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IR–UV Double Resonance Spectroscopic Investigation of Phenylacetylene–Alcohol Complexes. Alkyl Group Induced Hydrogen Bond Switching

Prashant Chandra Singh and G. Naresh Patwari*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076 INDIA

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The electronic transitions of phenylacetylene complexes with water and trifluoroethanol are shifted to the blue, while the corresponding transitions for methanol and ethanol complexes are shifted to the red relative to the phenylacetylene monomer. Fluorescence dip infrared (FDIR) spectra in the O–H stretching region indicate that, in all the cases, phenylacetylene is acting as a hydrogen bond acceptor to the alcohols. The FDIR spectrum in the acetylenic C–H stretching region shows Fermi resonance bands for the bare phenylacetylene, which act as a sensitive tool to probe the intermolecular structures. The FDIR spectra reveal that water and trifluoroethanol interact with the π electron density of the acetylene C–C triple bond, while methanol and ethanol interact with the π electron density of the benzene ring. It can be inferred that the hydrogen bonding acceptor site on phenylacetylene switches from the acetylene π to the benzene π with lowering in the partial charge on the hydrogen atom of the OH group. The most significant finding is that the intermolecular structures of water and methanol complexes are notably distinct, which, to the best of our knowledge, this is first such observation in the case of complexes of substituted benzenes.

Introduction

Phenylacetylene (PHA) is a simple yet multifunctional molecule vis-à-vis hydrogen bonding. It consists of a benzene ring and the acetylene moiety, which can act as π acceptors, and a relatively acidic acetylenic C–H group, which can act as a σ donor for the formation of hydrogen bonds. However, the exact hydrogen-bonded intermolecular structure with any interacting molecule will be a subtle competition between the various possibilities. Recently, we have reported on the intermolecular structure of PHA–water complex,[1] which is distinctly different from both the benzene–water[2] and acetylene–water[3] complexes, even though PHA combines the features of both benzene and acetylene. The resulting structure was an in-plane cyclic complex incorporating the O–H···π and C–H···O hydrogen bonding, wherein the acetylenic π bond electrons and the benzene C–H group in the ortho position are involved in hydrogen bonding with the water molecule. Formation of such a complex was rationalized on the basis of cooperativity between the two sets of hydrogen bonds.[1] Extending the investigation, we examined the complexes of PHA with various alcohols, viz., methanol (MeOH), ethanol (EtOH), and trifluoroethanol (TFE-tOH), to understand the effect of alkyl group substitution on the hydrogen bonding properties. These substitutions will allow us to explore how relatively bulky groups and the variation in the acidity of the OH group affect the intermolecular structure.

Experiment

The details of the complete experimental setup can be found elsewhere.[4] Briefly, helium buffer gas at 4 atm was bubbled through a mixture of PHA (Aldrich) and water/alcohol kept at room temperature and expanded supersonically through a 0.5 mm diameter pulsed nozzle (Series 9, Iota One; General Valve Corporation). The laser-induced fluorescence (LIF) excitation spectrum of PHA was recorded in the absence of any reagent and recorded once again in the presence of water/alcohol. It follows, straightforwardly, that the new transitions appearing after addition of the reagent are due to the water/alcohol complexes. The fluorescence dip infrared (FDIR) technique was used to record the IR spectra of the PHA monomer and its complexes.[5] In this technique, an UV laser is fixed on the band-origin of the $S_1 \leftarrow S_0$ electronic transition of a particular species, which gives a continuous fluorescence signal that reflects the ground-state population. A tunable infrared pulse is introduced 100 ns prior to the UV laser, which, when resonant with the vibrational transition of the species probed, creates population depletion in the ground state. The infrared absorption is then detected as a dip in the fluorescence signal, because of the population depletion. In our experiments, the UV laser was a frequency doubled output of a second harmonic Nd:YAG laser (Continuum, Surelite I-10) and pumped dye laser (Radiant Dyes, Narrow Scan G-R) operating with Rhodamine-19 dye. Total florescence was detected using a PMT (Electron tubes Limited, 9780SB + 1252–5F)/Filter (WG305 + BG3) combination. The tunable IR source was an idler output of a $LiNbO_3$ optical parametric oscillator (Euroscan Instruments, Custom $LiNbO_3$ OPO) pumped with an injection-seeded single-mode Nd:YAG laser (Quantel, Brilliant B). The dye laser was calibrated using an optogalvanic method, and the IR OPO was calibrated by recording the photoacoustic spectrum of ambient water vapor. The typical energies used were about 100 μJ/pulse and 2 mJ/pulse for the UV and IR lasers, respectively. The bandwidth of both UV and IR lasers is about 1 cm^{-1}, and the absolute frequency calibration is within ±2 cm^{-1}.

Results and Discussion

The LIF spectra of PHA in the presence of water and various alcohols are depicted in Figure 1. Trace A shows the spectrum of PHA, which also consists of a transition due to PHA–H_2O complex (marked with “W”), which is shifted by +14 cm^{-1}, relative to bare PHA at 35876 cm^{-1} (marked with “P”).[1,6] Traces

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* Corresponding author. E-mail: naresh@chem.iitb.ac.in.

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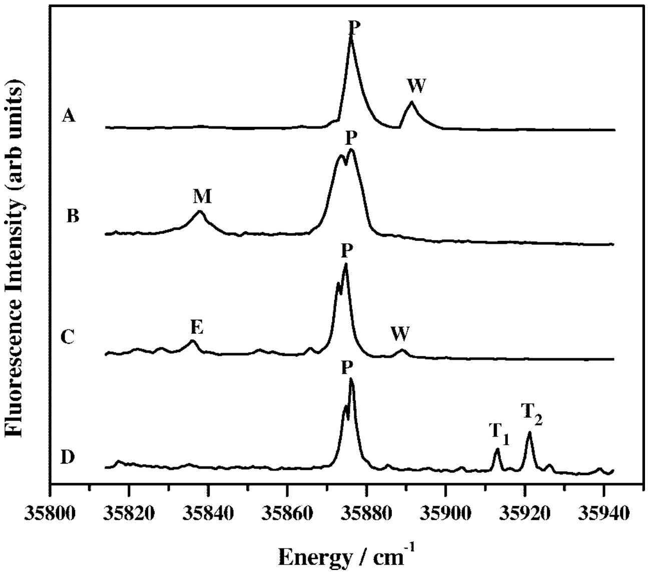

Figure 1. LIF spectra of PHA in the presence of (A) H_2O, (B) MeOH, (C) EtOH, and (D) TFEtOH. The peaks marked with P are due to PHA monomer, and those marked with W, M, E, and T's are due to clusters with H_2O, MeOH, EtOH, and TFEtOH, respectively.

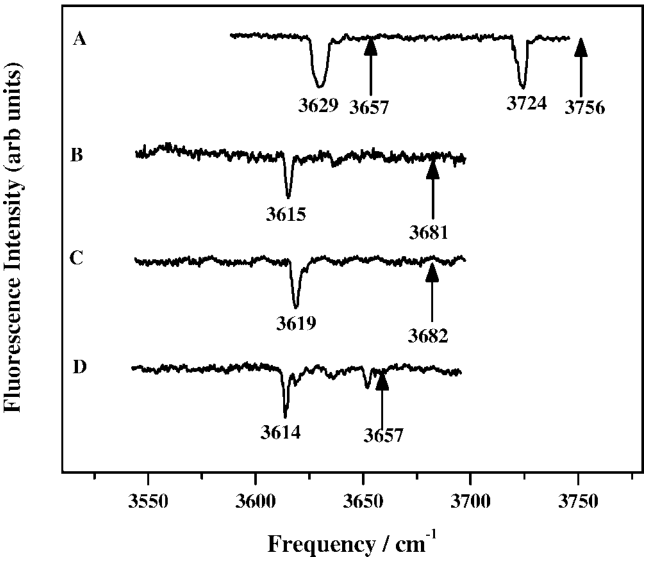

Figure 2. FDIR spectra of (A) PHA−H_2O, (B) PHA−MeOH, (C) PHA−EtOH, and (D) PHA−TFEtOH in the O−H stretching region. The arrows indicate the position of O−H oscillators of the monomers.

B, C, and D in Figure 1 correspond to the spectra in the presence of MeOH, EtOH, and TFEtOH, respectively. The addition of MeOH and EtOH leads to the appearance of new transitions at 35838 and 38836 cm^{-1}, respectively, which are marked with "M" and "E" in Figure 1. These transitions are shifted by −38 and −40 cm^{-1}, respectively, relative to the PHA band-origin. On the other hand, the addition of TFEtOH leads to the appearance of two new transitions at 35913 and 35921 cm^{-1} (marked with "T_1" and "T_2"). These transitions are shifted by +37 and +45 cm^{-1}, respectuvely, relative to the bare PHA. These two transitions can be assigned to arising out of the two isomers (*gauche* and *anti*) of TFEtOH. The complexes of H_2O and TFEtOH show a blue shift in the $S_1 \leftarrow S_0$ electronic transition and can be grouped together, while the complexes with MeOH and EtOH form another group with a red shift in the electronic transition. On the basis of the shifts in the electronic transitions, it appears that the intermolecular structure of PHA−TFEtOH should be similar to that of PHA−H_2O complex, while the complexes of MeOH and EtOH would have a different intermolecular structure.

The shifts in the electronic transitions provide, in the present scenario, the evidence for the formation of binary clusters. They also indicate similarity in the intermolecular structure of PHA−H_2O and PHA−TFEtOH complexes. On the other hand, it is also possible to infer that the intermolecular structures of PHA−MeOH and PHA−EtOH complexes are very similar but are unlike the structures of H_2O and TFEtOH complexes. In order to arrive at the intermolecular structure, it is imperative to carry out vibrational spectroscopic investigation in the hydride stretching region. Vibrational spectroscopy in the hydride (X−H; where X = O, N, C) stretching region is a convenient tool to investigate the formation of hydrogen bonding. This is because these stretching frequencies are very sensitive to hydrogen-bonded structures, as they are directly involved in the formation of hydrogen bonds and show characteristic shift to a lower frequency.[7] The FDIR spectra of all the four PHA complexes in the O−H stretching region are presented in Figure 2. The FDIR spectrum of the H_2O complex (Figure 2A) is similar to that reported earlier, which shows a sharp transition at 3724 cm^{-1} and a relatively broad band at 3629 cm^{-1} assigned to free and hydrogen-bonded O−H stretching vibrations of water molecule, respectively.[1] The FDIR spectra of PHA complexes with MeOH (Figure 2B) and EtOH (Figure 2C) show lone transitions at 3615 and 3619 cm^{-1}, respectively, which can been assigned to O−H stretching vibrations of the complex. The FDIR spectrum of PHA−TFEtOH complex, probed at T_1, is depicted in Figure 2D. This spectrum shows an intense transition at 3614 cm^{-1}, which once again can be assigned to the O−H stretching vibration of the complex, along with a weak band at 3652 cm^{-1}, which is likely to be the combination band of intermolecular vibration on the O−H stretching vibration. The FDIR spectrum of the T_2 band is identical to the T_1 band.[8] The O−H stretching frequencies of MeOH, EtOH, and TFEtOH in the complexes with PHA are shifted to the red by 66, 63, and 43 cm^{-1}, respectively. The shift in the O−H stretching frequency of the MeOH moiety in the complex with PHA (−66 cm^{-1}) is higher than that observed for the benzene−MeOH (−42 cm^{-1}) complex.[9] The low frequency shifts clearly indicate that the OH group in all the three alcohols is involved in the hydrogen bond formation. Further, the magnitude of shifts in the O−H stretching frequencies also rules out the possibility of the formation of C−H···O "σ" hydrogen-bonded complexes with PHA, in which case the shifts would have been marginal.

The FDIR spectra in the O−H stretching region clearly indicate that the OH groups of alcohols act has hydrogen bond donors. However, PHA has two acceptor sites: the benzene π and the acetylene π electron densities. To gain further insight into the nature of the interaction of PHA with alcohols, FDIR spectra in the acetylenic C−H stretching region were recorded. Figure 3 shows the FDIR spectrum of PHA along with the complexes of H_2O, MeOH, EtOH, and TFEtOH in the acetylenic C−H stretching region. The FDIR spectrum of bare PHA (Figure 3A) shows two intense transitions at 3325 and 3343 cm^{-1}, which have been assigned to the Fermi resonance bands involving the C−H stretching vibration and the combination band of one quantum of C≡C stretch and two quanta of out-of-plane acetylenic C−H bend.[10] Other weak features in the spectrum have been assigned to higher order coupling terms.[10] The deperturbation analysis places the pure acetylenic C−H stretching vibration at 3334 cm^{-1}.[1,4] The FDIR spectra of H_2O

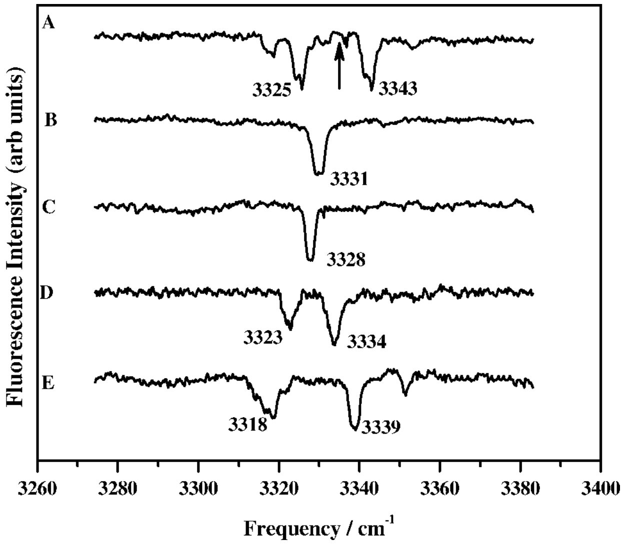

Figure 3. FDIR spectra of (A) PHA, (B) PHA−H_2O, (C) PHA−TFEtOH, (D) PHA−MeOH, and (E) PHA−EtOH in the acetylenic C−H stretching region. The arrow in A indicates the position of the unperturbed acetylenic C−H oscillator.

(Figure 3B) and TFEtOH (Figure 3C) complexes show lone transitions at 3331 and 3328 cm^{-1}, which can be assigned to the C−H stretching vibration of the respective complex. Once again, in the case of TFEtOH complex, the T_1 and T_2 bands show identical FDIR spectra.[8] The C−H stretching vibrations shifts to a lower frequency by 3 and 6 cm^{-1} for the H_2O and TFEtOH complexes, respectively, which implies rather straightforwardly that TFEtOH does not form a linear C−H···O "σ" hydrogen-bonded complex with PHA and is most likely interacting with the acetylenic π bond electrons, similar to H_2O. The FDIR spectra of PHA−MeOH (Figure 3D) and PHA−EtOH (Figure 3E) have two intense transitions, but their positions and intensities are marginally different from that of bare PHA. In the case of PHA−MeOH complex, the two bands are positioned at 3323 and 3334 cm^{-1}, while in the case of PHA−EtOH they are observed at 3318 and 3339 cm^{-1}. These spectra clearly show the presence of Fermi resonance, albeit with some minor changes in the position and relative intensities of the two bands. Few other bands observed in the case of PHA-EtOH can be assigned to transitions arising out of higher order coupling terms, similar to bare PHA.[10] These spectra once again establish, unequivocally, that neither MeOH nor EtOH form C−H···O "σ" hydrogen-bonded complexes and further rule out the possibility of interaction with acetylenic π bond electrons.

The FDIR spectra of all four complexes in the C−H stretching region unambiguously rule out the formation of linear C−H···O "σ" hydrogen-bonded complexes, wherein the acetylenic C−H group of PHA acts as a hydrogen bond donor to the oxygen atom of water and alcohols. The spectra in the O−H stretching region point out that the OH group is hydrogen-bonded to the PHA moiety in all four cases. PHA has two sets of π acceptor sites: the benzene ring and the acetylenic C−C triple bond. The electronic transitions for the MeOH and EtOH complexes are shifted to the red relative to bare PHA (Figure 1), similar to that of PHA−Ar complex, which is known to interact with the π electron density of the benzene ring.[4,11] On the other hand, the shift in the electronic transitions of H_2O and TFEtOH complexes is shifted to the blue (see Figure 1). The difference in the nature of the shifts in the electronic transitions clearly points to the fact that the mode of interaction of MeOH, EtOH, H_2O, and TFEtOH are different. The FDIR spectrum in the C−H stretching region for the MeOH and EtOH complexes is almost identical to that of bare PHA; on the other hand, the spectra of H_2O and TFEtOH show a lone transition around the predicted unperturbed acetylenic C−H oscillator. Since the Fermi resonance bands involves a C−C triple bond stretching vibration, any perturbation on this bond will lead to the disappearance of the Fermi resonance condition and the appearance of a single band corresponding to free C−H oscillator. The complexes of H_2O and TFEtOH therefore belong in this category. Alternatively, the interaction with the benzene π electron density will not perturb the C−C triple bond and the C−H oscillator (both C−H stretching vibration and C−H bends), thereby retaining the Fermi resonance bands. However, such an interaction can lead to marginal changes in the band positions and intensities, which is the case for MeOH and EtOH complexes.

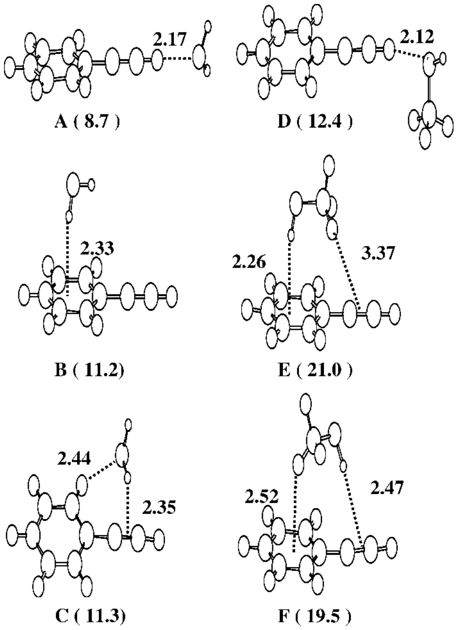

Figure 4. Calculated structures of PHA−H_2O and PHA−MeOH complexes at the MP2/aug-cc-pVDZ level. Distances are shown in angstroms (Å), and the binding energies (kJ mol^{-1}) are shown in parenthesis.

TABLE 1: Binding Energies (kJ mol^{-1}) and Scaled Vibrational Frequencies (cm^{-1}) and Their Shifts for the Water and Methanol Complexes of PHA Complexes Calculated at the MP2/aug-cc-pVDZ Level of Theory[a]

	ΔE	ν_{C-H}	$\Delta\nu_{C-H}$	ν_{O-H}	$\Delta\nu_{O-H}$
PHA		3335			
H_2O				3644 (s), 3772 (as)	
MeOH				3683 (f)	
PHA-H_2O (A)	8.7	3274	*−61*	3641 (s), 3769 (as)	−2, *−5*
PHA-H_2O (B)	11.2	3333	*−2*	3621 (hb), 3744 (f)	*−22, −29*
PHA-H_2O (C)	11.3	3328	*−7*	3587 (hb), 3735 (f)	*−59, −38*
PHA-MeOH (D)	12.4	3247	*−88*	3676 (f)	*−7*
PHA-MeOH (E)	21.0	3333	*−2*	3637 (hb)	*−46*
PHA-MeOH (F)	19.5	3330	*−5*	3633 (hb)	*−50*

[a] For the O−H vibrations, "s", "as", "hb", and "f" indicate symmetric, antisymmetric, hydrogen-bonded, and free stretching frequencies, respectively.

To supplement the experimental observations, we carried out ab initio calculations for the H_2O and MeOH complexes at the MP2/aug-cc-pVDZ level of theory using Gaussian 03.[12] In each case, three distinct minima were located, shown in Figure 4, and Table 1 lists the ZPE and 50% BSSE corrected binding energies along with the scaled vibrational frequencies (scaling factor 0.958).[13] The C−H···O "σ" hydrogen-bonded complex in both cases is the least stable structure and has not been observed experimentally. In the case of H_2O complex, both O−H···π (benzene π) (Figure 4B) and the cyclic complex (Figure 4C) have almost identical binding energy. However, only the cyclic complex has been observed experimentally, which was attributed to the cooperativity between the C−H···O and O−H···π (acetylene π) hydrogen bonds in the cyclic structure.[1] Preliminary microwave results from Arunan and coworkers confirm the cyclic structure of the PHA−H_2O complex.[14]

In the case of MeOH complex, the O−H···π (benzene π; Figure 4E) is marginally more stable than the O−H···π (acetylene π; Figure 4F). The intermolecular structures of C−H···O (σ) and O−H···π (benzene π) complexes of H_2O and MeOH complexes are very similar. However, the O−H···π (acetylene π) PHA−MeOH complex (Figure 4F) is distinctly different from that of the corresponding PHA−H_2O complex (Figure 4C). The H_2O complex is characterized by the presence of two hydrogen bonds leading to the formation of a cyclic structure; on the other hand, the MeOH complex can be characterized by the presence of O−H···π (acetylene π) and C−H···π (benzene π) hydrogen bonds. Several attempts were made to obtain the cyclic structure starting from modified initial geometries; however, in all the cases, the calculations converged on to the structure shown in Figure 4F. Since the structure shown in Figure 4F involves the interaction of the OH group of methanol with the acetylenic C−C triple bond, it consequently is expected to affect the Fermi resonance bands. However, the FDIR spectrum in the acetylenic C−H stretching region is almost identical to the PHA monomer. The vibrational frequencies listed in Table 1 can distinguish between "σ" and "π" hydrogen-bonded PHA−MeOH complexes. However, the differences in both the C−H and O−H stretching frequencies between the two "π" complexes is marginal. It would have therefore been difficult to assign the structure on the basis of the shifts in the vibrational frequencies. A similar situation holds for the C−H stretching frequencies of two "π" complexes of PHA−H_2O complexes. Fortunately, the appearance and disappearance of the Fermi resonance bands serves as a pointer to assign the intermolecular structures. The red shift in the electronic transition and the FDIR spectra in the O−H and C−H region in combination with the ab initio calculations overwhelmingly support the formation of O−H···π (benzene π) hydrogen-bonded complex between PHA and MeOH, the structure of which is shown in Figure 4E. Further, because of similarities between the spectra of PHA−EtOH with PHA−MeOH and PHA−TFEtOH with PHA−H_2O, one can infer that EtOH forms an O−H···π (benzene π) hydrogen-bonded complex, while TFEtOH forms a cyclic structure with PHA analogous to PHA−H_2O complex.

Reports on complexes of benzene[2,9] and substituted benzenes such as fluorobenzene,[15] phenol,[16] 2-pyridone,[17] and several others have clearly established that the intermolecular structure of H_2O and MeOH complexes are almost identical. However, the most significant observation of PHA complexes is the drastic change in the intermolecular structure between H_2O and MeOH. A seemingly noninvasive substitution by a ubiquitous single methyl group switches its intermolecular structure from a cyclic complex to an O−H···π (benzene π) hydrogen-bonded complex. In PHA complexes, H_2O and TFEtOH interact with acetylenic π electron density while MeOH and EtOH interact with the benzene π electron density. To rationalize the observed switching of hydrogen bonding in PHA alcohol complexes, we carried out the charge analysis of H_2O, MeOH, EtOH, and TFEtOH monomers using the natural population analysis (NPA) method at RHF, B3LYP, and MP2 levels of theory using the aug-cc-pVDZ basis set, and the results are listed in Table 2.[18] Though the absolute values of the partial charge on the hydrogen atom of the OH group varies with the level of calculation, it is amply clear from Table 2 that all the levels of theory consistently yield the charge on the hydrogen atom of the OH groups in the order TFEtOH > H_2O > MeOH > EtOH. H_2O interacts with the acetylene π, and substitution with a single methyl group marginally lowers the partial charge on the hydrogen atom of the OH group from +0.481*e* to +0.478*e* (at the MP2 level), which leads to switching of the interaction to the benzene π. The O−H···π (benzene π) interaction remains intact with further lowering of the partial charge on the hydrogen atom of the OH group to +0.476*e* in EtOH. On the other hand, increase in the partial charge of the hydrogen atom of the OH group in TFEtOH to +0.494*e* favors the formation of O−H···π (acetylene π). These results clearly indicate that OH groups with higher partial charge on the hydrogen atom prefer to interact with the π electron density of acetylenic C−C triple bond, and those with lower partial charge prefer benzene π electron density. The subtle variation in the partial charge on the hydrogen atom of the approaching OH group results in drastic changes in the intermolecular structure.

TABLE 2: NPA-Derived Charges on the Hydrogen Atom of OH Group in Various Alcohols Using the aug-cc-pVDZ Basis Set

	RHF	B3LYP	MP2
H_2O	0.478	0.481	0.481
MeOH	0.475	0.477	0.478
EtOH	0.474	0.475	0.476
TfEtOH	0.490	0.491	0.494

Conclusions

The hydrogen-bonded complexes of PHA complexes with water, methanol, ethanol, and trifluoroethanol were investigated using LIF and IR−UV double resonance spectroscopic methods. The electronic transitions of water and trifluorethanol complexes are shifted to blue, while those of methanol and ethanol complexes are shifted to the red relative to the bare PHA. The FDIR spectra in the O−H stretching region shows the presence of hydrogen-bonded and free OH oscillators for the water complex, while the OH groups of methanol, ethanol, and trifluoroethanol show a shift to a lower frequency upon interacting with PHA. This indicates that PHA is acting as a hydrogen bond acceptor in all four complexes. The FDIR spectra of water and trifluoroethanol complexes in the acetylenic C−H stretching region show a lone transition, pointing out that the OH group of these two molecules is interacting with the π electron density of the acetylene C−C triple bond. On the other hand, the FDIR spectra of methanol and ethanol complexes are very similar to the that of bare PHA, which indicates that the OH group is interacting with the π electron density of the benzene ring. It can be inferred that the intermolecular structure is governed by the partial charge on the hydrogen atom of the interacting OH group, and the hydrogen bond acceptor site switches from acetylene π to benzene π on lowering partial charge of the approaching OH group. Thus the hydrogen bond switching in PHA complexes can be used as a probe for the partial charge on the hydrogen atom of the approaching OH group. Finally, to the best of our knowledge, this is the first example in the case of substituted benzenes wherein the intermolecular structure of water complex differs from that of methanol complex.

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