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Can an OH Radical Form a Strong Hydrogen Bond? A Theoretical Comparison with H_2O

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Abstract: In this study, we apply UCCSD/6-31++G** to investigate the ability of an OH radical acting as a hydrogen bond acceptor with HF, HCl, and H_2O (HO...HX; X=F, Cl, OH) or as a hydrogen bond donor with H_2O and H_2S (OH...XH_2; X=O and S). We also replace OH with H_2O and make a fair comparison between them. Additionally, the counterpoise method (CP) has been used to examine the effect of basis set superposition error (BSSE). Our results reveal that OH is a stronger hydrogen bond donor but a weaker hydrogen bond acceptor than H_2O. This conclusion is independent of the correction for BSSE and can be rationalized by the NBO analysis, the results of which indicate that OH radical has a lower n_O and σ^*_{O-H} in energy than that of H_2O.

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Key words: hydrogen bond; counterpoise method; basis set superposition error; NBO; CCSD

Introduction

Although hydrogen-bonded complexes have been known for many years, they still attract a great deal of interest because of their ubiquity and fundamental importance in chemistry and biology. Copious amounts of research work are still devoted to this issue, with the attention focused on complexes formed between either two neutral molecules or a neutral molecule and an ion. There are several books dealing with hydrogen bonds from different angles,[1–3] and very recently, different aspects of these compounds have been reviewed.[4–7] However, far less attention has been paid to the hydrogen-bonded complexes involving radicals. One intriguing example is the photolysis of 2-methoxyphenol, shown in Scheme 1. According to their calculated results, Muller and coworkers concluded that the homolytic cleavage of the O—C bond did not disturb the O—H...O hydrogen bond strength.[8] Recently, studies of the O_nH radical complexes with different species have received much attention because of their importance in atmospheric chemistry.[9–20] For example, Anglada and Torrent-Scuarrat have performed theoretical calculations to investigate the possible hydrogen-bonded complexes between formic acid and an OH radical.[19] Also, it has been pointed out that the formation of intermediates or pre-reactive radical hydrogen-bonded complexes may influence considerably the kinetics of the reaction, and that the forces because of the hydrogen bonds are sufficient to influence the collision dynamics as the reagents approach each other.[21–24] The OH radical also plays a very important role in nonthermal plasma chemical reactions for decomposition of gaseous pollutants or in the synthesis of methanol from methane and is a major oxidant in many biological, environmental, and synthetic aqueous media. For example, the OH radical plays a key role in inducing free radical reactions by attacking cytosine-related compounds.[25]

Owing to the increasing importance of the O_nH radical in fundamental, atmospheric and biological approaches, in this study, we applied the smallest O_nH radicals, OH, to investigate the strength of the hydrogen bonding between OH and other neutral molecules (HF, HCl, H_2O, H_2S). We also carried out a competitive study on the hydrogen bonding strength between the OH radical and its closed-shell counterpart, H_2O. Furthermore, the counterpoise method (CP) is applied to correct for basis set superposition error (BSSE) in an attempt to examine its influence on the calculated results. The results, in combination with NBO analyses, indicate that OH is a stronger hydrogen bond donor but a weaker hydrogen bond acceptor than H_2O. Details are described in the following sections.

Theoretical Method

All calculations are done with the Gaussian 03 program.[26] We use the restricted coupled-cluster (CCSD) and unrestricted coupled-cluster (UCCSD) theoretical approaches for closed-shell

$$\Delta E[E(Q)-E(P)]=\Delta E'[E(Q^*)-E(P^*)]=-16 \text{ kJ/mol}$$
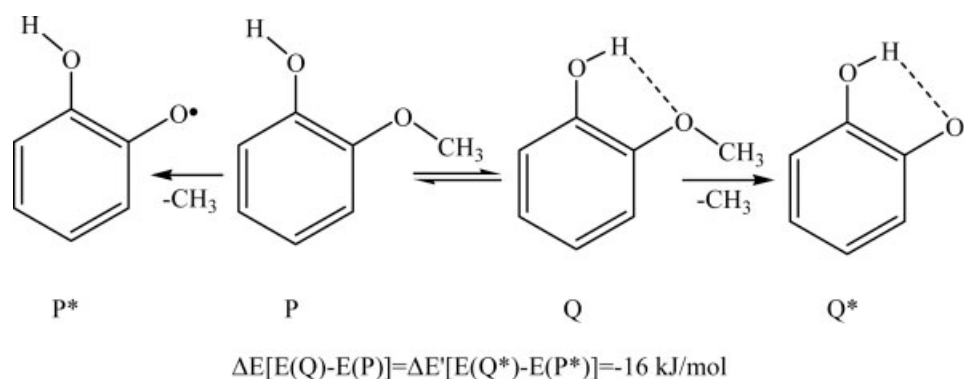
Scheme 1. The photolysis of 2-methoxyphenol.

and open-shell systems, respectively.[27,28] Both methods neglect the core electron excitations and are combined with 6-31++G** basis set. To simplify the comparison, we neglect the possibility of the formation of multiple hydrogen bonds and other conformers. All minima are checked by frequency analyses to confirm the number of imaginary frequencies as zero. All mentioned energetic values have been corrected for zero-point vibrational energy (ZPVE).

To correct for BSSE, we use the CP with full optimization (hereafter designated as CP optimized; the calculation without CP is designated as non-CP optimized).[29] BSSE is believed to be caused by the basis functions of the second unit in the associated complex, which may augment the basis functions of the first unit, resulting in lowering of the energy compared with a calculation of this unit alone. Likewise, the first unit will cause a similar error in the second. The CP proposed by Boys and Bernardi has been the most popular mean of correcting for BSSE, although several other approaches to correct this error have been discussed in the literature.[29,30] CP calculates each of the units with just the basis functions of the others (so called "ghost orbitals") and can be written as eq. (1):

$$\text{BSSE} = \sum_{i=1}^{n} \left(E_{m_f}^i - E_{m_f}^{i^*} \right) \quad (1)$$

where the E_m represent the energies of the individual monomers, with the subscript "f" denoting the monomer frozen in the geometry of the complex, and the asterisk (*) represents monomers calculated with "ghost orbitals."

The CP has proven to be somewhat controversial.[31] The origin of this controversy lies in the fact that the traditional use of CP, which incorporates an additional single-point calculation based on the previously optimized geometry.[29(b)] Since the intermolecular interactions are artificially too attractive in BSSE, CP is expected to make the complex less stable and to lengthen the intermolecular distance of the complex. Furthermore, the vibrational frequencies are generally reported on the uncorrected potential surface. This tends to make the intermolecular vibrations appear too strong, resulting in an incorrect ZPVE. A striking example is a well-defined minimum existing between acety-

lene and ozone, whereas they become repulsive with each other after CP and ZPVE corrections.[32] In search of improvement, several authors have addressed the importance of relocating stationary points in the CP-corrected potential energy surface. Furthermore, molecular orbital calculations that include CP in the optimization have been demonstrated.[33] For a brief introduction of the optimization that includes CP automatically, the CP-corrected energy of complex and interaction energy can be written as eqs. (2) and (3). More detailed discussion can be found in Dannenberg and coworkers[29(b)]

$$E_{\text{complex}}^{\text{CP}} = E_{\text{complex}} + \sum_{i=1}^{n} (E_{m_f}^i - E_{m_f}^{i^*}) \quad (2)$$

$$E_{\text{interaction}}^{\text{CP}} = E_{\text{complex}} - \sum_{i=1}^{n} E_{m_{\text{opt}}}^i + \sum_{i=1}^{n} (E_{m_f}^i - E_{m_f}^{i^*}) \quad (3)$$

where $E_{\text{complex}}^{\text{CP}}$ is the CP corrected energy of complex, E_{complex} is the energy of the complex, and $E_{m_{opt}}^i$ is the energy of the individually optimized monomer. To find a stationary point with respect to geometrical variation of the complex, the derivative of $E_{\text{complex}}^{\text{CP}}$ with respect to all internal coordinates of the complex [eq. (4)] is set equal to zero.

$$\frac{\partial E_{\text{interaction}}^{\text{CP}}}{\partial p_j} = \frac{\partial E_{\text{complex}}^{\text{CP}}}{\partial p_j} = \frac{\partial E_{\text{complex}}}{\partial p_j} + \sum_{i=1}^{n} \left(\frac{\partial E_{m_f}^i}{\partial p_j} - \frac{\partial E_{m_f}^{i^*}}{\partial p_j} \right) \quad (4)$$

where p_j is the geometric parameter of the complex. Since the energies of the optimized monomers are not a function of the complex calculation, their derivatives with respect to the geometric parameters of the complex are always zero. Force constants and vibrational frequencies can then be derived from the matrix of second derivatives (the Hessian matrix). Each element of the Hessian matrix can be calculated similar to eq. (4)

$$\frac{\partial^2 E_{\text{interaction}}^{\text{CP}}}{\partial p_j \partial p_k} = \frac{\partial^2 E_{\text{complex}}^{\text{CP}}}{\partial p_j \partial p_k} = \frac{\partial^2 E_{\text{complex}}}{\partial p_j \partial p_k} + \sum_{i=1}^{n} \left(\frac{\partial^2 E_{m_f}^i}{\partial p_j \partial p_k} - \frac{\partial^2 E_{m_f}^{i^*}}{\partial p_j \partial p_k} \right) \quad (5)$$

Table 1. Bonding Strengths, Bond lengths, Bond angles, ZPVEs, Dipole Moments and |BSSE/E_{HB}| of Hydrogen-Bonded Complexes H_2O...HX (X=F, Cl, and OH) and HOH...XH_2 (X=O, S).

	E_{HB}[a]	BSSE[b]	a	b	ZPVE	Dipole moment	|BSSE/E_{HB}| (%)[c]
H_2O...HX							
X=F	−21.72,[d] −22.84,[e] −28.76,[f] −33.47,[g] −25.94[h]	6.06,[d] 5.92[e]	1.775,[d] 1.812,[e] 1.740,[f] 1.768[g]	177.2,[d] 177.1,[e] 177.2[f]	93.33,[d] 92.43,[e] 93.69,[f] 92.95[g]	1.910,[d] 2.186,[e] 4.534[f]	27.89,[d] 25.90[e]
X=Cl	−13.31,[d] −18.67[e]	5.36[e]	2.080,[e] 1.951[f]	178.6,[e] 180.0[f]	81.54,[e] 83.18[f]	2.191,[e] 4.153,[f] 3.437[i]	40.25[e]
X=OH	−10.90,[e] −15.45,[f] −20.37[j]	4.55[e]	2.070,[e] 1.971[f]	175.8,[e] 175.6[f]	122.5,[e] 123.8[f]	2.196,[e] 3.205[f]	41.71[e]
HOH...XH_2							
X=O	−10.90,[e] −15.45,[f] −20.37[j]	4.55[e]	2.070,[e] 1.971[f]	175.8,[e] 175.6[f]	122.5,[e] 123.8[f]	2.196,[e] 3.205[f]	41.71[e]
X=S	−3.16,[e] −6.56[f]	3.40[f]	2.774,[e] 2.588[f]	161.1,[e] 160.1[f]	103.6,[e] 103.9[f]	1.324,[e] 1.895[f]	100.1[e]

Energy is expressed in kJ/mol, bond length in Å, angle in °, and dipole moment in debye.

[a] $E_{HB} = E$ (hydrogen-bonded complex) − E(hydrogen bond donor) − E(hydrogen bond acceptor).

[b] This value is calculated according to eq. (3).

[c] We adopt the CP-optimized E_{HB}.

[d] The CP optimized results of CCSD/cc-pVTZ.
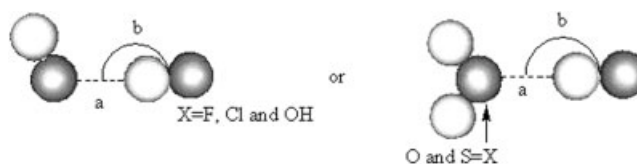
[e] The CP optimized results of CCSD/6-31++G**.

[f] The non-CP optimized results of CCSD/6-31++G**.

[g] The MP2/D95++** CP optimized results [ref. 29(b)].

[h] The experimental value, [ref. 34(a)].

[i] The experimental value, [ref. 34(b)].

[j] The experimental value, [ref. 34(c)].

In general, any molecular property, such as dipole moment, one-electron density, electric field values at nuclei, electrostatic potentials, polarizabilities, IR intensity, etc., can be defined as a derivative of the energy, and thus can be calculated by a variant of eq. (4). Although other correction methods for BSSE have been used in the literature, none of these have been programmed to obtain analytical derivatives of the BSSE-free surface.[30]

Finally, to comprehend the properties of hydrogen bonds formed by OH radical, we also perform NBO analyses according to the CP optimized complexes and individual optimized donors and acceptors.[34] In this study, CCSD/6-31++G** is carried out for the geometry optimization, followed by the frequency analysis to confirm that the species is at least a local minimum. The NBO analysis is then performed according to the saved information in the scratch file (.chk in Gaussian 03).

Results and Discussion

The Hydrogen-Bonded Complexes Involving H₂O

At first place, H_2O...HF is taken as a prototype and the results of the medium-sized basis set 6-31++G** are compared with those of Dunning's correlation consistent basis set (cc-pVTZ).[35] Such a comparison seems to be necessary since Dannenberg and coworkers have pointed out that the CP-optimized results for the same system might be dependent on the quality of the basis set (6-31G** versus D95++** at the MP2 level).[29(b)] Accordingly, both of our CCSD/6-31++G** and CCSD/cc-pVTZ results are listed in Table1. As shown in Table 1, the average difference between the results of 6-31++G** and those of cc-pVTZ is only 4.174%. Therefore, the economic basis set 6-31++G** seems to provide trustable results and will be applied throughout the text. Table 1 summarizes the physical parameters of hydrogen-bonded complexes H_2O...HX (X=F, Cl and OH) and HOH...XH_2 (X=O, S), including bonding strengths, bond lengths, ZPVEs, dipole moments, etc. In addition, the differences between CP optimized and non-CP optimized results are also listed. Applying CP for correcting BSSE results in an increase (decrease) of the hydrogen bonding length (strength). Furthermore, CP effectively affects the dipole moment of the hydrogen-bonded complex. The most significant case should be ascribed to FH...OH_2, for which the dipole moments are calculated to be 2.186 and 4.534 Debye for the CP and non-CP optimized complexes, respectively. The difference of ZPVE

Table 2. Bonding Strengths, Bond lengths, Bond angles, ZPVEs, Dipole Moments and $|BSSE/E_{HB}|$ of Hydrogen-Bonded Complexes HO...HX (X=F, Cl, and OH) and OH...XH$_2$ (X=O, S).

	E_{HB}[a]	BSSE[b]	a	b	ZPVE	Dipole moment	$\|BSSE/E_{HB}\|$ (%)[c]
HO...HX							
X=F	−13.72, −17.39[d]	3.66	1.941, 1.875[d]	174.9, 174.9[d]	54.89, 55.44[d]	1.854, 3.662[d]	26.69
X=Cl	−6.64, −10.45[d]	3.82	2.243, 2.117[d]	180.0, 180.0[d]	45.49, 46.03[d]	1.854, 3.317[d]	57.51
X=OH	−7.02, −9.83,[d] −10.46[e]	2.81	2.187, 2.108,[d] 2.234,[e] 2.033,[f] 2.107[g]	163.3, 163.3,[d] 164.1,[e] 158.5,[f] 161.4[g]	85.25, 85.59[d]	2.197, 1.718[d]	40.05
OH...XH$_2$							
X=O	−14.98, −19.21,[d] −19.87[e]	4.23	2.020, 1.939,[d] 2.031[e]	178.7, 178.7,[d] 180.0[e]	87.00, 88.52[d]	1.855, 4.437[d]	28.24
X=S	−4.02, −6.61[d]	2.58	2.748, 2.572[d]	175.0, 179.9[d]	69.33, 70.43[d]	1.324, 3.108[d]	64.22

Energy in kJ/mol, bond length in Å, angle in ° and dipole moment in debye.

[a] E_{HB} = E (hydrogen-bonded complex) − E (hydrogen bond donor) − E(hydrogen bond acceptor).
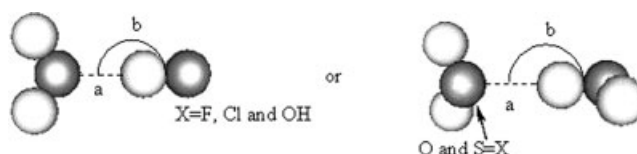[b] Calculated according to eq. (3).
[c] We adopt the CP optimized E_{HB}.
[d] The non-CP optimized results.
[e] Calculated by non-CP RASSCF method, [ref. 17(c)].
[f] Calculated by non-CP UB3LYP/6-311++G(2d,2p), [ref. 17(a)].
[g] Calculated by non-CP CISD/TZ2P, [ref. 17(b)].

between CP optimized and non-CP optimized complexes is calculated to be on average 1.16 kJ/mol with ZPVE of the non-CP optimized complex always larger than that of the CP optimized complex. Note that the largest difference in ZPVE occurs in the ClH...OH$_2$ complex.

In 1996, Dannenberg and coworkers developed a method to incorporate CP into the optimization and showed the differences between CP optimized and non-CP optimized results in three prototypes (HF/HCN, HF/H$_2$O, HCCH/H$_2$O) at the MP2 level.[29(b)] The CCSD method applied in the current study takes the advantage of greater electron correlation to calculate the complex H$_2$O...HF and thus may be considered as an improved method compared with the previous CP-optimized results. Data for both results are listed in Table 1. Apparently, the differences are on average 16.51%. It is thus concluded that electron correlation can moderately influence the CP-optimized results. Comparing with the experimental strength (−25.94 kJ/mol) of H$_2$O...HF, the CP-optimized CCSD method seems to underestimate the hydrogen bond strength regardless the basis sets.[34(a)] This may be mainly due to the fact that CP overemphasizes BSSE. It is clear that the formation of a complex requires certain degrees of charge transfer and/or charge polarization. Therefore, partial borrowing of the basis functions is necessary to reflect the chemical reality. However, CP treats the total borrowing of the basis functions as BSSE, resulting in an overemphasis of BSSE. For example, prior to the CP correction, Masamura analyzed some ion-hydrate clusters and found that interaction energies computed with basis set (e.g. augmented-polarized-double-zeta) were in closer agreement with that using the complete basis-set. Conversely, the deviation was larger after the CP correction.[36]

The Hydrogen-Bonded Complexes Involving OH Radical

Table2 lists the physical parameters of hydrogen-bonded complexes HO...HX (X=F, Cl and OH) and OH...XH$_2$ (X=O, S), including bonding strengths, bond lengths, ZPVEs, dipole moments, etc. In addition, the differences between CP optimized and non-CP optimized results are also listed. As expected, the length (strength) of the hydrogen bond increases (decreases) upon introducing CP to correct BSSE. Furthermore, it is found that CP can affect the dipole moment of the hydrogen-bonded complex significantly, as supported by the dipole moments of complex H$_2$O...HO, calculated to be 1.855 and 4.437 Debye for the CP and non-CP optimized complexes, respectively. As revealed in Table 2, the difference of the ZPVE is on average 0.81 kJ/mol between CP optimized and non-CP optimized complexes, and the ZPVE of the non-CP optimized complex is always larger than that of the CP optimized complex. Note that the largest difference in ZPVE occurs in the H$_2$O...HO complex. Of prime importance is that the Mulliken charges of H are calculated to be 0.3169 and 0.3407 for the OH radical and H$_2$O, respectively, implying that the hydrogen atom in the OH radical possesses a proton character similar to that of H$_2$O. We thus can view this type of hydrogen bond as a classical picture, in which

Table 3. The Energies of σ^*_{X-H} of the Donor and n_O of H_2O or OH, $E^{(2)}$ and occupation of σ^*_{X-H} in the XH...OH and XH...OH₂ systems (X=F, Cl, and OH).

	$E_{\sigma^*X-H}{}^a$	$E_{n_O}{}^a$	$E^{(2)}$ of $\sigma^*_{X-H} \leftrightarrow n_O$	Occupation of σ^*_{X-H}
HO...HX				
X=F	0.7810	−0.5610	1.63	0.0104
X=Cl	0.4539	−0.5610	12.94	0.0059
X=OH	0.8058	−0.5610	14.49	0.0049
H₂O...HX				
X=F	0.7810	−0.5057	72.58	0.0202
X=Cl	0.4539	−0.5057	31.75	0.0118
X=OH	0.8058	−0.5057	32.13	0.0088

^{a}Values are expressed in eV.

a hydrogen bond is formed by a pair of closed-shell molecules, namely a proton donor with a pertinent hydrogen atom covalently bound to an electronegative atom X and an acceptor Y containing an electronegative atom with at least one lone pair electrons. As the two molecules approach each other, the hydrogen atom forms a sort of "bridge" between them. Accordingly, the OH radical can form a strong hydrogen bond as long as it acts as the proton donor with respect to H_2O. This viewpoint is also true even if the complex is corrected for BSSE and ZPVE. When OH acts as a hydrogen bond donor, the energies of the hydrogen bond (E_{HB}) are calculated to be −14.98 and −4.00 kJ/mol for the acceptor H_2O and H_2S, respectively, the results of which are well correlated with the relative basicity of O and S atoms upon acting as a hydrogen bond acceptor. In contrast, as the OH radical acts as a hydrogen bond acctepor, E_{HB} are calculated to be −13.72, −6.636, −7.02 kJ/mol for the proton donors HF, HCl, and H_2O, respectively. This trend is essentially the same as in the case of its closed-shell analogue, H_2O.

Several comments can be made upon comparison of Tables 1 and 2. First, BSSE is found to be larger in the hydrogen-bonded complex containing H_2O than that in the complex with the OH radical. This may be due to the fact that the number of basis functions in OH is a smaller radical than that in H_2O, such that HF, HCl, or H_2O is influenced by fewer basis functions in the XH...OH complexes. Similarly, in comparison to the H_2X...HOH complexes (X=O, S), H_2O (or H_2S) is influenced by fewer basis functions in the H_2X...HO complexes. Secondly, the OH radical is found to be a stronger hydrogen bond donor but a weaker hydrogen bond acceptor than that of H_2O. For example, E_{HB} are calculated to be −14.98 and −10.90 kJ/mol for the OH radical and H_2O, respectively, upon forming a complex with the hydrogen bond acceptor H_2O. In contrast, E_{HB} are estimated to be −13.72 and −22.84 kJ/mol for the OH radical and H_2O, respectively, upon bonding with the hydrogen bond donor HF. Furthermore, it should be noted that the value of BSSE is <6 kJ/mol in all studied systems. To explore the importance of BSSE in this approach, we intuitively divide BSSE by the CP optimized E_{HB} and summarize the results in Tables 1 and 2. One thus can expect $|BSSE/E_{HB}|$ to be increasing as the contribution of BSSE increases or E_{HB} decreases. For example, E_{HB} are calculated to be −22.84 and −13.31 kJ/mol for

FH...OH₂ and ClH...OH₂, respectively, while the corresponding $|BSSE/E_{HB}|$ are 25.90 and 40.25%. Furthermore, while E_{HB} is only −3.16 kJ/mol in the case of the HOH...SH₂ complex, its $|BSSE/E_{HB}|$ is >100%. That is to say, BSSE must be taken into account if the weak hydrogen bonding is to be described properly.

NBO Analysis

As discussed above, we can qualitatively conclude that the OH radical is a stronger hydrogen bond donor but a weaker hydrogen bond acceptor than H_2O. From a more quantitative approach, we thus perform NBO analyses in an attempt to render a rationalization.[37] Note that except for the electrostatic interaction, which is a well-known factor in calibrating the hydrogen bond, insights into the hydrogen bonding property can also be gained by other factors. For example, Bickelhaupt et al. has pointed out that a hydrogen bond can be formed by the interaction of the lone pair of the acceptor atom Y with the unoccupied σ^* orbital of the X—H donor.[38] Accordingly, a hydrogen bond can be formed between HF and H_2O via the orbital interaction between σ^*_{H-F} and n_O. Since the interaction energy of two orbitals should be inversely proportional to the energy separation, with the assistance of NBO analyses, we then obtain the energies of the incorporated orbitals as well as their interaction energies according to the second perturbation theory. Taking the orbital interaction between σ^*_{H-F} and n_O as an example, the interaction energy can be expressed in eq. (6) according to the second perturbation theory.

$$E^{(2)} = 2\frac{\langle \sigma^*_{H-F}|H_{int}|n_O\rangle^2}{E_{\sigma^*} - E_n} \tag{6}$$

where H_{int} is the interacting Hamiltonian, E_{σ^*} and E_n are the energies of σ_{H-F^*} and n_O, respectively. "2" in the above equation indicates the number of electrons in the n_O orbital.

As summarized in Tables 3 and 4, the results clearly show that the OH radical possesses a lower n_O and σ^*_{O-H} in energy than H_2O (Scheme 2 for the orbital configuration). When the lone pair n_O is lower in energy, it is rather difficult for it to interact with other unoccupied orbitals, so the OH radical can be considered a weaker hydrogen bond acceptor than H_2O. In con-

Table 4. The Energies of σ^*_{O-H} of H_2O or OH and n_X of the Acceptor, $E^{(2)}$ and Occupation of σ^*_{O-H} in the H_2X...HO and H_2X...HOH systems (X=O and S).

	$E_{\sigma^*O-H}{}^a$	$E_{n_x}{}^a$	$E^{(2)}$ of $\sigma^*_{O-H} \leftrightarrow n_X$	Occupation of σ^*_{O-H}
OH...XH₂				
X=O	0.7441	−0.5057	15.12	0.0042
X=S	0.7441	−0.3886	7.35	0.0031
HOH...XH₂				
X=O	0.8058	−0.5057	32.13	0.0088
X=S	0.8058	−0.3886	12.52	0.0051

^{a}Values are expressed in eV.

$\sigma^*_{\text{O-H}}$ ——— 0.8058 ——— - - - ——— 0.7441 ———

n_{O} ——— -0.5057 ——— - - - ——— -0.5610 ———
H_2O OH radical
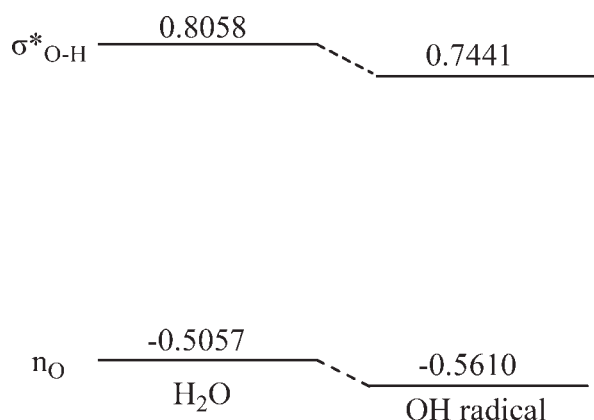
Scheme 2. The energies (in eV) of n_{O} and $\sigma^*_{\text{O-H}}$ of H_2O and OH radical.

trast, when the unoccupied orbital $\sigma^*_{\text{O-H}}$ is lower in energy, its interaction with other occupied orbitals should be facile, such that the OH radical may be realized as a stronger hydrogen bond donor than H_2O. Initially, the occupation of $\sigma^*_{\text{X-H}}$ should be zero in the donor. As the orbital interaction energy ($E^{(2)}$, Tables 3 and 4) increases, the occupation probability of $\sigma^*_{\text{X-H}}$ in the complex increases accordingly. For example, in the FH...OH_2 hydrogen-bonded complex, the occupation of $\sigma^*_{\text{H-F}}$ is 0.0202, and $E^{(2)}$ ($\sigma^*_{\text{H-F}} \leftrightarrow n_{\text{O}}$) is 72.58 kJ/mol. In comparison to FH...OH_2, the occupation of $\sigma^*_{\text{H-Cl}}$ is smaller (0.0118) in the ClH...OH_2 complex, as also indicated by the smaller $E^{(2)}$ ($\sigma^*_{\text{H-Cl}} \leftrightarrow n_{\text{O}}$) of 31.75 kJ/mol. Finally, E_{HB} of FH...OH_2 and ClH...OH_2 are calculated to be -13.72 and -6.64 kJ/mol, respectively, implying a good correlation between $E^{(2)}$ ($\sigma^*_{\text{H-X}} \leftrightarrow n_{\text{Y}}$) and E_{HB}. However, there is some inconsistency in Table 1 and 2 if we compare the hydrogen bond strength only by $E^{(2)}$. Note that in addition to the orbital interaction energy ($E^{(2)}$), there are other factors, such as electrostatic interaction, can influence the hydrogen bond strength as well. For simplicity, we make a fair comparison of the hydrogen bond strength via the interaction energy under the same conditions. For example, OH or H_2O acts as the acceptor with respect to HF, and likewise, HF or HCl acts as the donor with respect to H_2O.

Conclusion

In summary, we apply UCCSD/6-31++G** to investigate the ability of the OH radical to act as a hydrogen bond acceptor with HF, HCl and H_2O (HO...HX; X=F, Cl, OH) and as a hydrogen bond donor with H_2O and H_2S (OH...XH_2; X=O and S). We also replace OH with H_2O and compare them. Additionally, we use the CP to check the effect of BSSE.[29] Since the calculated Mulliken charges of H in the OH radical are similar to that of H_2O, the hydrogen bonding between OH and other neutral molecules can be viewed as a classical picture, consisting of a hydrogen bond formed by a pair of closed-shell molecules. According to our results, CP significantly affects the bond length, E_{HB}, and dipole moment of a hydrogen-bonded

complex. Based on the UCCSD/6-31++G** results, the OH radical can form a strong hydrogen bond with H_2O when it acts as the donor. The absolute value, $|\text{BSSE}/E_{\text{HB}}|$, increases upon decreasing E_{HB}, and it is >100% in the weakest complex, HOH...SH_2, manifesting the importance of incorporating BSSE if the weak hydrogen bonding is to be described properly. Our results also lead to the conclusion that OH is a stronger hydrogen bond donor but a weaker hydrogen bond acceptor than H_2O. As for a rationalization, OH radical possesses a lower n_{O} and $\sigma^*_{\text{O-H}}$ in energy than H_2O according to the NBO analysis.[33] In agreement with Fonseca's point of view,[37] $E^{(2)}$ ($\sigma^*_{\text{H-X}} \leftrightarrow n_{\text{Y}}$) is a key factor to influence the strength of a hydrogen bond. To the best of our knowledge, this is the first time that CP-optimization has been incorporated in hydrogen-bonded complexes containing an OH radical. We believe that the results should spark a broad spectrum of interest in the fields of atmospheric and biological chemistry.

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