Strength of the Benzene−Water Hydrogen Bond

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Very large basis set, correlated calculations of the benzene−water complex predict a geometry in which the water molecule sits above the aromatic ring with oxygen pointed away from the benzene center of mass. The purely electronic binding energy, in the complete basis set limit, was found to be −3.9 ± 0.2 kcal/mol, or only 20% weaker than the water−water interaction. When zero-point energies are included, the ΔE_0(0 K) values are identical within their estimated uncertainties. Core/valence and higher-order correlation recovery via coupled cluster calculations were found to play a minor role. The present ΔE_0(0 K) value of −2.9 ± 0.2 kcal/mol is in good agreement with a recent threshold photoionization experiment that yielded −2.4 ± 0.1 kcal/mol.

I. Introduction

As part of an effort to develop an improved benzene−water classical force field suitable for molecular dynamics simulations,[1] we have determined the binding energy of benzene and a single water molecule using high-level ab initio methods. An accurate treatment of this prototype system is important for developing models capable of handling complex systems in which benzene participates as an environmental contaminant. Previous theoretical work on the $C_6H_6-H_2O$ complex indicated the existence of a very weak hydrogen bond, in qualitative accord with the observation that liquid benzene is immiscible in water. Past work includes the self-consistent-field/configuration interaction (SCF CI) calculations of Karlström et al.[2] and five frozen-core, second-order Møller−Plesset perturbation theory (MP2(FC)) studies.[3−7] Values of the electronic binding energy, ΔE_e, range from −1.78 to −5.23 kcal/mol, with the smaller values resulting from calculations that accounted for basis set superposition error (BSSE). Even for the most extensive study reported in the literature,[6] BSSE contributed more than 1 kcal/mol to the binding energy. For smaller basis sets it can easily exceed 3 kcal/mol. Since the BSSE-adjusted binding energies range from −1.8 to −2.8 kcal/mol, the relative size of the basis set truncation error remains significant. A very recent theoretical investigation of the related $C_6F_6-H_2O$ complex found a similar ΔE_e value of −1.81 kcal/mol, after correcting for BSSE.[8]

Due to the expense of ab initio calculations on a complex of this size, very limited investigations of the sensitivity of ΔE_e to variations in basis set quality have been reported. In the study of Fredericks et al.,[6] the benzene basis set was increased from 6-31G* to 6-31+G*, resulting in a 0.01 kcal/mol weakening of the binding energy (−2.49 to −2.48). This suggests only a weak dependence of ΔE_e on the basis set. With the same set, the B3LYP[9−11] density functional method predicted a much smaller −1.46 kcal/mol. Binding energies from previous work are listed in Table 1. By way of contrast, the electronic binding energy of the water dimer has been estimated to be −5.0 ± 0.1 kcal/mol, after consideration of core/valence and higher-order correlation corrections.[12]

II. Procedure

All calculations in the present study were performed with the correlation-consistent basis sets, conventionally denoted cc-pV*x*Z, where x = D (double-ζ), T (triple-ζ), etc.,[13−16] or their diffuse function augmented counterparts (aug-cc-pV*x*Z). In previous studies of hydrogen-bonded systems, the addition of diffuse functions to the basis set significantly reduced BSSE. Although this observation comes largely from work on $(H_2O)n$ clusters and water−phenol complexes, we expect similar behavior for the $C_6H_6-H_2O$ complex. BSSE corrections to the binding energies were based on the full counterpoise correction of Boys and Bernardi[17] using the relaxed fragment geometries. Such results are denoted by the presence of the suffix (CP).

Although most calculations were performed at the MP2(FC) level, a limited number of coupled cluster calculations were carried out to assess the importance of higher-level correlation. The coupled cluster work included single and double excitations, plus a perturbative treatment of triples, CCSD(T).[18−20] All CCSD(T) calculations were carried out with MOLPRO-97[21] on SGI/Cray Origin 2000s or J90s.

MP2 geometries were optimized with a convergence criterion of $\sim 2 \times 10^{-4}$ E_h/a_o for the aug-cc-pVDZ and aug-cc-pVTZ basis sets. Due to the computational expense of aug-cc-pVQZ calculations, a larger threshold of 1×10^{-3} E_h/a_o was used. The same threshold was used for the CCSD(T)/aug-cc-pVDZ optimizations. Although the double- and triple-ζ MP2 geometry optimizations for $C_6H_6-H_2O$ were started in C_1 symmetry, they converged to structures that possessed C_s symmetry. Subsequent CCSD(T) and quadruple-ζ optimizations were begun in C_s symmetry to increase the efficiency of the calculations. While a geometry convergence threshold of 1×10^{-3} E_h/a_o is not sufficient to achieve convergence in bond lengths to 0.001 Å, the changes in total energy between subsequent optimization steps was small enough to ensure binding energies to ±0.02 kcal/mol. The aug-cc-pVDZ and aug-cc-pVTZ basis set optimizations were performed with Gaussian 98.[22] The MP2/aug-cc-pVQZ calculations were performed with NWChem[23] on a 512-node IBM SP2. The largest basis set used with the complex was the cc-pV5Z set, which entailed 1077 functions.

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TABLE 1: Benzene-Water Electronic Binding Energy (kcal/mol)

basis set						
C_6H_6	H_2O	theory	geometry	Δ*E*	Δ*E*(CP)[a]	reference
minimal	minimal	SCF CI	constrained	−4.05	−3.04	Karlström et al. [2]
6-31G*	6-31G*	MP2	RHF/3-21G	−3.81		Brédas et al. [3]
6-31G*	6-31G*	MP2(FC)	RHF/3-21G	−4.10		Cheney/Schulz [4]
6-31G**	6-31G**	MP2	MP2 constrained[b]	−4.21	−1.78	Suzuki et al. [5]
6-31G*	6-31+G[2d,p]	MP2(FC)	MP2 constrained[c]	−5.23	−2.49	Fredericks et al. [6]
		MP2(FC)	BSSE optimized[d]		−2.82	
6-31+G*	6-31+G[2d,p]	MP2(FC)	MP2 constrained[c]	−3.65	−2.48	
		B3LYP	B3LYP	−1.79	−1.46	
DZP	DZP	MP2(FC)	MP2 optimized	−4.37	−1.76	Gregory & Clary [7]
aVDZ	aVDZ	MP2(FC)	MP2/aVDZ	−4.84	−2.89	This work
		CCSD(T)(FC)	CCSD(T)/aVDZ	−4.56	−2.68	
aVTZ	aVTZ	MP2(FC)	MP2/aVTZ	−4.01	−3.13	
		CCSD(T)	MP2/aVTZ	−3.85		
VQZ	aVQZ	MP2(FC)	MP2/aVQZ	−4.06	−3.42	
V5Z	V5Z	MP2(FC)	MP2(aVQZ)	−3.75	−3.42	
est. CBS		MP2(FC)		−3.9 ± 0.2		

[a] Counterpoise-corrected binding energy. [b] All internal coordinates in the benzene and water fragments were frozen at their experimental gas-phase values. [c] The benzene fragment was contrained to remain planar. The geometry optimization was performed with the 6-31G* basis set on benzene and the 6-31+G[2d,p] basis set on water. [d] Binding energy with reoptimization of the benzene−water separation with inclusion of the counterpoise correction.

TABLE 2: Selected MP2 and CCSD(T) Energies and Geometry Parameters[a]

H_2O

basis	theory	*E*	r_{OH}	∠HOH	reference
aVDZ (41)[b]	MP2(FC)	−76.2609	0.966	103.9	Feller et al. [28]
	CCSD(T)(FC)	−76.2739	0.967	103.9	
aVTZ (92)[b]	MP2(FC)	−76.3290	0.961	104.1	
aVTQ (172)[b]	MP2(FC)	−76.3519	0.959	104.3	
expt[c]			0.957	104.5	

C_6H_6

basis	theory	*E*	r_{CC}	r_{CH}	reference
aVDZ (192)[b]	MP2(FC)	−231.5402	1.408	1.094	This work
	CCSD(T)(FC)	−231.6172	1.413	1.097	
aVTZ (414)[b]	MP2(FC)	−231.7447	1.394	1.082	
VQZ (510)[b]	MP2(FC)	−231.8027	1.393	1.082	
expt[d]			1.397	1.084	

$C_6H_6-H_2O$

basis	theory	E	r_{OX}[e]	r_{HX}	r_{OH}	reference
aVDZ (233)[b]	MP2(FC)	−307.8088	3.240	2.404	0.969	This work
	CCSD(T)(FC)	−307.8984	3.235	2.417	0.969	
aVTZ (506)[b]	MP2(FC)	−308.0801	3.212	2.413	0.965	
aVQZ[f] (682)[b]	MP2(FC)	−308.1611	3.211	2.414	0.963	
expt			3.32 ± 0.07[g] 3.347 ± 0.005[h] 3.329[i]			

[a] Energies are in hartrees, distances are in angstroms, and angles are in degrees; X represents the center of mass of the benzene ring; the OH distance listed under $C_6H_6-H_2O$ is the water bond length corresponding to the hydrogen point toward the benzene, i.e., the hydrogen involved in the hydrogen bond. [b] The total number of basis functions. [c] Experimental values take from Benedict et al., ref 23. [d] Experimental values take from Stoicheff, ref 24. [e] Distance between the water and benzene centers of mass. [f] The cc-pVQZ basis set was used on benzene. [g] Experimental r_0 value from Gotch and Zwier, ref 25. [h] Experimental r_0 value from Suzuki et al., ref 5. [i] Experimental r_0 value from Gutowski et al., ref 26.

III. Results

Total energies and selected geometry parameters for H_2O, C_6H_6, and $C_6H_6-H_2O$ are listed in Table 2, along with the available experimental geometry data.[5,24−27] The results for the water molecule have been reported previously.[28] Agreement between theory and experiment is very good for H_2O and C_6H_6, with differences in bond lengths < 0.005 Å. Large basis set MP2 bond lengths typically agree with experimental r_0 and r_e values for small molecules to within ±0.015 Å.[29] However, for the benzene−water complex the predicted distance between the C_6H_6 and H_2O centers of mass, denoted as r_{ox} in Table 2, is considerably shorter than any of the experimental values. Our best MP2 value of r_e (3.211 Å) compares with experimental r_0 values ranging from 3.32 to 3.35 Å. Vibrational averaging effects were estimated by numerically integrating the r_{ox} potential energy curve generated by stepping the benzene−oxygen distance and re-optimizing all remaining internal coordinates. This resulted in an r_0 of 3.23 Å, just outside the lower error bound of the Gotch and Zwier value.[26] The present r_e value is nearly identical to the MP2 value of 3.210 Å reported by Fredericks.[6] Similar problems in reproducing experimental r_0 distances in hydrogen-bonded systems have been demonstrated for the water dimer.[28,30]

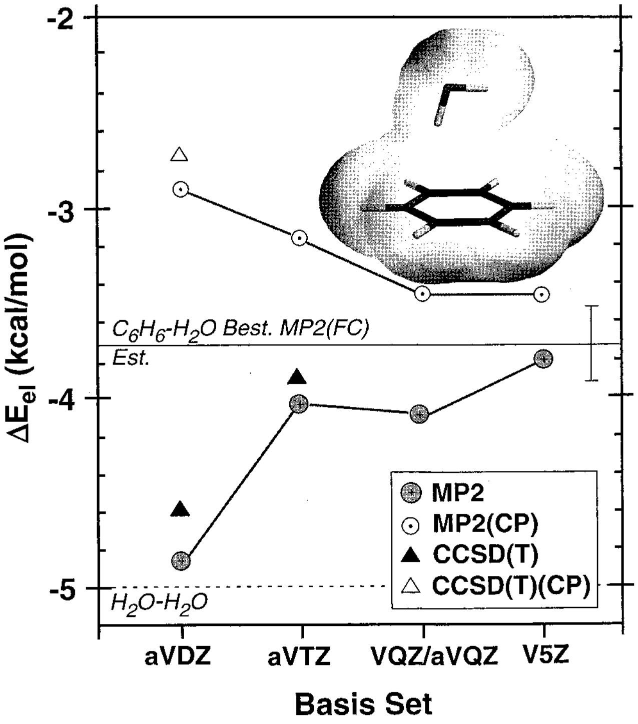

Figure 1. The convergence of the benzene−water electronic binding energy as a function of the basis set.

As found by previous studies, the minimum energy structure for the benzene−water complex has water sitting above the ring, forming a single hydrogen bond to one of the carbons. Gregory and Clary[7] have noted that vibrational averaging effects corresponding to a rocking motion of the water renders both water hydrogen atoms indistinguishable. The distance from the center of the benzene ring to the hydrogen atom involved in the hydrogen bond is 2.413 Å at the MP2/aug-cc-pVTZ level of theory. This value is ~0.1 Å longer than the distance reported by Fredericks et al.[6] with a smaller basis set, but the potential surface is quite flat.

Electronic binding energies obtained from the correlation consistent basis sets are listed in Table 1 and graphically depicted in Figure 1. Counterpoise-corrected results are presented beside the raw binding energies. Due to the degree of linear dependency encountered with the full aug-cc-pVQZ basis set on benzene, it was necessary to remove the diffuse functions. With the aug-cc-pVQZ basis set there were 21 eigenvalues of the overlap matrix with values less than 1.0×10^{-7}. NWChem would normally attempt to perform a rectangular transformation to eliminate linearly dependent vectors, but with this many vectors, problems in the self-consistent field convergence were anticipated. With the hybrid aug-cc-pVQZ(H_2O)/cc-pVQZ(benzene) basis set, only one eigenvalue fell below 1.0×10^{-6}. Comparable cc-pV*x*Z basis set calculations were carried out at the same geometries, but are not shown in Figure 1 to prevent the figure from becoming overly cluttered.

The raw MP2 and CP-corrected binding energies appear to be converging to a value between −3.5 and −4.1 kcal/mol. Unfortunately, even for the cc-pV5Z basis set, BSSE is still 0.33 kcal/mol, whereas for the water dimer it had dropped to less than half that amount with the same basis set. Although the presence of augmenting diffuse functions reduces BSSE by a factor of 2, diffuse functions also lead to excessive linear dependency in this case. With most widely used basis sets, CP-corrected binding energies provide a more realistic estimate of the binding energy. However, for the augmented correlation consistent basis sets it has frequently been observed that ΔE_e(CP) is in worse agreement with the complete basis set (CBS) limit than the uncorrected values.[12,31] To the extent this behavior persists for the benzene−water complex, the true CBS limit is likely to be nearer −4.0 than to −3.5 kcal/mol.

Improved CBS limit estimates can sometimes be achieved by fitting the raw or CP-corrected binding energies to a simple exponential functional form.[32−36] However, in this case the convergence patterns lacked the requisite exponential decay. Of the calculations performed in this study, only the CP-corrected cc-pV*x*Z data points exhibited approximate exponential decay. Fitting the TZ → 5Z sequence of binding energies with an exponential produced a CBS estimate of −3.7 kcal/mol. Combining this value with the raw aug-cc-pVQZ value (−4.1 kcal/mol), we arrive at our best estimate of the frozen core MP2 binding energy, $\Delta E_{\mathrm{MP2(CP)}}{}^{\mathrm{CBS}} = -3.9 \pm 0.2$ kcal/mol, with error bars based on the spread in the values. The comparable value for the water dimer is −4.9 ± 0.1 kcal/mol, or just 25% stronger than the benzene−water interaction. The present estimate is considerably stronger than the best previously reported MP2(FC) value, after adjusting for BSSE, and almost three times larger than the B3LYP result of Fredericks et al.

MP2 calculations with basis sets designed to recover core/valence correlation energy (cc-pCVTZ)[37] were performed at the MP2/aug-cc-pVTZ geometries. Experience with a large number of molecules has shown that this level of basis set typically recovers 80−90% of the true CBS limit core/valence effect. For the benzene−water complex, the computed change in the binding energy was −0.03 kcal/mol, i.e., it was strengthened. For the water dimer, the same level of theory produces a 0.04 kcal/mol core/valence correction.

Increasing the level of theory to CCSD(T) causes only slight shifts in the binding energy. With the aug-cc-pVDZ basis set, ΔE_e decreases in magnitude by 0.28 kcal/mol (0.21 with CP correction), having much the same affect as it did in the water dimer. With the larger aug-cc-pVTZ basis set, the difference in the raw MP2 and CCSD(T) binding energies falls to 0.16 kcal/mol. It was not practical to compute the CP correction at the CCSD(T)/aVTZ level of theory, since each 506 basis function calculation required ~36 days. We anticipate that at the complete basis set level the difference between MP2 and CCSD(T) will be ≤0.1 kcal/mol.

The four lowest-frequency normal modes obtained from an MP2/aug-cc-pVDZ calculation correspond primarily to twisting and rocking motions of the water molecule. These modes span a frequency range between 34 cm^{-1} and 102 cm^{-1}. Frequencies of this magnitude often possess a significant anharmonic component, but no attempt was made to determine this effect in the present work. The change in vibrational zero point energy (ZPE) for the reaction $C_6H_6{-}H_2O \rightarrow C_6H_6 + H_2O$ was obtained from normal-mode analyses and amounts to 1.0 kcal/mol. Adding this to our best estimate of the electronic binding energy, yields $\Delta E_0(0\ \mathrm{K}) = -2.9 \pm 0.2$ kcal/mol, in good agreement with the recent threshold photoionization value of −2.4 ± 0.1 kcal/mol,[38] and in reasonable agreement with the upper end of the −1.63 to −2.78 kcal/mol range determined from dispersed fluorescence spectra.[26] The corresponding value for the water dimer is $\Delta E_0(0\ \mathrm{K}) = -2.9 \pm 0.1$ kcal/mol, based on $\Delta E_e = -5.0$ kcal/mol and $\Delta \mathrm{ZPE} = -2.1$ kcal/mol.

IV. Conclusions

Large basis set, highly correlated calculations of the benzene−water complex predict a geometry in which the water sits above the aromatic ring with oxygen pointed away from the benzene center of mass and one of the water hydrogens is oriented toward the ring, in qualitative accord with previous reports. However, unlike previous reports, we find the electronic binding energy to fall into the −3.8 to −3.9 kcal/mol range, or only 20% weaker than the water−water interaction. When zero point energies are included, the $\Delta E_0(0\ \mathrm{K})$ values are identical within their estimated uncertainties. This suggests that the immiscibility of the bulk phases is predominantly the result of the disruption of the water−water hydrogen bond network by benzene, rather than the difference in the binding energies.

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