

Computational Study of Hydrogen Bonding in Phenol-acetonitrile-water Clusters

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Calculations are presented for phenol – acetonitrile - (water)_n (n = 1-3) clusters. We examine the nature of interactions in the mixed clusters by calculating and comparing the structures, relative energies and harmonic frequencies of isomers with different type of hydrogen bonding. The conformers exhibit quite different patterns in the shifts of the CN and OH stretching frequencies, depending on the type of hydrogen bonding. Cyclic hydrogen bonding among the water molecule(s), acetonitrile and phenolic OH proves very important in determining the relative stability. It is also shown that acetonitrile tends to bind to the OH group of phenol in low energy conformers.

Key Words : Hydrogen bonding, Mixed cluster

Introduction

Studying clusters is useful for elucidating the effects of solvation on the properties of the solute on the molecular level. Although considerable amount of information has been accumulated for the structures of the clusters, most of the investigations were focused either on “pure” clusters, consisting of identical solvent molecules such as water, methanol, ammonia, or “microsolvated” solute consisting of solute molecule and a number of identical solvent molecules. The latter type of clusters¹⁻⁹ were investigated extensively to unveil the properties of the solvated solute both in the clusters and in the solution phase. Recent studies of aromatic alcohol - water,¹⁰⁻¹² benzonitrile - water,¹³ amino acid - water^{14,15} and DNA base - water¹⁶ clusters are of this type. More intriguing and complicated “mixed” clusters may consist of a solute interacting with different kinds of solvent molecules of more or less equal molar ratio. In this situation, different type of functional groups may interact, producing a variety of conformers with interesting structural and thermodynamic properties. Studying this type of mixed clusters would also be useful to obtain information for the properties of the solute in mixed solution on the molecular level, because one may not simply use the weighted average of the dielectric constants of the constituent solvents to employ the polarizable continuum models (PCM) type approximations.¹⁷ Thus, one would study their properties by explicitly considering the molecular nature of the interactions, taking advantage of the cluster model.

In this work, we study the phenol – acetonitrile – (water)_n (n=1-3) cluster to examine the nature of interactions as a prototypical system for the mixed type clusters. Our focus in this work is on the interactions among the solute and the different kinds of solvent molecules. We investigate this type of system to elucidate the property of the clusters as a function of the number of the binding water molecules. We

calculate and compare the structures, relative energies and harmonic frequencies of the isomers with different types of hydrogen bonding.

Computational Methods

In this study all the calculations are carried out using the GAUSSIAN 94 and the GAUSSIAN 98W set of programs.¹⁸ The density functional theory method (BLYP^{19,20}) is employed with the 6-31+G(d,p) basis set, because it yields harmonic frequencies for the high frequency stretching modes that agree with the experimental observations mostly to within 30 cm⁻¹. All the energies are zero point energy (ZPE) corrected. Default criteria are employed for the optimization processes.

Results

Phenol – solvent clusters^{3,5,21-22} have been studied intensively as model system for elucidating the effects of solvation. It has been found that the spectroscopic properties of phenol, especially the infrared frequency of the OH group, depends significantly on the arrangement of the solvent molecules such as water or ammonia. This latter finding has proved very useful for determining the structures of phenol – solvent clusters by double resonance technique along with quantum chemical calculations.

We find two lowest energy isomers for the phenol – CH₃CN – (H₂O) cluster as presented in Figure 1. The isomer (ph1-1), in which the hydroxyl group acts as proton donor to the binding water molecule, is of lower energy than (ph1-2) by 1.18 kcal/mol (ZPE-corrected). (the relative energy calculated by the MP2/6-31+G(d,p)//BLYP/6-31+G(d,p) method, and the relative Gibbs function at 5 K (typical temperature at which these clusters are to be observed), G_{5K}, in the Figures also give similar relative stability of the conformers). This observation may stem from the fact that the water molecule is a better proton acceptor than the CN

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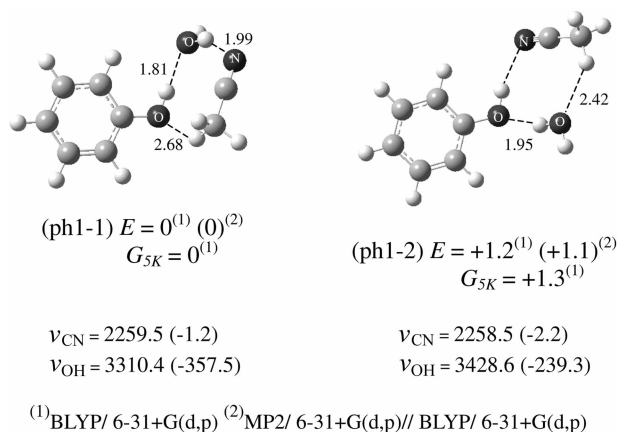


Figure 1. The structures and harmonic frequencies (CN and OH) of phenol (CH_3CN) - (H_2O) clusters (relative energy and Gibbs function in kcal/mol, and harmonic frequencies in cm^{-1}).

group in acetonitrile. The presence of acetonitrile seems to moderate the energy difference (2.6 kcal/mol) between the two type of isomers from the case of the phenol - (H_2O) cluster.²³ The methyl hydrogen in acetonitrile forms partial hydrogen bonding with the hydroxyl group and with the water molecule in (ph1-1) and (ph1-2), respectively. The acetonitrile molecule binds with the OH group and the water molecule in cyclic fashion in these isomers. Thus the hydrogen bonding may be described as " π -type".²⁴ The CN stretching frequencies are calculated to slightly red-shift (by 1.2 and 2.2 cm^{-1} , respectively) from that in the free acetonitrile molecule, in line with the case of water - acetonitrile cluster.²⁴ The stretching frequencies of the phenolic OH group, however, red shift profoundly (by 357 and 239 cm^{-1}) from the free phenol. Since the difference in the frequency shifts is considerable (118 cm^{-1}), it would be very useful signature for determining the structures of the two isomers.

Figure 2 presents the lowest energy conformers for the phenol - CH_3CN - (H_2O)₂ cluster, of which (ph2-1) is lower lying by 0.5 kcal/mol than (ph2-2). In these isomers the acetonitrile directly interacts with the phenolic OH group, forming cyclic hydrogen bonding with the two water molecules. These low energy structures seems quite interesting, because they indicate that the insertion of acetonitrile into the hydrogen bonding among the two water molecules and the hydroxyl group may contribute to the stability of the cluster, in contrast with the generally known fact that the interactions among the water molecules are stronger than that between water and other polar molecules. The difference between (ph2-1) and (ph2-2) consists in the position of acetonitrile relative to the hydroxyl group: in (ph2-1) the OH group is proton-donating to the water molecule, whereas it donates a proton to the CN group in (ph2-2). It should be noted, however, that the energy difference between these two conformers are quite small (0.5 kcal/mole), decreasing from that (1.2 kcal/mol) between the two lowest energy conformers (ph1-1) and (ph1-2) of the phenol - CH_3CN - (H_2O) cluster. The shifts of the CN stretching frequencies for (ph2-1) and

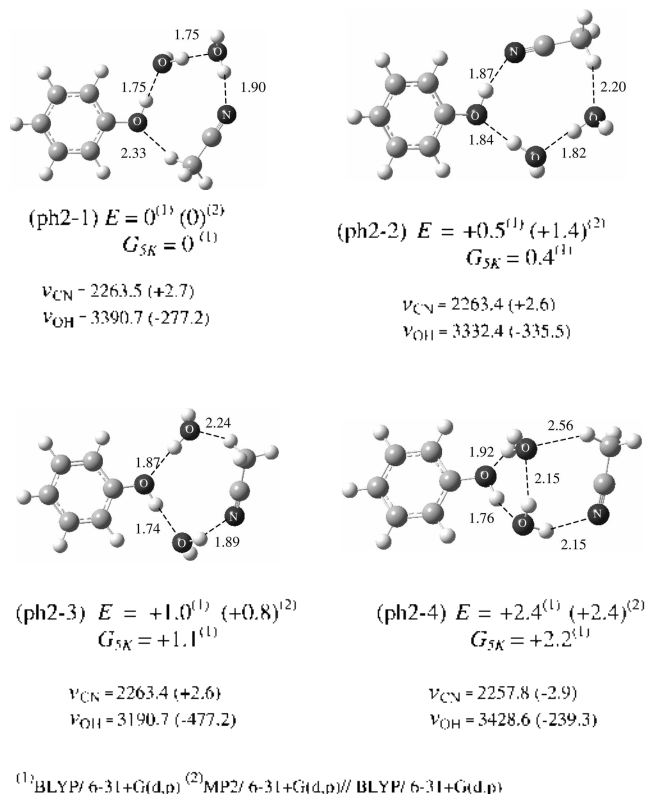


Figure 2. The structures and harmonic frequencies (CN and OH) of phenol - (CH_3CN) - (H_2O)₂ clusters (relative energy and Gibbs function in kcal/mol, and harmonic frequencies in cm^{-1}).

(ph2-2) are calculated to be very similar. Thus, assigning these two low energy conformers in the low temperature gas phase environment would rather be carried out by comparing the phenolic OH stretching frequencies that are red-shifted by 277 and 336 cm^{-1} , respectively. It is also interesting to observe that the methyl hydrogen atom contributes to the cyclic hydrogen bonding in these conformers, as noted in acetonitrile - water clusters.²⁴

In the conformer (ph2-4), the OH group and the two water molecules form cyclic hydrogen bonding with the O-O distance of 2.15 Å, with the acetonitrile moiety lying outside and not forming direct hydrogen bond with the OH group. In (ph2-3), the OH group, the two water molecules and acetonitrile forms 4-membered cyclic hydrogen bonding similarly to (ph2-1) and (ph2-2), but with the acetonitrile on the far side. In (ph2-2) the two waters are quite far apart, and this reduction of the strain from (ph2-1) to (ph2-2) may be the reason that the latter conformer is thermodynamically more stable. It is useful to note that the CN stretching frequency in (ph2-4) is slightly red-shifting (-2.9 cm^{-1}), whereas those for others conformers are blue-shifting. The disparate directions of the CN frequency shifts stem from the fact that acetonitrile interacts with water molecules almost in perpendicular fashion (π -type) in (ph2-3), whereas the acetonitrile - water hydrogen bonding in other conformers exhibits considerable σ -type character, as discussed in the case of water - acetonitrile cluster.²⁴ On the other hand, the phenolic OH stretching frequencies are calculated to red

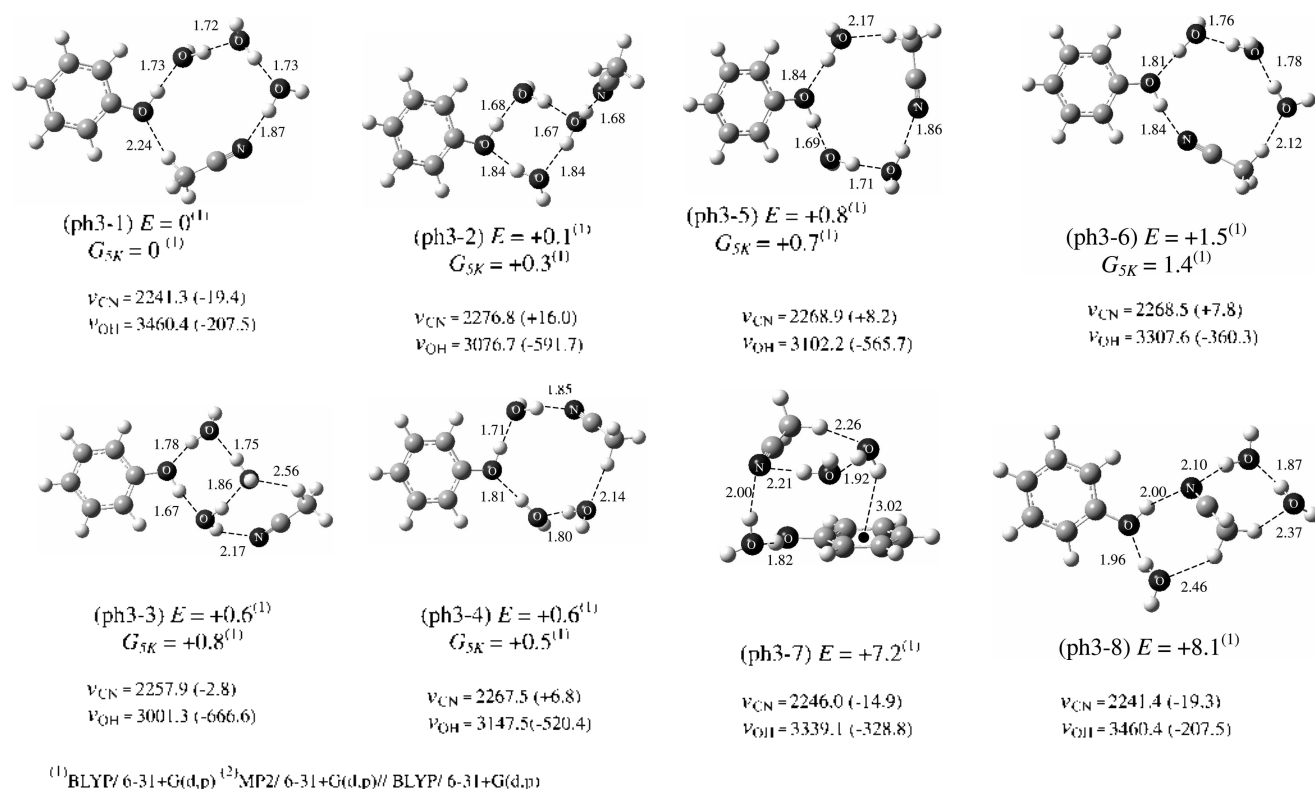


Figure 3. The structures and harmonic frequencies (CN and OH) of phenol-(CH₃CN)-(H₂O)_n clusters (relative energy and Gibbs function in kcal/mole, and harmonic frequencies in cm⁻¹).

shift tremendously (between 200 and 500 cm⁻¹) from that of free phenol.

For the phenol-CH₃CN-(H₂O)₃ cluster, the cyclic hydrogen bonding among the three water molecules, acetonitrile and phenolic OH again proves important. The calculated conformers are shown in Figure 3. In the conformer (ph3-1), acetonitrile participates in 5-membered cyclic hydrogen bonding, whereas it is expelled to the far side in the conformers (ph3-2) and (ph3-3) with the three water molecules and the phenolic OH interacting in 4-membered cyclic ring. Their energy differences, however, are very small (0.1 and 0.6 kcal/mole), and they may coexist in low temperature environment. The differences in the CN and phenolic OH stretching frequencies may help characterize them. The behavior of the CN frequencies is quite diverse, somewhat red-shifting for (ph3-1) and (ph3-3), while blue-shifting for (ph3-2) and (ph3-4). All the conformers exhibit red-shifted OH stretching frequencies, but the degree of shifts are also very different (207-667 cm⁻¹). Figure 3 also presents other conformers of higher energies. We find a conformer (ph3-7) in which a water molecule is located above the phenyl ring, forming a π -complex.⁹ This type of complex has been discussed for other type of clusters, but it is of much higher energy here. The binding energies of the clusters studied in this work is given in Table 1.²⁵

Although it would be dangerous to extrapolate the present results to the case of phenol dissolved in mixed water-acetonitrile solution, it is tempting to suggest that the configurations with acetonitrile directly binding to the

Table 1. Binding energies of phenol-(CH₃CN)-(H₂O)_n (n = 1-3) clusters

number of water molecule (s)		Binding energy (kcal/mole)
N=1	ph1-1	9.9
	ph1-2	8.7
N 2	ph2-1	19.2
	ph2-2	18.7
	ph2-3	18.2
	ph2-4	16.8
N=3	ph3-1	26.5
	ph3-2	26.4
	ph3-3	25.9
	ph3-4	25.9
	ph3-5	25.7
	ph3-6	25.0
	ph3-7	19.3
	ph3-8	18.4

phenolic OH group may largely contribute in the solution phase, despite the strength of the cyclic water chain. More accurate descriptions of this latter situation would be obtained by including more solvent molecules in the system, and also by employing the PCM type methods.

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25. The basis set superposition error of the binding energies may not be calculated unambiguously, but is estimated to be about 20-30% from our experience for phenol - water or water - acetonitrile clusters.