# Computational Study of Catechol-(H$_2$O)$_n$ ($n$ = 1-3) Clusters[†]

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Computations are presented for the catechol-(H$_2$O)$_n$ ($n$ = 1-3) clusters. A variety of conformers are predicted, and their relative energies are compared. Binding energies of the clusters are computed, and detailed analysis is presented on the harmonic frequencies of stretching modes involving the hydrogen bonding in the clusters, comparing with the experimental observations.

**Key Words :** Catechol, Cluster, Hydrogen bond, Binding energy

## Introduction

Clusters have been given a lot of attention due to the relevance to understanding the solvation processes. Since there are enormous number of solvent molecules in solution phase, they cannot explicitly be treated except by employing the approximations based on polarizable continuum model,[1,2] which is still being developed. Alternatively, the solution phase may be approximated as clusters,[3-16] in which a number of solvent molecules surround the solute to form a certain configuration. The properties of solution depending on the arrangement of solvent molecules around the solute may be efficiently studied by employing this approach. When a specific functional group of the solute interacts with solvent molecules, the cluster model can serve as good model system of the solution, since the interactions with the solvent molecules in the immediate vicinity of the functional group would largely determine the properties of the solution, while other solvent molecules may safely be considered as "spectators".

Hydrogen bonding,[17,18] which plays important role in physics, chemistry and biology, is such a case, in the sense that the solvent molecules (water, methanol or ammonia) in the immediate vicinity of the functional group such as hydroxyl, carbonyl or halogen atoms interact with the solute molecule to yield changes in the properties. Infrared (IR) spectroscopy is a very useful technique for this purpose and, in principle, measurements of the shifts of IR frequencies in the clusters from those of bare solute may give valuable information for the configuration of solvent molecules around the solute. However, direct correlation of the IR frequency shifts with the configuration of solvents is still very vague, and theoretical computations of IR frequencies for given solvent configuration can be very useful to make definite assignments of experimentally observed IR bands. Large-scale computations of the medium-sized clusters were made possible by rapidly increasing computational capability and efficient software to predict the structures and energies of

clusters. On the experimental side, the supersonic beam techniques allowed easy preparation of isolated ultracold clusters that can be employed to explore solvation processes on the molecular level. The strength of the hydrogen bonds may also be estimated by measuring the dissociation energy of the clusters, as recently carried out by Leutwyler and co-workers.[19]

The hydroxyl (OH) group is one of the simplest functional groups that can form hydrogen bonding with water molecules. Detailed studies on the structures and IR frequencies were carried out for the phenol-(H$_2$O)$_n$ clusters, up to $n$ = 10.[10-16] Comparison of experimentally observed and theoretically predicted IR frequencies has given detailed information on the arrangement of water molecules around the hydroxyl and on the nature of hydrogen bonding. Depending on the number of water molecules, OH group in the phenyl ring acts either as proton donor or acceptor. On the other hand, studies on other aromatic alcohol-water clusters are rare probably due to experimental difficulties and heavy computational cost. Catechol-water clusters may be quite intriguing in this sense, because the catechol molecule possesses two close-lying hydroxyl groups. The two hydroxyl 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$_2$O)$_n$ 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$_2$O)$_n$ system. Detailed study on the configuration of the water molecules in the vicinity of the two hydroxyl groups may also give invaluable information of the thermodynamic properties of the catechol molecule in aqueous solution. Since the catechol molecule exhibits many important biochemical functions such as nucleophilic catalysis of peptide bond formation,[20] the hydrogen bonding of catechol with other biomolecules

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or solvent molecules will be quite intriguing.

In this paper, we present computations on catechol-$(H_2O)_n$ ($n = 1$-3) clusters. A variety of isomers are predicted, and their relative energies are compared. Binding energies of the clusters are computed, and detailed analysis is presented on the harmonic frequencies of stretching modes involving the hydrogen bonding in the clusters comparing with the experimental observations.[10,21-23]

## Computational Methods

In this study all the calculations were carried out using the GAUSSIAN 98W set of programs.[22] Bond lengths and angles are computed along with the zero-point energies and harmonic frequencies by employing the HF/6-31+G** and BLYP/6-31+G** methods. The stationary structures of the clusters are obtained by verifying that all the harmonic frequencies be real.

## Results

The computational strategy adopted in this work is preliminary computations employing HF/6-31G level of theory followed by computations by HF/6-31+G** and BLYP/6-31+G** approximations. The gross structures and energies of the clusters are first determined by employing HF/6-31G method, and more accurate structures and harmonic frequencies are obtained by the HF/6-31+G** and BLYP/6-31+G** technique. It turned out that the HF/6-31G and HF/6-31+G** methods could give vastly different results, as we describe below. We also have specifically checked the relative accuracy of the BLYP and B3LYP methods, and have found that the harmonic frequencies of the OH stretching modes computed by the BLYP theory give results that agree well with the experimental observations without invoking the scaling factors. For example, the symmetric and antisymmetric stretching frequencies of the free water molecule computed by BLYP (B3LYP) method are 3663 (3809) and 3785 (3931) cm$^{-1}$, respectively, while the experimental frequencies are 3657 and 3756 cm$^{-1}$. Since the computed IR frequencies are the most important tool for analyzing the structures of the hydrogen bonding in the present systems, we employ the BLYP method in this work.

Figure 1 presents the computed structure of the free catechol molecule. The two OH groups lie in the plane of the phenyl ring (that is, catechol is planar) with the bond lengths of 0.980 Å. The catechol molecule possesses weak intramolecular hydrogen bonding with the distance of 2.710 Å between the hydrogen and the oxygen atoms. The harmonic frequencies of the two OH stretching modes ($O_1H$ and $O_2H$) obtained by HF/6-31+G** (BLYP/6-31+G**) method given in Table 1 are 4014 and 4065 cm$^{-1}$ (3636 and 3693 cm$^{-1}$), respectively. Those computed by BLYP/6-31+G** method (without employing the scaling factors) compare very well with the experimental frequencies of 3611 and 3673 cm$^{-1}$.[21] Although the computed results are harmonic frequencies without the effects of anharmonicity,
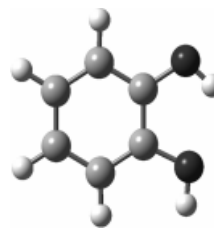


**Figure 1**. Computed structure of free catechol molecule.

the agreement (to within 30 cm$^{-1}$) between the computed and experimentally observed frequencies is quite good. We also carried out calculations for the catechol molecule employing the MP2/6-31+G** and MP2/6-311G** methods, but obtained imaginary frequencies for the planar structure of the molecule. For example, in the optimized stationary structure (that is, containing only real frequencies) of the catechol molecule obtained by the MP2/6-311G** method, the two OH bonds lie considerably out of the phenyl ring with the dihedral angles of 18.6° and 2.6°. Due to these results that are rather in disagreement both with intuition and with experimental observations, we do not employ the MP2 methodology further for larger clusters described below.

We have carried out the HF/6-31+G** and BLYP/6-31+G** computations for the catechol-$H_2O$ cluster, and find three isomers. The most stable isomer is the structure (1-1) both at HF/6-31+G** and BLYP/6-31+G** level of calculations, in which one of the two hydroxyl groups donates proton to the water molecule. The catechol moiety in the cluster does not much change from free catechol, and the two OH groups essentially lie in the phenyl ring. The water molecule forms very weak bond with the ortho-hydrogen in the phenyl ring with the bond distance of 2.910 (2.948) Å at HF/6-31+G** (BLYP/6-31+G**) approximation. The two OH bonds in the water molecule lie in perpendicular position with respect to the phenyl ring, as can be seen in (1-1b). 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 of catechol-$H_2O$, the water molecule interacts with two hydroxyl groups, forming a cycle. One of the OH groups acts as proton donor and the length of the hydrogen bonding between this OH and water is 1.800 (1.850 Å) at HF/6-31+G** (BLYP/6-31+G**) level of approximation. The other OH group is proton acceptor whose hydrogen bonding is significantly weaker. It should be noted that the two hydroxyl groups in the catechol become highly twisted (by 32.7° and 49.4° by BLYP/6-31+G** method) from the phenyl ring in the opposite directions in this isomer. This twisting of the hydroxyl groups is the result of the movements of the hydrogen atoms toward positions that are favorable for hydrogen bonding with the water molecule (see (2-1(b)): The hydrogen atom of the proton-accepting (donating) hydroxyl must twist away (toward) the water molecule to form hydrogen bonds. The energy of this isomer is slightly higher than the most stable structure (1-1) by about 1.83 (1.88) kcal/mol (ZPE corrected) at HF/6-31+G** (BLYP/6-31+G**) level of theory.

**Table 1**. Computed energies, zero point energies, binding energies and harmonic frequencies of the catechol-$(H_2O)_n$ ($n = 1$-$3$) clusters

| | Energy (Hartree) | ZPE (kcal/mol) | ΔE (kcal/mol) | Binding Energy (kcal/mol) | Harmonic Frequencies[b] (cm$^{-1}$) |
|---|---|---|---|---|---|
| $H_2O$ | -76.03123[a] | 14.51[a] | | | 3785 3663 |
| Catechol | -380.44690[a] | 73.23[a] | | | 3693 3636 |
| catechol-$H_2O$ (1-1) | -456.48938[a] | 89.64[a] | 0 | -5.15[a] | 3779 3665 3621 3444 |
| (1-2) | -456.48693[a] | 89.93[a] | 1.83[a] 1.88[b] | -3.33[a] | 3752 3601 3570 3357 |
| (1-3) | -456.48450[a] | 89.24[a] | 2.67[a] 3.55[b] | -2.49[a] | |
| catechol-$(H_2O)_2$ (2-1) | -532.53383[a] | 107.17[a] | 0 | -10.41[a] | 3745 3743 3511 3441 3317 |
| catechol-$(H_2O)_2$ (2-2) | -532.53284[a] | 106.82[a] | 0. 27[a] | -10.13[a] | 3748 3745 3621 3531 3419 3241 |
| (2-3) | -532.53140[a] | 107.02[a] | 1.38[a] | -9.03[a] | 3744 3743 3460 3456 3229 3215 |
| (2-4) | -532.52747[a] | 105.67[a] | 2.49[a] | -7.92[a] | |
| (2-5) | -532.52433[a] | 106.25[a] | 5.05[a] | -5.37[a] | |
| catechol-$(H_2O)_3$ (3-1) | -608.57958[a] | 124.01[a] | 0 | -17.16[a] | 3747 3742 3739 3483 3399 3302 |
| (3-2) | -608.57861[a] | 123.48[a] | 0.08[a] | -17.09[a] | 3741 3740 3736 3599 3527 3313 |
| (3-3) | -608.57984[a] | 123.92[a] | -0.26[a] | -17.42[a] | 3747 3745 3738 3617 3381 3275 |
| (3-4) | -608.57769[a] | 124.10[a] | 0.27[a] | -15.90[a] | |
| (3-5) | -608.57831[a] | 124.18[a] | 0.97[a] | -16.20[a] | |

[a]HF/6-31+G**. [b]BLYP/6-31+G**.

Since the water molecule and the two hydroxyl groups form a ring in this isomer, it may be considered to be more stable than the structure (1-1), in which there is only one hydrogen bonding. However, the effects of the twisting of the two hydroxyl groups from the phenyl ring seems to be more important than the increase in the number of hydrogen bonding in going from the structure (1-1) to (1-2). The computed harmonic frequencies of the two OH stretching modes are 3601 and 3357 cm$^{-1}$ (BLYP/6-31+G**).

The third isomer of catechol-H$_2$O cluster is (1-3), in which a hydroxyl group of catechol moiety accepts proton from the water molecule. The energy of this isomer is, however, 2.67 (3.55) kcal/mol higher than (1-1) at HF/6-31+G** (BLYP/6-31+G**) theory, and thus its contribution may not be significant at low temperature. Comparing the harmonic frequencies of these three isomers of the catechol-H$_2$O cluster with the experimental experimental frequencies of the two OH stretching modes (3597 and 3499 cm$^{-1}$), the catechol-H$_2$O cluster experimentally observed by Kleinermanns and coworkers can be safely assigned as the lowest energy structure (1-1), as discussed by them.[21] It is worth noting that the order of the total energy (including the ZPE) of the catechol-H$_2$O cluster remains the same for HF/6-31+G** and BLYP/6-31+G** methods. Since the HF/6-31+G** method gives similar ordering of the energies of the isomers that is similar to that obtained by employing the BLYP/6-31+G** methods containing the effects of electron correlation, it seems that the former method can be reliable for the clusters studied in this work.

For the catechol-(H$_2$O)$_2$ cluster, the most stable isomer obtained by the HF/6-31+G** method is the structure (2-1), in which the two hydroxyl groups and the two water molecules form a ring (Fig. 3). 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. This structure is similar to the most stable isomer of the phenol-(H$_2$O)$_3$ cluster, in which the phenolic hydroxyl and the three water molecules form a ring. The structure, which is computed to be higher in energy than (2-1) by only 0.27 kcal/mol at HF/6-31+G** level of approximation, is predicted to the most stable isomer (lying 0.86 kcal/mol below (2-1)) by the BLYP/6-31+G** method. In the structure (2-2), one of the two hydroxyl groups (twisted from the phenyl ring by 6.7° at HF/6-31+G** theory) remains noninteracting with the water molecules, while the other hydroxyl group (forming an angle of 16.6° with the phenyl ring) and the two water molecules form a ring. The latter hydroxyl group acts both as proton donor and acceptor, analogous to the phenol-(H$_2$O)$_2$ cluster. The hydrogen atom of the noninteracting hydroxyl forms a weak hydrogen bond (2.180 Å) with the oxygen atom of the other hydroxyl. One of the two water molecules lies more or less in the phenyl ring, while the other is located almost perpendicularly above it. The length (1.920 Å) of the hydrogen bond between the proton-donating hydroxyl and the water molecule is much shorter than the other (2.241 Å). The distance (2.030 Å) of the hydrogen bond between the
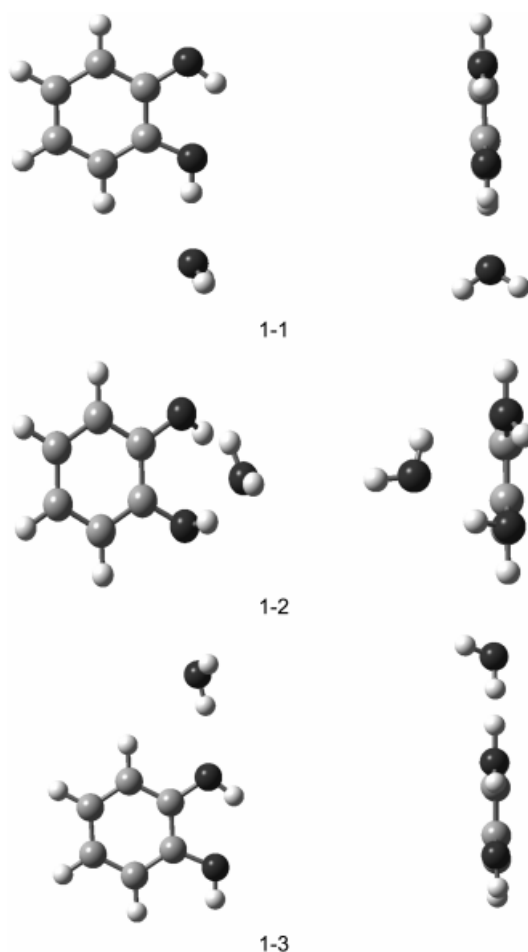


**Figure 2**. Computed structures of catechol-H$_2$O clusters.

two water molecules is in between. Compared with the case of catechol-H$_2$O cluster discussed above, this indicates that the effects of the addition of a hydrogen bond in the isomer with the largest ring structure consisting of the largest number of the hydroxyl groups and the water molecules, and those of the twisting of the two hydroxyl groups away from the phenyl ring acts in opposite way, that the relative magnitudes of the two effects are quite subtle.

The third stable structure (2-3) is also shown in Fig. 3. In this isomer, lying 1.38 (1.11) kcal/mol above (2-1) by HF/6-31+G** (BLYP/6-31+G**) theory, the two hydroxyl groups of the catechol moiety and the two water molecules form a distorted tetragon. In this structure, the two water molecules are located at the opposite sides of the phenyl ring, and the four oxygen atoms of the hydroxyl groups and the water molecules do not lie in a plane. Each of the hydroxyl groups of the catechol molecule acts both as proton donor and acceptor. The lengths of the hydrogen bonds between the proton-donating hydroxyl groups (1.948, 1.949 Å and 1.788 Å by HF/6-31+G** and BLYP/6-31+G** theory, respectively) are much shorter than those of the proton donating hydroxyl groups (2.130 Å and 1.956 by HF/6-31+G** and BLYP/6-31+G** theory, respectively). In another isomer, (2-4), lying 2.49 kcal/mol above (2-1) by HF/6-31+G** theory, one hydroxyl group is proton donor, while the other is proton
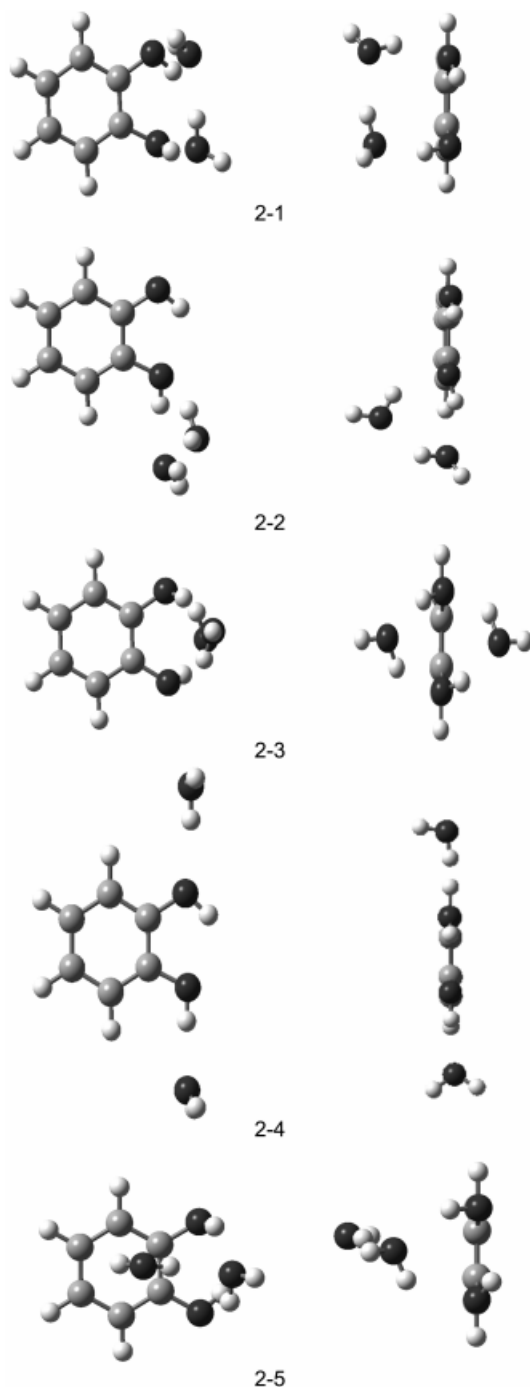
**Figure 3**. Computed structures of catechol-(H$_2$O)$_2$ clusters.

acceptor. The two hydroxyl groups in the catechol moiety are slightly (by about 2°) twisted from the phenyl ring. The lengths of the hydrogen bonds between these hydroxyl groups and the water molecule are 1.940 and 2.085 Å, respectively. The four oxygen atoms lie almost along a line parallel to the phenyl ring.

One of the intriguing questions concerning the aromatic acid-water clusters is whether the $\pi$ bonding between water molecule and the phenyl ring is important or not.[24] For the benzene-water clusters, this $\pi$ bonding is essentially the only possible interactions, because the benzene molecule does not

possess another functional group. For phenol-(H$_2$O)$_n$ clusters, on the other hand, the presence of the hydroxyl groups gives so strong hydrogen bonding with the water molecules that the isomers exhibiting $\pi$ 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 this regard, we checked whether a catechol-(H$_2$O)$_2$ cluster may contain such a $\pi$ bonding. In the isomer (2-5), one of the water molecules interacts with the two hydroxyl groups (the lengths of the hydrogen bonds are 2.130 and 2.318 Å), while the other water lies above the phenyl ring. The distance between the oxygen and the hydrogen atoms of the water molecules is 2.147 Å. The energy of this isomer is, however, quite high, 5.05 kcal/mol higher than that of the most stable structure (2-1) at HF/6-31+G** approximation. The lengths of the hydrogen bonds in this $\pi$ bonding isomer are relatively larger than for other isomers presumably due to the geometrical constraints (that is, the accessibility of water to the phenyl ring) caused by the formation of the $\pi$ bond, and the resulting increase in energy is not fully compensated by the bonding. Since the energy of the structure (2-5) is relatively higher than the low-energy structures, it may be inferred that this conformer including the $\pi$-bonding may not be important in low-temperature gas phase catechol-(H$_2$O)$_3$ 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, and indeed, the $\pi$ bonding cluster is very important for the catechol-(H$_2$O)$_3$ cluster, as we show below.

We have found that the relative energies of the catechol-(H$_2$O)$_3$ cluster depend very much on the methods and the basis sets employed. For example, the most stable isomer of the catechol-(H$_2$O)$_3$ cluster has been computed to be the structure (3-4) when employing the HF/6-31G method, while the structures (3-1), (3-2) and (3-3) are computed to more stable than (3-4) with almost the same energy (including ZPE) to within 0.3 kcal/mol by the HF/6-31+G** method. The structure of the isomer (3-1) of the catechol-(H$_2$O)$_3$ cluster is similar to that of the phenol-(H$_2$O)$_n$ ($n \geq 3$) clusters, in which the hydroxyl and the water molecules form a ring. In (3-1), the oxygen atoms of the two hydroxyl groups of the catechol moiety and the three water molecules form a pentagonal ring, and the five oxygen atoms lie almost in the ring. The lengths of the hydrogen bonds vary, from fairly short one between one of the hydroxyl and a water molecule 1.866 Å (1.681 Å) and a long one 2.188 Å (2.030 Å) for the intramolecular hydrogen bonding at HF/6-31+G** (BLYP/6-31+G**) level of theory. The other stable isomer of the catechol-(H$_2$O)$_3$ cluster is the structure (3-2), in which a water molecule forms a $\pi$ bond with the phenyl ring. This structure is not to be observed for phenol-(H$_2$O)$_n$ clusters, because the hydroxyl group in these clusters is more or less stiff with respect to the movement out of the phenyl ring, and thus, the binding water molecules cannot move back to the phenyl ring. Comparing the structures (3-1) and (3-2), it can
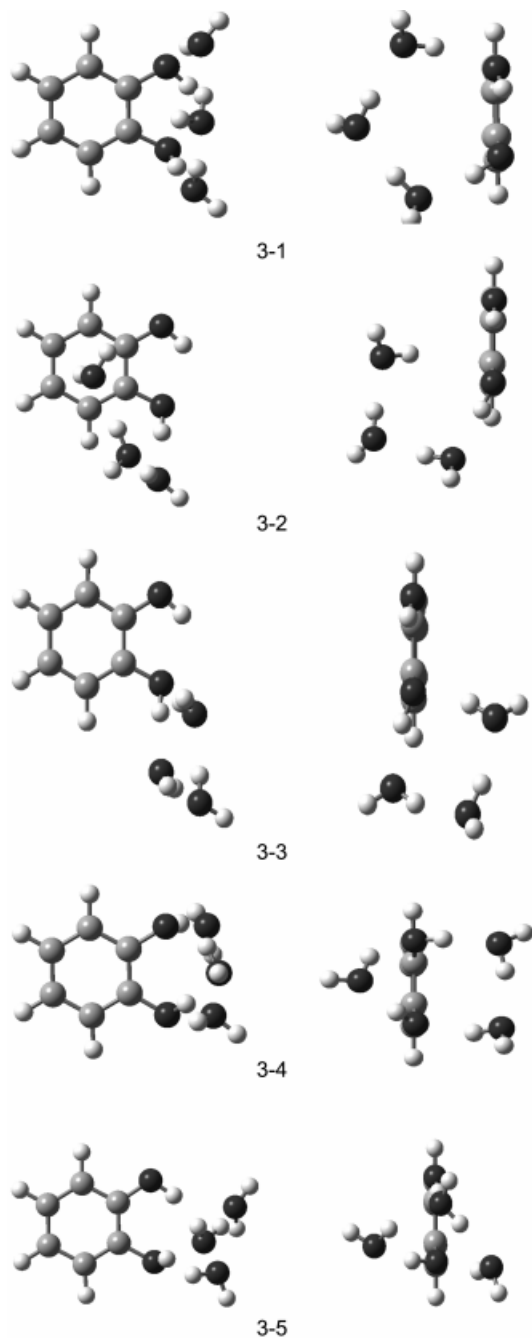
**Figure 4**. Computed structures of catechol-$(H_2O)_3$ clusters.

be seen that the weaker intramolecular hydrogen bonding (length of 2.157 or 2.120 Å by HF/6-31+G** and BLYP/6-31+G** method, respectively) in (3-2) is compensated by the presence of $\pi$ bonding, yielding very similar energies for (3-1) and (3-2). In the isomer (3-3), computed to be the most stable at HF/6-31+G** approximation, one of the two hydroxyl groups and the three water molecules form a rectangular ring, while the other hydroxyl group is essentially isolated from the ring. The four oxygen atoms in the ring form strict plane, and the lengths (strengths) of the hydrogen bonds decrease progressively from 1.640 to 1.848 Å.

Since these three isomers are essentially of identical

energy, they may contribute more or less equally to the infrared spectra of catechol in aqueous solution. Comparison of the computed harmonic frequencies with the experimentally observed (gas phase) infrared frequencies of catechol-water clusters may also give considerable insight into the configuration of the water molecules around the catechol molecule. The experimental frequencies obtained by Kleinermanns *et al.*[21] for the catechol-$(H_2O)_3$ cluster are, in decreasing order, 3720, 3714, 3704, 3571, 3450, 3423 and 3355 cm$^{-1}$. These frequencies correspond to OH stretching modes of the water molecules and the hydroxyl group in the phenyl ring. The harmonic frequencies of the corresponding OH stretching modes of the isomer (3-1) are 3747, 3742, 3739, 3483, 3398, 3302, 3205 cm$^{-1}$, while those of (3-2) and (3-3) are 3741, 3739, 3736, 3598, 3527, 3313, 3215 cm$^{-1}$, and 3747, 3745, 3738, 3617, 3381, 3275 cm$^{-1}$, respectively (see Table 1). The three modes with the highest frequencies are similar, and they agree very well (to within 35 cm$^{-1}$, which is typical of the BLYP/6-31+G** method) with the corresponding three experimental frequencies. The experimental frequency at 3571 cm$^{-1}$, however, seems to be accounted best by the computed band at 3598 cm$^{-1}$ for the conformer (3-2), which contains $\pi$ bonding with water molecule. The computed band at 3571 cm$^{-1}$ is characteristic of the conformer (3-2), and corresponds to the stretching of the water molecule that is $\pi$-bonding with the phenyl ring. Considering that the Kleinermanns *et al.*'s UV-IR double resonance experiments can select[25] different isomers of the catechol-$(H_2O)_3$ cluster, the observed bands seem to be that of the conformer (3-2), as pointed by Kleinermanns *et al.*[21]

The fourth most stable isomer is (3-4), lying 1.27 (0.71) kcal/mol above (3-1) (or (3-2)) at HF/6-31+G** (BLYP/6-31+G**) approximation. In this structure, two water molecules form hydrogen bonds with the two hydroxyl groups on one side of the phenyl ring forming a ring, while the third water molecule hydrogen bonds to the two hydroxyl groups on the other side of the ring. However, the five oxygen atoms do not lie in a plane. The 5th most stable isomer is (3-5) lying only 0.97 (0.70) kcal/mol above (3-1) at HF/6-31+G** (BLYP/6-31+G**) approximation. In this isomer, one of the hydroxyl groups and the three water molecules are interacting in a distorted tetragon that loosely bind to the remaining hydroxyl. In this structure, one of the water molecules interacts with both of the hydroxyl groups at one side of the phenyl ring, accepting proton from a hydroxyl and donating proton to another hydroxyl, while the other two water molecules form a slightly distorted ring with the two hydroxyl groups at the other side of the phenyl ring. It may be considered as the most stable catechol-$(H_2O)_2$ cluster (2-1) plus a water molecule interacting with the two hydroxyl. The lengths of the hydrogen bonds are between 1.660 and 1.830 Å. It should be noted that the five oxygen atoms are not in the same plane in this isomer.

The binding energies of these clusters are also of considerable interest, because they may be a good estimation of the interactions between the functional group (hydroxyl in the present case) in the phenyl ring and the water molecules

surrounding it in the clusters. This may also be the case for the aqueous solution of the aromatic alcohols, since the water molecules in the immediate vicinity of the functional group would largely determine the interactions, while other water molecules farther from it may act as "spectators". If this is the case, the cluster model could be quite useful for comparing the strengths of the functional group solvent interactions as recently studied by Cheong and co-workers[26-29] employing the chromatographic technique. Table 1 presents the binding energies of the catechol-$(H_2O)_n$ ($n$ = 1-3) clusters computed by the HF/6-31+G** method. The binding energies of the most stable isomers are about 5.1, 10.4 and -17.4 kcal/mol for $n$ = 1-3, respectively. The binding energies of catechol-$(H_2O)_n$ ($n$ = 1-3) are computed to be smaller than those[30] (-5.5, -12.6 and -21.3 kcal/mol, respectively) of the corresponding phenol-$(H_2O)_n$ ($n$ = 1-3) clusters computed by HF/6-31G** approximation, indicating that the interactions between the hydroxyl groups in the phenyl ring and the water molecules in catechol-water clusters are weaker than those in phenol-water clusters. This seems to be the result of the weakening of the two alcoholic hydroxyl groups interacting with the water molecules due to intramolecular hydrogen bonding in the catechol-$(H_2O)_n$ clusters. Experimental studies on the strength of the hydrogen bonding of catechol-$(H_2O)_n$ clusters or of the catechol molecule in aqueous solution will be highly intriguing.

## Conclusions

Since many conformers of aromatic alcohol-$(H_2O)_n$ clusters are of similar energy, the analysis of the experimental observations on these clusters is usually quite complicated. Since the differences between the energies of the conformers are typically less than a few kcal/mol, it is probable that several isomers may account for the configuration of water molecules near the catechol molecule in aqueous solution and also in gas phase environment at moderate temperature. We find that the binding energies of catechol-$(H_2O)_n$ clusters are a bit smaller than those of phenol-$(H_2O)_n$ clusters. If a few water molecules around the aromatic alcohol tend to determine the magnitude of the interactions between the alcoholic hydroxyl groups and the water molecules, these differences between the phenol-water and catechol-water clusters may be quite useful for elucidating the configurations of the water molecules around these aromatic alcohols and studying the nature of the solute-solvent interactions in aqueous solutions.

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