Water Complexes of Styrene and 4-Fluorostyrene: A Combined Electronic, Vibrational Spectroscopic and Ab-Initio Investigation

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Received: March 3, 2008; Revised Manuscript Received: June 3, 2008

The binary complexes of water with styrene and fluorostyrene were investigated using LIF and FDIR spectroscopic techniques. The difference in the shifts of $S_1 \leftarrow S_0$ electronic transitions clearly points out the disparity in the intermolecular structures of these two binary complexes. The FDIR spectra in the O−H stretching region indicate that water is a hydrogen bond donor in both complexes. The formation of a single O−H···π hydrogen-bonded complex with styrene and an in-plane complex with fluorostyrene was inferred based on the analysis of the FDIR spectra in combination with ab initio calculations. The in-plane complex with fluorostyrene is characterized by the presence of O−H···F and C−H···O hydrogen bonds, leading to formation of a stable six-membered ring. The synergistic effect of O−H···F and C−H···O hydrogen bonds overwhelms the O−H···π interaction in fluorostyrene−water complexes.

Introduction

The interaction of water with the π electron density of the benzene ring leading to the formation of a O−H···π hydrogen bond is now well established.[1−5] One of the most interesting features of the benzene−water complex is the nearly free rotation of H_2O over the benzene ring with a very low effective barrier for the V_6 potential, signatures of which have been captured in rotational as well as vibrational spectra.[3−5] The free rotation of H_2O over the benzene ring manifests in a multitude of transitions in the O−H stretching region of the benzene−water complex.[5] In the case of substituted benzenes, such as fluorobenzene and chlorobenzene, the formation of an in-plane hydrogen-bonded complex with water is favored over the O−H···π hydrogen-bonded complex.[6] This can be rationalized by the fact that both fluorine and chlorine atoms offer electron density (lone pairs) in the plane of the benzene ring, leading to the formation of the O−H···X (X = F, Cl) hydrogen bond. Further, the CH group of the benzene ring in the ortho position interacts with the oxygen of the water molecule, leading to formation of a C−H···O hydrogen bond, resulting in a stable six-membered cyclic structure. In the case of the benzonitrile−water complex, a similar situation holds.[7] However, the only difference is that the lone pair on the X atom is replaced by the π-bond electrons of the C≡N triple bond in the plane of the benzene ring. These results indicate that the presence of a heteroatom/group on the benzene ring favors the formation of an in-plane hydrogen-bonded complex. On the other hand, presence of strongly acidic or basic functional groups on the benzene ring, such as phenol, aniline, salicylic acid, phenylacetamide, and others, leads to formation of hydrogen-bonded complexes wherein the water molecule interacts exclusively with the functional group present on the benzene ring.[8−12]

The two functional groups ethenyl ($H_2C{=}CH{-}$) and ethynyl ($HC{\equiv}C{-}$) do not contain hetero atoms, and therefore, styrene (ethenylbenzene) and phenylacetylene (ethynylbenzene) can be expected to form O−H···π hydrogen-bonded complexes with water. However, we have recently shown that water forms of an in-plane hydrogen-bonded complex with phenylacetylene,[13] the structure of which is very similar to the water−benzonitrile complex.[7] Water complexes of styrene have been extensively investigated by El-Shall and co-workers using multiphoton ionization method to understand the role of water in the inhibition of the cationic polymerization of styrene.[14,15] Ab initio calculations and Monte Carlo simulations have indicated that water forms a π complex with styrene. The ab initio calculations identify two energetically closely spaced minima in which water interacts with the extended π electron cloud of styrene, leading to the formation of O−H···π hydrogen bonding. The fluorostyrene−water complex, the structure of which was recently reported by Chervenkov et al. using high-resolution electronic spectroscopy,[16] forms a cyclic complex involving O−H···F and C−H···O hydrogen bonds, similar to the fluorobenzene−water complex.[6] However, unlike benzene−water and fluorobenzene−water complexes, the IR spectra of binary complexes of water with styrene and fluorostyrene in the O−H stretching region have not been reported. Interestingly, even though the formation of the O−H···π hydrogen-bonded styrene−water complex has been discussed in the literature, the experimental proof is still missing.[14,15] To understand the nature of interaction of the water with styrene and fluorostyrene and to determine the fate of the O−H stretching vibrations of the water moiety upon complex formation, we have carried out an IR−UV double resonance spectroscopy investigation in the O−H stretching region, and the results are presented in this article.

Experimental Section

The details of the complete experimental setup can be found elsewhere.[17] Briefly, helium buffer gas at 4 atm was bubbled through a mixture of styrene/fluorostyrene and water kept at room temperature and expanded through a 0.5 mm diameter pulsed nozzle (Series 9, Iota One; General Valve Corporation). The electronic excitation of styrene/fluorostyrene and their water cluster was achieved using a frequency-doubled output of a tunable dye laser (Narrow Scan GR; Radiant Dyes) pumped with the second harmonic of a Nd:YAG laser (Surelite I-10; Continuum). The fluorescence excitation spectra were recorded by monitoring the total fluorescence with a photomultiplier tube

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10.1021/jp801856r CCC: $40.75

(9780SB+1252−5F; Electron Tubes Limited) and a filter (WG-320) combination while scanning the UV laser frequency. The IR spectra were obtained using the fluorescence dip infrared (FDIR) spectroscopic method. In this method, the population of a target species is monitored by the fluorescence intensity, following its electronic excitation to the $S_1 \leftarrow S_0$ origin band with a UV laser pulse. A tunable IR laser pulse is introduced 100 ns prior to the UV laser pulse. When the IR frequency is resonant with the vibrational transition of the target species, the ground-state population decreases, resulting in the depletion of the fluorescence signal. In our experiments, the source of tunable IR light was an idler component of a $LiNbO_3$ OPO (Custom IR OPO; Euroscan Instruments) pumped with an injection-seeded Nd:YAG laser (Briliant-B; Quantel). The IR OPO was calibrated by recording the photoacoustic spectrum of ambient water vapor, and the absolute frequency calibration was within ± 2 cm^{-1}. The typical energies used were about 100 μJ/pulse for the UV laser and about 2 mJ/pulse for the IR laser, and the bandwidth of both the UV and IR lasers was about 1 cm^{-1}.

To supplement the experimental observations, we carried out ab initio calculations using the Gaussian-03 suit of programs.[18] The equilibrium structures of the monomers and various complexes were calculated at the MP2(FC)/aug-cc-pVDZ level of theory. The nature of the stationary points obtained was verified by calculating the vibrational frequencies at the same level of theory. The stabilization energies were corrected for the zero-point vibrational energy (ZPVE) and basis set superposition error. Complete BSSE correction is believed to often underestimate the interaction energy, and 50% correction is a good empirical approximation;[19] therefore, we report the stabilization energies with 0, 50, and 100% BSSE correction. The calculated symmetric and antisymmetric O−H stretching frequencies of the water molecule at the MP2(FC)/aug-cc-pVDZ level were 3803 and 3937 cm^{-1}, respectively. However, the corresponding experimental values were 3657 and 3756 cm^{-1}. The scaling factor of 0.9576 was devised by taking the ratio of the average of experimental frequencies (3706 cm^{-1}) to the average of the calculated frequencies (3870 cm^{-1}). The same scaling factor was used for the styrene−water and fluorostyrene−water complexes. The agreement between the calculated and observed vibrational frequencies served as a benchmark for the structural assignment of the binary clusters.

Results and Discussion

Figure 1 shows the LIF excitation spectra of styrene (trace A) and fluorostyrene (trace C), and the transitions marked with “s” and “fw” correspond to their respective band-origin transitions at 34758 and 34315 cm^{-1}, respectively, which are in good agreement with the values reported in the literature.[20,21] In the presence of water, new transitions appear in the LIF excitation spectra of both styrene (trace B) and fluorostyrene (trace D). These newly appearing transitions are marked with “sw” and “fsw” and correspond to the binary complexes with water. The band-origin transition of the styrene−water complex appears at 34779 cm^{-1},[14] while for the LIF spectrum of the fluorostyrene−water complex, two transitions appear at 34418 and 34423 cm^{-1}, separated by 5 cm^{-1}, which can be assigned to two structural isomers, based on the observations made by Chervenkov et al.[16] The band-origin transitions of water complexes of styrene and fluorostyrene are shifted to the blue by 21 and 108 cm^{-1}, respectively, relative to the respective monomers. The large difference in the shifts of electronic transitions of styrene−water and fluorostyrene−water complexes, prima facie, indicates that the intermolecular structures of these two water complexes are very dissimilar.

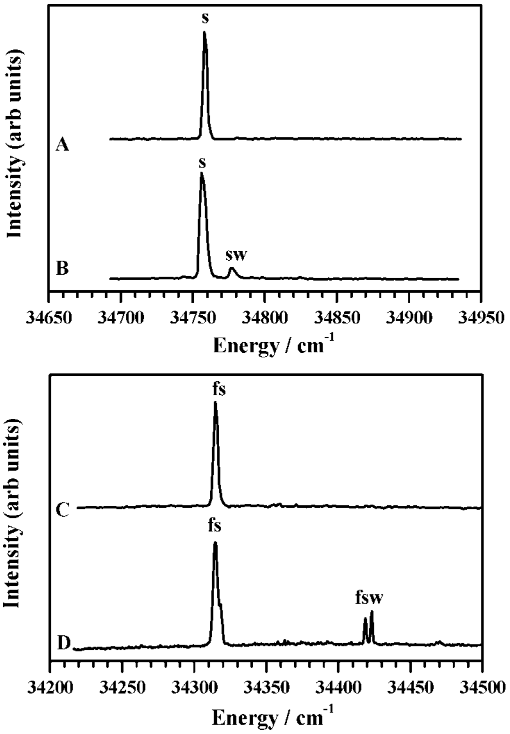

Figure 1. LIF excitation spectra of (A) styrene, (B) styrene−water, (C) fluorostyrene, and (D) fluorostyrene−water. The peaks marked with “s”, “sw”, “fs”, and “fsw” correspond to band-origin transitions of styrene, styrene−water, flurostyrene, and fluorostyrene−water, respectively.

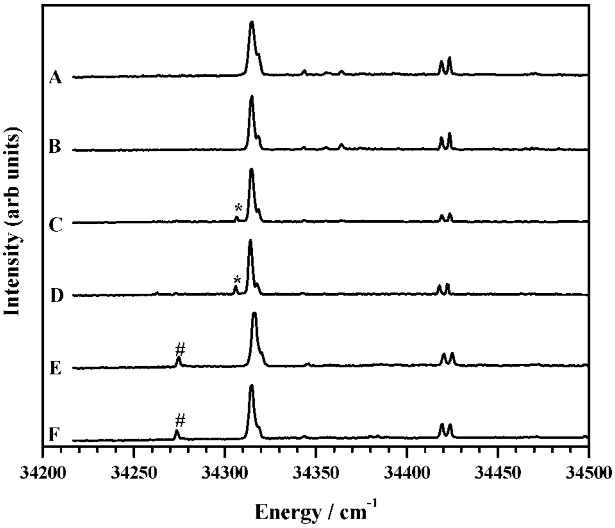

Figure 2. LIF excitation spectra of fluorostyrene−water recorded under various expansion conditions. (A) He at 3 atm, (B) He at 6 atm, (C) Ne at 2 atm, (D) Ne at 4 atm, (E) Ar at 1 atm, and (F) Ar at 2 atm. The nozzle temperature for all of the spectra was 298 K. The transitions marked with “*” and “#” are due to complexes with neon and argon, respectively.

The LIF excitation spectra of the fluorostyrene−water system were recorded by varying the expansion conditions, and the results are presented in Figures 2 and 3. Figure 2 shows the spectra recorded by varying the expansion conditions but maintaining the nozzle temperature at 298 K. These spectra reveal that the ratio of two peaks can be varied by changing the buffer gas. For instance, the ratio of the lower-energy

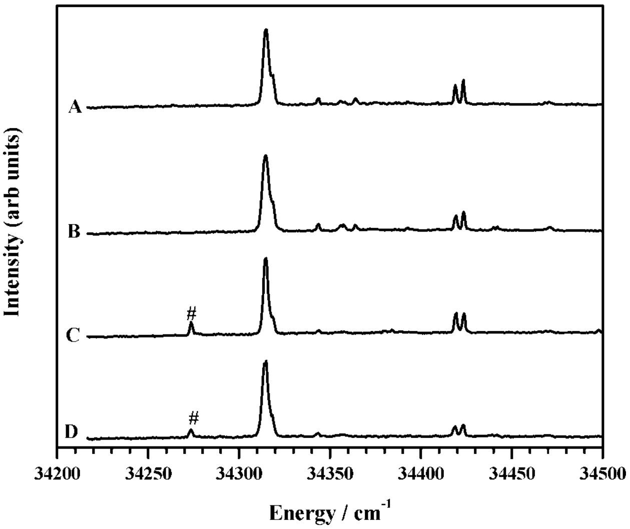

Figure 3. LIF excitation spectra of fluorstyrene−water recorded under various expansion conditions. (A) He at 3 atm and 298 K, (B) He at 3 atm and 330 K, (C) Ar at 1 atm and 298 K, and (D) Ar at 1 atm and 330 K. In C and D, the transition marked with "#" is due to a complex with argon.

transition (at 34418 cm^{-1}) to the higher energy transition (at 34423 cm^{-1}) increases progressively by changing the buffer gas from helium to neon to argon. On the other hand, just varying the backing pressure with the same buffer gas does not change the relative intensities of these two transitions. Figure 3 shows the LIF excitation spectra of the fluorostyrene−water complex with the change in the temperature of the nozzle (also the higher vapor pressure of water).[22] The formation of complexes is marginally disfavored at higher temperatures. However, the relative populations do not change with the temperature for both helium and argon buffer gases. These results indicate that stabilization energies of the two isomers are very close, and argon buffer gas is more effective in thermalizing the population, most probably due to its higher mass.

To understand the nature of interaction of water with styrene and fluorostyrene, FDIR spectra of water complexes in the O−H stretching region were recorded by monitoring the fluorescence following excitation at their corresponding band-origin transitions at 34779 and 34423 cm^{-1}, respectively, while scanning the IR laser frequency. The FDIR spectrum of the styrene−water complex, depicted in Figure 4A, shows two transitions at 3633 and 3727 cm^{-1} and is very much unlike the spectrum of the benzene−water complex.[5] This clearly signifies the quenching of the free rotation of the water molecule over the benzene ring. Shown in Figure 4B is the FDIR spectrum of the fluorostyrene−water complex, which also consists of two transitions at 3641 and 3744 cm^{-1}. The FDIR spectrum of the weaker transition observed in the LIF spectrum of fluorostyrene−water at 34418 cm^{-1} (see Figure 1D), was identical to the spectrum shown in Figure 4B. The arrows in Figure 4 point out the positions of the symmetric and antisymmetric stretching frequencies of the bare water molecule at 3657 and 3756 cm^{-1}, respectively. Clearly, the shifts in the O−H stretching frequencies of the styrene−water complex are higher than those of the fluorostyrene water complex. The total shift [$\Sigma(\Delta\nu)$] for the water complexes of the styrene and fluorostyrene complexes are 53 and 28 cm^{-1}, respectively.

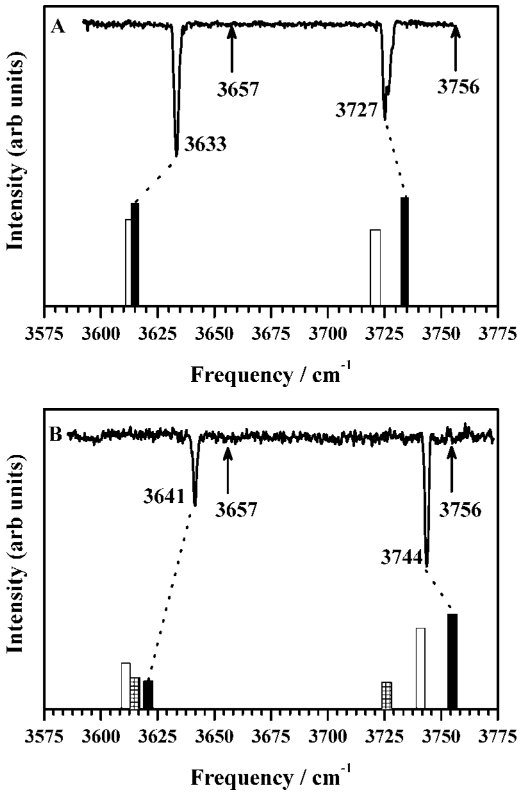

Figure 4. FDIR spectra of (A) styrene−water and (B) fluorostyrene−water complexes in the O−H stretching region. The arrows indicate the positions of symmetric (3657 cm^{-1}) and antisymmetric (3756 cm^{-1}) stretching frequencies of the bare water molecule. In (A), the solid and open solid bars represent the calculated vibrational (stick) spectra for complexes **A** and **B**, respectively. In (B) the open, mesh, and solid bars represent the calculated vibrational (stick) spectra for complexes **C**, **D**, and **E**, respectively. In each case, the solid bars correspond to the experimentally observed structure.

The ab initio calculations at MP2/aug-cc-pVDZ level converge on to two minima for the styrene−water system and four minima for the fluorostyrene−water system. The optimized structures of styrene−water and fluorostyrene−water complexes are shown in Figure 5, and the stabilization energies are listed in Table 1. The first styrene−water complex is an O−H···π hydrogen-bonded complex, **A**, in which a single OH group of water points toward the benzene ring. In the second complex, **B**, both OH groups of water are hydrogen-bonded, one each with benzene and ethylene π electron densities. The singly O−H···π hydrogen-bonded complex, **A**, Figure 5A, is marginally (~0.5 kJ mol^{-1}) more stable than the other isomer, **B**. Even in the case of the fluorostyrene−water system, two π hydrogen-bonded complexes with single, **C**, and double, **D**, O−H···π contacts were identified. The structures of these two complexes are similar, but not identical, to the corresponding styrene−water complexes. Interestingly, the doubly O−H···π hydrogen-bonded complex, **D**, is marginally more stable than the singly O−H···π hydrogen-bonded complex, **C**. The lower of the stabilization energies of the π complexes of fluorostyrene relative to styrene and the switching of the preferred conformation from single O−H···π to double O−H···π contacts can be attributed to the reduction of the π electron density on the benzene ring following substitution with fluorine.[23] Further, two in-plane minima were also identified, the structures of which are shown Figure 5E and F, which differ by the orientation of water molecule relative to the ethenyl group of styrene and can be recognized as trans and cis isomers. The structures of the in-plane complexes are characterized by the presence of O−H···F and C−H···O hydrogen bonds leading to formation of a six-membered cyclic complex, similar to the fluorobenzene−

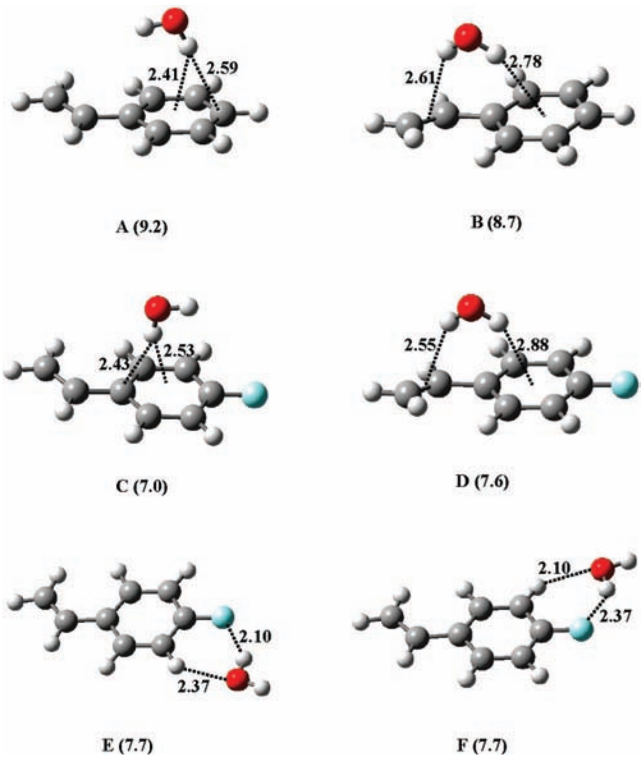

Figure 5. Calculated structures of styrene−water and fluorostyrene−water complexes at the MP2/aug-cc-pVDZ level. Distances are given in angstroms, and the 50% BSSE-corrected stabilization energies (kJ mol^{-1}) are shown in parenthesis.

TABLE 1: ZPVE-Corrected Stabilization Energies (kJ mol^{-1}) for the Water Complexes of Styrene and Fluorostyrene Calculated at the MP2/aug-cc-pVDZ Level of Theory

	ΔE^a	ΔE^b	ΔE^c
A	17.9	9.2	13.6
B	17.5	8.7	13.1
C	16.3	7.0	11.7
D	16.4	7.6	12.0
E	13.1	7.7	10.4
F	13.0	7.7	10.4

[a] No BSSE correction. [b] 100% BSSE correction. [c] 50% BSSE correction.

TABLE 2: O−H Stretching Frequencies (cm^{-1}) and Their Shifts for Water Complexes of Styrene and Fluorostyrene Calculated at the MP2/aug-cc-pVDZ Level of Theory[a]

	ν_1	ν_3	$\Delta\nu_1$	$\Delta\nu_3$	$\Sigma(\Delta\nu)$
water	3642 (4)	3770 (67)			
A	3615 (50)	3734 (53)	27	36	63
B	3613 (42)	3721 (37)	29	49	78
C	3611 (64)	3741 (113)	31	29	60
D	3615 (44)	3726 (37)	27	44	71
E	3620 (37)	3755 (130)	22	15	37
F	3621 (39)	3755 (133)	21	15	36

[a] The calculated intensities (km mol^{-1}) are shown in parentheses.

water complex.[6] The intermolecular structures and the stabilization energies of these two in-plane complexes are almost identical. The stabilization energies with 0 and 100% BSSE correction predict that the π complexes, **C** and **D**, are relatively more stable than the in-plane complexes, **E** and **F**. On the other hand, with 50% BSSE correction, the complexes **D**, **E**, and **F** are almost isoenergetic, which is in good agreement with the values reported by Chervenkov et al. using the MP2/6-311(d,p) level of theory.[16] Similar observations were made by Tarakeshwar et al. for the fluorobenzene−water complex.[24] From the above discussion, it is amply clear that the structural assignment of both styrene−water and fluorostyrene−water complexes is not justified on the basis of binding energies.

The IR spectroscopy in the hydride (X−H) stretching region is the most important spectroscopic tool for the identification of hydrogen bonding.[25] This is due to the fact that the groups involved directly are very sensitive to hydrogen-bonded structures and show a characteristic shift to a lower frequency upon hydrogen bonding. Comparison of the experimental with the calculated vibrational spectrum provides the basis for the structural assignment, for the reason stated above. In the case of the water monomer, the experimentally observed two O−H stretching frequencies of the water molecule are at 3657 and 3756 cm^{-1}, corresponding to symmetric (ν_1) and antisymmetric (ν_3) stretching vibrations, respectively. In the event of hydrogen bond formation to one of the OH groups of the water moiety, the two frequencies will now correspond to the hydrogen-bonded and free O−H stretching vibrations. Though only one of the OH groups is involved in hydrogen bond formation, both stretching frequencies are lowered due to decoupling of the two OH oscillators. The vibrational frequencies corresponding to the hydrogen-bonded and free O−H stretching vibrations are lower than the symmetric and antisymmetric stretching vibrations, respectively. Since both O−H stretching frequencies are lowered due to hydrogen bond formation, we have used the total shift in the O−H stretching frequencies [$\Sigma(\Delta\nu)$] as a tool to assign the intermolecular structures. Figure 4 also shows the comparison between the experimental and calculated (stick) vibrational spectra in the O−H stretching region. For the styrene−water system, the calculated positions for the ν_1 band are almost the same for both isomers, while the frequency of the ν_3 band for **B** is lower by 13 cm^{-1} relative to **A**. This additional lowering of the ν_3 band in **B** can attributed to the fact that both OH groups are involved in hydrogen bonding in **B**. Further, the total shift in the O−H stretching frequencies [$\Sigma(\Delta\nu)$] for the isomer **A** (63 cm^{-1}) is relatively in good agreement with the experimental value of 53 cm^{-1}, in comparison with the that of isomer **B** (78 cm^{-1}). Thus, the IR spectrum in the O−H stretching region clearly favors the formation of a singly O−H···π hydrogen-bonded styrene−water complex, the structure of which is shown in Figure 3A.

In the case of the fluorostyrene−water complexes, the calculated vibrational frequencies for the two π complexes are different, as expected from the structures. On the other hand, the vibrational frequencies for the two in-plane complexes are almost identical (see Table 2). The calculated total shifts in the O−H stretching frequencies [$\Sigma(\Delta\nu)$] for the two π complexes of fluorostyrene−water (**C** and **D**) are marginally lower than those for the two corresponding styrene−water complexes (see Table 2). This can be attributed to the lowering of the π electron density of the benzene ring following substitution with fluorine. On the other hand, the calculated $\Sigma(\Delta\nu)$'s for the two in-plane complexes (**E** and **F**) are much lower in comparison with those for the styrene−water complex. Experimentally, the ν_1 and ν_3 bands for the fluorostyrene−water complex are lowered by 16 and 12 cm^{-1}, respectively, which implies that the observed $\Sigma(\Delta\nu)$ for the fluorostyrene−water complex is 28 cm^{-1}. This total shift is much lower than the experimentally observed $\Sigma(\Delta\nu)$ for the styrene−water complex of 53 cm^{-1}. Comparison of the total shift of the water complexes of styrene and fluorostyrene clearly indicates the differences in the interaction in these two sets of complexes. The comparison between the calculated and experimental vibrational frequencies of the fluorostyrene–water complex is also shown in Figure 4. In the case of the fluorostyrene–water complex, these calculations favor the in-plane hydrogen-bonded complexes, **E** and **F**. This structural assignment is consistent with the assignment of Chervenkov et al.[16]

One of the notably interesting features of the FDIR spectrum of the fluorostyrene–water complex (Figure 4B) is the relative intensities of the ν_1 and ν_3 bands. These two bands correspond to stretching vibrations of the hydrogen-bonded and free OH groups of the water moiety in the complex, respectively. Surprisingly, the intensity of the free O–H band is significantly higher than that of the hydrogen-bonded OH group, unlike the styrene–water complex, wherein the intensity of the hydrogen-bonded OH group is higher than that of the free OH group (see Figure 4A). This observation can be rationalized as follows. The symmetric O–H stretching vibration of bare water molecule has very low infrared intensity. On the other hand, it is well-known that the hydrogen-bonded O–H stretching vibration gains intensity and is indicative of the strength of the interaction. The normal-mode analysis reveals that for the in-plane fluorostyrene–water complexes, the two O–H stretching vibrations of the water moiety almost retain the symmetric and antisymmetric stretching characteristics of the bare water molecule. This clearly indicates that the O–H···F hydrogen bond in the fluorostyrene–water complex is very weak.

According to Pimentel and McClellan, the shifts in the X–H stretching frequencies of the donor in hydrogen-bonded complexes provide a quantitative index for the properties of the hydrogen bond.[25] This implies that for a given donor, the lowering of the X–H stretching frequency upon hydrogen bonding should be correlated to the strength of the hydrogen bond with any acceptor. Graton et al. investigated the complex formation between *p*-fluorophenol with a wide variety of secondary amines in CCl_4 and showed that the $\Delta\nu_{OH}$ for *p*-fluorophenol is linearly correlated to the equilibrium constant for the hydrogen bond formation.[26] In the case of water complexes of styrene and fluorostyrene, the total shifts in the O–H stretching frequencies [$\Sigma(\Delta\nu)$] are 53 and 28 cm^{-1}, respectively. A simplistic consideration would indicate that the strength of the fluorostyrene–water complex is significantly lower or perhaps roughly one-half that of the styrene–water complex ($28/53 = 0.53$). A similar conclusion can be drawn from the calculated $\Sigma(\Delta\nu)$ for the fluorostyrene–water complexes, wherein the stabilization energy of the in-plane complex, **E**, would be roughly one-half that of the doubly O–H···π hydrogen-bonded complex, **D**. However, the difference in the calculated stabilization energies of the complexes **D** and **E** is only marginal. On the other hand, the present experimental results and those reported by Chervenkov et al. clearly establish the formation of the in-plane hydrogen-bonded complex between fluorostyrene and water, which indicates that the in-plane complex is preferred over the π hydrogen-bonded complex. Further, in the case of water complexes of benzene and fluorobenzene, it has been experimentally established that the water forms an O–H···π hydrogen-bonded complex with benzene[1–5] and an in-plane complex with fluorobenzene.[6] However, for the fluorobenzene–water system, the calculations predict that the in-plane complex is only marginally more stable then the π complex, and the $\Sigma(\Delta\nu)$ for the O–H stretching frequencies for the water moiety for the π complex is higher than those for the in-plane complex.[24] For the water complexes, the two sets of observations (styrene–fluorostyrene and benzene–fluorobenzene) clearly indicate that the formation of the in-plane hydrogen-bonded complex is preferred with the substitution of a single fluorine atom on the benzene ring. As mentioned earlier, the in-plane complexes of water with both fluorostyrene and fluorobenzene are characterized by O–H···F and C–H···O hydrogen bonds leading to the formation of a cyclic six-membered ring. The difference in the O–H···F and the O–H···π interaction should be more than compensated for by the formation of C–H···O hydrogen bond. In other words, the synergistic effect of O–H···F and C–H···O hydrogen bonds present in the in-plane complex outweighs the formation of the π complex.

Conclusions

The electronic transitions for the water complexes of styrene and fluorostyrene were shifted to the blue by 21 and 108 cm^{-1}, respectively. The larger difference in the shift is a primary indicator for the dissimilarity in the intermolecular structures. The FDIR spectrum for the styrene–water complex shows two transitions in the O–H stretching region at 3633 and 3727 cm^{-1}, while the FDIR spectrum of the fluorostyrene–water complex shows two transitions at 3641 and 3744 cm^{-1}. The structural assignment of the binary clusters was based on the agreement between the experimental and the computed spectra. The total shift in the O–H stretching frequencies was the criterion used for the structural assignment. Water forms a single O–H···π hydrogen-bonded complex with the styrene. The styrene–water complex is the only water complex of substituted benzenes in which water is bound to the π electron density of the benzene ring. On the other hand, the fluorostyrene–water complex consists of O–H···F and C–H···O hydrogen bonds leading to formation of a six-membered cyclic structure. The cooperativity of these two hydrogen bonds prevails over the O–H···π hydrogen bond.

Acknowledgment. This material is based upon work supported by Department of Science and Technology (Grant No. SR/S1/PC-40/2003), Board of Research in Nuclear Sciences (Grant No. 2004/37/5/BRNS/398), and Council of Industrial and Scientific Research (Grant No. 01(1902)/03/EMR-II). P.C.S. thanks CSIR for a senior research fellowship.

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JP801856R