

Hydrogen-Bonded Complexes Involving Benzene as an H Acceptor

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Abstract: Ab initio molecular theory has been used to study π hydrogen bonding in dimers involving benzene and the following H donors: NH_3 , H_2O , HF, H_2S , and HCl. Symmetry-restricted geometry optimization was carried out at the Hartree-Fock level using a small split-valence basis set. Effects of electron correlation were assessed by second-order Møller-Plesset perturbation theory with a larger basis set in single-point calculations at the final geometry. The structures feature weak association and a flat potential surface in the region where π hydrogen bonding occurs. At all levels of theory employed in this study, the binding strength of the H donors follows the order $\text{HF} > \text{H}_2\text{O}$, $\text{HCl} > \text{H}_2\text{S}$, NH_3 . In every case, the dimer exhibits a substantially larger calculated dipole moment than the polar monomer, which suggests that complex formation is accompanied by significant redistribution of electronic charge.

1. Introduction

The structures of heterodimers joined by unconventional π hydrogen bonds have been the subject of several experimental¹⁻¹⁰ and theoretical¹¹⁻¹³ investigations. In most of the systems, small unsaturated hydrocarbons served as H acceptors in complexes with Lewis acids. Although the features of complexes with aromatic H acceptors are of considerable interest, few structural studies have been carried out on such systems due to the complications of size.

Weak 1:1 complexes between benzene and the hydrogen halides HF and HCl have recently been characterized in the gas phase by means of the Fourier transform microwave molecular beam technique.¹⁻³ In each case, the spectral results show that, on average, the structure is a symmetric top with the hydrogen lying between the ring center and the halogen. Large-amplitude oscillations in both complexes made it difficult to determine equilibrium structures. Although the π -electron system of benzene may play the role of proton acceptor in associations with other electrophilic hydrides, no measurements on such complexes have been reported as yet.

Kollman and co-workers¹¹ performed limited ab initio molecular orbital calculations on $\text{C}_6\text{H}_6 \cdots \text{HF}$ using the minimal STO-3G basis set. No relaxation of the subunit geometry was allowed in the calculations. The vertical approaches of HF along the C_6 axis of the ring and toward the center of a CC bond were found to be equally favorable, with $\Delta E = 0.9$ kcal/mol.

In this paper, we discuss the findings from an ab initio theoretical study of π hydrogen bonding in the complexes of benzene with ammonia, water, hydrogen fluoride, hydrogen sulfide, and hydrogen chloride. Structures and energies have been calculated with Roothaan-Hall^{14,15} self-consistent field molecular orbital theory, and dispersion effects on the binding energies have been estimated by means of Møller-Plesset¹⁶ perturbation theory. Pople et al.¹² obtained satisfactory descriptions of hydrogen-bonded complexes between small unsaturated hydrocarbons (acetylene and ethylene) and hydrogen halides with techniques similar to those employed here.

Since the focus of this work is the examination of π hydrogen bonding, no effort has been made to locate other minima in the potential surface of the $\text{C}_6\text{H}_6 \cdots \text{AH}_n$ systems. Although experimental evidence indicates that HF and HCl preferentially act as H donors in complexes with benzene, some of the other AH_n molecules may favor a different approach to the ring. In such a case, the population of the π hydrogen-bonded species may be too small for easy experimental detection. Nevertheless, in view

of the interest in complexes featuring unconventional H bonds, it is worthwhile to assess the capability of benzene to engage in such interactions with a variety of potential H donors.

2. Calculations

The CADPAC program was employed in all computations.¹⁷ Structural variations were made with Hartree-Fock (HF) wave functions using the split-valence 3-21G(*) basis set,¹⁸ which includes d-type polarization functions only on second-row atoms. Owing to the large number of atoms in each system, we made no attempt to establish an equilibrium structure through full-geometry optimization. At first, the $\text{C}_6\text{H}_6 \cdots \text{AH}_n$ complexes were energy minimized with the heavy atom A constrained to lie on the C_6 axis of benzene. Furthermore, the orientation of AH_n above the ring was fixed to maintain C_{nv} (C_{6v} if $n = 1$) symmetry throughout the calculation. Since the orientation of H_2O , H_2S , and NH_3 relative to the benzene ring may be taken in two different ways without loss of symmetry, both geometries were considered. Bond lengths of all molecules were allowed to vary in the energy-minimization process, as were the bond angles in H_2O , H_2S , and NH_3 . Final values of the variables, total energies, and complex binding energies are listed in Tables I-III, respectively. At convergence, no Cartesian energy gradient exceeded 5×10^{-4} hartree/bohr in magnitude. Although some improvement might result from relaxation of the planarity of the benzene ring, the small size of the gradients implies that further changes in energy and geometry would be minor. A second series of energy-minimization computations was performed with the bond lengths and angles obtained from the initial

(1) Baiocchi, F. A.; Williams, J. H.; Klemperer, W. J. *J. Phys. Chem.* **1983**, *87*, 2079.

(2) Read, W. G.; Campbell, E. J.; Henderson, G.; Flygare, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7670.

(3) Read, W. G.; Campbell, E. J.; Henderson, G. *J. Chem. Phys.* **1983**, *78*, 3501.

(4) Read, W. G.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 2238.

(5) Legon, A. C.; Aldrich, P. D.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 625.

(6) Aldrich, P. D.; Kukolich, S. G.; Campbell, E. J. *J. Chem. Phys.* **1983**, *78*, 3521.

(7) Shea, J. A.; Bumgarner, R. E.; Henderson, G. *J. Chem. Phys.* **1984**, *80*, 4605.

(8) Shea, J. A.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 4857.

(9) Aldrich, P. D.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 2126.

(10) Kukolich, S. G.; Read, W. G.; Aldrich, P. D. *J. Chem. Phys.* **1983**, *78*, 3552.

(11) Kollman, P.; McKelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975**, *97*, 955.

(12) Pople, J. A.; Frisch, M. J.; Del Bene, J. E. *Chem. Phys. Lett.* **1982**, *91*, 185.

(13) Frisch, M. J.; Pople, J. A.; Del Bene, J. E. *J. Chem. Phys.* **1983**, *78*, 4063.

(14) Roothaan, C. C. *J. Rev. Mod. Phys.* **1951**, *23*, 69.

(15) Hall, G. G. *Proc. R. Soc. London, A* **1951**, *A205*, 541.

(16) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(17) Amos, R. D. CADPAC: The Cambridge Analytic Derivatives Package, issue 3.0, Cambridge, 1986.

(18) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 63-100.

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Table I. Optimized^a Distances and Angles^b of C₆H₆...AH_n Complexes with C_{nv} Symmetry

	C ₆ H ₆ ...HF: C _{6v}		C ₆ H ₆ ...HCl: C _{6v}		C ₆ H ₆ ...H ₂ O ^c		C ₆ H ₆ ...H ₂ S ^c		C ₆ H ₆ ...NH ₃ ^d	
					C _{2v} -1	C _{2v} -2	C _{2v} -1	C _{2v} -2	C _{3v} -1	C _{3v} -2
R ^e	3.28 ^f	3.79 ^g			3.41	3.40	4.12	4.12	3.65	3.66
HA	0.939 (0.937)	1.269 (1.267)			0.966 (0.967)	0.967	1.326 (1.327)	1.326	1.005 (1.003)	1.005
HAH					106.3 (107.6)	106.2	93.8 (94.4)	93.8	110.3 (112.4)	110.3
CC	1.386 (1.385)	1.386			1.386	1.386	1.385	1.385	1.385	1.385
CH	1.072 (1.072)	1.072			1.072	1.072	1.072	1.072	1.072	1.072

^aEnergy-minimized at HF3-21G(*). ^bLengths in angstroms and angles in degrees. Values for isolated molecules given in parentheses. ^cAH₂ nuclear plane bisects benzene ring through carbon atoms (C_{2v}-1) or CC bonds (C_{2v}-2). ^dMirror planes of complex contain ring atoms (C_{3v}-1) or CC bond centers (C_{3v}-2). ^eDistance from ring center to heavy atom, A, of hydrogen donor. ^fThe experimental value of R for the vibrationally averaged symmetric top structure is given in ref 1 as 3.18 Å. ^gIn ref 3, the value of R is reported to be 3.63 Å for the symmetric top structure.

Table II. Total Energies^a of C_{nv} Structures

system	case	HF3-21G(*)	HF6-31G*//3-21G(*)	MP2(FC)/6-31G*//3-21G(*)
HF		-99.460 22	-100.002 10	-100.182 16
HCl		-457.981 41	-460.049 96	-460.181 90
H ₂ O		-75.585 96	-76.009 74	-76.196 50
H ₂ S		-396.819 64	-398.666 48	-398.787 55
NH ₃		-55.872 20	-56.182 48	-56.351 93
C ₆ H ₆		-229.419 44	-230.703 07	-231.455 89
C ₆ H ₆ ...HF	C _{6v}	-328.886 80	-330.710 97	-331.646 45
C ₆ H ₆ ...HCl	C _{6v}	-687.405 77	-690.756 40	-691.644 20
C ₆ H ₆ ...H ₂ O	C _{2v} -1	-305.010 76	-306.716 79	-307.658 86
	C _{2v} -2	-305.010 74	-306.716 79	-307.658 88
C ₆ H ₆ ...H ₂ S	C _{2v} -1	-626.241 57	-629.371 39	-630.247 40
	C _{2v} -2	-626.241 57	-629.371 39	-630.247 20
C ₆ H ₆ ...NH ₃	C _{3v} -1	-285.293 39	-286.887 71	-287.812 02
	C _{3v} -2	-285.293 39	-286.887 64	-287.811 93

^aAtomic units: 1 hartree = 627.47 kcal/mol.

Table III. Binding Energies (kcal/mol) of C_{nv} Structures

system	case	HF3-21G(*)	HF6-31G*//3-21G(*)	MP2(FC)/6-31G*//3-21G(*)
C ₆ H ₆ ...HF	C _{6v}	4.5	3.6	5.3
C ₆ H ₆ ...HCl	C _{6v}	3.1	2.1	4.0
C ₆ H ₆ ...H ₂ O	C _{2v} -1	3.4	2.5	4.1
	C _{2v} -2	3.4	2.5	4.1
C ₆ H ₆ ...H ₂ S	C _{2v} -1	1.6	1.1	2.5
	C _{2v} -2	1.6	1.1	2.5
C ₆ H ₆ ...NH ₃	C _{3v} -1	1.1	1.3	2.6
	C _{3v} -2	1.1	1.3	2.6

calculations, but the position of AH_n (represented by R, θ, and φ in Figure 1) was allowed to vary in systems with C_s symmetry. The mirror plane in which the motion of A is confined may contain either a pair of benzene ring carbons or two CC bond centers. Furthermore, for a given choice of R, θ, and φ, the angle χ governing the orientation of AH_n may be selected in two different ways if the molecule is water, hydrogen sulfide, or ammonia. As a result, two C_s geometries were examined for each hydrogen halide, and four were investigated in the other cases. The final geometries, force constants, and binding energies from these calculations are given in Table IV.

Table IV. Geometries,^a Force Constants,^b and Binding Energies^c of C_s Structures^d Using the HF3-21G(*) Model

	C ₆ H ₆ ...HF: C _s		C ₆ H ₆ ...HCl: C _s		C ₆ H ₆ ...H ₂ O ^e		C ₆ H ₆ ...H ₂ S ^e		C ₆ H ₆ ...NH ₃ ^f	
					C _s -1	C _s -2	C _s -1	C _s -2	C _s -1	C _s -2
R	3.42	3.81	3.39	3.39	4.07	4.07	3.92	3.70		
θ	17.0 (2)	9.3 (1)	0.0	0.0	0.0	0.0	13.6 (2)	4.7 (1)		
φ	9.5 (1)	12.2 (1)	-0.3	0.0	-5.6 (6)	0.0	-52.9	-45.6		
k _{RR}	0.0057 (3) ^g	0.0041 (1) ^h	0.0047 (3)	0.0043	0.0022 (1)	0.0023 (1)	0.0015	0.0025 (1)		
k _{Rθ}	0.0096 (3)	0.0059 (6)	0.0006 (4)	0.0001	0.0006	0.0001	0.0035	0.0024 (3)		
k _{Rφ}	0.0006	0.0017 (1)	0.0000 (1)	-0.0001 (1)	-0.0001	0.0001	-0.0022 (7)	0.0005 (4)		
k _{θθ}	0.0271 (1)	0.0165 (1)	0.027 (1)	0.0135	0.017 (1)	0.0079 (1)	0.0107 (3)	0.012 (2)		
k _{θφ}	-0.0064 (2)	0.0003 (1)	0.000 (3)	0.0008 (2)	-0.0002 (1)	0.0011 (1)	0.0034 (1)	0.004 (3)		
k _{φφ}	0.0154 (4)	0.0144 (1)	0.0011 (6)	0.0078 (2)	0.0003 (1)	0.0061	0.0054 (1)	0.006 (3)		
ΔE	4.6	3.2	3.4	3.4	1.6	1.6	1.5	1.4		

^aDistances in angstroms and angles in degrees. ^bAtomic units: hartree/bohr², hartree bohr⁻¹ rad⁻¹, or hartree/rad² where 1 bohr = 0.529 177 Å and 1 rad = 57.295 78°. ^cEnergy in kilocalories per mole. ^dValues are the means of the two systems that differ in the orientation of the benzene ring relative to the mirror plane. The deviation in the last digit is shown in parentheses. ^eAH₂ lies in the mirror plane (C_s-1) or perpendicular to it (C_s-2). ^fThe NH bond lying in the mirror plane is directed toward either the edge (C_s-1) or the interior (C_s-2) of the benzene ring. ^gThis force constant is 0.090 mdyn/Å, which may be compared with the experimental radial force constant k_r = 0.073 mdyn/Å given in ref 1. ^hIn ref 3 the experimental radial force constant, k_r, is given as 0.080 mdyn/Å while the value of k_{RR} is 0.065 mdyn/Å.

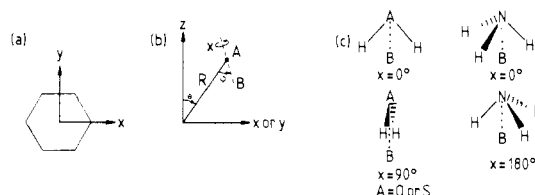


Figure 1. Coordinate system used to describe C_s complexes: (a) benzene ring in the xy plane with its center at the origin; (b) mirror plane of the complex containing A, the heavy atom of molecule AH_n, as well as the AH_n symmetry axis passing through point B in the vicinity of the H atom(s); (c) orientations of AH_n relative to the mirror plane of the complex and the corresponding values of χ for the cases where n > 1. In the text, C_s-1 denotes the system with χ = 0° and C_s-2 represents the case with χ = 90° or 180°.

To obtain better estimates of the complex stabilization energy, additional calculations were made using the 6-31G* basis set, which includes polarization functions on all atoms other than hydrogen. The final geometries of the C_{nv} systems were used in single-point Hartree-Fock calculations with the larger basis, a procedure represented by the notation¹⁸ HF6-31G*//3-21G(*). An attempt was also made to assess the effects of electron correlation by employing second-order Møller-Plesset perturbation theory with the frozen-core approximation, a method denoted by MP2(FC)/6-31G*//3-21G(*). The results of these calculations are listed in Tables II and III.

The rearrangement of charge that accompanies complex formation is an important indicator of hydrogen bonding. Comparison of the calculated dipole moment of the dimer with that of the polar monomer provides evidence of polarization and charge transfer within the system. Table V contains results from the C_{nv} systems using the theoretical models discussed above.

3. Discussion

At the HF3-21G(*) level, all complexes with C_{nv} geometry exhibit modest binding. Calculated structural changes in the component molecules arising from complex formation are generally quite small. A slight 0.002-Å increase in the HA bond length occurs for HF, HCl, and NH₃. On the other hand, the bond lengths in H₂O and H₂S decrease by 0.001 Å. The HAH angles in hydrogen sulfide, water, and ammonia contract by amounts

Table V. Calculated Dipole Moments^a and Charge Shifts^b Accompanying Complex Formation

AH _n	$\mu(\text{C}_6\text{H}_6\cdots\text{AH}_n)^c$			$\mu(\text{AH}_n)$			ΔQ_A^c		ΔQ_H^c		$\Delta Q_{\text{C}_6\text{H}_6}^c$	
	3-21G(*)	6-31G*	MP2(FC)	3-21G(*)	6-31G*	MP2(FC)	3-21G(*)	6-31G*	3-21G(*)	6-31G*	3-21G(*)	6-31G*
HF	2.58	2.52	2.51	2.17	2.01	2.00	0.0242	0.0271	-0.0145	-0.0141	-0.0097	-0.0130
HCl	1.98	1.95	1.96	1.51	1.44	1.44	0.0367	0.0298	-0.0281	-0.0176	-0.0086	-0.0122
H ₂ O	2.77	2.63	2.63	2.39	2.18	2.17	0.0164	0.0226	-0.0021	-0.0040	-0.0123	-0.0146
H ₂ S	1.73	1.75 (1)	1.75 (1)	1.42	1.41	1.41	0.0274	0.0225	-0.0099	-0.0070	-0.0076	-0.0084
NH ₃	2.10	1.90	1.90	1.75	1.55	1.55	-0.0094	-0.0087	0.0051	0.0048	-0.0058	-0.0057

^aDebye units. ^bMulliken population analysis: $\Delta Q_i = Q_i(\text{dimer}) - Q_i(\text{monomer})$. ^cValues given for C_{nv} complexes. In those cases exhibiting two different C_{nv} geometries, the value is the mean with any deviation in the last figure shown in parentheses.

from 0.6 to 2.1°. In addition, the benzene CC bonds stretch 0.001 Å in the complexes with HF, HCl, and H₂O. The calculated distance, *R*, from the ring center to the heavy atom A ranges from 3.28 to 4.12 Å and follows the order HF < H₂O < NH₃ < HCl < H₂S. Vibrationally averaged values of *R* have been obtained for the hydrogen halide complexes through analysis of the rotational spectra.^{1,3} The experimental F and Cl distances from the ring center are, respectively, 0.10 (3%) and 0.16 Å (4%) shorter than the calculated values.

Values of the binding energies, ΔE , obtained with the C_{nv} geometries lie between 1 and 6 kcal/mol for all three levels of computation. HF exhibits the strongest π hydrogen bonding; H₂O and HCl form bonds of intermediate strength; and the weakest associations occur with NH₃ and H₂S. The orientation of H₂O, H₂S, or NH₃ relative to the benzene ring has no effect on ΔE at any level of calculation. With the exception of the C₆H₆...NH₃ binding energy, the HF6-31G* results are smaller in magnitude than those obtained with the 3-21G(*) basis set. Since the improved basis should yield a reduction in the basis set superposition error, such a change might be expected in all cases, and the result for the ammonia complex seems anomalous. Although the Hartree-Fock calculations with the larger basis set suggest that association is very weak in these complexes, the binding energies are significantly increased by the incorporation of dispersion effects using second-order Møller-Plesset theory.

The anomalous value of ΔE for the ammonia complex produced by the HF6-31G*/3-21G(*) calculations may be ascribed to the geometry obtained through optimization with the smaller basis. The NH₃ bond angles appear to be less satisfactory for the isolated molecule (which is not sufficiently pyramidal) than the complex when the structures are employed in calculations using the 6-31G* basis. This leads to slight overestimation of the HF6-31G* stabilization energy for C₆H₆...NH₃.

It is of interest to compare calculated π hydrogen bond strengths from the benzene systems with results obtained using simpler unsaturated hydrocarbons as the H acceptors. The HF3-21G(*) and HF6-31G*/3-21G(*) hydrogen bond energies for C₆H₆...HF and C₆H₆...HCl are similar to the values reported for the hydrogen-halide complexes with acetylene and ethylene.¹² Frisch et al.¹³ have optimized the C₂H₂...H₂O system with water as the H donor at the HF6-31G* level yielding an energy without zero-point correction of 2.3 kcal/mol. This value is comparable to the HF6-31G*/3-21G(*) binding energy for C₆H₆...H₂O. However, when dispersion contributions are taken into account, the benzene complexes appear to have somewhat greater stability than complexes involving the simpler unsaturated hydrocarbons. While no stable π complex could be found for C₂H₂...NH₃, the findings of this study suggest that ammonia does act as an H donor with benzene.

In order to conduct a limited examination of the potential surface governing the motions of the component molecules, geometry optimizations were carried out in the systems with C_s symmetry, where the heavy atom A was initially placed above a carbon atom or CC bond of the aromatic ring. In every case, the change in θ shifted AH_n from its location above the edge of the ring toward the axis. However, only in the H₂O and H₂S complexes did the heavy atom actually lie on the C₆ axis at convergence. At the final value of ϕ , at least one hydrogen atom in AH_n approached closer to the face of the aromatic ring than

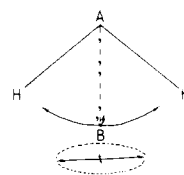


Figure 2. Oscillations in ϕ for AH₂ complexes with C_s symmetry. The sweep of the AB axis pushes one hydrogen down into the π -electron cloud of the ring in C_s-1, while this motion lifts both hydrogens away from the π cloud in C_s-2.

the heavy atom A. In C₆H₆...NH₃, the swing of the ammonia symmetry axis pushed the hydrogen(s) nearest the outside of the ring down into the π -electron cloud. The binding energies of the C_s complexes are negligibly lower than the C_{nv} energies, and the force constants are all quite small. This is indicative of wide-amplitude, low-frequency oscillations on a relatively flat potential surface. Since it makes little difference whether the mirror plane bisects the ring through the carbon atoms or the CC bonds, the results presented in Table IV are mean values from the two systems. On the other hand, orientation of the small molecule relative to the mirror plane is of importance in revealing subtle features of the potential surface for H₂O, H₂S, and NH₃. For example, in the H₂O and H₂S complexes, $k_{\phi\phi}$ is 1 order of magnitude smaller in C_s-1 than C_s-2. Hence, as illustrated in Figure 2, the side-to-side pendulum swings of the AB axis in C_s-1 are much less restricted than the back-and-forth swings in C_s-2. Examination of the results for C₆H₆...NH₃ reveals that the stretching force constant, k_{RR} , in C_s-1 is almost half the size of the C_s-2 value. Furthermore, coupling between the radial and angular motions, represented by $k_{R\theta}$ and $k_{R\phi}$, is much greater in the ammonia complex with C_s-1 geometry than the C_s-2 system. Therefore, *R* tends to increase with θ in both C_s structures, but the change is greater if the orientation of ammonia is such that a single hydrogen atom lies near the perimeter of the aromatic ring. Concerted stretch-rocking motions also occur in the hydrogen halide complexes since the force constants exhibit significant positive coupling between *R* and θ .

Baiocchi et al.¹ found that the dipole moment of C₆H₆...HF is 2.282 D, which exceeds the value for HF by 0.455 D. This dipole enhancement indicates that significant redistribution of electronic charge takes place in the process of complex formation. Similar enhancements are noted in the calculated dipole moments of the C_{nv} dimers when compared to the polar monomers. Although polarization within atom A and the carbons of benzene accounts for a good share of the enhancement, Mulliken population analysis suggests that weak charge transfer from benzene to AH_n contributes significantly. Intramolecular charge transfer within AH_n also takes place. In all but one case, the net negative charge on atom A is increased at the expense of the hydrogen(s) in the small molecule. The exception is the nitrogen atom of ammonia, which experiences a slight loss of electronic charge in the dimer.

4. Conclusions

On the basis of the results of the HF3-21G(*) calculations, the subunits in the C₆H₆...AH_n complexes undergo wide-amplitude oscillations on potential surfaces that are best described as broad shallow valleys in the π hydrogen-bonding region. Changes in the geometry of the component molecules due to complex for-

mation are quite small. Although the magnitude of the binding energy varies when a larger basis set is employed and electron correlation effects are included, the qualitative trends for the series under study remain essentially unchanged. At all levels of calculation, the relative affinity of the hydrogen donors for benzene is found to be $\text{HF} > \text{H}_2\text{O}$, $\text{HCl} > \text{H}_2\text{S}$, NH_3 . Where comparison is possible, the results of the calculations appear to be in fair agreement with experimental findings. The theoretical distances from the halide atoms to the ring center are slightly longer than the values obtained from analysis of the rotational spectra. According to both experiment and theory, the dipole moment of $\text{C}_6\text{H}_6 \cdots \text{HF}$ is substantially larger than that of HF. Since the theoretical calculations predict similar dipole moment enhancements for all dimers, the benzene ring seems to act as an electron donor in these systems.

Although this work has been concentrated on a limited domain of complex geometries, the results suggest that further use of this theoretical approach may be fruitful for exploring other configurations of the $\text{C}_6\text{H}_6 \cdots \text{AH}_n$ systems. It is of particular interest to determine whether the theory predicts other structures to be more favorable than those involving π hydrogen bonding. Investigations undertaken to answer this question will be the subject of a future report.

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Registry No. C_6H_6 , 71-43-2; HF, 7664-39-3; HCl, 7647-01-0; H_2O , 7732-18-5; H_2S , 7783-06-4; NH_3 , 7664-41-7.

Molecular Dynamics Simulation of Interfacial Water Structure and Dynamics in a Parvalbumin Solution

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Abstract: A 106-ps molecular dynamics simulation of the calcium-binding protein parvalbumin in water has been used as a basis for studying interfacial water. A general conclusion is that structure and dynamics of the interfacial water are only marginally affected by the presence of the protein. A few water molecules, which reside close to charge groups, are immobilized throughout the simulation. In the analysis the water molecules have been classified according to the distance to the nearest protein atom. Close to the protein we find a decrease in radial diffusion, while lateral diffusion is enhanced. In the inner water layers the dipole moment vector is preferentially oriented perpendicular to the radius vector of the protein. The reorientational correlation times have a minimum 4–5 Å from the protein, with values similar to those obtained from simulations of pure water.

It is commonly believed that a foreign body in a water solution imposes some ("clathrate-like" or icelike) structure on the water, in order to minimize the number of nonfulfilled hydrogen bonds. This applies especially to hydrophobic bodies since they are unable to form any hydrogen bonds at all but also to nonionic hydrophilic ones since they do not normally form hydrogen bonds as easily as water. Such a structure would, of course, affect the dynamics near the surface.

Experimental Results. The structure and dynamic behavior of a solvent close to a surface have received considerable attention. In particular, the influence of biological macromolecules on water structure and dynamics has been the subject of several experimental studies with varying methods, among others infrared spectroscopy,¹ Mössbauer and microwave spectroscopy,² and nuclear magnetic resonance. Koenig et al.³ studied interfacial water in protein solutions by means of ^2H and ^1H NMR relaxation measurements. However, as was pointed out by Piculell and Halle,⁴ ionizable groups at the protein contribute considerably to deuterium and proton relaxation rates, which are thus unsuitable for studies of interfacial water. Instead, the latter authors used ^{17}O relaxation data to obtain information about water dynamics around several proteins, among these carp parvalbumin.⁵ They

found that the local water reorientation at the protein surface was anisotropic and could be characterized by two relaxation times. They concluded that approximately two water layers close to the protein were affected by the surface with significantly reduced reorientational dynamics as compared to bulk water. On assumption of time-scale separation, they also concluded that the local rapid motion at the protein surface, which by necessity is anisotropic, is followed by a much slower reorientation with a correlation time in the nanosecond region. Another approach was made by Polnaszek and Bryant,⁶ who studied proton relaxation of interfacial water using a spin label bound to a protein surface. They found a 5–10-fold decrease in the translational diffusion near (<10 Å) the protein surface.

In another study⁷ of water in silica sols, Halle and Piculell found qualitatively the same behavior. For this system they also applied a dynamic model in order to interpret the long correlation time. Their conclusion⁸ was that the translational mobility of the hydration water is strongly reduced; the radial diffusion is decreased by 2 orders of magnitude, and the lateral diffusion is decreased by 1 order of magnitude compared to bulk water.

Simulations of Water at Surfaces. Both Monte Carlo (MC) and molecular dynamics (MD) simulations are well suited to study water at interfaces. Preferentially, a simplified model system is

(1) Poole, P. L.; Finney, J. L. In *Biophysics of Water*; Franks, F., Mathias, S., Eds.; Wiley-Interscience: Chichester, U.K., 1982; p 36.

(2) Parak, F. *Methods Enzymol.* **1986**, *127*, 196.

(3) Koenig, S. H.; Hallenga, K.; Sphorer, M. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2667.

(4) Piculell, L.; Halle, B. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 401.

(5) Halle, B.; Andersson, T.; Forsén, S.; Lindman, B. *J. Am. Chem. Soc.* **1981**, *103*, 500.

(6) Polnaszek, C. F.; Bryant, R. G. *J. Chem. Phys.* **1984**, *81*, 4038.

(7) Piculell, L. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 387.

(8) Halle, B.; Piculell, L. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 415.