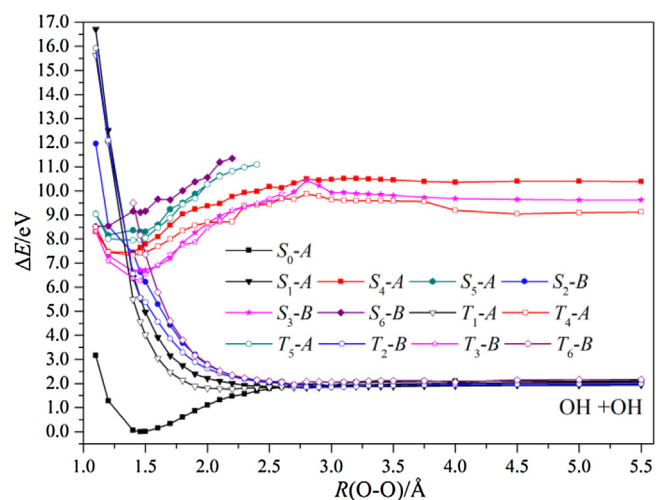

Fig. 1. The MS-CASPT2//CASPT2 calculated diabatic PECs along the O—O bond of 13 states of H_2O_2 in the gas phase.

Table 1
The ground-state structure of H_2O_2. (Bond length is in Å; angle is in degrees).

	Theor.				Expt.	
	CCSD(T) [24]	MP2 [16]	QCISD(T) [25]	CASPT2	Expt. [26]	Expt. [27]
R_{OO}	1.453	1.471	1.462	1.459	1.463	1.464
R_{OH}	0.963	0.972	0.967	0.966	0.967	0.965
∠HOO	99.9	99.1	99.8	100.0	99.3	99.4
∠HOOH	112.5	112.9	112.1	114.9	120.2	111.8

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