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Ionized State of Hydroperoxy Radical−Water Hydrogen-Bonded Complex: $(HO_2-H_2O)^+$

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Ab initio molecular orbital calculations have been employed to characterize the structure and bonding of the $(HO_2-H_2O)^+$ radical cation system. Geometry optimization of this system was carried out using unrestricted density functional theory in conjunction with the BHHLYP functional and 6-311++G(2df,2p) as well as 6-311++G(3df,3p) basis sets, the second-order Møller−Plesset perturbation (MP2) method with the 6-311++G(3df,3p) basis set, and the couple cluster (CCSD) method with the aug-cc-pVTZ basis set. The effect of spin multiplicity on the stability of the $(HO_2-H_2O)^+$ system has been studied and also compared with that of oxygen. The calculated results suggest a proton-transferred hydrogen bond between HO_2 and H_2O in $H_3O_3^+$ wherein a proton is partially transferred to H_2O producing the $O_2\cdots H_3O^+$ structure. The basis set superposition error and zero-point energy corrected results indicate that the $H_3O_3^+$ system is energetically more stable in the triplet state; however, the singlet state of $H_3O_3^+$ is more stable with respect to its dissociation into H_3O^+ and singlet O_2. Since the resulting proton-transferred hydrogen-bonded complex $(O_2\cdots H_3O^+)$ consists of weakly bound molecular oxygen, it might have important implications in various chemical processes and aquatic life systems.

1. Introduction

The investigation of structure and bonding of hydrogen-bonded complexes is of great theoretical and experimental interest because it plays an important role in various chemical, biological, and atmospheric reactions and processes. This has led to a large number of theoretical and experimental investigations of several systems and processes involving hydrogen bonds.[1,2] The strength of a hydrogen bond depends on the proton-donating and proton-accepting ability of the donor and the acceptor, respectively. The nature of bonding is mainly governed by the type of electronegative atom/group attached to the donor hydrogen atom.[3] However, in some cases the type of interaction involved in the hydrogen bonding has been found to be controversial.[4]

Hydrogen-bonding interaction between H_xO_y species is very important because of their formation and presence in a variety of processes, especially in the atmosphere. Various stable and transient chemical species of H_xO_y type, which are present in the atmosphere, interact among themselves and also form complexes with water molecules. In this context, hydroperoxy (HO_2) radical is an important chemical species, which is involved in atmospheric chemical reactions. Further, self-reaction of HO_2 radical is the primary source of H_2O_2 in the atmosphere.[5,6] HO_2 is involved in gas-phase processes, gas−aqueous phase chemistry, and aqueous phase reactions.[7,8] It plays a significant role in the stratospheric chemistry and oxidation processes in the troposphere. HO_2 also plays an important role in the oxidation of SO_2 to H_2SO_4, a major constituent of acid rain.[9] It can take part not only in redox processes but also in forming a variety of intermolecular complexes both as a hydrogen bond donor and acceptor. The experimental and theoretical studies suggest that HO_2 forms complexes with water molecules, viz., HO_2-H_2O.[10−15] In the earlier studies, the abundance of HO_2 in the atmosphere has been found to be affected by the presence of water.[16,17]

The hydroperoxy radical that is associated with high gas-phase acidity has been found to form complexes due to its charge distribution, $^{\delta+}H-O-O^{\delta-}$. The existence of radical−molecule hydrogen-bonded complexes of HO_2 and their impact on the atmospheric processes has been an active field of research. It has been postulated that as much as 30% of free HO_2 radical in the troposphere may actually be complexed with H_2O under ideal conditions.[14] Experimental studies have demonstrated that reactivity of the HO_2 radical is increased when complexed with NH_3 and H_2O.[17−20] It has also been shown that in addition to the enhanced reactivity observed for a number of radicals as a result of complex formation, their photochemistry can also be perturbed.[21] Due to the tendency of radical−molecule complexes to alter both the reactivity and photochemistry of molecules, studies of the effects of complex formation on the HO_2 molecules are of importance to atmospheric chemistry. Although reactions of HO_2 radical in the atmosphere are well studied, there has been a discrepancy between the model predictions for the loss of HO_2 radical in the atmosphere and measured HO_2 concentration.[22] It has been suggested that some important and unknown process for HO_2 loss is missing in the model predictions. Interestingly, the additional loss of HO_2 has been found to be directly proportional to the observed H_2O concentration.[22] Formation of HO_2-H_2O complex in the atmosphere is suggested to enhance the rate of H_2O_2 formation by a factor

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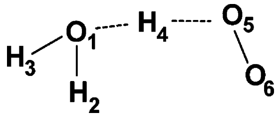
SCHEME 1: Structure of $H_3O_3^+$ Denoting the Atom Labels



of 3.[10−15] This indicates that reactions of complexes of HO_2 with H_2O play some role in the loss of HO_2.

The nature of bonding and energy in isolated HO_2 and the excited state of HO_2-H_2O (H_3O_3) complexes have been well studied.[5−15] However, ionization of the HO_2-H_2O complex has not been reported even though it is very important and relevant in the atmospheric reactions. The H_3O_3 has also been considered as a transition state in the reaction of H_2O_2 with OH radical.[23] It is known that photolysis of chemical species in the atmosphere causes their ionization resulting in a large number of chemical processes induced by their radical cations and/or anions. In this context, ionization of the HO_2-H_2O complex (H_3O_3) in the atmosphere producing $H_3O_3^+$ might be important and relevant to understand the reactions of HO_2 and the unaccountable loss of HO_2. In view of this, we have been motivated to investigate the stability, structure, and bonding of the $H_3O_3^+$ species. The study of $H_3O_3^+$ is also of interest for the solubility of oxygen in acidic aqueous solutions ($O_2-H_3O^+$) and radiolysis of O_2/air-saturated aqueous solutions. Formation of solvent radical cation is the first step in the ionizing radiation effects on the aqueous systems leading to the formation of H_3O^+, OH, e^-(aq), H, H_2, and H_2O_2.[24] Reduction in solubility of oxygen with increase in H_3O^+ (decrease in pH) is relevant to chemical processes as well as life in aquatic systems.[25]

2. Computational Methods

The geometry of the $H_3O_3^+$ species has been fully optimized using density functional theory with Becke's half and half (BH) exchange and Lee−Yang−Parr (LYP) correlation functional (BHHLYP), and also with the second-order Møller−Plesset perturbation (MP2) method. The ab initio calculations have been performed using the GAMESS[26] electronic structure program with 6-311++G(2df,2p) and 6-311++G(3df,3p) basis sets. Stable structures were characterized using vibrational analysis. It has also been attempted to study the multiplicity effects on the stability of $H_3O_3^+$. The binding energy of $H_3O_3^+$ has been calculated by subtracting the total energy of the structure from the total energy of the constituent species. The basis set superposition error and zero-point energy correction have also been included to refine the binding energy values. To further ascertain the stability order of the three structures, their geometries and energies have been calculated using the more accurate CCSD/aug-cc-pVTZ method followed by single-point energy calculations using CCSD(T)/aug-cc-pVTZ level of theory with the Gaussian03 program.[27] Single-point energy calculations have also been performed using the restricted open-shell BHHLYP and MP2 methods. Single-point energy calculations have also been performed using the restricted open-shell CCSD(T)/aug-cc-pVTZ method (RCCSD(T)) with the MOLPRO 2006 program.[28]

3. Results and Discussion

The structures of $H_3O_3^+$, O_2, and H_3O^+ have been optimized using various methods as listed above. In the initial geometry of $H_3O_3^+$, it has been assumed that an electron is removed from a chemical species in which the H-atom of HO_2 is hydrogen-bonded with the O-atom of H_2O (Scheme 1). This structure has been considered to investigate the effect of ionization on the structure and bonding of the HO_2-H_2O complex. In an earlier study, hydrogen from the HO_2 has been shown to form a hydrogen bond with the oxygen of the water.[14,15] An attractive interaction between the terminal oxygen in the peroxyl radical and one of the hydrogens on the water has also been reported which causes the structure to have a floppy five-membered ringlike structure.[14] As stated above, we have considered this neutral HO_2-H_2O structure as the initial guess for the ionized state to obtain an insight about the process of ionization. The effect of spin multiplicity on the structure and stability of O_2 and $H_3O_3^+$ systems has also been investigated. The structures of $H_3O_3^+$ optimized using the UCCSD method with the aug-cc-pVTZ basis set are presented in Figure 1, parts a and b. Various structural parameters of singlet and triplet states of $H_3O_3^+$ as calculated by different methods and basis sets are reported in Table 1.

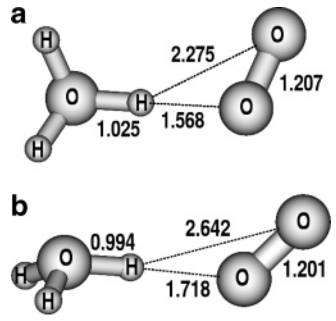


Figure 1. (a) CCSD/aug-cc-pVTZ optimized structure of singlet $H_3O_3^+$. (b) CCSD/aug-cc-pVTZ optimized structure of triplet $H_3O_3^+$.

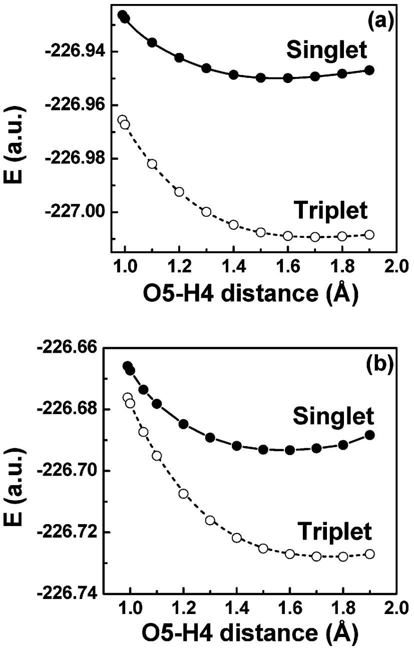


Figure 2. Variation of total energy along the reaction coordinate corresponding to the proton-transfer coordinate (O_5-H_4 distance) in the $H_3O_3^+$ system as calculated using (a) the BHHLYP method with the 6-311++G(2df,2p) basis set and (b) the MP2 method with the 6-311++G(3df,3p) basis set.

A comparison of our calculated results for $H_3O_3^+$ (UCCSD/aug-cc-pVTZ) with that of neutral H_3O_3 (B3LYP/6-311+G-(3df,3p) and MP2/6-311G(2df,2p)) of Aloisio and co-workers[14,15] has also been made. This comparison suggests that ionization of H_3O_3 results in increase in O−H bond lengths in H_2O and HO_2. However, the bond lengths of the O_5-O_6 bond (in HO_2) and O_1-H_4 bond (between H_2O and HO_2) have been

TABLE 1: Optimized Geometrical Parameters for the Singlet (Triplet) States of $H_3O_3^+$ and O_2 as Calculated Using Different Methods and Basis Sets (the Bond Length, *R*, in angstroms, and θ and δ in deg)[a]

	BHHLYP (6-311++G(2df,2p)	BHHLYP (6-311++G(3df,3p)	MP2 (6-311++G(3df,3p)	UCCSD (aug-cc-pVTZ)
$R(O_1-H_2)$	0.964 (0.966)	0.965 (0.966)	0.973 (0.976)	0.972 (0.975)
$R(O_1-H_4)$	1.019 (0.987)	1.020 (0.988)	1.028 (0.990)	1.025 (0.994)
$R(H_4-O_5)$	1.562 (1.705)	1.565 (1.703)	1.565 (1.764)	1.568 (1.718)
$R(O_5-O_6)$	1.175 (1.179)	1.175 (1.179)	1.243 (1.205)	1.207 (1.201)
$\theta(H_2-O_1-H_3)$	112.2 (112.8)	111.9 (112.5)	110.7 (111.2)	110.8 (111.1)
$\theta(H_3-O_1-H_4)$	114.8 (113.6)	114.5 (113.3)	113.0 (111.8)	113.3 (111.9)
$\theta(O_1-H_4-O_5)$	177.4 (176.7)	176.9 (176.5)	173.6 (178.9)	174.9 (178.4)
$\theta(H_4-O_5-O_6)$	114.1 (134.4)	112.8 (131.2)	103.6 (138.3)	109.4 (128.8)
$\delta(H_3-H_2-O_1-H_4)$	133.6 (131.4)	132.5 (130.4)	127.9 (125.7)	128.4 (126.0)
$\delta(H_3-O_1-H_4-O_5)$	113.6 (47.2)	108.1 (42.3)	72.2 (34.3)	104.9 (48.0)
$\delta(O_1-H_4-O_5-O_6)$	9.1 (154.9)	2.5 (150.9)	49.8 (148.2)	69.1 (165.9)
$R(O-O)$[b]	1.178 (1.180)	1.177 (1.179)	1.245 (1.221)	1.209 (1.202)

[a] Geometrical parameters for the triplet states are given within the parentheses. [b] $R(O-O)$ refers to the bond length in the oxygen molecule.

TABLE 2: Singlet−Triplet Energy Difference [ΔE(S−T)] for $H_3O_3^+$ and O_2 as Calculated using Different Methods and Basis Sets

ΔE(S−T) (kcal/mol)	BHHLYP (6-311++G(2df,2p)	BHHLYP (6-311++G(3df,3p)	MP2 (6-311++G(3df,3p)	UCCSD (aug-cc-pVTZ)	UCCSD(T) (aug-cc-pVTZ)
$H_3O_3^+$	37.3 (31.6)[a]	37.0 (31.4)[a]	21.7 (24.8)[a]	27.3	24.0 (23.3)[a]
O_2	42.4 (36.6)[a]	42.5 (36.6)[a]	29.1 (37.6)[a]	32.9	29.9 (29.3)[a]

[a] Correspond to restricted open-shell calculated values for open-shell systems; see text for details.

reduced. This reduction of the O_1-H_4 bond suggests a stronger interaction between H_2O and HO_2 on ionization of H_3O_3. Further, the UCCSD calculated data reported in Table 1 show the effect of spin multiplicity on the bond lengths in $H_3O_3^+$. It shows that the lengths of O−H bonds (in H_2O and HO_2) are slightly elongated but O_5-O_6 (in HO_2) and O_1-H_4 (between H_2O and HO_2) bond lengths are slightly shortened on increase in multiplicity from the singlet to triplet state. The calculated O−H bond length in HO_2 (doublet) has been found to increase from 0.974 to 1.568 Å for $^1[H_3O_3^+]$ and to 1.718 Å for $^3[H_3O_3^+]$. This increase in bond length of O−H in HO_2 (∼1.61−1.76 times) and a comparison of O−H bond length of O_1-H_4 and H_4-O_5 suggests a proton-transferred hydrogen bond between HO_2 and H_2O in $H_3O_3^+$ wherein a proton is partially transferred to H_2O. It is evident that ionization of H_2O-HO_2 results in the formation of a structure in which H_3O^+ and O_2 are hydrogen-bonded, i.e., $HO_2-H_2O - e^- \rightarrow O_2\cdots H_3O^+$. The optimum distance at which H_3O and O_2 are held together in $^3[H_3O_3^+]$ as calculated by BHHLYP/6-311++G(2df,2p), BHHLYP/6-311++G(3df,3p), MP2/6-311++G(3df,3p), and UCCSD/aug-cc-pVTZ levels of theory is 1.705, 1.703, 1.764, and 1.718 Å, respectively. Similarly, the optimum distance at which H_3O and O_2 are held together in $^1[H_3O_3^+]$ as calculated by BHHLYP/6-311++G(2df,2p), BHHLYP/6-311++G(3df,3p), MP2/6-311++G(3df,3p), and UCCSD/aug-cc-pVTZ levels of theory is 1.562, 1.565, 1.565, and 1.568 Å, respectively. It is also evident from Table 1 that the calculated O_5-O_6 bond length in the singlet and triplet state of $H_3O_3^+$ is close to that of the O−O bond length in the oxygen molecule in the singlet and triplet state, respectively. In other words, ionization of H_2O-HO_2 results in the $O_2\cdots H_3O^+$ structure. In this context it is important to note that the formation and stability of singlet oxygen in acidic medium is of importance in photodynamic therapy.[29] No significant differences in geometrical parameters have been observed on using BHHLYP method with either the 6-311++G-(2df,2p) or 6-311++G(3df,3p) basis set. The O_5-O_6 bond lengths calculated with MP2/6-311++G(3df,3p) and UCCSD/aug-cc-pVTZ levels of theory for $H_3O_3^+$ are larger than those calculated with the BHHLYP method. In general, geometrical parameters calculated with the MP2/6-311++G(3df,3p) method are closer to those obtained with the UCCSD/aug-cc-pVTZ method. A comparison of bond lengths and angles of $^1[H_3O_3^+]$ as calculated by MP2/6-311++G(3df,3p) with that of neutral H_3O_3 as calculated by MP2/6-311++G(2df,2p) shows that the O−H bond lengths in H_2O and HO_2 are increased, whereas the O−H bond length between HO_2 and H_2O and the O−O bond length in HO_2 are reduced on ionization of H_3O_3.

Though $H_3O_3^+$ is an even electron system, its total energy indicates that the triplet system is lower in energy than the singlet system. Further, the $H_3O_3^+$ triplet system has been calculated to have longer distance between H_3O^+ and O_2 as compared to the singlet system. Table 2 lists the singlet−triplet energy difference [ΔE(S−T)] of $H_3O_3^+$ and O_2 as calculated with various methods. The difference in calculated total energy of the triplet and singlet state of $H_3O_3^+$ falls in the infrared region. It can be inferred from the Table 2 that the ΔE(S−T) value of O_2 is reduced by 5.1, 5.5, 7.4, 5.6, and 5.9 kcal/mol on interaction with H_3O^+ as calculated using BHHLYP/6-311++G(2df,2p), BHHLYP/6-311++G(3df,3p), MP2/6-311++G(3df,3p), UCCSD/aug-cc-pVTZ and UCCSD(T)/aug-cc-pVTZ levels of theory, respectively. It indicates that the singlet and triplet states of O_2 come closer on interaction with H_3O^+. Table 2 reveals that the BHHLYP method overestimates the ΔE(S−T) value in both $H_3O_3^+$ and O_2 species. To analyze this aspect further, we have calculated the ΔE(S−T) using restricted open-shell BHHLYP (ROBHHLYP), restricted open-shell MP2 (ROMP2), and ROHF-RCCSD(T) (RCCSD(T)) methods. Indeed, it has been found that the ΔE(S−T) values calculated using ROBHHLYP method are smaller as compared to the corresponding unrestricted values. Thus, it is the spin-polarization effect which is responsible for the overestimation of ΔE(S−T) values as calculated by the BHHLYP method. On the contrary, the ROMP2 calculated values have been found to be larger with respect to the corresponding UMP2 values. Nevertheless, ROBHHLYP and ROMP2 values are close to each other. ΔE(S−T) values calculated using the RCCSD(T) and UCCSD(T) methods are almost the same. Hence, electron correlation as well as spin-polarization effects are equally important in the prediction of the singlet−triplet energy difference in the $H_3O_3^+$ system.

TABLE 3: Binding Energy (BE, in kcal/mol) of $H_3O_3^+$ with Respect to H_3O^+ and O_2 as Calculated Using Different Methods and Basis Sets[a]

	BHHLYP (6-311++G(2df,2p))		BHHLYP (6-311++G(3df,3p))		MP2 (6-311++G(3df,3p))		UCCSD (aug-cc-pVTZ)	UCCSD(T) (aug-cc-pVTZ)
species	BE	ZPE_{corr}	BE	ZPE_{corr}	BE	ZPE_{corr}	BE	BE
$^1[H_3O_3^+]$	11.9	1.4	12.4 (0.5)[b]	1.5	12.8 (1.2)[b]	1.3	12.2	12.9
$^3[H_3O_3^+]$	6.7	1.4	6.9 (0.3)[b]	1.5	5.5 (0.7)[b]	1.9	6.7	7.0

[a] $H_3O^+ + O_2 \rightarrow H_3O_3^+$; BE $= E(H_3O^+) + E(O_2) - E(H_3O_3^+)$. [b] Within the parenthesis BSSE values are given.

TABLE 4: Infrared Frequencies (cm^{-1}) of Singlet and Triplet $H_3O_3^+$ as Calculated Using BHHLYP and MP2 Methods with the (6-311++G(3df,3p) Basis Set[a]

$H_3O_3^+$	$^1[H_3O_3^+]$		$^3[H_3O_3^+]$	
vibration mode	BHHLYP	MP2	BHHLYP	MP2
O_1-H_2; O_1-H_3 asymmetric stretch	3859.4 (413.7)	3772.0 (377.4)	3846.2 (443.6)	3726.8 (434.2)
O_1-H_2; O_1-H_3 symmetric stretch	3779.1 (226.7)	3679.3 (226.4)	3770.0 (290.0)	3648.4 (394.4)
O_1-H_4 stretch	2786.0 (2396)	2717.2 (2121)	3317.6 (1525)	3422.8 (1145)
O=O stretch	1793.7 (2.9)	1762.1 (64.1)	1795.0 (28.2)	1921.3 (32.1)
$H_4-O_1-H_3$ bend	1717.1 (38.0)	1680.1 (29.5)	1731.0 (78.7)	1707.4 (68.0)
$H_2-O_1-H_3$ bend	1712.6 (65.6)	1311.6 (3.8)	1718.1 (63.1)	1698.1 (73.8)
$H_4-O_1-H_3-H_2$ torsion	1091.7 (232.0)	972.5 (299.0)	916.1 (367.6)	942.8 (366.9)
$O_5-H_4-O_1$ in-plane bend[b]	566.3 (199.0)	538.3 (123.7)	437.5 (83.8)	389.8 (97.8)
$O_5-H_4-O_1$ out-of-plane bend[c]	429.0 (3.3)	533.5 (31.8)	289.4 (11.6)	267.4 (6.8)
O_5-H_4 stretch	323.8 (112.9)	320.2 (76.1)	224.1 (55.2)	201.6 (74.9)
$O_5-H_4-O_1-H_3$ torsion	219.1 (46.4)	160.6 (49.6)	222.3 (83.1)	113.4 (52.3)
$O_6-O_5-H_4-O_1$ torsion	129.9 (4.4)	113.6 (7.4)	111.5 (4.7)	83.9 (8.7)

[a] IR Intensities (km/mol) are given within the parentheses. [b] Bending motion in the plane containing O_6, O_5, H_4, and O_1 atoms. [c] Bending motion perpendicular to the plane containing O_6, O_5, H_4, and O_1 atoms.

Further, stabilization energies of singlet as well as triplet states of $H_3O_3^+$ have been calculated using different methods and basis sets with respect to its dissociation into H_3O^+ and singlet/triplet O_2 (Table 3). The calculated interaction energy values suggest that the singlet state of $H_3O_3^+$ is more stable than its triplet state with respect to its dissociation into H_3O^+ and O_2. Thus, H_3O^+ is more strongly bound with singlet O_2 than triplet O_2. In other words, ionization of HO_2-H_2O should produce more stable triplet $H_3O_3^+$, which exists as $O_2-H_3O^+$. However, decay of $H_3O_3^+$ to singlet O_2 is less favorable. This is clearly due to the higher interaction energy of H_3O^+ with singlet O_2 as compared to triplet O_2. It also suggests that decay of $^1[O_2-H_3O^+]$, produced in photodynamic therapy, into singlet O_2 is less favorable. Earlier, Young et al. have shown that the decrease in lifetime of singlet oxygen in protic solvents is due to hydrogen bonding which plays an important role in deactivation of singlet oxygen.[30] Table 3 also lists basis set superposition error (BSSE) and zero-point energy (ZPE) correction values for the singlet as well as triplet $H_3O_3^+$ system as calculated using different methods and basis sets. BSSE values suggest that the selected basis sets are adequate to calculate the interaction energy in $H_3O_3^+$ system. The ZPE correction values are also small enough to affect the general trend in the binding energy values of the $H_3O_3^+$ system. Further, the energy of singlet and triplet $H_3O_3^+$ has been calculated using the BHHLYP method with 6-311++G-(2df,2p) and the MP2 method with 6-311++G(3df,3p) basis sets by varying the hydrogen bond length between H_3O^+ and O_2 (as a function of proton-transfer coordinate, O_5-H_4 distance in Scheme 1). For this purpose the neutral structure of HO_2-H_2O has been considered, and the hydrogen atom of HO_2 has been moved gradually toward the H_2O fragment in $H_3O_3^+$. The variation of the energy in going from the initial state (with O_1-H_4 hydrogen bond) structure, $(HO_2-H_2O)^+$ to the final state (with O_5-H_4 hydrogen bond) proton-transferred structure $(O_2-H_3O)^+$ is shown in Figure 2 as function of O_5-H_4 distance.

It has been observed that the total energy of singlet as well as triplet $H_3O_3^+$ reduces with increase in separation between H_3O^+ and O_2, passes through a minimum, and increases thereafter (Figure 2). The $(O_2-H_3O)^+$ system is calculated to be the most stable at ∼1.56 and ∼1.71 Å for the singlet and triplet state, respectively, as calculated using the BHHLYP method with 6-311++G(2df,2p) and MP2 with 6-311++G-(3df,3p) basis sets, which clearly denote the corresponding equilibrium hydrogen bond lengths.

The vibrational frequencies of the $H_3O_3^+$ system as calculated using the BHHLYP and MP2 methods with the 6-311++G-(3df,3p) basis set are reported in Table 4. All the vibrational frequencies reported in this table are assigned approximately in terms of the stretching, bending, and torsional modes. It is well-known that formation of a hydrogen bond generally involves shift in the frequency value of the stretching modes that are relevant to the formation of a hydrogen bond. Also, the extent of shift, in general, is directly related to the strength of a hydrogen bond. Thus, it is interesting to compare the frequency values of the relevant bonds before and after the formation of the hydrogen bond. On analysis of the BHHLYP calculated vibrational frequencies it is revealed that the stretching frequency of the O−H bond in H_3O^+ that is involved in the formation of $H_3O_3^+$ through hydrogen bonding with O_2, is red-shifted by an amount of 991 cm^{-1} (3777 cm^{-1} in H_3O^+ to 2786 cm^{-1} in $H_3O_3^+$) in the singlet state. The corresponding shift for the triplet state is 459 cm^{-1} (3777 cm^{-1} in H_3O^+ to 3317.6 cm^{-1} in $H_3O_3^+$). These singlet/triplet frequency shift values are in agreement with the larger/smaller O_1-H_4 bond length for the corresponding singlet/triplet states of $H_3O_3^+$. Again, a weaker (stronger) O_1-H_4 bond is consistent with the stronger (weaker) H_4-O_5 hydrogen bond for the singlet (triplet) state. All these parameters are directly related to the relative stability of the singlet/triplet state toward the respective dissociated products. It is to be noted that the shift in the O=O stretching mode is negligible both for the singlet (1799.8 cm^{-1} in $^1O_2$ to 1793.7 cm^{-1} in $^1H_3O_3^+$) as well as triplet (1803.0 cm^{-1} in $^1O_2$ to 1795.0 cm^{-1} in $^1H_3O_3^+$) states. From the table it is also clear that the stretch frequency value corresponding to the H_4-O_5 hydrogen bond is larger by ~100 cm^{-1} for the singlet state as compared to the triplet state, which indicates a stronger H_4-O_5 hydrogen bond in the former state. Again, it is in agreement with the higher stability of $H_3O_3^+$ with respect to its dissociation into H_3O^+ and singlet O_2.

4. Conclusion

Ab initio molecular orbital methods have been employed to study the ionization of the hydroperoxy radical−water hydrogen-bonded complex. It has been inferred that ionization of the HO_2-H_2O system results in proton transfer from HO_2 to H_2O leading to the formation of the $O_2\cdots H_3O^+$ structure. The effect of spin multiplicity on the structure and the stability of $(HO_2-H_2O)^+$ has been investigated, and its comparison with that of oxygen molecule has also been done. Similar to the O_2 molecule, the $H_3O_3^+$ system is found to be energetically more stable in the triplet state than in the singlet state. A comparison of $H_3O_3^+$ and O_2 suggests that singlet−triplet separation of O_2 is reduced by ~5.0 kcal/mol on interaction with H_3O^+. The interaction between O_2 and H_3O^+ in $H_3O_3^+$ is stronger in the singlet state with a binding energy of 12.9 kcal/mol at the UCCSD(T)/aug-cc-pVTZ level of theory as compared to that in the triplet state, for which the binding energy is 7.0 kcal/mol at the same level. The calculated hydrogen bond length for the singlet and triplet state is consistent with the corresponding binding energy value. The shift in the O−H stretching frequency and the frequency corresponding to the $O_2\cdots H_3O^+$ hydrogen bond for the singlet and triplet states are in agreement with the calculated stability trend. The ionized state of the HO_2-H_2O hydrogen-bonded complex ($O_2\cdots H_3O^+$) consists of weakly bound molecular oxygen as a fragment and might have importance in various chemical processes and aquatic life systems.

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