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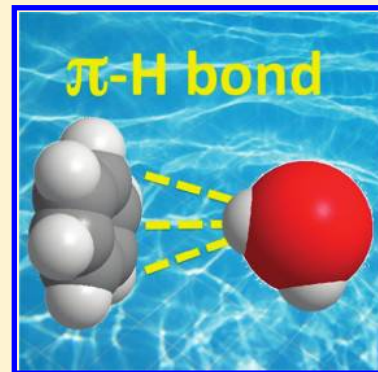
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S Supporting Information

ABSTRACT: We report the experimental observation and quantitation of π -hydrogen bond formation between liquid water and benzene using Raman multivariate curve resolution (Raman-MCR) combined with quantum and classical (cluster and liquid) calculations. Our results establish that π -hydrogen bonds between liquid water and benzene are weaker and more flexible (have a more positive enthalpy and entropy) than bulk water hydrogen bonds. We further establish that such bonds also form between water and other aromatics, including the amino acid phenylalanine, thus implying their common occurrence at hydrated biological interfaces.

SECTION: Kinetics, Spectroscopy



The biologically ubiquitous $\text{OH}\cdots\text{O}$ and $\text{NH}\cdots\text{O}$ bonds are members of a much larger class of hydrogen-mediated $\text{AH}\cdots\text{B}$ interactions, all of which may reasonably be called hydrogen bonds.¹ Among the more unusual members of this class is the π -hydrogen bond (πHB) $\text{AH}\cdots\phi$ where ϕ represents an aromatic ring and A may be a N, O, or C atom.^{1,2} Such bonds have previously been well characterized in cold (matrix and gas phase) clusters^{3–9} and the interiors of native proteins,^{10,11} but not at protein surfaces in liquid water. Here we report the experimental observation of the quintessential πHB between liquid water and benzene (as well as other aromatics), and quantify the corresponding πHB probability, flexibility, and dynamic equilibrium between the benzene–water πHB and water–water hydrogen bond (wHB). Our results imply that πHB formation is likely to be common at biological interfaces, and thus may well participate in various binding, recognition, and signaling processes.

Early evidence of πHB formation was obtained from vibrational spectroscopic studies of liquid benzene containing a trace amount of dissolved water.^{1,12} These seminal studies were followed by many others, including detailed investigations both under ambient conditions¹³ and at high pressure and temperature,^{14–17} as well as in low temperature benzene–water clusters.^{3–6} However, an aqueous solution containing benzene is quite different from any of the above systems, in that liquid water wHB formation provides an energetically and statistically competitive alternative to πHB formation.

Previous experiments have found that πHBs are far more flexible than $\text{OH}\cdots\text{O}$ hydrogen bonds. For example, high-resolution rotational and vibrational spectra of the πHB in benzene– H_2O , benzene– HOD , and benzene– NH_3 dimers

indicate that the formation of a πHB leaves water (or ammonia) remarkably free to rotate.^{4–9} Moreover, recent time-resolved infrared studies of the πHB between phenol and benzene (as well as other aromatics) confirm that the OH group may readily reorient and translate parallel to the aromatic plane even in systems with substantially different πHB strengths.^{18–20} Our results reveal that benzene–water $\text{OH}\cdots\phi$ configurations in liquid water are also more flexible (have greater entropy) than water–water $\text{OH}\cdots\text{O}$ structures.

A substantial number of prior theoretical investigations have focused on characterizing the interaction between benzene and water. These include quantum calculations of benzene–(H_2O)_n clusters containing between $n = 1$ and $n = 10$ water molecules,^{4,21–23} as well as both classical^{24,25} and quantum mechanical^{26,27} molecular dynamics simulations of benzene in liquid water. Although all of these studies suggest that a πHB may form between water and benzene, detailed predictions obtained using different theoretical methods are not entirely consistent with each other, particularly with regard to πHB strengths, probabilities, and structural distribution functions.

Here we employ a recently developed experimental strategy that combines ultralow-noise Raman scattering measurements and multivariate curve resolution (Raman-MCR)²⁸ to obtain a solute-correlated (SC) spectrum that reveals OH vibrational features arising from benzene's hydration-shell. The same Raman-MCR method has previously been used to discover dangling water OH bonds around dissolved saturated hydrocarbon

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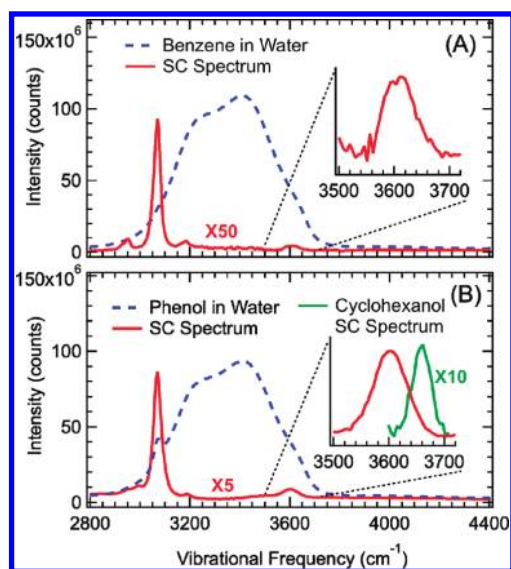


Figure 1. Aqueous solutions containing dissolved aromatic (and alkane) groups reveal vibrational peaks assigned to water π HB (and dangling) OH groups. (A) The total Raman scattering spectrum of a dilute (~ 22 mM) solution of benzene in water (dashed blue curve) looks virtually identical to that of bulk water. The resulting Raman-MCR SC spectrum (red curve) reveals a small, relatively narrow peak at ~ 3610 cm^{-1} assigned to a π HB between benzene and liquid water (expanded in the insert). (B) The latter π HB peak is similar to that observed in the SC spectrum of phenol in water (red curve, expanded in the insert) and is about 50 cm^{-1} red-shifted with respect to the dangling OH peak that appears in the SC spectrum of cyclohexanol in water (green curve). The full SC spectrum of phenol in water is given in the Supporting Information (Figure S3).

(alkane) groups, as well as to provide preliminary evidence of the formation of a π HB between water and benzyl alcohol.²⁹ Extending these results to benzene in water poses formidable challenges because the low aqueous solubility of benzene (~ 20 mM) means that the π HB OH vibrational peak of interest is more than 1000 times smaller than the broad overlying bulk water OH stretch band. Thus, Raman spectra of benzene in water must be obtained with a signal-to-noise ratio of at least 10,000:1. Figure 1A shows such a Raman spectrum and the relatively narrow blue-shifted OH peak at ~ 3610 cm^{-1} that appears in the resulting SC spectrum of benzene in water (obtained as further described in the Supporting Information).

Our assignment of the ~ 3610 cm^{-1} peak to water molecules in the benzene hydration shell is supported in part by our isotopic studies of C_6D_6 in H_2O , and C_6H_6 in D_2O , which confirm that the above peak only appears when benzene is present and is not a vibrational combination band of benzene, but rather arises from the interaction between water and benzene (see Supporting Information for details). Our assignment of the ~ 3610 cm^{-1} peak to a π HB is further supported by the results shown in Figure 1B, which reveal that a similar peak appears in the SC spectrum of phenol ($\text{C}_6\text{H}_5\text{OH}$) dissolved in water, and is red-shifted by ~ 50 cm^{-1} with respect to the dangling (free) OH peak (at ~ 3660 cm^{-1}) that appears in the SC spectrum of cyclohexanol ($\text{C}_6\text{H}_{11}\text{OH}$).²⁹ Note that the latter red-shift is similar to the ~ 60 cm^{-1} red-shift of a π HB with respect to a free OH previously observed in both benzene–water clusters and liquid benzene containing a trace amount of water.^{1,12,30} Moreover, the much larger intensity of the SC peaks of benzene and phenol,

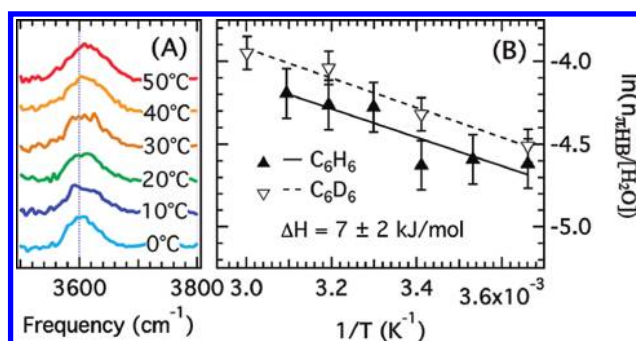


Figure 2. Temperature dependent measurements are used to obtain the enthalpy difference between π HB and wHB structures in liquid water. (A) The temperature dependence of the benzene–water π HB peak reveals a slight broadening and blue-shift with increasing temperature. These π HB peaks are all normalized by dividing the SC spectra by the area of the benzene ring breathing peak at ~ 992 cm^{-1} , thus assuring that the areas of the π HB peaks are proportional to $n_{\pi\text{HB}}$. (B) The temperature dependence of the π HB peak areas are used to obtain the corresponding average number of π HBs between water and either benzene (C_6H_6) or deuterated benzene (C_6D_6), both of which imply that $\Delta H \sim 7 \pm 2$ kJ/mol for the conversion of a wHB to a π HB structure (see text for details).

relative to the dangling OH peak in the SC spectrum of cyclohexanol (see Figure 1B), clearly implicates the role of aromaticity in giving rise to the ~ 3610 cm^{-1} peak. We have further verified that a virtually identical π HB peak appears in the SC spectrum of aqueous phenylalanine (see Supporting Information). Thus, there is little doubt that the observed peak at ~ 3610 cm^{-1} arises from a π HB between liquid water and benzene as well as other aromatic solutes.

Figure 2A shows how the benzene–water π HB peak depends on temperature. The areas of these π HB peaks, combined with those arising from benzene and bulk water, may be used to determine the average number $n_{\pi\text{HB}}$ of π HBs formed between liquid water and a dissolved benzene molecule (as further described below, and in the Supporting Information). In order to improve the accuracy of the resulting $n_{\pi\text{HB}}$ values, we have made use of the fact that the OH Raman scattering cross section of $\text{OH} \cdots \text{O}$ is predicted to be ~ 1.21 times larger than that of $\text{OH} \cdots \phi$ (obtained using ab initio MP2/aug-cc-pVTZ level calculations of the OH Raman cross sections in $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ and $\text{C}_6\text{H}_6 \cdots \text{H}_2\text{O}$ dimers, as further described in the Supporting Information). The resulting average number of π HBs between benzene and liquid water $n_{\pi\text{HB}}$ is $\sim 0.64 \pm 0.12$ at 20 $^\circ\text{C}$, and increases mildly with temperature from $\sim 0.51 \pm 0.12$ (at 0 $^\circ\text{C}$) to $\sim 0.83 \pm 0.12$ (at 50 $^\circ\text{C}$).

The above experimental results are in reasonable agreement with the predicted value of $n_{\pi\text{HB}} \sim 1.1 \pm 0.03$, which we have obtained from classical simulations of benzene in liquid water (with OPLS-AA/TIP4P potentials, and OH vibrational frequency predictions obtained from a semiempirical Stark-shift correlation, as further described in the Supporting Information). The fact that the predicted value of $n_{\pi\text{HB}}$ is larger than the experimental value is consistent with the fact that such classical simulations are known to be overstructured, and thus overestimate π HB probabilities, when compared to higher level quantum calculations²⁶ (as further discussed below, as well as in the Supporting Information).

Both the simulation and experimental results agree in indicating that increasing temperature produces a slight increase in

both the mean frequency and width of the π HB peak. More specifically, while our experimental results indicate a frequency increase of $\sim 10\text{ cm}^{-1}$ (from $\sim 3603 \pm 1\text{ cm}^{-1}$ to $\sim 3613 \pm 1\text{ cm}^{-1}$) and a full-width-at-half-maximum (fwhm) increase of $\sim 17\text{ cm}^{-1}$ (from $\sim 61 \pm 4\text{ cm}^{-1}$ to $\sim 78 \pm 4\text{ cm}^{-1}$) over a 0 to 50 °C temperature range, the simulations predict frequency and width increases of $\sim 25\text{ cm}^{-1}$ and $\sim 10\text{ cm}^{-1}$, respectively, over the same temperature range (see Supporting Information for further details).

The temperature dependence of the experimental π HB peak areas may be used to obtain a quantitative estimate of the enthalpy difference ΔH between a benzene–water π HB configuration and an average wHB in liquid water, as shown in Figure 2B. More specifically, the Gibbs–Helmholtz relation implies that $\Delta H = -R[\partial \ln K / \partial (1/T)]_p$, where $K = [\pi\text{HB}] / [\text{wHB}]$ is the ratio of the π HB and wHB concentration in a benzene–water solution (of fixed benzene concentration), and $R \sim 8.3\text{ J/(K mol)}$ is the gas constant. Since $[\pi\text{HB}] \propto n_{\pi\text{HB}}$ and $[\text{wHB}] \propto [\text{H}_2\text{O}]$, we expect that $\ln K = \ln(n_{\pi\text{HB}}/[\text{H}_2\text{O}]) + C$ (where C is a temperature-independent constant) and thus $\Delta H = -R\{\partial \ln(n_{\pi\text{HB}}/[\text{H}_2\text{O}]) / \partial (1/T)\}_p \sim 7 \pm 2\text{ kJ/mol}$, as shown in Figure 2B. A similar analysis of the temperature-dependent SC spectra of phenol in water yields $\Delta H \sim 3 \pm 2\text{ kJ/mol}$. Although the above ΔH values have significant uncertainty, repeated measurements as well as alternative analysis procedures invariably produce positive experimental ΔH values of similar magnitude, which implies that a π HB is weaker than a wHB in liquid water.

The positive signs of the above ΔH values are consistent with previous experimental and theoretical benzene–water cluster results. For example, fragmentation threshold studies imply that a benzene–water dimer is slightly more weakly bound (by about 10–20%) than a water–water dimer.^{2,31} Moreover, hybrid quantum-classical effective fragment potential (EFP) calculations of benzene–water clusters imply that replacement of one water molecule by benzene in water clusters with 4–8 water molecules leads to an intermolecular binding energy change of $+7.5 \pm 2.5\text{ kJ/mol}$.²² Note that the latter energy difference is remarkably similar to our experimental ΔH result for the enthalpy difference between π HB and wHB configurations in liquid water (see Figure 2B).

Additional information regarding the thermodynamics of π HB formation may be obtained by focusing on a single water molecule situated nearest to the center of the benzene ring. Such a water molecule may be assumed to either form a π HB to benzene $\text{HOH} \cdots \text{C}_6\text{H}_6$ (with a probability of p), or not $\text{H}_2\text{O} \cdots \text{C}_6\text{H}_6$ (with a probability of $1 - p$). This simplified two-state description assumes that each of the OH groups on such a nearest neighbor water molecule either form a π HB to benzene or a wHB to another water. Thus, the transformation of a $\text{HOH} \cdots \text{C}_6\text{H}_6$ structure to a $\text{H}_2\text{O} \cdots \text{C}_6\text{H}_6$ structure involves exchanging one π HB for one wHB. The ratio of the probabilities of finding the system in the latter two configurations, $\kappa = p/(1 - p) = n_{\pi\text{HB}}/(2 - n_{\pi\text{HB}})$, represents the equilibrium constant for the $\text{H}_2\text{O} \cdots \text{C}_6\text{H}_6 \rightarrow \text{HOH} \cdots \text{C}_6\text{H}_6$ transformation. Note that the second of the above equalities is obtained by identifying $p = n_{\pi\text{HB}}/2$ as the probability that a water molecule closest to one side of the benzene ring will form a π HB. The equilibrium constant κ may be used to estimate the free energy ΔG and entropy ΔS of the $\text{H}_2\text{O} \cdots \text{C}_6\text{H}_6 \rightarrow \text{HOH} \cdots \text{C}_6\text{H}_6$ process. For example, at 20 °C $n_{\pi\text{HB}} \sim 0.64$, so $p \sim 0.32$ and $\kappa \sim 0.32/(1 - 0.32) \sim 0.47$, which implies that $\Delta G = -RT \ln(0.47) \approx +2\text{ kJ/mol}$.

This experimental free energy is in remarkably good agreement with value of $\Delta G \approx +3\text{ kJ/mol}$ inferred from the benzene–water π HB potential of mean force, obtained from our classical molecular dynamics simulations (as further described in the Supporting Information). The experimental ΔG , combined with the fact that $\Delta H > 2\text{ kJ/mol}$, clearly implies that $\Delta S = (\Delta H - \Delta G)/T > 0$. This conclusion is also consistent with the value of ΔS obtained from the temperature derivative of ΔG , $\Delta S = -(\partial \Delta G / \partial T)_p = R[\partial (\ln \kappa) / \partial T]_p \approx +30\text{ J/(K mol)}$. The positive sign of ΔS indicates that $\text{HOH} \cdots \text{C}_6\text{H}_6$ (π HB) configurations have a larger entropy than $\text{H}_2\text{O} \cdots \text{C}_6\text{H}_6$ (non- π HB) configurations. In other words, the water molecule nearest to benzene's center of mass has a greater conformational flexibility when one of its two OH groups forms a π HB than it does when both of its OH groups form a wHB.

Our experimental results imply that the conversion of a wHB to a π HB in liquid water is entropically favored ($\Delta S > 0$) but enthalpically disfavored ($\Delta H > 0$). The observed entropy increase is consistent with previous observations of the remarkably high orientational freedom of a π HB in benzene–water clusters⁶ as well as phenol dissolved liquid benzene.²⁰ We have further found that, in spite of the fact that a π HB is somewhat weaker than a wHB (and the statistically greater number of potential wHB partners), approximately one π HB is formed between liquid water and each dissolved benzene molecule, as well as between water and other aromatic solutes including phenylalanine. The observed ubiquity of π HB formation in liquid water implies that such bonds are undoubtedly common at biological interfaces containing aromatic amino acids, nucleic acids, or metabolites, and thus π HB formation may well prove to play an important role in biological binding, recognition, and signaling processes.

■ ASSOCIATED CONTENT

S Supporting Information. Materials and methods, data analysis procedures, and theoretical results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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