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Benzene Forms Hydrogen Bonds with Water

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Fully rotationally resolved spectra of three isotopic species of 1:1 clusters of benzene with water (H_2O, D_2O, and HDO) were fit to yield moments of inertia that demonstrate unambiguously that water is positioned above the benzene plane in nearly free internal rotation with both hydrogen atoms pointing toward the π cloud. Ab initio calculations (MP2 level of electron correlation and 6-31G basis set with basis set superposition error corrections) predict a binding energy $D_e \gtrsim 1.78$ kilocalories per mole. In both the experimental and theoretical structures, water is situated nearly 1 angstrom within the van der Waals contacts of the monomers, a clear manifestation of hydrogen bond formation in this simple model of aqueous–π electron interactions.**

We report the ground-state microwave spectra of jet-cooled C_6H_6-H_2O along with an ab initio calculation of the intermolecular potential energy surface (IPS). Our goals are, first, to establish experimentally the structure and ground-state energy levels of the complex free of external perturbations, such as many-body solvent interactions and macromolecular structures and, second, to gain a global theoretical understanding of the IPS in order to guide future searches and to provide estimates of the binding energy and anisotropy of this prototypical model of aromatic-hydrophilic interactions. Compared to other methods, fully rotationally resolved cluster spectra of the type presented below are perhaps the most direct approach to an understanding of the structural implications and energetics of weak intermolecular forces at the two-body level.

It has been speculated for several years that aromatic rings can act as hydrogen-bond acceptors (*1, 2*). Recently, compelling but indirect evidence for the hydrogen-bonding character of aromatic rings to water and other biologically significant materials has been found in a number of experiments, ranging from low-resolution ultraviolet (UV) and infrared (IR) spectroscopy of molecular clusters in supersonic jets (*3*) and in matrices (*4*) to x-ray crystallographic structures of a variety of proteins (*2*) as well as specifically designed synthetic materials (*5*). Although the hydrogen positions were not directly located in these studies, they provided strong support for an interaction of hydrogen bond donors with the high electron density of the aromatic π cloud. Aromatic-polar interactions may also play significant roles in many natural chemical systems and reactions, ranging from the tertiary structure (*6*) and function (*7*) of biopolymers to reactions on atmospheric aerosols (*8*). They may also provide a variety of molecular recognition motifs (*9*).

That aromatic rings act as hydrogen bond acceptors illustrates dramatically the need for a molecular description of phenomena such as the hydrophobic effect so familiar at macroscopic scales. Aromatic hydrogen bonds, like essentially all weak interactions, are not well characterized at the molecular level, and much of our understanding is based on chemical intuition and theories in which the practical limitations of current computing power forces us to make what are often drastic assumptions and simplifications with unknown consequences.

An arbitrary structure of the benzene-water complex that shows the intermolecular coordinate system used is presented in Fig. 1. Weak intermolecular forces allow a number of large amplitude motions to occur in clusters such as C_6H_6-H_2O and necessitates the use of permutation-inversion (PI) theory [(*3*) and references therein], in which all "feasible" motions are considered, in order to understand the vibration-rotation-tunneling (VRT) spectra of these clusters. Such VRT spectra should allow intermolecular forces in weakly bound clusters to be probed at unprecedented levels of detail (*10, 11*). Here, there are two potentially feasible motions: (i) an internal rotation of the water relative to the benzene in a sixfold potential; and (ii) assuming the monomer C_2 and C_6 axes are not aligned, an interchange of the H_2O protons in a double minimum potential. Several studies, such as the matrix isolation work of Engdahl and Nelander (*4*) and especially the resonance ionization experiments through the S_1 state of benzene by Gotch and Zwier (*3*), have unambiguously demonstrated that the internal rotation is nearly free and that, on a vibrationally averaged basis, the hydrogens are equivalent.

A detailed experimental investigation of these large amplitude motions, and by extension the IPS, requires the measurement of all of the VRT modes of C_6H_6-H_2O, which occur in the far-IR (FIR) region of the spectrum. We have used the Caltech tunable FIR laser spectrometer to measure the VRT states for a range of water-containing complexes such as CO-H_2O and NH_3-H_2O (*12, 13*). However, high-resolution microwave spectra, which often provide good structural estimates and form a useful starting point for FIR work, do not exist for the C_6H_6-H_2O complex.

We have previously described our microwave version of the Caltech cluster spec-

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trometer (*14*). In this work, clusters were formed by mixing two Ar streams saturated with water and benzene vapor in varying proportions. Spectra were obtained for the C_6H_6-H_2O, C_6H_6-D_2O, and C_6H_6-HDO isotopomers by using two methods, frequency-modulated (FM) and Stark-modulated (SM) direct absorption spectroscopy of an unskimmed planar supersonic expansion. We surveyed several regions between 18 and 40 GHz, which covered angular momentum (J) values ranging from 4 to 10.

Spectra from the $J = 7 \leftarrow 6$ transitions of all three isotopic species taken by SM are shown in Fig. 2. Far too many lines were observed for the complex to be acting as a rigid molecule. One can easily observe similar patterns labeled A, A′, and A″, with additional patterns labeled B and B′ for the H_2O and D_2O complexes. The low rotational and collisional temperatures of molecules in the jet combined with the slow nuclear spin exchange (*15*) lead to separate $J_{K_pK_o}$ (water) $= 0_{00}$ and metastable $J_{K_pK_o}$ (water) $= 1_{01}$ states for the H_2O and D_2O complexes, but not for HDO. These states are analogous to the *para* and *ortho* states of H_2 and D_2.

The relative intensities suggest that A, A′, and A″ result from transitions originating in the $J_{K_pK_o}$ (water) $= 0_{00}$ state and that B and B′ result from the $J_{K_pK_o}$ (water) $= 1_{01}$ state. This conclusion is in complete accord with that deduced from partially rotationally resolved multiphoton ionization spectra by Gotch and Zwier (*3*). If water is selected as the top and benzene as the frame, then in the G_{24} PI group of C_6H_6-H_2O the two water nuclear spin states correlate with the internal rotation quantum number m, whereas the four benzene nuclear spin states correlate with the projection of J onto the z axis of Fig. 1, K (*3*). States are uniquely labeled by their values of J, K, and m, and those with $|mK| \geq 1$ are split by the internal rotation. The measured line intensity ratios and the absence of a similar B pattern for HDO are consistent with this assignment.

In the limit of free internal rotation of two symmetric top subunits, the simple formula

$$\nu = 2(J + 1)[B - D_{JK}K^2 - D_{Jm}m^2 - D_{JKm}Km - H_{JKm}m^2K^2] - 4(J + 1)^3D_J$$

has been found to provide an adequate fit for species such as CF_3H-NH_3 (*16*). The rotational and distortion constants found with this approach are shown in Table 1. The fit, which is well within experimental error for the $m = 0$ states, tightly constrains the moments of inertia used below and illustrates the nearly free character of the internal rotation (a complete listing of the transition frequencies is available from the authors). The larger residuals for the $m = \pm 1$ states are most likely due to the overly simplistic model as well as the nonrigidity of the complex.

The observed spectral patterns and moments of inertia, which demand that the water protons lie between the monomer centers of mass (cm), rule out structures where H_2O is not bound to the face of benzene. Two methods were used to extract more structural information. The simplest analysis treated the complex as a pseudodiatomic molecule and assumed that the C_6 axis of benzene and the C_2 axis of water were colinear. In the second method, if we describe the angular orientations of H_2O with θ and ψ (Fig. 1), assume $\langle\psi\rangle = 0$, place the H_2O cm on the C_6H_6 C_6 axis and integrate over the sixfold potential in ϕ, θ can be expressed in relation to $R_{(cm\text{-}cm)}$ (the

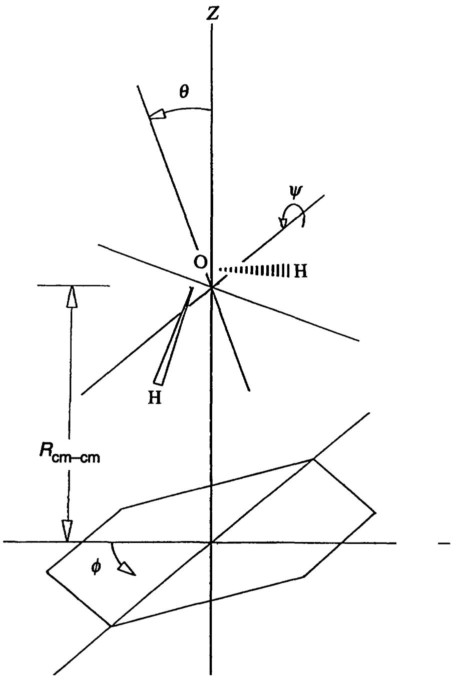

Fig. 1. An arbitrary structure for C_6H_6-H_2O; $R_{cm\text{-}cm}$ is the center-of-mass to center-of-mass distance between the monomers, θ is the angle between the C_6 axis of benzene and the C_2 axis of water, ϕ is the torsion angle about the *a*-axis of the complex (very close to the *z*-axis drawn) from an arbitrary reference configuration, and ψ is the angle between the water plane and the C_6 axis of benzene.

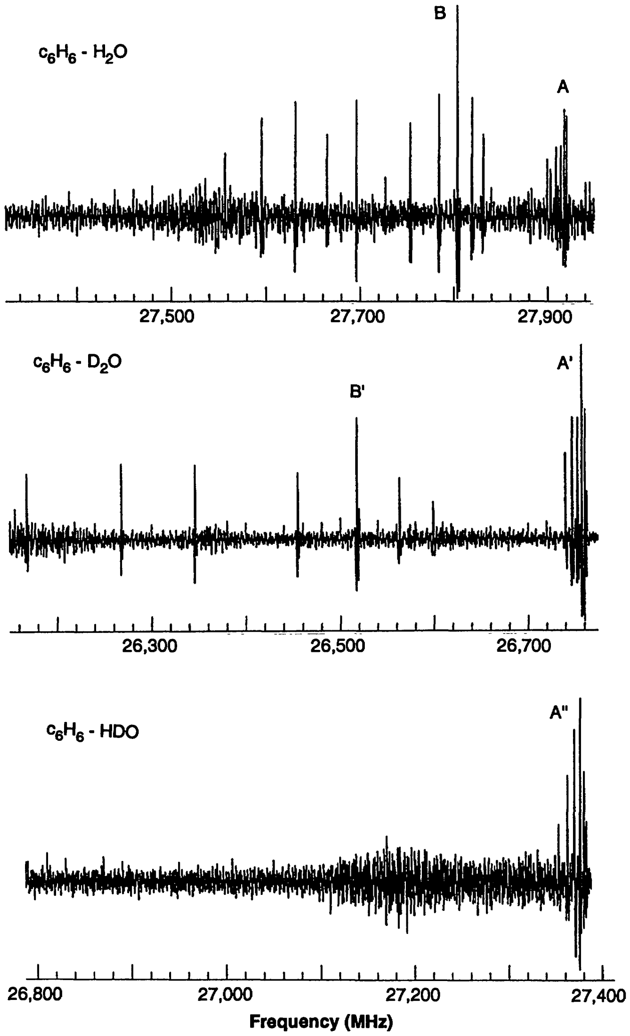

Fig. 2. Spectra of the $J = 7 \leftarrow 6$ transitions of all three isotopic species by using Stark modulation.

Table 1. Spectroscopic fits to experimental data (errors in last digit or digits in parentheses); σ is the standard deviation of the fit.

Parameter	Complex		
	C_6H_6-H_2O	C_6H_6-HDO	C_6H_6-D_2O
		m = 0	
$\bar{B}$ (MHz)	1994.83(2)	1956.357(7)	1921.068(8)
D_J (kHz)	3.58(6)	3.641(12)	3.877(27)
D_{JK} (kHz)	37.87(26)	60.48(5)	46.41(7)
σ (MHz)	0.27	0.11	0.13
		m - ±1	
D_{Jm} (MHz)	12.49(5)		
D_{JKm} (MHz)	1.650(8)		
H_{JKm} (kHz)	58.9(25)		
σ (MHz)	3.9		

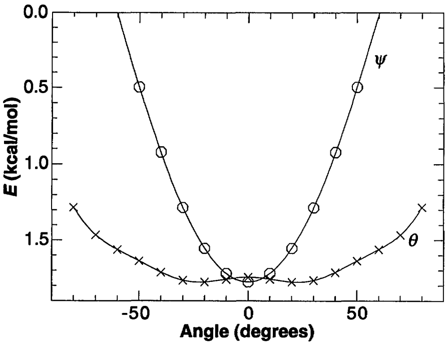

Fig. 3. Ab initio IPS cuts along θ (X) and ψ (O). Solid lines are polynomial fits to the calculated points.

Table 2. Structural parameters obtained from spectroscopic constants.

Complex	$R_{\text{cm-cm}}$ (Å)		θ (degrees)
	Pseudo-diatomic	Averaged over ϕ	
C_6H_6-H_2O	3.32	3.347(5)	20(15)
C_6H_6-HDO	3.31	3.322(5)	
C_6H_6-D_2O	3.28	3.308(5)	20(15)

distance between the monomer cm) and moments of inertia I of the monomers and the complex as

$$I_{\text{bb}(C_6H_6\text{-}H_2O)} = \mu R^2_{(\text{cm-cm})} + \frac{I_{\text{aa}(H_2O)}}{2}\langle 1 + \cos^2\theta\rangle + \frac{I_{\text{bb}(H_2O)}}{2}\langle \sin^2\theta\rangle + I_{\text{bb}(C_6H_6)}$$

where the reduced mass $\mu = m_{C_6H_6}m_{H_2O}/(m_{C_6H_6} + m_{H_2O})$ (*16*). Assuming that the distance from the oxygen atom (O) to the benzene plane (bz) was the same for benzene-H_2O and benzene-D_2O led to an independent constraint on R and θ. The derived constants clearly demonstrated that the water protons must be pointing toward the benzene. Mathematically, $R_{(\text{O-bz})} = 3.411$ and $\theta = 20°$, but the model is consistent with a range of ± 0.005 Å for $R_{(\text{O-bz})}$ and ±15° for θ_0^{expt}. A summary of the structural fits is presented in Table 2. Our results fall well within the range of $R_{(\text{cm-cm})} = 3.32(7)$ Å reported by Gotch and Zwier (*3*).

Because the hydrogen atoms are light, θ^{expt} can be greatly affected by vibrational averaging. We therefore used ab initio calculations to estimate the IPS minimum and vibrationally averaged dimer geometry. There are a number of previous calculations on C_6H_6-H_2O that have used ab initio and semiempirical methods (*17–21*), but only the variational calculations of Linse (*18*) and the MMC approach of Augspurger *et al.* (*21*) scan the complete IPS as we have. By using the 6-31G** basis set and MP2 level of electron correlation, we investigated all degrees of freedom with the Gaussian 90 suite of programs (*22*). We used counterpoise calculations to estimate the basis set superposition error (BSSE) (*23*) for all points on the IPS. The internal coordinates of the components were frozen at their gas-phase values to make the calculations more tractable.

The search for the IPS minimum started with $R_{(\text{cm-cm})} = 3.341$ Å and varied only θ (see Fig. 3). The optimized equilibrium configuration had $\theta_e^{\text{calc}} = \pm 21°$. An important point to note is that Hartree-Fock wave functions led to a single minimum at $\theta_e = 0°$. Thus, the details of the double-welled potential, similar to that reported by Linse (*18*), are sensitive to higher order interactions. The MP2 curve has a minimum at $\theta_e^{\text{calc}} = 21°$, and we estimate that $\theta_0^{\text{calc}} = 24°$. To ensure that this feature was not due to constraints on the other intermolecular degrees of freedom, we performed several scans where R, θ, ϕ, and ψ were allowed to vary. The optimum $R_{(\text{cm-cm})}$ was somewhat shorter than that deduced from experiment [$R^{\text{calc}}_{\text{e(cm-cm)}} = 3.168$ Å and $R^{\text{calc}}_{0(\text{cm-cm})} = 3.195$ Å, MP2 (*24*); $R^{\text{expt}}_{0(\text{cm-cm})} = 3.347(5)$ (errors in last digit or digits in parentheses) Å], but the minimum was again at $\theta_e^{\text{calc}} = \pm 21°$. The Morse parameters that fit the ab initio radial cut are $R^{\text{fit}}_{\text{e(cm-cm)}} = 3.124(11)$ Å, $D_e^{\text{fit}} = 630(30)$ cm^{-1}, and $\alpha = 2.1(1)$ Å^{-1}.

Earlier calculations reported that the potential about the z-axis is very flat, which is consistent with our experimental data. We calculated the optimum position in the case where $\phi = 0°$ (eclipsed over a C atom) and also where $\phi = 30°$ (staggered, bisecting two C–C bonds), and these two minima differ by only 0.0005 kcal/mol. Cuts along θ and ψ are depicted in Fig. 3.

Final scans allowed the H_2O cm to move away from the z-axis in order to determine if an off-center geometry would favor a better bonding pattern. The preferred mode of binding was for the H_2O cm to be on the benzene C_6 axis. This result agrees with the initial vibrationally averaged structure presented by Gotch and Zwier (*3*) and the symmetric rotor patterns in the microwave spectra, but disagrees with the equilibrium structure calculated by Augspurger *et al.* (*21*). The D_e^{calc} value was 1.78 kcal/mol with and 4.21 kcal/mol without BSSE correction for the complex, which falls within the experimental boundaries ($1.63 < D''_0 < 2.78$ kcal/mol) placed by Gotch and Zwier (*3*). The large BSSE correction was very flat across the IPS, and although the value of D_e must be treated with caution, the anisotropy should be reasonably accurate.

It is this anisotropy which governs the nature of the VRT spectrum, and one-dimensional eigenvalue generation on the ab initio surface yielded estimates of 101, 47, 260 cm^{-1} for the intermolecular stretch (R) and the two (θ, ψ) water bends. Experimental estimates of the stretch obtained from D_J range from 90 to 100 cm^{-1}, with a binding energy of $D_0 = 1.9$ kcal/mol.

From both the experimental and ab initio structures of the 1:1 benzene-water complex [$R^{\text{expt}}_{0(\text{cm-cm})} = 3.347(5)$ Å, $\theta_0^{\text{expt}} = 20 \pm 15°$; $R^{\text{calc}}_{0(\text{cm-cm})} = 3.195$ Å, $\theta_0^{\text{calc}} = 24°$], it is clear that benzene acts as a hydrogen bond acceptor for both H_2O hydrogens. The potential well is extremely flat over the C_6H_6 surface, however, which makes benzene an excellent "target" as a hydrogen-bond acceptor. The fundamental character of this aromatic-hydrophilic attraction is reflected in the occurrence of many similar structures in nature; it does not require any external constraining forces.

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Synthesis of Fluoropolymers in Supercritical Carbon Dioxide

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Fluoropolymers are used in many technologically demanding applications because of their balance of high-performance properties. A significant impediment to the synthesis of variants of commercially available amorphous fluoropolymers is their general insolubility in most solvents except chlorofluorocarbons (CFCs). The environmental concerns about CFCs can be circumvented by preparing these technologically important materials in supercritical fluids. The homogeneous solution polymerization of highly fluorinated acrylic monomers can be achieved in supercritical carbon dioxide by using free radical methods. In addition, detailed decomposition rates and efficiency factors were measured for azobisisobutyronitrile in supercritical carbon dioxide and were compared to those obtained with conventional liquid solvents.

The dissemination of CFCs into the atmosphere has been identified as one of the main causes of the depletion of the ozone layer (*1*). As a result, extensive research efforts have focused on alternatives to CFCs in applications such as refrigerants and aerosols. Additionally, CFCs are used as solvents for a variety of standard commercial processes. An important example of this is the solubilization of highly fluorinated polymers—known generally as fluoropolymers—in CFCs to form homogeneous solutions for polymer processing and synthesis. These fluoropolymers, used extensively as lubricants in computer disk drives, protective coatings, aircraft fuel sealants, and so forth, are generally insoluble in many traditional organic solvents (*2*) and therefore both their synthesis (using solution polymerization methods) and their processing depend on CFC solvents. We have found a way to circumvent the environmental concerns about CFCs by preparing these technologically important materials in supercritical fluids (SCFs). We report here the successful synthesis of high molar mass fluoropolymers by using homogeneous free radical polymerization methods in supercritical carbon dioxide (CO_2).

In addition to offering an environmentally sound alternative to CFCs, SCFs can provide insight into the general role that solvents play in polymerization reactions. Heretofore, research into the role of solvent strength in chemical reactions has been limited by the need to use multicomponent solvents in order to manipulate the bulk solvent strength, that is, the solubility parameter δ. The mean δ-value in mixed solvents is often masked by specific solute-solvent interactions. Because of their large compressibilities, researchers can use SCFs to produce a wide range of solvent strengths by varying the pressure rather than the composition of the solvent. The resulting significant and controllable changes in density readily allows investigations into solvent effects without changing the solvent composition (*3*, *4*). We illustrate the generality of polymerizations in SCFs with the determination of the decomposition kinetics and efficiency factor for the initiator, azobisisobutyronitrile (AIBN), followed by homopolymerization studies of 1,1-dihydroperfluorooctyl acrylate (FOA) and the synthesis of statistical copolymers of FOA with ethylene, styrene, butyl acrylate, and methyl methacrylate in supercritical CO_2.

The insolubility of most amorphous fluoropolymers in common organic solvents necessitates the use of CFC solvents when homogeneous solution polymerizations of fluoromonomers are desired. Although it has been known for some time that oligomeric perfluoropolyethers and poly(chlorotrifluoroethylene) are soluble in CO_2 (*3*), we have discovered that many other fluoropolymers are very soluble in both liquid and supercritical CO_2. In general, the only other solvents known for these highly fluorinated polymers are CFCs. Specifically, high molar mass (>250,000 g/mol) homopolymers of a variety of fluorinated acrylic monomers are soluble in CO_2 up to 25% (w/v) in some cases depending on pressures and temperatures (*5*). These are exceedingly high solubility values for a polymer in CO_2. For comparison, the hydrocarbon analogs of these polymers, such as poly(methyl methacrylate), are essentially insoluble in CO_2. We believe the high solubility of these fluoropolymers in CO_2 is indicative of a specific solute-solvent interaction between fluorine and CO_2.

As a result of the very high solubilities of these materials in supercritical CO_2, we set out to investigate the synthesis of fluoropolymers with the use of homogeneous solution free radical polymerization methods in CO_2 as an inert solvent. The rate of radical generation through the thermal decomposition of an initiator will influence both the overall rate of polymerization and the molar mass of the resulting polymer. Specifically, the rate of polymerization, R_P, is dependent on the square root of the initiator concentration [I]:

$$R_P = k_P[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2}$$

and the kinetic chain length, ν (the average

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