Thermochemical Properties and Structure of Phenol−$(H_2O)_{1-6}$ and Phenoxy−$(H_2O)_{1-4}$ by Density Functional Theory

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Structural, vibrational, and thermochemical properties of phenol−$(H_2O)_{1-6}$ and phenoxy radical−$(H_2O)_{1-4}$ complexes were calculated by using density functional theory. The insertion of a phenol molecule in a water cluster keeps some similarities with the addition of a water molecule. The interaction of the phenoxy radical with water clusters shows a strong dependence on the cluster size. The results are compared with theoretical and experimental data for the vibrational structure of phenol−water complexes and with thermochemical data for the phenol O−H bond dissociation enthalpy.

1. Introduction

The study of hydrogen bonding between water molecules and organic systems is important to understand the solvation of these systems and therefore their chemical reactivity in solution. Some relatively simple molecular structures can be considered as model systems in this type of studies. One of them is the phenol molecule. Several experimental and theoretical studies on phenol[1−10] and phenol−water complexes[5,11−29] have been reported, focusing on some relevant aspects, including vibrational spectrum, structure, and binding energies.

It is known that the O−H breaking mechanism in ionized phenol−water clusters is crucial for the understanding of proton-transfer reactions.[30−32] One of the most interesting aspects of this mechanism is the dependence of the proton-transfer reaction on the number of water molecules in the cluster.[31,32] In addition, the importance of the phenoxy radical is well recognized since this is an intermediate in many biological and industrial processes. The reactive nature of the phenoxy radical makes difficult its direct structure determination[33−35] and several quantum chemical studies contributed to characterize the radical structure, bonding, and vibrational spectrum.[36−39] Most of the studies for the phenoxy radical dealed with the isolated system. However, the chemical reactivity of this radical in solution makes the study of its interactions with water clusters of great interest. It is also expected that studies on the complexation of phenol and phenoxy radical with water clusters will contribute to understand their solvation in water, at a molecular level.

In the present work we report data for the structures, vibrational spectra, and thermochemical properties of phenol−water [PhOH−$(H_2O)_{1-6}$] and phenoxy radical−water [PhO$^\bullet$−$(H_2O)_{1-4}$] complexes, based on density functional theory. Our main objectives are to provide accurate theoretical data on these systems and to establish a closer link with recent experimental data on the vibrational structure[25,28,29] and thermochemical properties of phenol in the condensed phase.[40−43]

2. Computational Details

Molecular energies (E) were calculated by using eq 1

$$E = V_{NN} + H^{CORE} + V_{ee} + E_X[\rho] + E_C[\rho] \qquad (1)$$

where V_{NN} is the nuclear-nuclear interaction, H^{CORE} is a monoelectronic contribution to the total energy, including electron kinetic and electron-nuclear interaction energies, and V_{ee} is the Coulombic interaction between the electrons. $E_X[\rho]$ and $E_C[\rho]$ are respectively the exchange and correlation energies, functionals of the electronic density ρ.

Complete geometry optimizations have been carried out with different exchange and correlation functionals and the following combinations were used: a Becke representation for the exchange[44] and the gradient-corrected Lee, Yang, and Parr correlation functional[45] (BLYP); the Becke's three parameter hybrid method[46] with the LYP correlation functional (B3LYP) and with the Perdew and Wang[47] nonlocal correlation functional (B3PW91).

Calculations with different basis set including 6-31G(d,p),[48] 6-311+G(d,p),[49] D95V(d,p),[50] and cc-pVTZ[51] have been carried out. Phenol−water [PhOH−$(H_2O)_{1-6}$], phenoxy−water [PhO$^\bullet$−$(H_2O)_{1-4}$], and water clusters [$(H_2O)_{1-6}$] have been fully optimized with the B3LYP and B3PW91 functionals using Dunning's D95V(d,p)[50] basis set. In our geometry optimizations we have selected the most stable conformer for the complexes of phenol and phenoxy with water molecules and also for the water clusters. Experimental[52,53] and theoretical[53−56] works indicate that the water trimer, tetramer, and pentamer have cyclic minimum energy structures. The water hexamer is the first to adopt a three-dimensional cage structure.[53,55] However, in the case of the water hexamer, recent MP2 calculations of Kim and Kim[56] indicate that the five most stable conformers of the water hexamer are isoenergetic within ~3 kJ mol^{-1} at 0 K. Thus, we have directed our geometry optimizations to the water [$(H_2O)_{3-6}$]

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TABLE 1: Theoretical Results for the Phenol Molecule (PhOH) and for the Phenoxy Radical (PhO$^•$)[a]

	E			
	PhOH	PhO$^•$	H$^•$	D(PhO−H)[b,c]
BLYP/6-31G(d,p)[d]	−307.254 03	−306.633 45	−0.495 44	331.0
BLYP/6-311+G(d,p)[e]	−307.341 75	−306.718 85	−0.497 55	331.5
B3LYP/6-31G(d,p)[d]	−307.373 66	−306.743 78	−0.500 27	342.7
B3LYP/6-311+G(d,p)[f]	−307.453 78	−306.821 73	−0.502 16	343.5
B3LYP/cc-pVTZ[f]	−307.480 67	−306.847 25	−0.502 16	347.1
B3LYP/D95V(d,p)[d]	−307.413 99	−306.783 38	−0.498 91	348.2
B3LYP/cc-pVTZ[g]	−307.480 51	−306.846 99	−0.502 16	347.3
B3PW91/6-31G(d,p)[d]	−307.256 02	−306.623 45	−0.502 17	344.8
B3PW91/cc-pVTZ[h]	−307.356 35	−306.720 32	−0.503 98	349.1
B3PW91/D95V(d,p)[d]	−307.298 52	−306.665 26	−0.501 01	349.7
B3PW91/6-311+G(d,p)[d]	−307.329 99	−306.695 46	−0.503 98	345.2

[a] Total energies E corrected for zero point vibrational energies in a.u.; D(PhO−H) (in kJ mol^{-1}) is the enthalpy for the reaction PhOH(g) → PhO$^•$(g) + H$^•$(g) at 298.15 K. [b] D(PhO−H) has been estimated as $D(\text{PhO−H}) = \Delta E + RT$, where $\Delta E \approx \Delta E_e + \Delta E_v$. ΔE_e is the electronic energy difference and ΔE_v is the difference between zero point energies. [c] The recommended experimental value is 371.3 ± 2.3 kJ mol^{-1} (ref 42). [d] Optimized geometry at this level of the theory. [e] Single-point calculation with the BLYP/6-31G(d,p) geometry. [f] Single-point calculation with the B3LYP/6-31G(d,p) geometry. [g] Single-point calculation with the B3LYP/D95V(d,p) geometry. [h] Single-point calculation with the B3PW91/6-31G(d,p) geometry.

cyclic conformers. Single-point energy calculations with a larger basis set (cc-pVTZ) with the geometries optimized at the B3LYP/D95V(d,p) level are also reported.

All the calculations were performed with the Gaussian-94/DFT program.[57]

3. Results and Discussion

A. Thermochemical Properties. *1. O-H Bond Dissociation Enthalpy in PhOH.* The results obtained for the homolytic O−H bond dissociation enthalpy in phenol (reaction 2) by using different functionals and basis sets are reported in Table 1.

$$\text{PhOH(g)} \rightarrow \text{PhO}^•\text{(g)} + \text{H}^•\text{(g)} \qquad (2)$$

In agreement with Wu and Lai,[9] D(PhO−H) at 298.15 K from BLYP/6-31G(d,p) calculations (331 kJ mol^{-1}), is much lower than the recommended experimental value (371 ± 2 kJ mol^{-1}).[42] B3LYP results are in better agreement with experiment than BLYP predictions. D(PhO−H) from B3LYP/cc-pVTZ with the geometry optimized at B3LYP/D95V(d,p) is 347.3 kJ mol^{-1}. The combined functional B3PW91 also gives values in reasonable agreement with experiment and our better prediction, $D(\text{PhO−H}) = 349.7$ kJ mol^{-1}, is from a B3PW91/D95V(d,p) calculation. However, this value is still 6% lower than the recommended experimental value.

2. Phenol−Water and Phenoxy−Water Clusters. Several works[24,42,43] including a recent review article,[42] have addressed the energetics of the phenol O−H bond dissociation enthalpy in the gas phase, D(PhO−H), and in solution, D_{sln}(PhO−H).

A route to estimate D_{sln}(PhO−H), starting from gas phase data, is based on eq 3

$$D(\text{PhO−H}) = D_{\text{sln}}(\text{PhO−H}) + \Delta_{\text{sln}}H°(\text{PhOH,g}) - \Delta_{\text{sln}}H°(\text{PhO}^•\text{,g}) - \Delta_{\text{sln}}H°(\text{H}^•\text{,g}) \qquad (3)$$

where $\Delta_{\text{sln}}H°$(PhOH,g) and $\Delta_{\text{sln}}H°$(PhO$^•$,g) represent the enthalpies of solvation of phenol and phenoxy radical, and $\Delta_{\text{sln}}H°$(H$^•$,g) represents the enthalpy of solvation of the hydrogen atom, which is considered to be similar to the enthalpy of solvation of H$_2$, $\Delta_{\text{sln}}H°(\text{H}_2\text{,g})$.[58] A value proposed by Wilhelm[59] for $\Delta_{\text{sln}}H°(\text{H}_2\text{,g})$ in water (−4 kJ mol^{-1}) will be adopted.

A possible approach for estimating the enthalpies of solvation of PhOH and PhO$^•$ in water is to assume that these quantities can be identified with the enthalpies of reactions 4 and 5, respectively, provided that n (the number of water molecules in the cluster) is large enough.

$$\text{PhOH(g)} + (\text{H}_2\text{O})_n\text{(g)} \rightarrow [\text{PhOH} - (\text{H}_2\text{O})_n]\text{(g)} \qquad (4)$$

and

$$\text{PhO}^•\text{(g)} + (\text{H}_2\text{O})_n\text{(g)} \rightarrow [\text{PhO}^• - (\text{H}_2\text{O})_n]\text{(g)} \qquad (5)$$

In fact, we would anticipate that the enthalpies of these reactions would be nearly constant (within ca. 10 kJ mol^{-1}) for $n \geq 2$. A preliminary study involving the same type of phenol−water clusters with one and two water molecules confirmed the obvious idea that the strongest interactions with one and two water molecules would be through a pair of hydrogen bonds and therefore that the OH group would be “saturated” with two water molecules.[43] On the other hand, the early results for the phenoxy radical indicated a fairly strong hydrogen bond between the oxygen and the first water molecule, and a weaker interaction between the second water molecule and a hydrogen from the aromatic ring.

By examining larger clusters we can now test those ideas and get a better understanding about the influence of the “spectator” water molecules (those which do not interact directly with the organic solute) on the solvation energetics.

Total energies for the phenol−water clusters [PhOH−(H$_2$O)$_{1-6}$], phenoxy−water clusters [PhO$^•$−(H$_2$O)$_{1-4}$], and water clusters [(H$_2$O)$_{1-6}$] are reported in Table 2. These values were used to calculate enthalpies of reactions 4, 5, and 6 at $T = 298.15$ K, which are collected in Table 3.

$$\text{H}_2\text{O(g)} + (\text{H}_2\text{O})_n\text{(g)} \rightarrow (\text{H}_2\text{O})_{n+1}\text{(g)} \qquad (6)$$

Let us first consider the data obtained for the water clusters. Based on simple considerations, similar to those made above, we would expect a fairly constant value for the enthalpy of reaction 6 for $n \geq 3$. Indeed, our early calculations using a semiempirical method (AM1)[43] lead to a fairly constant value for the enthalpy of reaction 6, −38 ± 3 kJ mol^{-1} ($n = 3-6$). Moreover, the negative of this value is similar to the enthalpy of vaporization of water, $\Delta_{\text{vap}}H°(\text{H}_2\text{O}) = 44.0$ kJ mol^{-1}.[60] The data in Table 3, calculated from the energies of the cyclic conformers for $n = 3-6$, also indicate that the enthalpies of reaction 6 (in the reverse direction) are in reasonable agreement with the experimental $\Delta_{\text{vap}}H°(\text{H}_2\text{O})$, particularly those based on the B3LYP optimization.

TABLE 2: Total Energies *E* (in a.u.) for the Phenol−Water Complexes [PhOH−$(H_2O)_{1-6}$], Phenoxy−Water Complexes [$PhO^\bullet-(H_2O)_{1-4}$], and Water Clusters [$(H_2O)_n$][a]

	B3PW91/D95V(d,p)	B3LYP/D95V(d,p)	B3LYP/cc-pVTZ[b]
	E	*E*	*E*
PhOH−$(H_2O)_1$	−383.703 70	−383.848 13	−383.928 33
PhOH−$(H_2O)_2$	−460.111 51	−460.285 97	−460.378 82
PhOH−$(H_2O)_3$	−536.526 65	−536.730 42	−536.834 72
PhOH−$(H_2O)_4$	−612.936 36	−613.169 17	−613.283 94
PhOH−$(H_2O)_5$	−689.343 54	−689.606 38	−689.736 22
PhOH−$(H_2O)_6$	−765.751 53	−766.044 90	−766.187 37
$(H_2O)_1$	−76.395 62	−76.423 49	−76.438 33
$(H_2O)_2$	−152.796 98	−152.853 84	−152.882 61
$(H_2O)_3$	−229.207 98	−229.294 79	−229.335 86
$(H_2O)_4$	−305.623 39	−305.739 42	−305.791 70
$(H_2O)_5$	−382.032 85	−382.177 88	−382.242 76
$(H_2O)_6$	−458.441 95	−458.616 46	−458.693 22
$PhO^\bullet-(H_2O)_1$	−383.068 44	−383.216 07	−383.293 73
$PhO^\bullet-(H_2O)_2$	−459.476 28	−459.653 55	−459.744 01
$PhO^\bullet-(H_2O)_3$	−535.882 88	−536.088 22	−536.192 18
$PhO^\bullet-(H_2O)_4$	−612.286 94	−612.523 74	−612.641 27

[a] Total energies are corrected for zero point vibrational energies. [b] Single-point calculations with geometries optimized at the B3LYP/D95V(d,p) level.

TABLE 3: Theoretical Reaction Enthalpies at 298.15 K ($\Delta_r H$ in kJ mol^{-1}) for Phenol−Water Clusters, Phenoxy Radical−Water Clusters, and Water Clusters[a]

	$-\Delta_r H$[b]					
			$PhOH + (H_2O)_n \rightarrow PhOH-(H_2O)_n$			
n	1	2	3	4	5	6
B3LYP/D95V(d,p)	30.4	50.1	59.2	43.8	40.5	40.4
B3LYP/cc-pVTZ[c]	27.3	43.7	50.6	33.2	36.4	38.2
B3PW91/D95V(d,p)	27.5	44.5	55.3	40.4	34.4	31.5
			$PhO^\bullet + (H_2O)_n \rightarrow PhO^\bullet-(H_2O)_n$			
n	1	2	3	4		
B3LYP/D95V(d,p)	26.6	45.3	28.8	4.9		
B3LYP/cc-pVTZ[c]	24.5	40.3	26.9	9.2		
B3PW91/D95V(d,p)	22.3	39.3	27.7	−1.9		
			$(H_2O)_n + H_2O \rightarrow (H_2O)_{n+1}$			
n	1	2	3	4	5	
B3LYP/D95V(d,p)	20.4	48.3	57.9	41.7	42.0	
B3LYP/cc-pVTZ[c]	18.1	41.6	48.4	35.9	34.3	
B3PW91/D95V(d,p)	17.5	42.8	54.4	38.8	37.8	

	D_{sln}(PhO−H)[d]				*D*(PhO−H)
n	1	2	3	4	
B3LYP/D95V(d,p)	348.0	349.0	374.6	383.1	348.2
B3LYP/cc-pVTZ[c]	346.1	346.7	367.0	367.3	347.3
B3PW91/D95V(d,p)	350.9	350.9	373.3	388.0	349.7

[a] D_{sln}(PhO−H) (in kJ mol^{-1}) is the PhO−H bond dissociation enthalpy in the water clusters. *D*(PhO−H) (in kJ mol^{-1}) is the enthalpy for the reaction $PhOH(g) \rightarrow PhO^\bullet(g) + H^\bullet(g)$ at 298.15 K. [b] $\Delta_r H = \Delta E - RT$, where $\Delta E \approx \Delta E_e + \Delta E_v$. ΔE_e is the electronic energy difference and ΔE_v is the difference between zero point energies. [c] Single-point calculations with the geometry optimized at the B3LYP/D95V(d,p) level. [d] Experimental data (ref 42) for D_{sln}(PhO−H) in several solvents are (in kJ mol^{-1}): 378.7 (benzene); 373.9 (isooctane); 402.3 (acetonitrile); 402.1 (ethyl acetate).

The results for the phenol−water clusters in Table 3 exhibit the same general pattern of the water clusters. This is made clear in Figure 1. Here, $D[(H_2O)_n-PhOH]$ and $D[(H_2O)_n-H_2O]$ represent, respectively, the dissociation enthalpies of a phenol molecule and a water molecule from a [$(H_2O)_n$] cluster and are equal (but have opposite signs) to the enthalpies of reactions 4 and 6. If the trends for $D[(H_2O)_n-PhOH]$ and $D[(H_2O)_n-H_2O]$ were identical, all the points would be in the unit slope straight line drawn in Figure 1. While this is not exactly the case, it is observed that the line fits the data within ca. 10 kJ mol^{-1}. In other words, from a thermochemical point of view, the insertion of one phenol molecule in water clusters of these sizes is quite similar to the addition of one water molecule.

As discussed above, our attempt to model solvation energetics by using few solvent molecules must be used with caution. Nevertheless, it is interesting to compare the experimental value for the enthalpy of solvation of phenol in water, $\Delta_{sln}H°$(PhOH,g), with the data shown in Table 3, for the phenol−water clusters. The well-known sublimation enthalpy of phenol, $\Delta_{sub}H°(PhOH) = 68.7 \pm 0.5$ kJ mol^{-1},[61] and a value for the enthalpy of solution of phenol in water, $\Delta_{sln}H°(PhOH,cr) = 10.7 \pm 0.5$ kJ mol^{-1},[62] obtained by reaction-solution calorimetry, lead to $\Delta_{sln}H°(PhOH,g) = -58.0 \pm 0.7$ kJ mol^{-1}. We observe that this value is fairly close to the enthalpy of reaction 4 for $n = 3$ but significantly more exothermic than the enthalpy of the same reaction for $n = 4-6$.

The enthalpy of reaction 5 is very dependent on the cluster size (Table 3) and $D[(H_2O)_n-PhO^\bullet]$ (the dissociation enthalpy of a phenoxy radical from a [$(H_2O)_n$] cluster, equal to minus the enthalpy of reaction 5) is quite small for $n = 4$, reflecting

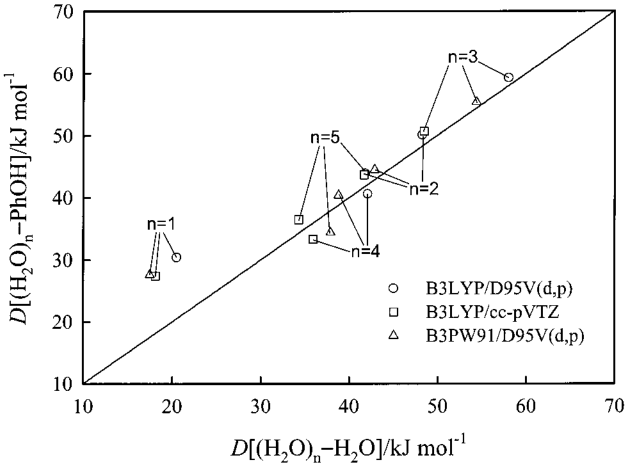

Figure 1. Dissociation enthalpy of phenol, $D[(H_2O)_n-PhOH]$, versus dissociation enthalpy of a water molecule, $D[(H_2O)_n-H_2O]$, from a $[(H_2O)_n]$ cluster, calculated at different theoretical levels.

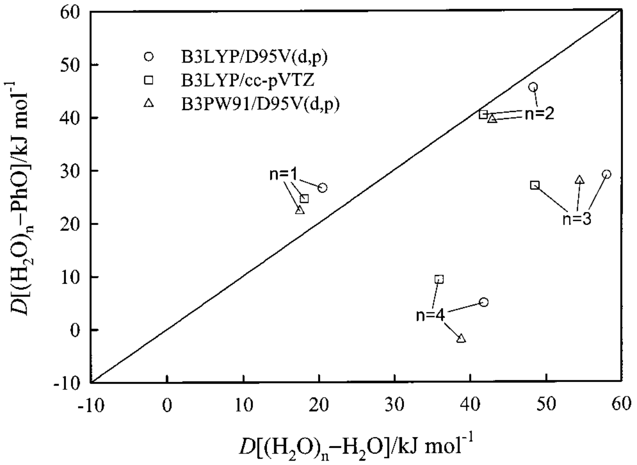

Figure 2. Dissociation enthalpy of the phenoxy radical, $D[(H_2O)_n-PhO^\bullet]$, versus dissociation enthalpy of a water molecule, $D[(H_2O)_n-H_2O]$, from a $[(H_2O)_n]$ cluster, calculated at different theoretical levels.

a weak interaction between the phenoxy radical and the water tetramer, and also the stability of the water tetramer. These conclusions are stressed in Figure 2, which shows a plot of $D[(H_2O)_n-PhO^\bullet]$ against $D[(H_2O)_n-H_2O]$. As in the case of the PhOH, here it is also observed that the complexation of the phenoxy radical with one water molecule is more stable than water dimerization (the point is above the unit slope straight line in Figure 2), reflecting the importance of the radical as a proton acceptor. On the other hand, in contrast to the case of phenol (Figure 1), the interaction between the radical and the water clusters with $n \geq 2$ is weaker than the interaction of one water molecule with the water clusters of the same size.

Our predictions for the PhO−H bond dissociation enthalpy in the water clusters, which we call D_{sln}(PhO−H), are also displayed in Table 3. They were derived from eq 3, by using the theoretical gas phase D(PhO−H) data and "solvation" enthalpies from the same table. The dependence of D_{sln}(PhO−H) on the number of water molecules in the cluster reflects the above discussion for $D[(H_2O)_n-PhOH]$ and $D[(H_2O)-PhO^\bullet]$ (or the enthalpies of reactions 4 and 5). D_{sln}(PhO−H) ≈ D(PhO−H) when $n = 1$ and 2 but D_{sln}(PhO−H) becomes considerably higher (by 20−30 kJ mol^{-1}) than D(PhO−H), for the larger clusters.

It is interesting to point out that data for D_{sln}(PhO−H) in various solvents were recently compiled.[42] Some of these values are collected in a footnote for Table 3. We can observe a strong solvent dependence of the difference between D_{sln}(PhO−H) and D(PhO−H). This difference ranges from ∼5 kJ mol^{-1} (benzene) to ∼20 kJ mol^{-1} (ethyl acetate). Our theoretical predictions for this difference, when $n = 4$, are 34.9 kJ mol^{-1} (B3LYP/D95V-(d,p)), 20 kJ mol^{-1} (B3LYP/cc-pVTZ), and 38.4 kJ mol^{-1} (B3PW91/D95V(d,p)). Although these values are in keeping with the observed experimental trend, we should stress once again that the comparison is based on the assumption that the dominant effect in the solvation enthalpy is related to the interactions of the solute with a few water molecules in the first coordination shell.

B. Structure and Vibrational Spectrum. *1. Structure*. The structure of phenol−water complexes has been analyzed by numerous experimental[22,23,27−29] and theoretical[16−18,21,22,26,28,29] works. Theoretical studies were based on ab initio Hartree−Fock (HF) theory[16−18,21,26,28,29] and Møller−Plesset perturbation theory.[17,21,26] The ionization of phenol−water and phenol−ammonia complexes has been recently analyzed by calculations using different theoretical methods, including B3LYP, MP2, and modified coupled pair MCPF.[31] Very recently, DFT calculations on the structure of ionized phenol−$(H_2O)_{1-4}$ clusters have been reported.[32]

The structures of neutral [phenol−$(H_2O)_{1-6}$] clusters, as obtained in this work by density functional theory, are displayed in Figure 3, and the corresponding Cartesian coordinates are available as Supporting Information.

We have directed our calculations to the most stable conformer for each phenol−water complex. These structures are in keeping with those found by Watanabe and Iwata[26] for the most stable conformers and some bond distances from their work are also shown in Figure 3.

Table 4 reports data for the phenol O−H bond in the different clusters. We can observe an increase of the phenol O−H bond length (d_{O-H}) and a reduction of the H−OH$_2$ distance between the hydrogen in the phenol OH group and the water oxygen (d_{H-OH_2}) when n increases from 1 to 5. However, while d_{H-OH_2} increases by about 3%, d_{H-OH_2} decreases by 14%, reflecting the relevant role played by the water oxygen as a proton acceptor. This feature is reinforced by the collective coupling of the hydrogen bonding interactions among the water molecules, which increases with n but seems to stabilize after $n = 5$.

Although our results stress the role of the phenol molecule as a proton donor in water, it is interesting to establish a comparison with the situation in the ionized $[PhOH-(H_2O)_{1-4}]^+$ complexes. Table 4 also reports d_{O-H} and d_{H-OH_2} for the ionized clusters, obtained by Re and Osamura.[32] From these values it is clear that proton transfer only occurs for $n \geq 3$ in the ionized complexes. The only similarity with the neutral complexes concerns the enhancement of the proton acceptor character of the oxygen atom closer to the phenol O−H bond by increasing the number of water molecules. For the neutral complexes, our calculations indicate that this collective effect levels off when phenol is surrounded by five water molecules.

Figure 4 presents the geometric structures of the phenoxy radical and phenoxy radical−water complexes. Table 5 reports the C−O bond length (d_{C-O}) and the distance between the phenoxy oxygen and the water hydrogen atom (d_{O-HOH}). The C−O bond length is not significantly modified by the presence of the water molecules but d_{O-HOH} is reduced by about 0.1 Å when we move from the complex with one water molecule to the complex with two water molecules. A smaller change is

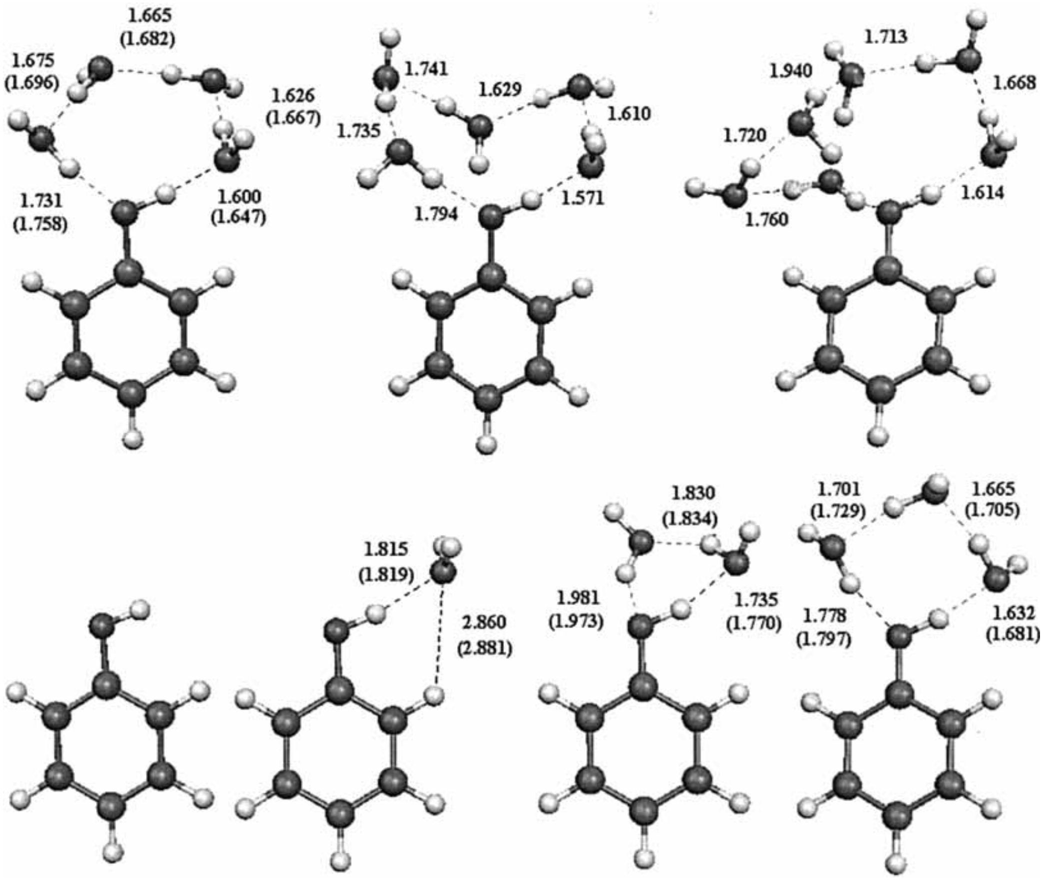

Figure 3. Structures of phenol−water clusters [PhOH−$(H_2O)_{1-6}$] showing hydrogen bond distances (in Å). The values in parentheses are from Watanabe and Iwata (ref 26).

TABLE 4: O−H Bond Lengths in Phenol (d_{O-H} in Å), Distances Between the Hydrogen of the Phenol O−H Group and the Water Oxygen (d_{H-OH_2} in Å), and Frequencies (ν_{O-H} in cm^{-1}) for Phenol and Phenol−Water Clusters [PhOH−$(H_2O)_{1-6}$][a]

	B3LYP/D95V(d,p)			exp.[b]
	d_{O-H}	d_{H-OH_2}	ν_{O-H}	ν_{O-H}
PhOH[c]	0.967		3845	3657
PhOH−$(H_2O)_1$	0.980 (1.027)	1.819 (1.532)	3600	3524
PhOH−$(H_2O)_2$	0.990 (1.074)	1.748 (1.393)	3393	3388
PhOH−$(H_2O)_3$	1.001 (1.354)	1.650 (1.091)	3310	3236
PhOH−$(H_2O)_4$	1.007 (1.4)	1.626 (1.069)	3088	3167
PhOH−$(H_2O)_5$	1.012	1.591	3141	
PhOH−$(H_2O)_6$	1.004	1.632	3133	

[a] Values in parentheses are from Re and Osamura (ref 32) for the ionized complexes. [b] Experimental values are from Watanabe et al. (ref 25). [c] Density functional results for ν_{O-H} in isolated phenol are (in cm^{-1}): 3658 (BLYP/6-31G(d,p)); 3822 (B3LYP/6-31G(d,p)); 3861 (B3PW91/6-31G(d,p); 3863 (B3PW91/6-311+G(d,p)).

observed when a third water molecule is introduced. Complexation of the phenoxy radical with four water molecules increases d_{O-HOH} relative to the system with three water molecules and two different d_{O-HOH} distances are now observed (see Figure 4).

2. O−H Stretch Vibrations. The vibrational spectrum of phenol−water clusters[15,19,20,22,25,27,28] is characterized by a strong red-shift of the phenol O−H vibrational frequency (ν_{O-H}) with increasing number of water molecules.[22,25,26] This red-shift reflects a weakening of the phenol O−H bond strength due to hydrogen bonding with water molecules. Table 4 shows experimental data[25] and DFT frequencies assigned to the phenol O−H bond vibrations. For isolated phenol, unscaled ν_{O-H} from BLYP/6-31G(d,p) (3658 cm^{-1}) calculations are in very good agreement with experiment (3657 cm^{-1}).[2] B3LYP and B3PW91 (see Table 4) results clearly overestimate ν_{O-H} by ~200 cm^{-1}. Comparison between ν_{O-H} from DFT calculations and experimental data for phenol−water complexes shows a much better agreement.

Recently, Curtiss et al.[63] suggested that DFT zero-point energies should be scaled for comparison with experimental data. In particular, B3LYP/6-31G(d) zero-point energies should be scaled by 0.96.[63] If such scaling is used in our results, our prediction for ν_{O-H} in the phenol molecule improves significantly but the agreement between scaled frequencies for the phenol−water complexes worsens. If scaling is to be used, in our case the factor 0.98 proposed by Bauschlicher[64] seems to be more appropriate.

Table 5 reports vibrational frequencies represented by $\nu_{O\cdots H-OH}$ and assigned to the O−H stretch in the water molecule closer to the phenoxy radical oxygen. This vibrational mode is red-shifted by about 100 cm^{-1} when the phenoxy radical complexates with two water molecules in comparison with the complex with one water molecule, indicating that the role of the phenoxy radical as a proton acceptor is increased by the presence of a second water molecule. A similar trend is observed in the complexation of the phenoxy radical with three water molecules. However, $\nu_{O\cdots H-OH}$ is blue-shifted by about 100 cm^{-1} relative to the complex with one water molecule, when the phenoxy radical is coupled to four water molecules, reflecting a weaker interaction of the phenoxy radical with the water tetramer.

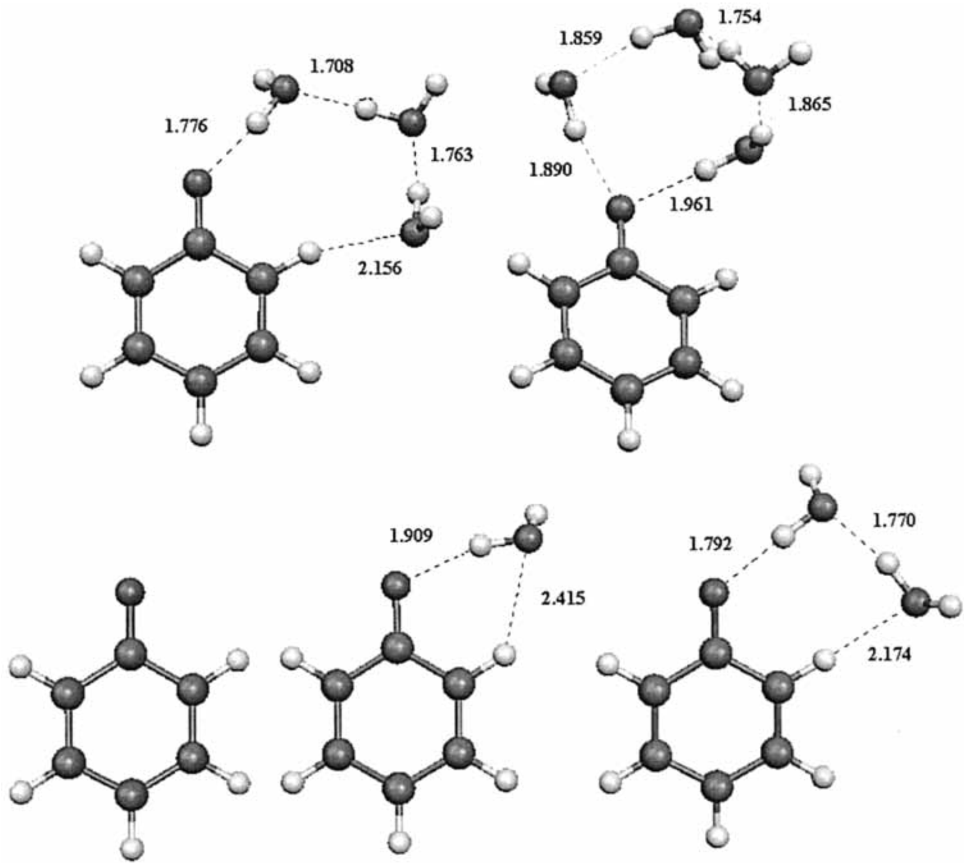

Figure 4. Structures of phenoxy radical−water clusters [$PhO^{\bullet}-(H_2O)_{1-4}$] showing hydrogen bond distances (in Å).

TABLE 5: C−O Bond Length (d_{C-O} in Å), Distances Between the Phenoxy Oxygen and the Water Hydrogen (d_{O-HOH} in Å), and Water O−H Frequencies ($\nu_{O\cdots H-OH}$ in cm^{-1}) for the Phenoxy−Water Complexes [$PhO^{\bullet}-(H_2O)_{1-4}$]

	B3LYP/D95V(d,p)			B3PW91/D95V(d,p)		
	d_{C-O}	d_{O-HOH}	$\nu_{O\cdots H-OH}$	d_{C-O}	d_{O-HOH}	$\nu_{O\cdots H-OH}$
$PhO^{\bullet}$	1.261				1.258	
$PhO^{\bullet}-(H_2O)_1$	1.267	1.904	3660	1.263	1.909	3690
$PhO^{\bullet}-(H_2O)_2$	1.268	1.795	3574	1.264	1.792	3592
			3502			3518
$PhO^{\bullet}-(H_2O)_3$	1.269	1.742	3450	1.264	1.776	3570
$PhO^{\bullet}-(H_2O)_4$	1.268	1.951	3750	1.264	1.890	3720
		1.890	3783		1.961	

4. Conclusions

This work reports data for the energetics, structure, and vibrational spectrum of phenol, phenol−water complexes, phenoxy radical, and phenoxy radical−water complexes, based on density functional theory calculations. The O−H bond dissociation enthalpy of phenol calculated by density functional theory show some dependence on the basis set and on the exchange-correlation functionals. We have verified that BLYP underestimates *D*(PhO−H) and that a better agreement with experiment is observed for calculations with hybrid functionals B3LYP and B3PW91. However, our better prediction for *D*(PhO−H), based on density functional calculations, is still 6% lower than the recommended experimental value. In addition, density functional calculations based on the B3LYP and B3PW91 exchange-correlation functionals overestimate the phenol ν_{O-H} frequency by $\sim$200 cm^{-1}.

The insertion of a phenol molecule in a water cluster has some similarities, at least from a thermochemical point of view, with the insertion of a water molecule. A significant increase of the phenol O−H bond length and a corresponding reduction of the distance $PhOH\cdots OH_2$ is observed in neutral phenol−water clusters when the number of water molecules increases, showing the relevant role played by the phenol molecule as a proton donor in water. The analysis of the interactions of the phenoxy radical with water clusters evidences the role played by this system as a proton acceptor in water.

By analyzing the energetics of phenol−water, phenoxy radical−water complexes, and water clusters, we were able to estimate the phenol O−H bond dissociation enthalpy in water clusters, D_{sln}(PhO−H). Our predictions for D_{sln}(PhO−H) in water clusters are in qualitative agreement with literature data for the solvation of phenol in other solvents.

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Supporting Information Available: The Supporting Information includes tables (1S to 10S) including the identification of B3PW91/D95V(d,p) optimized structures (Cartesian coordinates). The tables are in Gaussian input format and are numbered from 1S to 10S corresponding to phenol−$(H_2O)_{1-6}$ and phenoxy−$(H_2O)_{1-4}$. At the end of each table the set of O−H stretch frequencies is also reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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