Influence of Substitution, Hybridization, and Solvent on the Properties of C−HO Single-Electron Hydrogen Bond in CH_3-H_2O Complex

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Received: October 29, 2007; Revised Manuscript Received: February 19, 2008

The effect of substitution, hybridization, and solvent on the properties of the C···HO single-electron hydrogen bond has been investigated with quantum chemical calculations. Methyl radical, ethyl radical, and vinyl radical are used as the proton acceptors and are paired with water, methanol, HOCl, and vinyl alcohol. Halogenation (Cl) of the proton donor strengthens this type of hydrogen bond. The methyl group in the proton donor and proton acceptor plays a different role in the formation of the C···HO single-electron hydrogen bond. The former is electron-withdrawing, and the latter is electron-donating, both making a constructive contribution to the enhancement of the interaction. The contribution of the methyl group in the proton acceptor is larger than that in the proton donor. The increase of acidity of the proton is helpful to form a single-electron hydrogen bond. As the proton acceptor varies from the methyl radical to the vinyl radical, the interaction strength also increases. The solvent has an enhancing influence on the strength of the C···HO single-electron hydrogen bond. These factors affect the C···HO single-electron hydrogen bond in a similar way that they do other types of hydrogen bonds.

1. Introduction

Hydrogen bonding is an important molecular interaction between a hydrogen atom with a partial positive charge and an electronegative region in a proton-acceptor molecule. Because of its crucial roles in chemistry, physics, and biology,[1–3] hydrogen bonding has attracted extensive attention from researchers. Conventional hydrogen bonding is usually presented in form of X−H···Y, where X and Y are F, O, or N elements. Accompanied with in-depth studies, other types of hydrogen bondings have also been proposed during the past few decades. For example, C−H hydrogen bonds, π hydrogen bonds, dihydrogen bonds, anion hydrogen bonds, and single-electron hydrogen bonds have been proposed. For the C−H hydrogen bond, the proton donor is a hydrogen atom adjoined to carbon atom.[4] For the π hydrogen bond, the proton acceptor is a π system.[5] For the dihydrogen bond, the proton acceptor is a hydrogen atom with a partial negative charge.[6] For the anion hydrogen bond, the proton acceptor is an anion.[7]

Beside the above closed-shell hydrogen bonds, open-shell hydrogen-bonded systems also exist. These open-shell hydrogen bonds are of importance in regulating the electron transfer in many enzymatic systems[8,9] and determining the chemical properties of many radical species, such as bond dissociation energies and reduction/oxidation potentials.[10] As a radical is taken as a proton acceptor, the open-shell hydrogen bond is named as a single-electron hydrogen bond. In the single-electron hydrogen bond, methyl radical (CH_3) is often taken as a proton acceptor because it is a simple prototype for a wide class of organic radicals and plays a key role as an intermediate in the field of chemistry and biochemistry.[11,12] Up to now, the investigated single-electron hydrogen-bonded complexes have been CH_3-HF,[13–15] CH_3-HCl,[16] CH_3-HBr,[16] CH_3-H_2O,[17] CH_3-CH_4,[18] $CH_3-C_2H_2$,[13] CH_3-HCN,[19] and CH_3-HNC.[19] Wang et al. evaluated the single-electron hydrogen bonds in CH_3-HF, and $CH_3-C_2H_2$ complexes had similar characteristics to the conventional hydrogen bond,[13] such as a red shift of X−H stretching frequency upon formation of a single-electron hydrogen bond. Igarashia and co-workers studied the finite temperature effect on the hyperfine coupling constant of CH_3-H_2O and CH_3-HF complexes.[15,17] Tang and Shi elucidated that the blue-shifted single-electron hydrogen bond in the CH_3-HCN complex and the red-shifted single-electron hydrogen bond in the CH_3-HNC complex have no essential difference.[19]

The properties of hydrogen bonds are not only dependent on the properties of X, Y, and H but related with other factors as well, such as substitution, hybridization, and solvation. In C−H···O, C−H···N, C−H···F, and C−H···S hydrogen bonds, it was found that their strengths increase in the following sequence: $C(sp^3)-H < C(sp^2)-H < C(sp)-H$.[20–23] The presence of an electron-withdrawing group in the proton donor strengthens the hydrogen bond,[21] while the presence of an electron-withdrawing group in the proton acceptor weakens the hydrogen bond.[22] The effect of solvent on the strength of the hydrogen bond is more complicated. For example, the interaction between 4-nitrophenylnitromethane and triethylamine increases in the solvent, [24] while the interaction in a pyrrole−hydrogen cyanide complex decreases in the solvent.[25] However, a study on the effect of substitution, hybridization, and solvent on the properties of a single-electron hydrogen bond has not been reported. Considering that water is an ubiquitous solvent in biological systems, it is very necessary to investigate the effect of these factors on the interaction of the methyl radical with a water molecule (in the CH_3-H_2O complex). Such a study would be helpful for understanding the stabilization and functions of the methyl radical in biological systems.

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10.1021/jp710414g CCC: $40.75

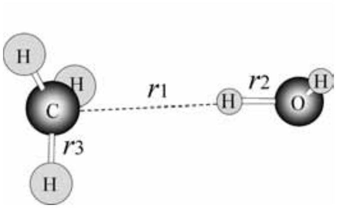

Figure 1. Optimized structure of the CH_3-H_2O complex.

Thus, the goal of this work is to investigate the radicals of methyl, ethyl, and vinyl as the proton acceptors and water, methanol, hypochlorous acid, and vinyl alcohol as the proton donors to have deeper insight into the properties of C···HO single-electron hydrogen bonds. The Bader theory and natural bond orbital (NBO) analysis are applied to characterize such interactions. The aim of this study is also to examine if the effects of substitution, hybridization, and solvent on the interaction are similar to those on the other types of hydrogen bonds.

2. Computational Details

All of the complexes and monomers were fully optimized at the UMP2/6-311++G(3df,2pd) level and UB3LYP/aug-cc-pVTZ level developed by Dunning and co-workers.[26–30] Harmonic frequency analyses were performed at the same levels to confirm that these structures were local minima on the energy surfaces. The interaction energies were corrected with the basis set superposition error (BSSE). The BSSE was evaluated using the counterpoise method of Boys and Bernardi.[31] Single-point energy calculations for the UMP4(SDQ)/6-311+G(d,p) optimized geometries were also carried out with UMP4(SDQ)/aug-cc-pVTZ method. The atoms-in-molecules (AIM) theory of Bader[32] was applied to find the bond critical points (BCP)[33] and to analyze them in terms of electron densities and their Laplacians. The AIM calculations were carried out using the AIM2000 program.[34] The NBO analyses were carried out using the NBO package included in the Gaussian 03 suite of programs.[35] The calculations in solutions were performed with the conductor polarized continuum model (CPCM)[36] at the UB3LYP/aug-cc-pVTZ level. All calculations were carried out with the Gaussian 03 program.[37]

3. Results and Discussion

Figure 1 shows the optimized structure of the CH_3-H_2O complex. The C···HO single-electron hydrogen bond in the CH_3-H_2O cluster is a weak interaction; thus, it is crucial to select a proper method for calculating the interaction energy. To determine the influence of theoretical methods and basis sets on the complexation energy, we performed calculations of the CH_3-H_2O complex with UB3LYP, UMP2, UMP4(SDQ), and UQCISD(T) theories with various basis sets. The results of the complexation energies, together with bond lengths, are summarized in Table 1. For the UMP2 method, it can be seen that the complexation energy and bond lengths are sensitive to the used basis sets as the size of basis sets is smaller than 6-311++G(2df,2p), while they are insensitive to the used basis sets as the size of basis sets is larger than 6-311++G(2df,2p). This is consistent with the conclusion that it is necessary to use a sufficiently flexible basis set, such as 6-311++G(2df,2p), to get reliable interaction energies for open-shell hydrogen bonds.[38] As the result of the MP4 method with two different basis sets is compared, it is clear that the basis sets also have a big effect on the interaction energy. As the used basis set is aug-cc-pVTZ, the complexation energy is calculated to be 1.35, 1.54, 1.42, and 1.58 kcal/mol for UB3LYP, UMP2, UMP4(SDQ), and UQCISD(T) methods, respectively. It is seen that the complexation energy calculated with the UMP2/aug-cc-pVTZ method is almost equal to that with the UQCISD(T) method, and its difference with that of UMP4(SDQ) method is also small. As the 6-311+G(d,p) basis set is adopted, the complexation energy and bond lengths with the UMP2 method are very close to those with the UMP4(SDQ) method. With these comparisons in hand, together with the consideration of computation cost, the UMP2/6-311++G(3df,2pd) method was selected to investigate single-electron hydrogen bonds of larger systems. As compared to the results of UB3LYP/aug-cc-pVTZ and UMP4/aug-cc-pVTZ, it is found that the UB3LYP/aug-cc-pVTZ is also proper to describe the complexation energy and bond lengths of the CH_3-H_2O complex. Thus, the UB3LYP/aug-cc-pVTZ method is also used in this paper for some occasions.

TABLE 1: Calculated Complexation Energy (ΔE, kcal/mol) and Bond Lengths (r, Å) of the CH_3-H_2O Complex with Different Methods[a]

methods	ΔE	$r1$	$r2$	$r3$
UB3LYP/aug-cc-pVTZ	1.35	2.382	0.966	1.078
UMP2/6-31G+(d)	1.09	2.464	0.973	1.080
UMP2/6-31+G(d,p)	1.05	2.496	0.965	1.076
UMP2/6-311+G(d,p)	1.06	2.513	0.961	1.080
UMP2/6-311++G(d,p)	1.06	2.524	0.961	1.080
UMP2/aug-cc-pVDZ	1.27	2.431	0.968	1.088
UMP2/6-311++G(2d,2p)	1.29	2.431	0.961	1.074
UMP2/6-311++G(2df,2p)	1.33	2.415	0.962	1.075
UMP2/6-311++G(3df,2pd)	1.39	2.414	0.962	1.075
UMP2/aug-cc-pVTZ	1.54	2.383	0.965	1.076
UMP4(SDQ)/6-311G+(d,p)	0.99	2.543	0.961	1.083
UMP4(SDQ)/aug-cc-pVTZ	1.42			
UQCISD(T)/aug-cc-pVTZ	1.58			

[a] Note: The ΔE with UMP4(SDQ)/aug-cc-pVTZ and UQCISD(T)/aug-cc-pVTZ methods is calculated with single-point energy.

3.1. Effect of Substitution. The effect of substitution in the proton donor and proton acceptor on the strength of the hydrogen bond is often the subject of investigation on hydrogen bonds. Taking the O···HO conventional hydrogen bond in a dimethyl sulfoxide (DMSO)−methanol complex as an example, it was found that the methyl groups in DMSO and methanol enhance the strength of the O···HO H-bond.[39] Thus, the hydrogen atom of the methyl radical and water in the CH_3-H_2O complex is replaced with a methyl group, respectively. The structures of the CH_3-HOCl complex are also optimized to compare with that of the CH_3-HOCH_3 complex. Table 2 presents the calculated C···H binding distance, O−H bond length, binding energy, OH stretching frequency, stabilization energy, methyl charge transfer, electron density, and Laplacian of electron density in the four complexes (CH_3-H_2O, CH_3-HOCH_3, CH_3-HOCl, and $CH_3CH_2-H_2O$) at the UMP2/6-311++G(3df,2pd) level.

For the CH_3-H_2O complex, the bond angle ∠C···H−O is 169° and the C···H binding distance is 2.414 Å; this intermolecular contact is shorter than the sum of the van der Waals radii (2.6−3.0 Å). As the H atom of the methyl radical or water molecule in the CH_3-H_2O complex is substituted with a methyl group or Cl atom, the C···H binding distance decreases. The decrease is largest in the CH_3-HOCl complex (0.245 Å) and smallest in the CH_3-HOCH_3 complex (0.053 Å). The decrease of the C···H binding distance indicates that these substitutions lead to an enhancement of the C···HO single-electron H-bond.

Selected bond lengths for the four complexes and their submolecules are summarized in Table 2. Inspection of this table

TABLE 2: Calculated Bond Lengths (r), Binding Energy (ΔE), OH Stretching Frequency (v), Stabilization Energy (E), Methyl Charge Transfer (Δq), Electron Density (ρ), and Laplacian of Electron Density ($\nabla^2\rho$) for Four Complexes at the UMP2/6-311++G(3df,2pd) Level

	CH_3-H_2O	CH_3-HOCH_3	CH_3-HOCl	$CH_3CH_2-H_2O$
r(C···H) (Å)	2.414	2.362	2.169	2.313
r(O−H)[a] (Å)	0.962 (0.958)	0.962 (0.958)	0.973 (0.965)	0.963 (0.958)
ΔE[b] (kJ/mol)	−5.83 (−5.96)	−6.64 (−6.49)	−11.47 (−10.92)	−9.19 (−8.93)
v(O−H)[a] (cm^{-1})	3835 (3875)	3837 (3908)	3657 (3817)	3807 (3875)
E_{ij}[c] (kJ/mol)	9.20	12.77	29.78	11.54
E_{ij}[d] (kJ/mol)	3.19	5.12	7.05	3.86
Δq[e] (e)		−0.0051		0.0157
ρ(C···H)	0.010	0.011	0.017	0.013
$\nabla^2\rho$(C···H)	0.032	0.034	0.045	0.039

[a] Data in brackets are from water, methanol, and HOCl, respectively. [b] Data in brackets are calculated with single-point energy. [c] The E_{ij} is the stabilization energy due to the n(C)→σ*(O−H) orbital interaction. [d] The E_{ij} is the stabilization energy due to the σ(O−H)→n*(C) orbital interaction. [e] The methyl charge transfer Δq is a difference between the methyl charge in the complex and that in the respective monomer.

indicates that the interaction results in an elongation of the OH group bonded to the C atom of the radicals. In the three CH_3 complexes, the elongation ranges between 0.004 and 0.008 Å. The elongation of the OH bond is greatest in the CH_3-HOCl complex (0.008 Å). The elongation of the O−H bond results in a red shift of the OH stretching frequency. The changes of OH stretching frequencies are consistent with those of O−H bond lengths. The red shift of the OH stretching frequency is 40, 71, 160, and 68 cm^{-1} for the CH_3-H_2O, CH_3-HOCH_3, CH_3-HOCl, and $CH_3CH_2-H_2O$ complexes, respectively.

The interaction energies of the four clusters were also calculated with the UMP4(SDQ)/aug-cc-pVTZ method. The results are also given in Table 2. It is seen in Table 2 that the results calculated with the UMP4(SDQ)/aug-cc-pVTZ method are very close to those calculated with the UMP2/6−311++G(3df,2pd) method for each complex, and the change of the interaction energies is similar for the two methods. Here, we only analyze the results with UMP2/6-311++G(3df,2pd) method. For the CH_3-H_2O complex, the interaction energy of the C···HO single-electron H-bond is −5.83 kJ/mol, which is in absolute value smaller than −12.87 kJ/mol in the CH_3-HF complex and larger than −4.02 kJ/mol in the CH_3-HCCH complex (MP2/aug-cc-pVDZ).[13] The result shows that the strength of the single-electron H-bond is also related to the acidity of the proton. As in other types of hydrogen bonds, the more the acidity of the proton is, the stronger the hydrogen bond is. As the hydrogen atom in water is replaced with a methyl group and chlorine atom (in the CH_3-HOCH_3 and CH_3-HOCl complexes), the hydrogen-bonded energy increases. Here, the chlorine atom is electronegative; thus, the methyl group in methanol also has a similar effect. However, the electronegativity of the methyl group in methanol is smaller than that of the chlorine atom in HOCl. The interaction energy is thus larger in the CH_3-HOCl complex. As compared with −5.83 kJ/mol of the CH_3-H_2O complex, the interaction energy in the CH_3-HOCl complex is increased in magnitude by about 97%. Considering that the C···HO single-electron H-bond is a weak intermolecular interaction, the role of the electronegative group in the proton donor is much more prominent in the C···HO single-electron H-bond. As a hydrogen atom in the methyl radical is substituted with a methyl group (in the $CH_3CH_2-H_2O$ complex), the hydrogen-bonded energy also increases. This increase due to the presence of a methyl group in the proton acceptor is −3.36 kJ/mol, which is four times as large as −0.81 kJ/mol due to the presence of a methyl group in the proton donor. The results indicate that the contribution of the methyl group in the proton acceptor is more prominent than that in the proton donor.

The second-order perturbation approach provides a convenient way to evaluate hyperconjugation interactions. For open-shell systems, the density matrices for α and β spin systems are different. There are two main orbital interactions [n(C)→σ*(O−H) and σ(O−H)→n*(C)] in the C···HO single-electron H-bond. This case is different from that in closed-shell systems, where there is one main orbital interaction, for example, n(O)→σ*(O−H) in the O···HO conventional hydrogen bond between DMSO and methanol. The stabilization energy E_{ij} due to the n(C)→σ*(O–H) orbital interaction is almost 2−4 times as large as that due to the σ(O−H)→n*(C) orbital interaction for all complexes. For the σ(O−H)→n*(C) orbital interaction, the stabilization energy increases in the following order: $CH_3-H_2O < CH_3CH_2-H_2O < CH_3-HOCH_3 < CH_3-HOCl$. For the n(C)→σ*(O−H) orbital interaction, the stabilization energy in the CH_3-HOCl complex is much larger than those in other complexes. We attribute it to the stronger electron-withdrawing ability of the Cl atom.

The strength of the C···HO single-electron H-bond increases whether the methyl group is adjoined to the proton donor or the proton acceptor. To explore their role in the formation of the H-bond, the methyl charge transfer Δq is analyzed with natural population analysis (NPA). The methyl charge transfer Δq is a difference between the methyl charge in the complex and that in the respective monomer. As seen in Table 2, the Δq of the proton acceptor is positive (0.0157 e), while that of the proton donor is negative (−0.0051 e). Positive (negative) Δq values demonstrate a decrease (increase) in electron density of the methyl group. The negative Δq of the methyl group in methanol indicates that it plays an electron-withdrawing role upon the formation of a hydrogen bond. Similarly, the positive Δq of the methyl group in ethyl radical indicates that it plays an electron-donating role upon the formation of a hydrogen bond. The result is consistent with the role of methyl groups in the O···HO hydrogen bond of the DMSO−methanol complex.[39] Upon further analysis, it is seen that the positive Δq of the methyl group in the ethyl radical is larger than the negative Δq of the methanol methyl group in absolute. Such charge changes are consistent with the interaction energies in the CH_3-HOCH_3 and $CH_3CH_2-H_2O$ systems.

The topological parameters are very helpful in studying the formation of the H-bond. There is a BCP between the proton acceptor (methyl radical) and the proton donor (water) in the CH_3-H_2O complex. The electron density and its Laplacian at the BCP of C···H in the CH_3-H_2O complex are 0.009 and 0.032 au, respectively, which are within the proper range of 0.002−0.034 au for the electron density and 0.024−0.139 au for its Laplacian, as was pointed out by Koch and Popelies.[40]

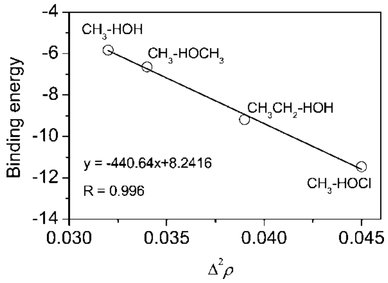

Figure 2. Relationship between the binding energy (kJ/mol) and the Laplacian of electron density ($\nabla^2\rho$) at the C···H BCP at the UMP2/6-311++G(3df,2pd) level.

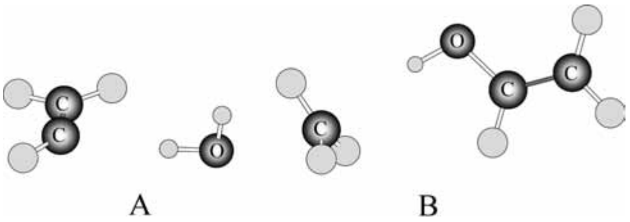

Figure 3. Optimized structures of the C_2H_3−H_2O (A) and CH_3−HOC_2H_3 (B) complexes.

All of these topological parameters confirm the formation of C···HO single-electron H-bonds in the complex. As the methyl group replaces the H atom of the methyl radical and water, both ρ(C···H) and $\nabla^2\rho$(C···H) increase. There is good relation between binding energy and $\nabla^2\rho$(C···H) with the linear correlation coefficient equal to 0.996 (Figure 2). It is worth mentioning that for the CH_3−HOCl complex, the hydrogen bond is strongest and the Laplacian of the electron density at C···H BCP is greatest if it is compared with the other complexes analyzed here.

3.2. Effect of Hybridization. In exploring the hydrogen bonds of C−H···O, C−H···F, C−H···N, and C−H···S, the effect of hybridization of proton donor atom (C) on the strength of the H-bond was studied. It was found that the strength of the hydrogen bond decreases in the following order: C(sp)−H > C(sp^2)−H > C(sp^3)−H.[20-23] In this paper, other than the hybridization of the proton acceptor (carbon atom in radical), the influence of hybridization in the proton donor on the C···HO single-electron H-bond is also investigated. As C_2H_3−H_2O and C_2H−H_2O molecular pairs are optimized with the MP2 method, the π···HO hydrogen bond, not C···HO single-electron H-bond, is always formed. Their structures, together with that of the CH_3−H_2O complex, are thus optimized at the UB3LYP/aug-cc-pVTZ level. Unluckily, an imaginary frequency is found in the C_2H−H_2O complex and the angle of C′C−H is 161° (much deviation from 180° in the monomer) at this level; thus, it is not analyzed here. Vinyl alcohol is still calculated at the UMP2/6-311++G(3df,2pd) level. Their optimized structures are shown in Figure 3. Table 3 shows the calculated bond lengths, binding energy, OH stretching frequency, stabilization energy, electron density, and Laplacian of electron density in the three complexes.

TABLE 3: Calculated Bond Lengths (r), Binding Energy (ΔE), OH Stretching Frequency (v), Stabilization Energy (E), Electron Density (ρ), and Laplacian of Electron Density ($\nabla^2\rho$) for Three Complexes[a]

	CH_3−H_2O	C_2H_3−H_2O	CH_3−HOC_2H_3
r(C···H) (Å)	2.382	2.275	2.276
r(O−H)[b] (Å)	0.966 (0.962)	0.968 (0.962)	0.963 (0.958)
ΔE (kJ/mol)	−5.67	−7.63	−9.27
v(O−H)[b] (cm^{-1})	3720 (3796)	3686 (3796)	3838 (3913)
E_{ij}[c] (kJ/mol)	11.63 (3.19)	14.95 (4.58)	19.39 (5.75)
ρ(C···H)	0.012	0.016	0.013
$\nabla^2\rho$(C···H)	0.029	0.034	0.039

[a] The data of the CH_3−H_2O and C_2H_3−H_2O complexes were calculated at the UB3LYP/aug-cc-pVTZ level, while those of the CH_3−HOC_2H_3 complex were calculated at the UMP2/6-311++G(3df,2pd) level. [b] Data in brackets are from water and HOC_2H_3 monomer, respectively. [c] The E_{ij} is the stabilization energy due to the n(C)→σ*(O−H) (σ(O−H)→n*(C)) orbital interaction.

The binding energy and C···H binding distance of the CH_3−H_2O complex calculated at the UB3LYP/aug-cc-pVTZ level (−5.67 kJ/mol and 2.382 Å) are almost equal to those at the UMP2/aug-cc-pVTZ level (−6.45 kJ/mol and 2.383 Å). The results show that the UB3LYP/aug-cc-pVTZ method can also be used to study the C···HO single-electron H-bond. As compared with the CH_3−H_2O complex, the interaction energy of the C_2H_3−H_2O complex is increased in absolute value by 35%. The C···H binding distance in the C_2H_3−H_2O complex (2.275 Å) decreases relative to that in the CH_3−H_2O complex (2.382 Å). A larger shortening of about 0.11 Å is found for the C···H binding distance as the carbon hybridization of proton acceptor is from $sp^{2.7}$ (methyl radical) to $sp^{2.1}$ (vinyl radical). The results demonstrate that the strength of C···HO single-electron H-bond is increased in the C_2H_3−H_2O complex. In the C_2H_3 radical, the radical is joined with a π bond; thus, its ability of electron-donating increases and the interaction with water is stronger. The stronger interaction results in a larger elongation of the O−H bond length and a larger red shift of the OH stretching frequency. The data of the stabilization energies, electron density, and its Laplacian at the C···H BCP also evaluate such conclusions.

As the calculated parameters of the CH_3−HOC_2H_3 complex are compared with those of the CH_3−$HOCH_3$ complex (Table 2), it is found that the C···H binding distance decreases, the binding energy in the absolute value increases, the stabilization energies increase, and the electron density and Laplacian of the electron density at the BCP of the C···H bond also increase. These results indicate that the C···HO single-electron H-bond between methyl radical and vinyl alcohol is stronger than that in the CH_3−$HOCH_3$ complex. The OH group is adjoined with sp^2 and sp^3 carbon atoms in HOC_2H_3 and $HOCH_3$ molecules, respectively. Because of a conjugation effect, the acidity of the H atom of the OH group in the HOC_2H_3 molecule is greater. Thus, this H atom is easier to form a single-electron H-bond. This conclusion is similar to those found in other types of hydrogen bonds. The changes of OH bond length and OH stretching frequency also support such a conclusion. For example, the OH bond length increases by 0.005 Å in the CH_3−HOC_2H_3 complex, while it increases by 0.004 Å in the CH_3−$HOCH_3$ complex. The change of OH stretching frequency is consistent with elongation of the OH bond length in both complexes.

3.3. Effect of Solvent. On most occasions, hydrogen bonds take place in liquid phase. It is thus necessary to consider how the strength of a single-electron hydrogen bond is affected by its surroundings. The CH_3−H_2O complex was therefore immersed in two solvents (heptane and water) and calculated with the CPCM at the UB3LYP/aug-cc-pVTZ level. Heptane and water represent nonpolar and polar solvents, respectively. Table 4 shows the calculated C···H binding distance, O−H bond length, binding energy, OH symmetrical stretching frequency, stabilization energy, charge transfer, NPA atom charge, and hybridization of the C atom of the CH_3−H_2O complex in the gas phase and solvents at the UB3LYP/aug-cc-pVTZ level.

TABLE 4: Calculated Bond Lengths (r), Binding Energy (ΔE), OH Stretching Frequency (v), Stabilization Energy (E), Charge Transfer (CT), NPA Atom Charge (q), and Hybridization of C Atom of the CH_3-H_2O Complex in the Gas Phase and Solvents at the UB3LYP/aug-cc-pVTZ Level

	gas	heptane	water
r(C···H) (Å)	2.382	2.365	2.351
r(O−H)[a] (Å)	0.966 (0.962)	0.967 (0.966)	0.968 (0.972)
ΔE[b] (kJ/mol)	−5.67	−6.12	−7.38
v(O−H)[a] (cm^{-1})	3720 (3796)	3693 (3713)	3601 (3594)
E_{ij}[c] (kJ/mol)	11.63	12.64	13.52
E_{ij}[d] (kJ/mol)	3.19	3.32	3.40
CT (e)	0.0056	0.0066	0.0078
q(C) (e)	−0.494	−0.498	−0.503
q(H) (e)	0.464	0.467	0.470
q(O) (e)	−0.928	−0.947	−0.972
sp^n(C)	2.70	2.70	2.68

[a] Data in brackets are from water monomer. [b] The ΔE in the gas phase was corrected with BSSE and that in solvent was calculated with the method of ref 46. [c] The E_{ij} is the stabilization energy due to the n(C)→σ*(O−H) orbital interaction. [d] The E_{ij} is the stabilization energy due to the σ(O−H)→n*(C) orbital interaction.

As the CH_3-H_2O complex is transferred from vacuum to heptane (nonpolar solvent), the C···H binding distance is decreased by 0.017 Å and the interaction energy is increased in the absolute value by 0.45 kJ/mol. These results indicate that the strength of the C···HO single-electron H-bond is enhanced in heptane. Further enhancement of the interaction is found as the CH_3-H_2O complex is moved from heptane to water (polar solvent). With an increase in the dielectric constant of the medium, the stabilization energy due to the σ(O−H)→n*(C) orbital interaction has a little increase, while that due to the n(C)→σ*(O−H) orbital interaction increases greatly. As compared with that in the gas phase, the OH stretching vibration is shifted to low frequency in the solvent, which is consistent with the elongation of the O−H bond length in the solvent. Upon formation of the hydrogen bond, the red shift of the OH stretching frequency is 24 and 20 cm^{-1} in the gas phase and heptane, respectively. However, a blue shift (7 cm^{-1}) of the OH stretching vibration is found as the CH_3-H_2O complex is immersed in water. The changes of the O−H bond length support such a shift of OH stretching frequency with the change of the dielectric constant of the medium. This result is a good complement to the conclusion of solvent effect on the type (red-shifted or blue-shifted) of hydrogen bond.[41] From the transformation of X−H stretching frequency shift in the gas phase and solvent, it can be inferred that the red-shifted hydrogen bond and blue-shifted hydrogen bond have no essential difference.[19,42,43]

From the above data, it is concluded that the solvent has an enhancing effect on the strength of C···HO single-electron hydrogen bond in the CH_3-H_2O complex. The similar solvent effect is also found in the CH···O hydrogen bond between DMSO and water[44,45] and the O···HO hydrogen bond between *N*-methylacetamide and water.[46] For a "low-barrier" hydrogen bond in the formamidine−formic acid complex, however, the solvent has a weakening influence on the interaction.[47] Thus, the effect of solvent is different for hydrogen bonds of different strengths. How does the solvent imposes its effect on the C···HO single-electron hydrogen bond? As the CH_3-H_2O complex is moved from the gas phase to heptane, the stabilization energy due to the σ(O−H)→n*(C) orbital interaction is changed from 3.19 to 3.32 kJ/mol and that due to the n(C)→σ*(O−H) orbital interaction is changed from 11.63 to 12.64 kJ/mol. The stabilization energies have a further increase as the CH_3-H_2O complex is placed in water. As seen in Table 4, it is found that the sp^n hybrid orbital of the C atom is almost not changed as the CH_3-H_2O complex is immersed in the solvents. There is a charge transfer (0.0056 e) to the σ*(O−H) antibonding orbital in the gas phase. This charge transfer causes the O−H bond length to elongate (0.962 Å in monomer and 0.966 Å in complex). The charge transfer increases in the solvent; thus, it leads to a further polarization of the O−H bond and makes the H atom more positive and the O atom more negative. The increase of the C negative charge and H positive charge indicates an enhancement of the interaction. According to the above analyses, we think that the solvent affects the C···HO single-electron hydrogen bond mainly through influencing the interactions of hyperconjugation and charge transfer. It is noted that the effect of solvent on the single-electron hydrogen bond is not prominent as compared with that of substitution and hybridization.

4. Conclusions

The present study performs the first systematic investigation of the effect of substitution, hybridization, and solvent on the properties of single-electron hydrogen-bonding interactions. As the proton donor adjoins with an electronegative group and the proton acceptor adjoins with an electropositive group, the strength of the single-electron H-bond increases. The methyl group in the proton donor is electron-withdrawing, and the methyl group in the proton acceptor is electron-donating, both making a positive contribution to the formation of single-electron H-bond. The contribution of the methyl group in the proton acceptor is larger than that in the proton donor. As the acidity of the H atom in the proton donor increases, the strength of the single-electron H-bond increases. As the proportion of the p orbital in carbon atom hybridized orbital of the radical decreases, the strength of the single-electron H-bond also increases. Solvents have an enhancing effect on the strength of the single-electron H-bond. The interactions of hyperconjugation and charge transfer play an important role in the effect of the solvent on the interaction. The effects of these factors on the single-electron H-bond are like those in other types of hydrogen bonds. We hope that the theoretical work in this paper can provoke experimental researchers to study it in the future.

Acknowledgment. This work was supported by doctoral funds (HY06B22) and young funds (HY07Z17) from Yantai University, China.

References and Notes

(1) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.
(2) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
(3) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: Oxford, United Kingdom, 1999.
(4) Desiraju, G. R. *Chem. Commun. (Cambridge)* **2005**, 2995.
(5) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.
(6) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963.
(7) Meot-Ner (Mautner) , M. *Chem. Rev.* **2005**, *105*, 213.
(8) De Visser, S. P.; Shaik, S. *J. Am. Chem. Soc.* **2003**, *125*, 7413.
(9) Whittaker, J. W. *Chem. Rev.* **2003**, *103*, 2347.
(10) Lucarini, M.; Mugnaini, V.; Pedulli, G. F.; Guerra, M. *J. Am. Chem. Soc.* **2003**, *125*, 8318.
(11) Romieu, A.; Bellon, S.; Gaparutto, D.; Cadet, J. *Org. Lett.* **2000**, *2*, 1085.
(12) Hix, S.; Kadiis, M. B.; Mason, R. P.; Augusto, O. *Chem. Res. Toxicol.* **2000**, *13*, 1056.
(13) Wang, B. Q.; Li, Z. R.; Wu, D.; Hao, X. Y.; Li, R. J.; Sun, C. C. *Chem. Phys. Lett.* **2003**, *375*, 91.
(14) Misochko, E. Y.; Benderskii, V. A.; Goldschleger, A. U.; Akimov, A. V.; Shestakov, A. F. *J. Am. Chem. Soc.* **1995**, *117*, 11997.

(15) Tachikawa, H. *J. Phys. Chem. A* **1998**, *102*, 7065.

(16) Chen, Y. H.; Tschuikow-Roux, E.; Rauk, A. *J. Phys. Chem.* **1991**, *95*, 9832.

(17) Igarashia, M.; Ishibashia, T.; Tachikawa, H. *J. Mol. Struct. (THEOCHEM)* **2002**, *594*, 61.

(18) Jursic, B. S. *Chem. Phys. Lett.* **1995**, *244*, 263.

(19) Tang, K.; Shi, F. Q. *Int. J. Quantum Chem.* **2007**, *107*, 665.

(20) Allerhand, A.; Schleyer, R. *J. Am. Chem. Soc.* **1963**, *85*, 1715.

(21) Scheiner, S.; Grabowski, S. J.; Kar, T. *J. Phys. Chem. A* **2001**, *105*, 10607.

(22) Domagala, M.; Grabowski, S. J. *J. Phys. Chem. A* **2005**, *109*, 5683.

(23) Alkorta, I.; Rozas, I.; Elguero, J. *J. Fluorine Chem.* **2000**, *101*, 233.

(24) Volkov, V. N.; Afanasev, V. N. *Internet J. Chem.* **2001**, *4*, 2.

(25) Shi, F. Q.; Jiang, X. M.; Xu, Z. C.; An, J. Y.; Yu, J. Y. *Acta Phys.-Chim. Sin.* **2004**, *20*, 1324.

(26) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503.

(27) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275.

(28) Woon, D. E.; Dunning, T. H., Jr *J. Chem. Phys.* **1993**, *98*, 1358.

(29) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(30) Davidson, E. R. *Chem. Phys. Lett.* **1995**, *241*, 432.

(31) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(32) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, United Kingdom, 1990.

(33) Carrol, M. T.; Chang, C.; Bader, R. F. W. *Mol. Phys.* **1988**, *63*, 387.

(34) Biegler-König, F. *AIM2000*; University of Applied Sciences: Bielefeld, Germany, 2000.

(35) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

(36) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian03*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(38) Qi, X. J.; Liu, L.; Fu, Y.; Guo, Q. X. *Struct. Chem.* **2005**, *16*, 347.

(39) Li, Q. Z.; Wu, G. S.; Yu, Z. W. *J. Am. Chem. Soc.* **2006**, *128*, 1438.

(40) Koch, U.; Popelier, P. L. A. *J. Phys. Chem. A* **1995**, *99*, 9747.

(41) Liu, G. Q.; Wang, H. F.; Li, W. Z. *J. Mol. Struct. (THEOCHEM)* **2006**, *772*, 103.

(42) Joseph, J.; Jemmis, E. D. *J. Am. Chem. Soc.* **2007**, *129*, 4620.

(43) Li, X. S.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639.

(44) Li, Q. Z.; Wang, N. N.; Yu, Z. W. *J. Mol. Struct. (THEOCHEM)* **2007**, *847*, 68.

(45) Li, Q. Z.; An, X. L.; Gong, B. A.; Cheng, J. B. *J. Phys. Chem. A* **2007**, *111*, 10166.

(46) Wang, Z. X.; Duan, Y. *J. Theor. Comput. Chem.* **2005**, *4*, 689.

(47) Kim, Y.; Lim, S.; Kim, Y. *J. Phys. Chem. A* **1999**, *103*, 6632.

JP710414G