Hydrogen Bonding in Aromatic Alcohol-Water Clusters: A Brief Review

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Recent experimental and theoretical advances on the aromatic alcohol-water clusters are reviewed, focusing on the structure of the hydrogen bonding between the alcoholic OH group and the binding water molecules. The interplay of experimental observations and theoretical calculations for the elucidation of the structure is demonstrated for phenol-water, benzyl alcohol-water, substituted phenol-water, naphthol-water and tropolone-water clusters. Discussion is made on assigning the role (either proton-donating or -accepting) of the hydroxyl group by measuring the shifts of infrared frequency of the OH stretching mode in the cluster from that of bare aromatic alcohol for the experimental determination of the cluster structure.

Key Words : Hydrogen bonding, Aromatic alcohol, Water, Cluster

Introduction

Hydrogen bonding[1,2] is extremely important in chemistry and biology, profoundly affecting the properties of the molecule. It is well known, for example, that the three dimensional structures of protein are mostly the results of the hydrogen bonding between the constituting amino acids. In the aqueous solution, the interactions of the amino acids with the solvent molecules,[3-8] another example of hydrogen bonding, may also play a fundamental role of the structure and reaction of protein. Therefore, systematic study on the hydrogen bond can reveal invaluable information for the structure and biochemical activity of protein. Since there are extremely many solvent molecules in the solution phase, however, it is more useful to study the hydrogen bonding in the clusters[9-23] consisting of a solute and a few solvent molecules.

Hydrogen bonding between the hydroxyl (OH) group and the water molecule(s) in organic alcohol-water clusters has been studied intensively as a prototypical model for more complex system. The organic alcohol-water clusters are of moderate size for quantum chemical calculations, allowing the comparison with the experimental observations by the molecular beam and the UV-IR double resonance techniques. Elucidation of the structures of their conformers lying closely in energy may also give a lot of useful information for the interactions between the alcohol molecule and the water molecules in the solution phase[24] on the molecular level.

In the present review we discuss recent advances on the understanding of hydrogen bonding in aromatic alcohol-water clusters. Experimental measurements and theoretical calculations of the structure, binding energy,[25,26] and infrared frequency of phenol-water, benzyl alcohol-water, substituted phenol-water, β-naphthol-water and tropolone-water clusters are reviewed. Elucidation of the nature of hydrogen bonding

in these clusters by the analysis of the shifts in the vibronic bands observed by spectroscopic techniques is exemplified. Electrostatic and steric effects of substitution at the phenyl ring on the structure of hydrogen bonding in the substituted phenol-water clusters are discussed. The OH stretching frequency is described in relation to the structure and the strength of the hydrogen bond in the clusters.

Phenol-water, benzyl alcohol-water and phenylpropyl alcohol-water clusters. The phenol-$(H_2O)_n$ clusters have been studied most intensively by many investigators[15-22] as the prototypical system for organic alcohol-water cluster. As depicted in Figure 1, the role of the OH group in the phenol-$(H_2O)_n$ cluster can be either proton-donating or -accepting. The conformer (P11) with the proton-donating OH group is calculated to be of lower energy than the proton-accepting one (P12). Experimentally, only the conformer with the proton-donating OH has been observed so far, and its measured binding energy is 5.47($\pm$0.09) kcal/mol.[27] The kinetic stability of the conformer with the proton-accepting OH group is not known, however, if the latter conformer may be observed experimentally, the different behavior of the OH stretching frequencies in the complexes P11 and P12 (significant red shift for P11 and slight blue shift for P12; see Table 1) from that of the bare phenol would be key observable for distinguishing the two conformers.

Figure 2 presents the benzyl alcohol-H_2O clusters corresponding to the phenol-H_2O clusters in Figure 1. In the
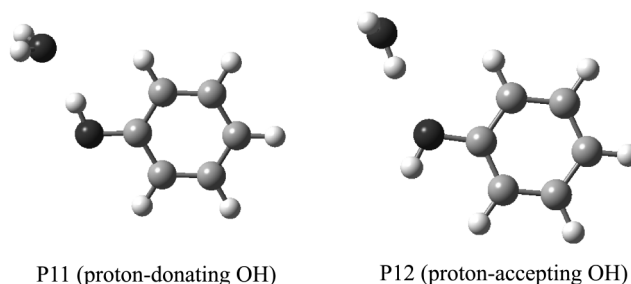
P11 (proton-donating OH)   P12 (proton-accepting OH)

Figure 1. Structures of phenol-H_2O complexes.

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Table 1. Calculated energies, zero point energies (ZPE), binding energies (BE), and OH stretching frequencies of phenol-H_2O and substituted phenol-H_2O complexes

	Energy[a] (Hartree)	ZPE[a] (kcal/mol)	ΔE[a] (kcal/mol)	BE[a] (kcal/mol)	ν_{OH} (cm^{-1})	Role of OH group
H_2O	-76.26397	13.71				
phenol	-306.65428	64.95			3883.5	
phenol-H_2O					3706.7	
(P11)	-382.93428	80.64	0	8.07[b] (5.48)[c]	3884.7	p-donating
(P12)	-382.92986	80.49	+2.61	5.46 (3.20)	3885.7	p-accepting
p-fluorophenol	-405.72475	60.03				
p-fluorophenol-(H_2O)						
(p-FP11)	-482.00546	75.77	0	8.47 (5.86)	3706.1	p-donating
(p-FP12)	-482.00026	75.55	+3.04	5.43 (2.52)	3887.9	p-accepting
p-aminophenol	-361.87858	75.62			3888.9	
p-aminophenol-H_2O						
(p-AP11)	-438.15794	91.39	0	7.65 (5.09)	3722.5	p-donating
(p-AP12)	-438.15472	91.17	+1.85	5.80 (2.81)	3890.9	p-accepting
p-chlorophenol	-765.71075	59.00			3883.8	
p-chlorophenol-H_2O						
(p-CP11)	-841.99188	74.75	0	8.72 (6.09)	3694.6	p-donating
(p-CP12)	-841.98607	74.47	+3.37	5.35 (2.45)	3884.5	p-accepting
hydroquinone	-381.72816	67.45			3888.6	
hydroquinone-H_2O					3889.8	
(HQ11)	-458.00800	83.14	0	7.97 (5.38)	3717.4	p-donating
(HQ12)	-458.00418	83.08	+2.33	5.64 (2.67)	3890.7	p-accepting
o-fluorophenol						
(o-FP1)	-405.72547	60.19	0		3862.1	
(o-FP2)	-405.72109	59.94	+2.50		3888.6	
o-fluorophenol-H_2O						
(o-FP11)	-482.00511	75.86	0	7.87 (4.70)	3603.1	p-donating
(o-FP12)	-482.00225	75.71	+1.63	6.24 (3.58)	3686.3	p-donating
(o-FP13)	-482.00081	75.67	+2.50	5.37 (2.50)	3859.5	p-accepting
o-chlorophenol						
(o-CP1)	-765.71320	59.24	0		3831.8	
(o-CP2)	-765.70886	59.00	+2.49		3880.8	
o-chlorophenol-H_2O						
(o-CP11)	-841.99039	74.76	0	6.48 (3.84)	3674.6	p-donating
(o-CP12)	-841.98977	74.70	+0.33	6.15 (3.47)	3633.7	p-donating
(o-CP13)	-841.98849	74.68	+1.12	5.36 (2.49)	3822.9	p-accepting

[a]MP2/6-311G**. [b]Binding energy (not corrected for BSSE). [c]Binding energy (corrected for counterpoise BSSE).

B11 (proton-donating OH)　　　　B12 (proton-accepting OH)
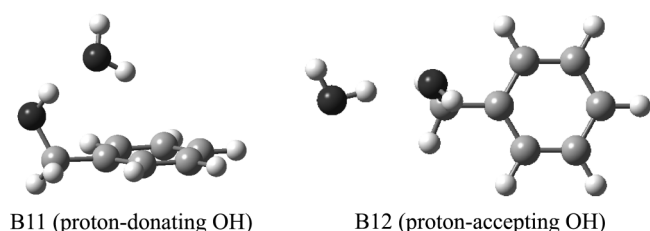
Figure 2. Structures of benzyl alcohol-H_2O complexes.

structure (B11), the hydroxyl at the phenyl ring is a proton donor to the water molecule, while it is a proton acceptor in (B12). The lowest energy isomer corresponds to Conformer I of benzyl alcohol-H_2O cluster obtained by Mikami *et al.*[28] For the benzyl alcohol-H_2O cluster, the high-frequency stretching modes experimentally observed by Mikami and co-workers[28] are at 3733, 3622 and 3568 cm^{-1}, assigned as antisymmetric and symmetric stretching of water molecule

and the stretching of alcoholic OH, respectively.

Figure 3 shows the phenol-$(H_2O)_2$ cluster (P21) and the benzyl alcohol-$(H_2O)_2$ cluster (B21) of the lowest energy. In both clusters, the oxygen atoms of the hydroxyl and those of the two water molecules form a ring. In their discussions on the infrared frequencies, Mikami *et al.*[28] proposed an isomer (B22) of the benzyl alcohol-$(H_2O)_2$ cluster, in which a water molecule forms a π bond to the phenyl ring, to account for the spectrum. Specifically, the observed band at 3595 cm^{-1}, assigned as the stretching of the π-bonding water molecule, was found to be reasonably close to the harmonic frequency of 3629 computed by HF/6-31G(d,p) method.

The most stable phenol-$(H_2O)_3$ cluster is well-known and has been studied by many groups. In this structure (P31) the four oxygen atoms form a ring as shown in Figure 4. Since the alcoholic hydroxyl group lies almost in the phenyl ring, the four-membered ring lies beyond the phenyl ring. The isomer of the benzyl alcohol-$(H_2O)_3$ cluster of the lowest
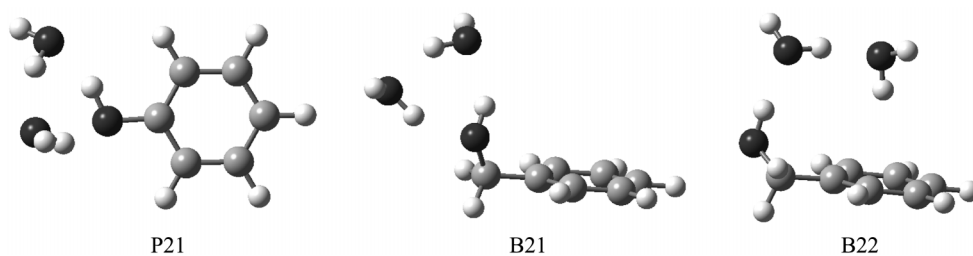
Figure 3. Structures of lowest-energy phenol- and benzyl alcohol-$(H_2O)_2$ clusters.
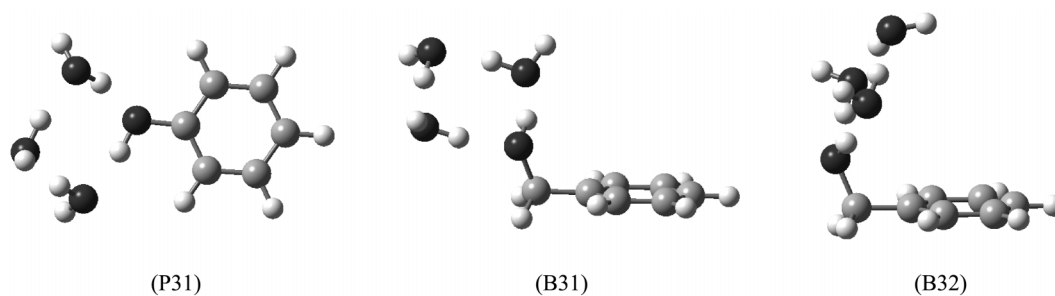

Figure 4. Structures of lowest-energy phenol- and benzyl alcohol-$(H_2O)_3$ clusters.
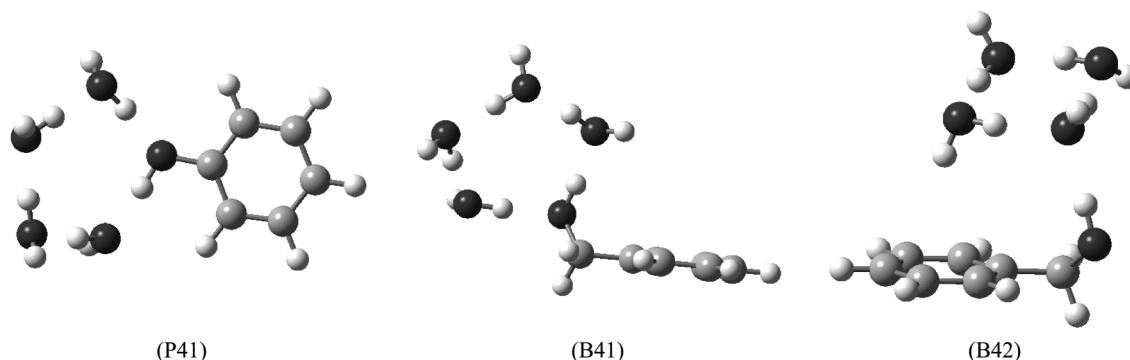

Figure 5. Structures of lowest-energy phenol- and benzyl alcohol-$(H_2O)_4$ clusters.

energy is (B31) shown in Figure 4. In this isomer the three water molecules and the hydroxyl group form a ring. Since the ring lies away from the phenyl ring, π bond cannot be formed between water and the phenyl ring in this isomer. The structures of the lowest energy phenol-$(H_2O)_4$ and the benzyl alcohol-$(H_2O)_4$ clusters are shown in Figure 5. In the isomer (P41) of the phenol-$(H_2O)_4$ cluster, the five oxygen atoms of the hydroxyl group and the four water molecules form a 5-membered ring. The isomer (B42) discussed by

Mikami and coworkers[28] contains π-bond between a water molecule and the phenyl ring.

As the carbon sidechain gets longer in the aromatic alcohol, the acidity of the hydroxyl group may decrease, rendering the energy difference between the isomer containing the proton-donating OH and that with the proton-accepting OH group to become smaller. It is found that this energy difference is 2.61 and 1.55 kcal/mol for phenol-H_2O and benzyl alcohol-H_2O complexes, respectively, demonstrating that this is
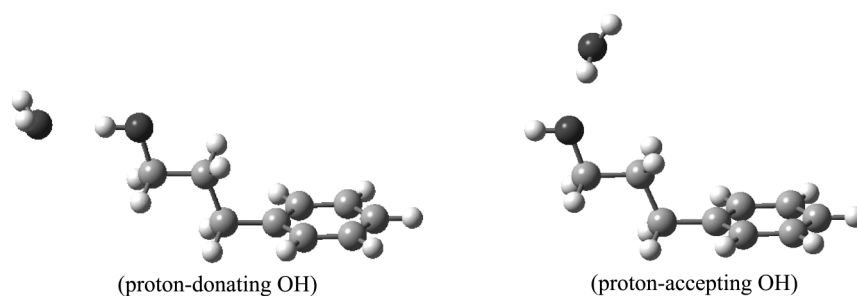

Figure 6. Structures of lowest-energy phenylpropanol-(H_2O) complexes.

indeed the case. Figure 6 depicts the lowest-energy proton-donating and -accepting conformers of the phenylpropanol-H_2O complex,[29] with very small energy difference (only 0.07 kcal/mol) (MP2 /6-31+G**, ZPE-uncorrected). Since the carbon sidechain is quite floppy, more numerous conformers exist for this complex with much smaller energy differences than for phenol-H_2O or benzyl alcohol-H_2O complexes.

Catechol-water clusters. Catechol-water clusters are quite intriguing, because the catechol molecule possesses two close-lying hydroxyl groups. The two OH groups may act either as proton donor or acceptor or both, and the strength of the hydrogen bonding could be more versatile depending on the structure of the clusters. It is known that water molecules form cyclic structures with themselves, while only very few of them directly interact with the hydroxyl group in phenol-$(H_2O)_n$ system. For catechol-water clusters more water molecules may interact with the water molecules due to the presence of multiple functional groups. Also, the intramolecular hydrogen bonding between the two alcoholic hydroxyl groups may significantly influence the interactions between the hydroxyl-water interactions in the catechol-water clusters (for example, in terms of the binding energies), as compared with the phenol-$(H_2O)_n$ system. Detailed study on the configuration of the water molecules in the vicinity of the two hydroxyl groups may also give invaluable information for the thermodynamic properties of the catechol molecule in aqueous solution. The catechol molecule exhibits many important biochemical functions such as nucleophilic catalysis of peptide bond formation,[30] and the interaction with the water molecules may also reveal valuable information for the biochemical reactivity in aqueous solution.

Figure 7 presents the computed structure of the free catechol molecule.[31] The two OH groups lie in the plane of the phenyl ring (that is, catechol is planar). The catechol molecule
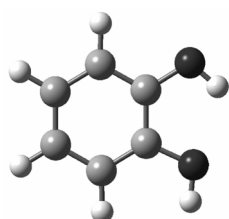

Figure 7. Free catechol.
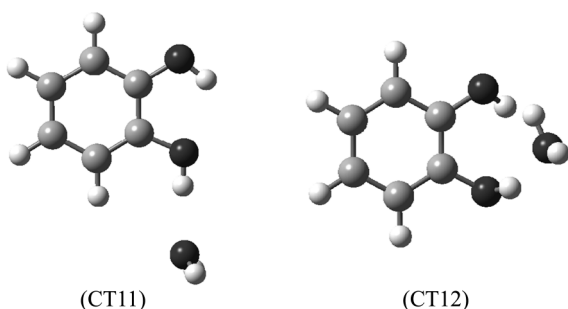

(CT11)   (CT12)

Figure 8. Structures of catechol-H_2O complexes.

possesses weak intramolecular hydrogen bonding between the hydrogen and the oxygen atoms. The harmonic frequencies of the two OH stretching modes calculated by BLYP/6-31+G** method (without employing the scaling factors) compare very well with the experimental frequencies of 3611 and 3673 cm^{-1}.[32] For the catechol-H_2O cluster (Figure 8), the most stable isomer is the structure (CT11) at BLYP/6-31+G** level of calculations, in which one of the two hydroxyl groups donates proton to the water molecule. The water molecule forms very weak bond with the ortho-hydrogen in the phenyl ring. The two OH bonds in the water molecule lie in perpendicular position with respect to the phenyl ring. The harmonic frequencies of the two OH stretching modes computed by the BLYP/6-31+G** method are 3621 and 3444 cm^{-1}. In the next stable isomer (CT12) of catechol-H_2O, the water molecule interacts with two hydroxyl groups, forming a cycle. One of the OH groups acts as proton donor. The other OH group is proton acceptor whose hydrogen bonding is significantly weaker. The energy of this isomer is slightly higher than the most stable structure (CT11) by about 1.88 kcal/mol (ZPE corrected) at BLYP/6-31+G** level of theory. The calculated harmonic frequencies of the two OH stretching modes are 3601 and 3357 cm^{-1} (BLYP/6-31+G**). Comparing the harmonic frequencies of these two isomers of the catechol-H_2O cluster with the experimental frequencies of the two OH stretching modes (3597 and 3499 cm^{-1}), the catechol-H_2O cluster experimentally observed by Kleinermanns and coworkers can be safely assigned as the lowest energy structure (CT11), as discussed by them.[32]

For the catechol-$(H_2O)_2$ cluster, the most stable isomer obtained is the structure (CT21), in which the two hydroxyl groups and the two water molecules form a ring (Figure 9). In this isomer all of them act both as proton donors and acceptors, that is, each oxygen atom in the ring accepts a proton from a neighboring member, and gives a proton to the next. Other isomers are also depicted in Figure 9. One of the intriguing questions concerning the aromatic alcohol-water clusters is whether the π bonding between water molecule and the phenyl ring is important or not.[23] For the benzene-water clusters, this π bonding is essentially the only possible interactions, because the benzene molecule does not possess another functional group. For phenol-$(H_2O)_n$ clusters, on the other hand, the presence of the hydroxyl groups gives so strong hydrogen bonding with the water molecules that the isomers exhibiting π bonding are predicted to be much higher in energy than those containing a hydrogen bonding between the hydroxyl group and a water molecule and a ring consisting of water molecules. In the isomer (CT25), one of the water molecules interacts with the two hydroxyl groups, while the other lies above the phenyl ring. The energy of this isomer is, however, quite high, 5.05 kcal/mol above that of the most stable structure (CT21) at HF/6-31+G** approximation. The lengths of the hydrogen bonds in this π bonding isomer are relatively longer than for other isomers presumably due to the geometrical constraints (that is, the accessibility of water to the phenyl ring) caused by the
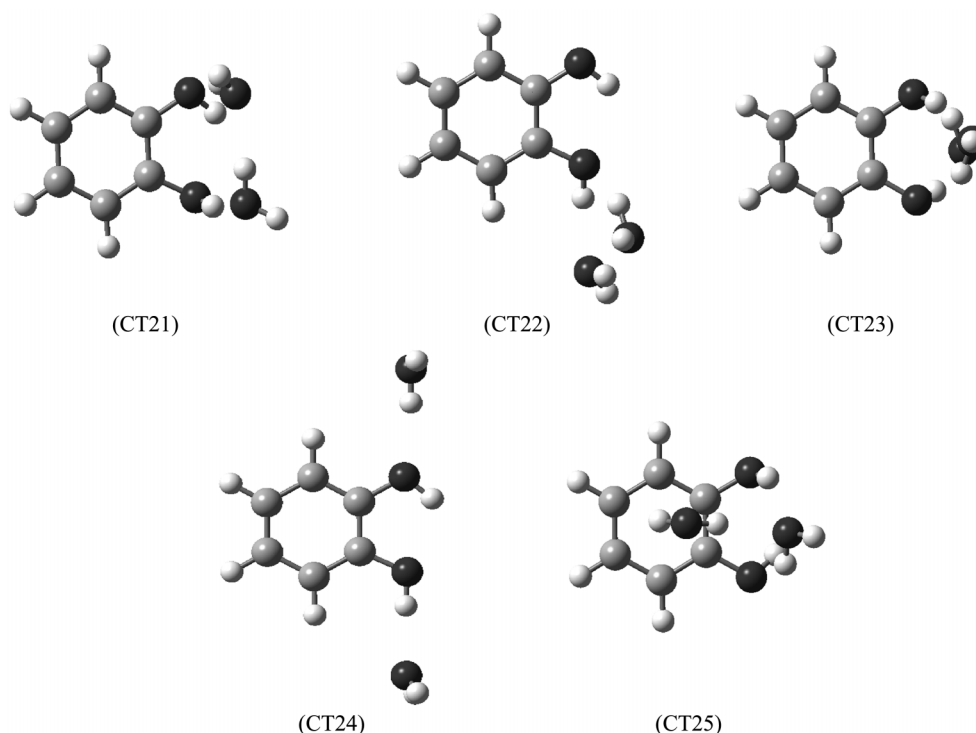
(CT21)   (CT22)   (CT23)
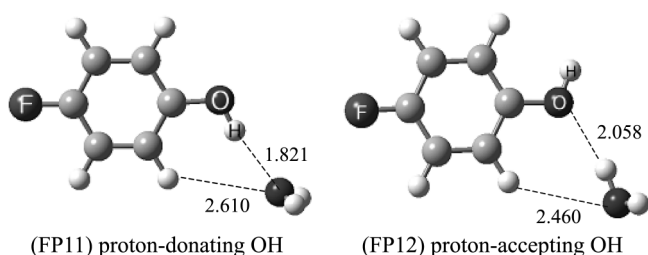

(CT24)   (CT25)

Figure 9. Structures of catechol-(H_2O)$_2$ clusters.

(FP11) proton-donating OH   (FP12) proton-accepting OH

Figure 10. Structures of p-fluorophenol-H_2O complexes.

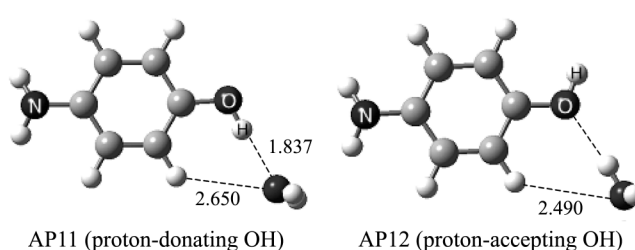AP11 (proton-donating OH)   AP12 (proton-accepting OH)

Figure 11. Structures of p-aminophenol-H_2O complexes.

formation of the π bond, and the resulting increase in energy is not fully compensated by the bonding. Since the energy of the structure (CT25) is relatively higher than the low-energy structures, it may be inferred that this conformer including the π-bonding may not be important in low-temperature gas phase catechol-(H_2O)$_2$ cluster, although higher level theory must be employed to verify this point clearly. Increase in the number of clustering water molecules, however, may somewhat relax this geometrical constraints in the clusters containing more water molecules.

Other substituted phenol-water clusters. There have not been many studies for the other substituted phenol-water clusters yet. Lee and co-workers[33] have recently investigated the effects of substitution at the phenyl ring on the strength of the hydroxyl-water hydrogen bonding systematically, by calculating the binding energies of the complexes. For all the complexes studied, they predicted that those conformers with the proton-donating OH group will be of lower energy than the proton-accepting one. Table 1 presents the calculated results for p-fluoro-, p-chloro-, p-aminophenol- and hydroquinone-

H_2O complexes, and Figure 10 and Figure 11 depict the calculated structures of the p-fluoro- and p-aminophenol H_2O complexes, respectively.

Based on a qualitative reasoning for the influence of substituting group at the para position on the strengths of the hydroxyl group as acid or hydrogen bonding basicity, it was predicted[33] that, when the hydroxyl group acts as proton-donor (acid), the hydrogen bonding is strengthened by the electron-withdrawing group. On the other hand, when the OH group is proton-accepting, the binding energy decreases because the hydrogen bonding basicity of the oxygen atom of the hydroxyl group is reduced due to the substituted fluorine. For the electron-donating groups, the reverse trend was predicted. They carried out calculations (by employing the MP2/6-311G** method) for -F and -Cl (-NH$_2$ and -OH) as electron-withdrawing (-donating) substituents, and found that their predictions are indeed correct. The changes in the binding energies due to the substituents were calculated to be about 0.5 kcal/mol. Natural Population Analysis (NPA) for the p-substituted phenol-H_2O complexes also corroborated

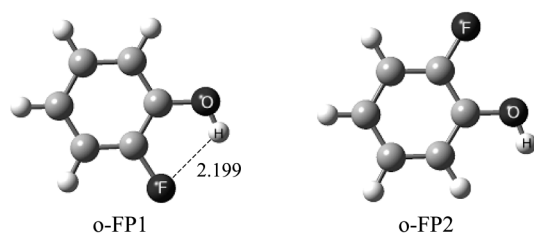o-FP1   o-FP2

Figure 12. Structures of o-fluorophenol complexes.

their explanations. For the ortho-substituted complexes, the analysis is much more difficult, because the OH group and the substituent lie very close to each other. For example, as depicted in Figure 12 for the o-fluorophenol, some conformers may possess the intramolecular hydrogen bonding, while others may not. These differences in the geometrical arrangements of OH, substituting group, and the binding water molecule may produce various effects to affect the strength of the hydrogen bonds in the complexes. In addition to the electrostatic effects, the substituents may directly bond with the hydroxyl group or the water molecule, or induce considerable change in the local structure near the hydrogen bonds.

The calculated infrared frequencies also exhibited very interesting pattern: It was found that the harmonic frequency of the stretching mode of the proton-*donating* OH group in the substituted phenol moiety in the complexes significantly decrease from that of bare substituted phenol (for example, while the OH stretching mode frequency of the p-fluorophenol is computed to be 3886 cm^{-1}, that of the corresponding complex p-FP11 is calculated to be only 3706 cm^{-1}), and that the harmonic frequency of the stretching mode of the proton-*accepting* OH group in the substituted phenol moiety in the complexes remained more or less the same as that of bare substituted phenol (for example, the harmonic frequency of the p-fluorophenol-water complex p-FP12, which possess proton-accepting phenolic OH group, is computed to be 3888 cm^{-1}, while that of bare p-fluorophenol is computed to be 3886 cm^{-1}). This latter observation may help elucidate the structures of the substituted phenol-water complexes by the infrared spectroscopic methods, determining whether the phenolic OH group is proton-donating or -accepting.

On the experimental side, the p-aminophenol-H$_2$O complex was studied by Wategaonkar and co-workers,[34] and by Gerhards and Unterberg.[35] They found that the most stable conformer of the p-aminophenol-(H$_2$O) complex is the one
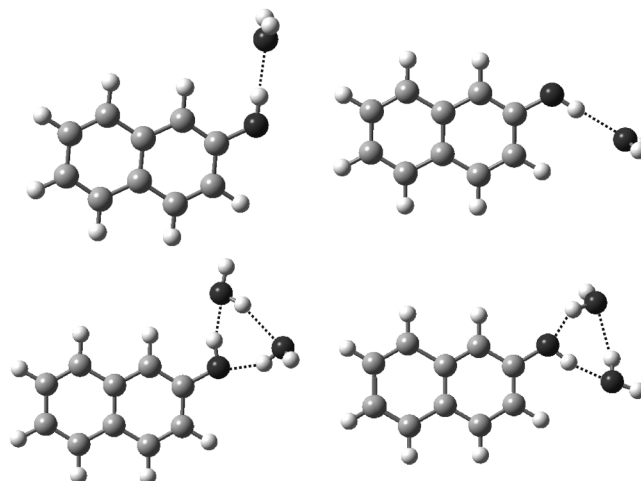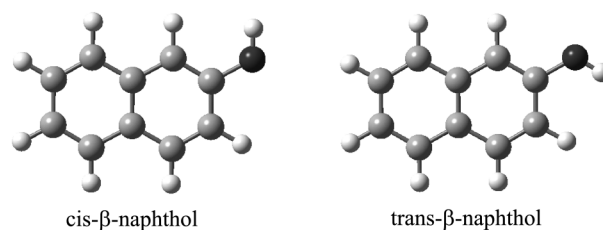

cis-β-naphthol   trans-β-naphthol

Figure 14. Structures of β-naphthol and β-naphthol-(H$_2$O)$_n$ (n = 1,2) clusters.

in which the OH group acts as proton donor (AP11 in Figure 11), in agreement with the predictions by Lee and co-workers.[33] The conformers with the water molecule binding to the amino group of the p-aminophenol moiety was calculated to be higher than AP11 or AP12, and they were not observed experimentally. Kleinermanns and co-workers[36] studied the structures of the p-cresol-(H$_2$O)$_{1-3}$ clusters by two-photon resonant ionization spectroscopy in detail. The structures of the clusters they assigned are depicted in Figure 13. They found that the (0,0) band of the $\pi - \pi^*$ transitions of the p-cresol-(H$_2$O)$_1$ cluster significantly (by 357 cm^{-1}) red shifts from that of the bare cresol, while those of the p-cresol-(H$_2$O)$_{2,3}$ clusters red shift to a lesser degree (107 and 76 cm^{-1}, respectively). They explained this behavior of the electronic spectra by carrying out the *ab initio* calculations for the HOMO-LUMO gap for the $\pi - \pi^*$ transitions, and by analyzing the effects of proton-accepting or -donating water molecule(s) on the HOMO and LUMO of the clusters, in good agreement with the experimental observations. They also found that the intermolecular stretching frequency (185
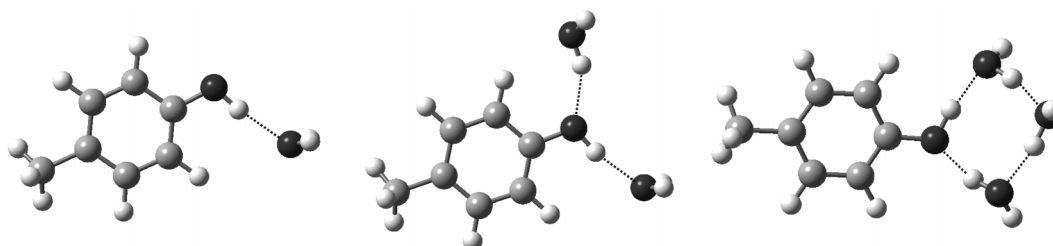

Figure 13. Structures of p-cresol-(H$_2$O)$_n$ (n = 1-3) clusters.

cm^{-1}) of p-cresol-(H$_2$O)$_3$ is significantly higher than that (146 cm^{-1}) of p-cresol-(H$_2$O)$_3$, and attributed this observation to the more rigid O-O potential of the cyclic water trimer in p-cresol-(H$_2$O)$_3$ cluster.

β-Naphthol-water clusters. The β-Naphthol-(H$_2$O)$_n$ (n = 1-3,5) clusters were investigated by Mikami and co-workers[37] both experimentally and computationally. By employing the IR-UV double resonance technique, they observed the hydrogen-bonded OH stretching frequencies, and assigned the structures of the clusters by comparing with the *ab initio* calculations. As in the case of p-cresol-water clusters discussed above, the (0,0) band of β-Naphthol-(H$_2$O)$_1$ shifts to red from that of bare β-Naphthol, while those of the clusters with n ≥ 2 blue shift with respect to that of the n = 1 cluster. The bare β-Naphthol molecule may exhibit two rotamers, *cis*- and *trans*-, as depicted in Figure 14. Of the two rotamers, the *cis*- form is of lower energy, and the measured population ratio of the *cis*- and *trans*-forms was 3:1. The assigned structures for the β-Naphthol-H$_2$O cluster are also shown in Figure 14. In both structures, the OH group in the naphthol moiety is proton-donating. The weakening of the OH bond is observed as red shifts (by 142 and 138 cm^{-1}, for *cis*- and *trans*-forms, respectively) from that of the bare β-Naphthol. The β-Naphthol-(H$_2$O)$_{2,3}$ clusters were assigned to contain three-membered, and four-membered water ring, respectively, while the structure of the β-Naphthol-(H$_2$O)$_5$ cluster was predicted to be of ice (I) type.

Tropolone-water clusters. The tropolone-water clusters contain both intramolecular and intermolecular hydrogen bonds, and thus it proved quite intriguing to study how the intermolecular hydrogen bond between water and tropolone affects the intramolecukar hydrogen bonding between the OH and the carbonyl groups in tropolone. Mikami and co-workers,[38] and Zwier and co-workers[39] carried out extensive investigations for the tropolone-(H$_2$O)$_n$ (n = 1-3) clusters to determine their structures by the IR-UV double resonance

spectroscopy. The former group found that the (0,0) frequencies for the tropolone-(H$_2$O)$_n$ (n = 1-3) clusters blue shift more and more (289, 451 and 623 cm^{-1}, respectively, for n = 1-3), indicating that tropolone acts as proton acceptor in these clusters. By observing that the IR spectra for the tropolone-(H$_2$O)$_1$ cluster exhibited two distinct band for the two OH stretching modes of the water moiety, the two groups proposed TP11 and TP12 (Figure 15) as the probable structures for the tropolone-(H$_2$O)$_1$ cluster. Preference of the two groups differed (for example, Mikami and co-workers[38] preferred the structure TP11 on the basis of several spectroscopic arguments and by comparing the IR spectra for the tropolone-(CH$_3$OH)$_1$ cluster, while Zwier and co-workers[39] expressed slight preference for TP12), however, and further detailed analysis would be needed for unambiguous elucidation of the structure. For the tropolone-(H$_2$O)$_2$ cluster, Mikami and co-workers proposed TP21 and TP22 as the two most probable structures, but definite assignment was not made. Based on the fact that the aqueous solution of tropolone is slightly acidic (*p*Ka = 6.7), Mikami *et al.* suggested that the intramolecular hydrogen bond in tropolone would break to free the OH group as a proton donor to the water molecule. By inferring that the stretching frequency of the tropolone OH in the tropolone-(H$_2$O)$_n$ cluster dramatically increases to about 3300-3500 cm^{-1} from that (~3100 cm^{-1}) of the tropolone-(H$_2$O)$_n$ (n = 0-3) clusters, Mikami *et al.* indicated that the intramolecular hydrogen bond in tropolone would indeed break in the former cluster. By comparing the spectra for the tropolone-(CH$_3$OH)$_3$ cluster, they also proposed a ring structure for tropolone-(H$_2$O)$_3$.

Concluding Remarks

Since the isomers of aromatic alcohol-(H$_2$O)$_n$ clusters are of similar energy, at most within a few kcal/mol, the analysis of the experimental observations is usually nontrivial. The interplay between calculations and experimental observations is thus very important to unambiguously elucidate the structures of the clusters. Systematic studies on the hydrogen bonding in small clusters would also shed considerable light to the structures and reactions of organic and biomolecules in the solution phase. Therefore, more extensive studies for this interesting system would be highly desirable.

Figure 15. Structures of tropolone-(H$_2$O)$_n$ (n = 1,2) clusters.

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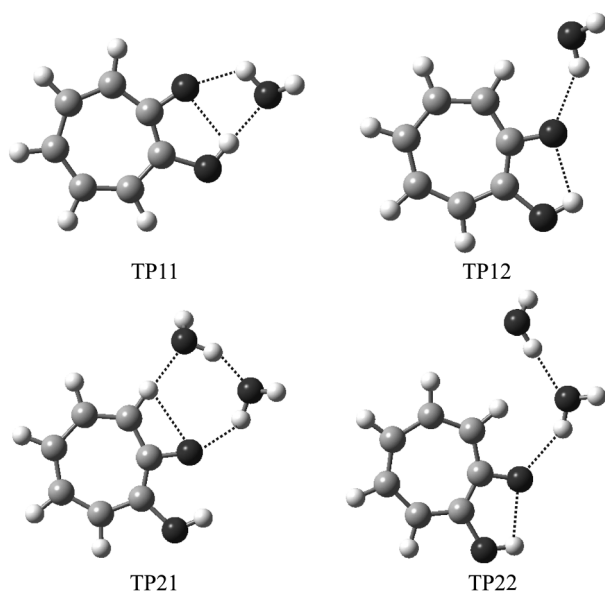6. Lee, K. T.; Sung, J.; Lee, K. J.; Kim, S. K.; Park, Y. D. *J. Chem. Phys.* **2002**, *116*, 8251.

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