Uptake of OH radical to aqueous aerosol: a computational study

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The OH radical is one of the most important species influencing diverse chemical processes in the atmosphere. Yet, little is known about the hydroxyl radical solvation thermodynamics. In this paper, the hydration of OH radical is studied using quantum chemical methods. Hydrogen-bonded complexes of OH radical with water have been studied using MP2 and DFT levels of theory. Optimized structures and binding energies for $OH(H_2O)_i$ clusters were determined using cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets. It was shown that aug-cc-pVTZ results are very close to basis set limit in the DFT calculations of OH-H_2O system. Moreover, the basis set superposition error is less than 1% for the X3LYP functional and aug-ccpVTZ basis set.

1. Introduction

The OH radical has been proven to be one of the most important oxidants in the atmosphere chemical cycle (Manahan, 2000; Stumm and Morgan, 1996). It is formed by different mechanisms including photolysis of water at higher altitudes, photolysis of ozone followed by the reaction of the excited oxygen atoms with water molecules, etc. Hydroxyl radical can enter water droplets from gas phase atmosphere or can be formed in aqueous particles by decomposition of HO_2 and further reaction with ozone. Several solutes can react photochemically in aqueous particles to produce hydroxyl radical. The characterization of interaction of hydroxyl radicals with its aqueous environment is particularly important for atmospheric chemistry, as many atmospherical chemical reactions occur in or on aqueous atmospheric aerosols, cloud droplets, and thin water films on particles. The reactivity of OH radical is influenced by its hydration structure and energetics. Values of the thermodynamic parameters of solvation of OH radical are also required for understanding of its uptake on aqueous surfaces.

We present here the results of theoretical study aimed to clarify the structure and behavior of mixed OH radical and H_2O clusters. Clusters with different OH:H_2O ratio were studied. For each of the clusters several alternative local minima were found. Vibration frequencies were calculated to verify that all the obtained structures are stable points on the potential energy surfaces. The frequency data were also used to estimate enthalpies and free energies. The binding energies were corrected for the basis set superposition error by counterpoise method.

2. Computational details

Different theoretical techniques were used in the research on interaction of OH radical with water. It was first studied by MP2 and CISD techniques using DZP and TZ2P basis sets (Kim et al., 1991; Xie and Shaefer, 1993). The larger basis set 6-311++G(2d,2p) and DFT technique were used in the later work (Wang et al., 1999). It was found that the most stable OH-H_2O complex contains OH acting as a donor in a hydrogen bond to water. This interaction was found to be 1-2 KJ/mol stronger than the hydrogen bond in water dimer. B3LYP density functional technique with 6-311++G(2d,2p) basis set were used to identify ten stationary points on the potential energy surface of the OH-H_2O system (Zhou, 2002). The binding energy ~26 KJ/mol for OH-H_2O cluster was found using MP2, the energy was calculated using 6-311++G(d,p) basis set at the geometry optimized with cc-pVDZ (Hamad et al., 2002). BLYP functional was found to described incorrectly the OH-H_2O interaction. This problem was solved in BHLYP calculations resulting in value of binding energy equal to ~29 KJ/mol. The optimized geometry of OH-H_2O cluster obtained at QCISD/6-311++G(2d,2p) level of theory was used to calculate vertical excitation energies and oscillator strengths using MRCI with aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z and aug-cc-pV6Z basis sets (Schofield and Kjaergaard, 2004). The MP2/6-31++G(d,p) resuts were compared with B3LYP/6-31++G(d,p), B3LYP/6-31++G(2d,2p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,2p) calculations (Dong et al., 2005). Du et al. (2006) employed CCSD(T) with aug-cc-pVTZ basis set to scan potential energy surface of OH-H_2O cluster for the ground state and low-lying excited state for systematically selected separation distances and orientations of OH radical with respect to H_2O molecule. These results were used to parameterize polarizable Thole-type potential (Burnham and Xantheas, 2002). The new potential was fitted to describe both ground and excited states. The binding enrgies equal to 5.88 kcal/mol and 5.99 kcal/mol were obtained for CCSD(T)/aug-cc-pVTZ and new OH potential, respectively. The excited state was found to be very important in determining chemical behavior of OH radical since its energy is very close to that of the ground state.

It is well known that the accurate description of weak interactions requires treatment of electronic correlations. In the past, the calculations of hydrogen bonded structures have been performed using different functionals. However, recent investigations proved that all these functionals, including the most popular B3LYP, does not correctly account for nonbonded interactions. That is why we employed the X3LYP extended functional with improved descriptions of the equilibrium properties of hydrogen bonded and van der Waals systems (Xu et al., 2005). This functional have shown the best performance in predicting binding energy and geometry of water dimer as compared to CCSD(T) calculation with basis set extrapolated to infinity (Klopper et al., 2000). In order to estimate the quality of this functional we also made MP2 calculations on OH-H_2O cluster.

The MP2 calculations were made usung GAMESS quantum chemistry package (Gordon and Schmidt, 2005), while MP2 calculations were performed using PC GAMESS code (Nemukhin et al., 2004).

3. Results

3.1 OH-H_2O system

We first performed MP2 and X3LYP optimization and energy calculation of OH-H_2O system using cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, cc-pVQZ and aug-cc-pVQZ basis sets. All optimized structures were proved to be local minima by the presence of real frequencies only. The binding energy values were calculated as

$$E = E(\mathrm{OH}(\mathrm{H}_2\mathrm{O})_\mathrm{i}) - E(\mathrm{OH}) - iE(\mathrm{H}_2\mathrm{O}),$$

where E(OH) and $E(H_2O)$ were calculated at the optimized ground state geometries at the same level of theory.

It is generally accepted that the binding energies need to be corrected for the basis superposition error, and it is especially important for weakly bound complexes, where the BSSE correction is known to change the order of local minima from that predicted by the uncorrected results (Tzeli et al., 2001). We used counterpoise correction scheme to estimate BSSE. The counterpoise-corrected binding energy is equal to

$$E^{CP} = E - CP \ ,$$

where correction CP is expressed as

$$CP = E_{WR}^{WR}(W) - E_{WR}^{W}(W) + E_{WR}^{WR}(R) - E_{WR}^{R}(WR) \ .$$

Here, W and R denote water molecule and hydroxyl radical, respectively, and $E_Y^Z(X)$ is defined as the energy of subsystem X at geometry Y calculated using basis set Z.

Zero-point energies were calculated from the harmonic frequencies in the simplest approximation:

$$ZPE = \frac{1}{2}\sum_i h\nu_i \ ,$$

where ν_i is the frequency for i-th mode obtained at the optimized geometry. The counterpoise and zero-point corrected binding energy is equal to

$$E^{CP,ZP} = E^{CP} + ZPE \ .$$

For the OH-H_2O complex several local minima and transition states were determined, the geometry corresponding to the lowest energy is presented in Fig. 1. Table 1 represents the most important structural parameters of the complex and dipole momentum. It can be seen that for X3LYP calculations cc-pVDZ basis sets is not sufficient to describe both the distance between OH and H_2O fragments and their orientation, cc-pVTZ and cc-pVQZ basis sets describes the separation distance well, but the convergence in the orientation of water molecule in the respect to hydroxyl radical is not achieved, as can be estimated by change of <H_W-O_R> and <H_W-H_R> distances. For the aug-cc-pVXZ basis sets, the convergence in geometries and dipole momentum is attained at aug-cc-pVTZ level. The root-mean-square difference between the structures optimized by two techniques is equal to 0.005 Å. For MP2 method the convergence is slower and the larger basis set should be used. We can conclude that the results obtained by MP2/aug-cc-pVQZ and X3LYP/aug-cc-pVTZ methods are similar. At the same time, the O_W-O_R and O_W-H_R distances are slightly underestimated as compared to high level CCSD(T) predictions, which are 2.89 and 1.91 Å, respectively (Ohshima et al., 2005). The IR spectrum of OH-H_2O complex calculated at X3LYP/aug-cc-pVQZ level is presented in Fig. 2.

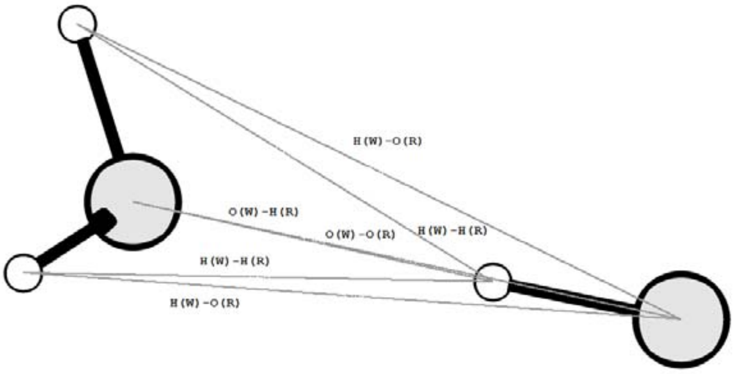

Fig. 1. The structure of optimized OH-H_2O complex.

Table1. Selected geometrical parameters (Å) and dipole momentum (D) of OH-H_2O complex

	O_w-O_R	O_W-H_R	<H_W-O_R>	<H_W-H_R>	Dipole
			X3LYP		
cc-pvdz	2.828	1.840	3.276	2.358	3.890
aug-cc-pvdz	2.858	1.874	3.432	2.490	4.081
cc-pvtz	2.854	1.870	3.360	2.434	4.002
aug-cc-pvtz	2.865	1.882	3.437	2.500	4.059
cc-pvqz	2.859	1.878	3.387	2.458	4.008
aug-cc-pvqz	2.867	1.886	3.440	2.503	4.055
			MP2		
cc-pvdz	2.862	1.883	3.352	2.432	3.976
aug-cc-pvdz	2.899	1.918	3.470	2.533	3.998
cc-pvtz	2.875	1.902	3.410	2.485	4.000
aug-ac-pvtz	2.882	1.904	3.466	2.532	4.022
cc-pvqz	2.874	1.902	3.442	2.512	4.043
aug-cc-pvqz	2.875	1.884	3.464	2.529	4.058

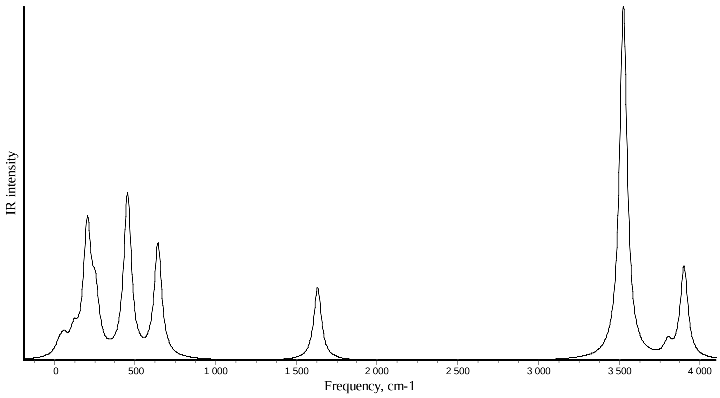

Fig. 2. Calculated IR spectrum of OH-H_2O complex.

Table 2. Binding energy E (kcal/mol), counterpoise correction CP (kcal/mol), zero-point energy (kcal/mol), counterpoise corrected energy E^{CP} (kcal/mol), counterpoise and zero-point corrected energy $E^{CP,ZPE}$ (kcal/mol) and counterpoise correction to corrected energy ratio CP/E^{CP} for OH-H_2O complex.

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
			X3LYP			
E	-9.705	-6.028	-7.431	-5.883	-6.622	-5.885
CP	-3.894	-0.280	-1.548	-0.054	-0.717	-0.033
ZPE	2.528	2.276	2.332	2.273	2.278	2.278
E^{CP}	-5.810	-5.748	-5.883	-5.829	-5.905	-5.852
$E^{CP,ZPE}$	-3.282	-3.471	-3.550	-3.557	-3.628	-3.573
CP/E^{CP}	0.401	0.047	0.208	0.009	0.108	0.005
			MP2			
E	-8.226	-5.874	-6.785	-5.938	-6.195	-5.948
CP	-2.157	-0.280	-0.778	-0.087	-0.302	-0.046
ZPE	2.554	2.274	2.348	2.263	2.200	2.282
E^{CP}	-6.070	-5.593	-6.005	-5.851	-5.892	-5.902
$E^{CP,ZPE}$	-3.515	-3.322	-3.658	-3.588	-3.692	-3.620
CP/E^{CP}	0.262	0.048	0.115	0.015	0.048	0.008

The binding energies, counterpoise corrected and zero-point corrected energies for OH-H_2O complex are presented in Table 2. It can be seen that aug-cc-pVXZ basis sets behave better than cc-pVXZ. For X3LYP the convergence is observed at the aug-cc-pVTZ level even for uncorrected binding energy (Fig. 3). At this level the basis set superposition error becomes negligible (less than 1 %). In contrast, cc-pVXZ basis sets need the BSSE correction to converge. At the same time the CP corrections is about two times less for MP2 technique and cc-pVXZ basis sets than for X3LYP. For aug-cc-pVXZ basis sets two methods behave in similar manner.

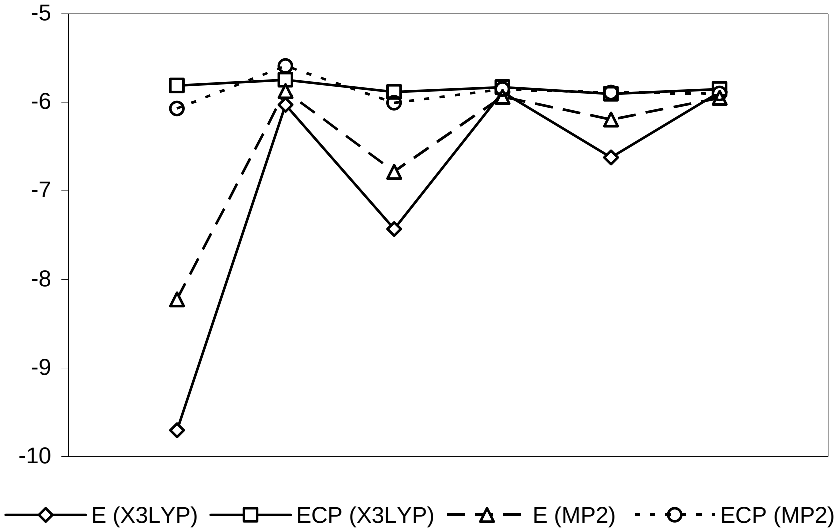

Fig. 3. Binding energy as a function of the correlation consistent basis set (cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, cc-pVQZ, aug-cc-pVQZ).

Table 3. Comparison of uncorrected binding energies calculated using different methods and basis sets.

Method	E, kcal/mol	Reference
X3LYP/aug-cc-pVTZ	-5.88	this work
CCSD(T)	-5.88	Ohshima et al., 2005
B3LYP/6-31++G(d,p)	-6.97	Dong et al., 2005
B3LYP/6-31++G(2d,2p)	-5.84	Dong et al., 2005
B3LYP/6-311++G(d,p)	-6.80	Dong et al., 2005
B3LYP/6-311++G(2d,2p)	-5.84	Dong et al., 2005
MP2/6-31++G(d,p)	-7.12	Dong et al., 2005
MP2/6-311++G(d,p)//MP2/cc-pVDZ	-6.24	Hamad et al., 2002
BLYP/6-311++G(d,p)//BLYP/cc-pVDZ	-7.65	Hamad et al., 2002
BHLYP/6-311++G(d,p)//BHLYP/cc-pVDZ	-7.04	Hamad et al., 2002
MP2/6-311++G(d,p)	-6.67	Hamad et al., 2002
BLYP/6-311++G(d,p)	-8.32	Hamad et al., 2002
BHLYP/6-311++G(d,p)	-7.22	Hamad et al., 2002
RCISD(Q)/TZ2P	-5.67	Xie and Shaefer, 1993

By this means, aug-cc-pVTZ/X3LYP method exhibits results similar to those of aug-cc-pVQZ/MP2 and aug-cc-pVQZ/X3LYP and does not need to be corrected to account for basis set superposition error. Moreover, the calculated binding energy value, 1.583 kcal/mol, is identical to that obtained using high level CCSD(T) calculation (Ohshima et al., 2005). It is seen from Table 3 that X3LYP/aug-cc-pVTZ method outperforms other techniques. So, we used this method for studying $OH(H_2O)_i$ clusters.

3.2 OH-$(H_2O)_i$ systems (i=2-5)

We performed stationary point searches for OH-$(H_2O)_i$ systems (i=2-5) using X3LYP/aug-cc-pVTZ method. The lowest energy optimized structures are presented in Fig. 4, the binding energies and hydrogen bond lengths for OH acting as donor and acceptor are listed in Table 4.

Table 4. Binding energy and structural parameters of OH-$(H_2O)_i$ clusters.

i	E, kcal/mol	Number of H-bonds	Donor	Acceptor
1	5.883	1	1.882	
2	15.022	2	1.884	2.092
3	26.848	2	1.822	1.980
4	35.029	2	1.820	1.942
5	42.988	2	1.809	1.948

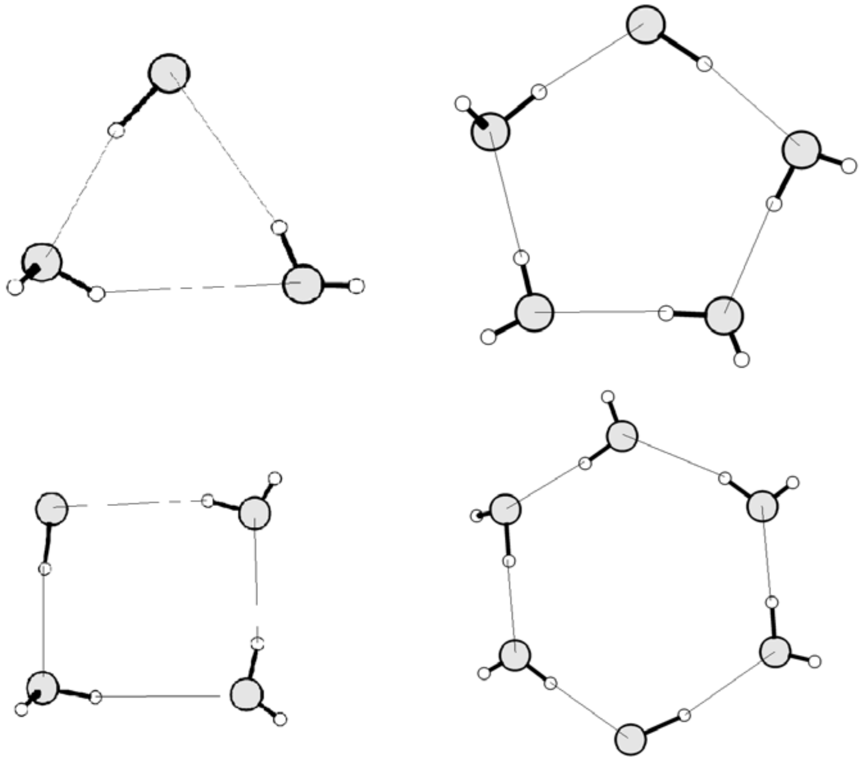

Fig. 4. The structures of optimized OH-$(H_2O)_2$, OH-$(H_2O)_3$, OH-$(H_2O)_4$ and OH-$(H_2O)_5$ complexes.

4. Conclusion

In this work, we have performed extensive *ab initio* study of the hydration of OH in aqueous clusters. Two different quantum chemical methods were employed. First, we have done MP2 calculation of OH-H_2O cluster, which is reliable enough to be considered as reference. Then we conducted DFT calculations using X3LYP functional. We used cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, cc-pVQZ and aug-cc-pVQZ basis sets. We found that convergence in energy and geometry is achieved at X3LYP/aug-cc-pVTZ level and the results of this calculation are identical to those obtained using high level CCSD(T) technique (Ohshima, et al., 2005). Moreover, at this level of theory the basis set superposition error becomes negligible. Then geometry optimization and energy calculation of larger clusters, OH-$(H_2O)_i$ (i=2-5), was conducted at X3LYP/aug-cc-pVTZ level.

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