IR-UV double resonance spectroscopy of phenylacetylene-water complex revisited: observation of cyclic and π complexes

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This article is dedicated to Prof Pradeep K Gupta for his contributions to optics and photonics with biomedical applications

The binary complex between phenylacetylene and water is investigated using 1C-R2PI and IDIR spectroscopic techniques combined with high-level *ab initio* calculations. A cyclic complex between phenylacetylene and water incorporating C_{bz}–H···O and O–H···π_{ac} hydrogen bonds was reported earlier. A new phenylacetylene-water complex that incorporates a single O–H···π_{bz} hydrogen bond is reported here. Stabilization energy calculated at CCSD(T)/CBS//MP2/aug-cc-pVDZ level of theory indicates that the new complex is local minima which is about 1.5 kJ mol^{-1} higher in energy than the earlier observed global minimum. © Anita Publications. All rights reserved.

Keywords: Double resonance spectroscopy, Mass resolved IR spectroscopy, *Ab-initio* calculations

1 Introduction

Observing multiple minima on an intermolecular potential energy surface is an interesting proposition, however, can be challenging. It is well known that many a times homo/hetero dimers having different intermolecular structures are energetically close, but elude experimental corroboration. One such interesting case is that of benzene dimer. The two most important structural minima for the benzene-dimer are the slipped π–stacked and the T–shaped (C–H···π) structures. The relative stability of the two minima depends on the level of calculation. However, calculations at the CCSD(T)/CBS level indicate both the that π–stacked structure and the T–shaped structures are almost isoenergetic [1,2]. There is now overwhelming experimental evidence for the formation of (Tilted)-shaped structure for the benzene dimer [3-7]. Interestingly, none of the experimental investigations have been able to determine the presence of the π–stacked dimer. It must be pointed out here that "absence of evidence cannot be the evidence for absence", which implies that the absence of π–stacked benzene-dimer cannot be unambiguously ruled out.

Phenylacetylene (PHA) is a versatile multifunctional molecule that offers multiple binding sites for hydrogen bond formation. PHA forms a plethora of intermolecular structures depending on the nature of the interacting molecule and is termed as hydrogen bonding chameleon [8,9]. We had earlier investigated hydrogen-bonded complex of PHA with water and only one structure was observed, in which the water forms a quasi-planar cyclic complex with O–H group of water interacting with the π electron density of the C≡C bond and the oxygen atom is hydrogen-bonded to the C–H group in the *ortho* position to the acetylene group [10]. Goswami and Arunan confirmed the quasi-planar cyclic structure of the PHA-H$_2$O complex using Fourier transform microwave spectroscopy [11]. On the other hand, the matrix isolation spectroscopy revealed the formation of C–H···O σ hydrogen-bonded complex [12]. Since PHA does not have either strongly acidic or strongly basic groups, *ab-initio* calculations reveal the presence of several energetically closely

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spaced minima on the intermolecular potential energy surface. High-level *ab-initio* calculations indicate the presence of four low energy minima of PHA-H_2O complex of which only two have been experimentally observed [10-12]. Many attempts to identify other elusive minimum on the intermolecular potential energy of PHA-H_2O complex and this work reports the first observation of π-bound PHA-H2O complex.

2 Experimental and computational methodology

The spectra presented in this article were acquired using time-of-flight (TOF) mass spectrometer coupled with supersonic jet expansion technique described elsewhere [13]. Briefly, complexes were created by expanding PHA (Aldrich) diluted in about 4 atm He buffer gas, through a 0.5 mm diameter pulsed nozzle (Series 9, Iota One; General Valve Corporation) operating at 10 Hz into a vacuum chamber operating at 10^{-6} Torr. The expanded molecular beam was crossed with the frequency-doubled output of a dye laser (Narrow Scan GR; Radiant Dyes; operating with the Rhodamine-19 dye) pumped with the second harmonic of a Nd:YAG laser (Surelite I-10; Continuum). One-color resonant two-photon ionization (1C-R2PI) spectra of PHA and its complex with H_2O were recorded by monitoring the appropriate mass ion signal with a two-stage Wiley-McLaren TOF spectrometer [14], using a channeltron (KBL-25RS; Sjuts) detector and a preamplifier (SR445A; Stanford Research Systems). The IR spectra of PHA and its complex with H_2O were obtained using an ion-dip infrared (IDIR) spectroscopic technique [15,16]. The tunable IR for our experiments was an idler component of a $LiNbO_3$ OPO (Custom IR OPO; Euroscan Instruments) pumped with an injection-seeded Nd:YAG laser (Brilliant-B; Quantel). The typical bandwidth of both UV and IR lasers was about 1 cm^{-1} and the absolute frequency calibration was within ±2 cm^{-1}.

Ab initio calculations were carried out to support the experimental results using the GAUSSIAN 09 suite of programs [17]. A detailed conformational search was followed by geometry optimization at the second-order Moller–Plesset perturbation (MP2) theory using the aug-cc-pVDZ (aVDZ) basis set using frozen core (FC) approximation. The stabilization energy was determined as the difference between the dimer energy and the sum of monomer energies. The calculated stabilization energies were corrected for the vibrational zero-point energy (ZPE) and the basis-set superposition error (BSSE). The BSSE correction was made after geometry optimization. The nature of the equilibrium structure obtained was verified by performing vibrational frequency calculations at the same level of theory. All the structures reported herein are true minima with real positive vibrational frequencies. A scaling factor of 0.9576 was chosen to match the experimental vibrational frequencies of the monomers and the same scaling factor was used for the complexes. The CCSD(T)/CBS stabilization energies were determined as a sum of MP2/CBS energies and CCSD(T) correction term, which is due to the fact that both the CCSD(T) and MP2 methods exhibit approximately the same basis set dependence [18]. The extrapolations were performed using the method proposed by Helgaker and co-workers [19], wherein the electron-correlation error is proportional to N^{-3} for the aug-cc-pVNZ (aVNZ) basis set [20]. The structures and the vibrations were visualized by GaussView-5 [21]. Further, the energy decomposition analysis was carried out using the simplest SAPT approach i.e. SAPT0 [22] using cc-pVTZ basis along with the cc-pVTZ-JKFIT RI basis for SCF [23]. The SAPT method uses density fitting approach to reduce the computational time. The main advantage of SAPT calculations is that it dissociates the total binding energy into the electrostatic (E_{Elec}), dispersion (E_{Disp}), exchange (E_{Exch}), and induction (E_{Ind}) terms. In the present analysis, the exchange-induction and exchange-dispersion terms will be included in the parent induction and dispersion terms. It has been found that the SAPT0 along with reasonable basis sets provide sufficiently acceptable intermolecular interaction energies. All the SAPT calculations were carried out using PSI4 *ab initio* package [24].

3 Result and Discussion

1C-R2PI spectra of PHA and its water complex were recorded by monitoring the mass signals at 102 and 120 amu, respectively, and are depicted in Fig 1. Earlier we had reported the LIF excitation spectrum

of PHA-H_2O complex [10]. The 1C-R2PI spectrum of PHA-H_2O complex, recorded earlier, showed only a single isomer of PHA-H_2O complex similar to the LIF excitation spectrum [10]. With improved ion collection efficiency, we re-visited the 1C-R2PI spectrum of the PHA-H_2O complex. The 1C-R2PI spectrum of PHA (Fig 1A) shows a single strong band at 35876 cm^{-1}, which corresponds it band-origin 20 . On the other hand 1C-R2PI spectrum of PHA-H_2O complex (Fig 1B) shows two bands at 35890 (W1) and 35871 cm^{-1} (W2) which are shifted by +14 and –5 cm^{-1} from the band origin of PHA monomer at 35876 cm^{-1}, respectively. The W2 band is very close (almost underneath!) to the band origin of PHA monomer, therefore probably remained elusive.
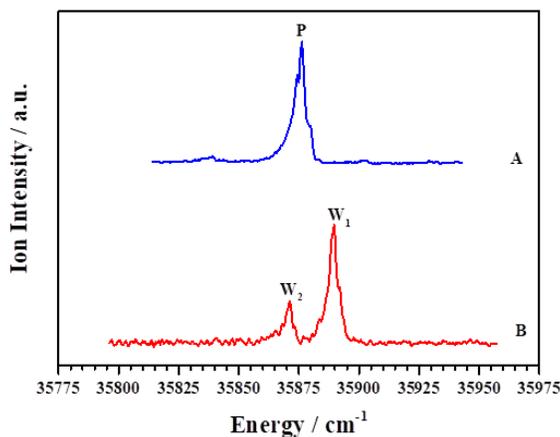

Fig 1. 1C-R2PI spectrum of (A) PHA and (B) PHA-H_2O. The spectra were recorded by monitoring the parent mass signals at 102 and 120 amu, respectively. In (A) the band marked with 'P' is the band-origin of PHA monomer and in (B) the two bands 'W1' and 'W2' represent the two isomers of PHA-H_2O complex.
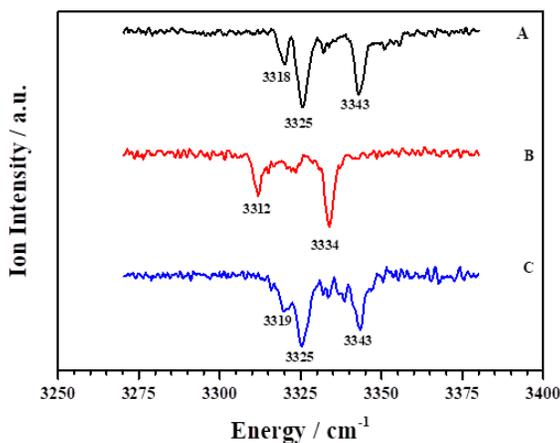

Fig 2. IDIR spectrum in the acetylenic C−H stretching region of (A) PHA monomer, (B) PHA-H_2O W1 complex, and (C) PHA-H_2O W2 complex.

The IR spectra in the acetylenic C–H stretching region for the PHA and its H_2O complexes were recorded using IDIR spectroscopic technique, and the results are shown in Fig 2. The IDIR spectrum of bare PHA (Fig 2A) shows two strong bands at 3325 and 3343 cm^{-1} along with few weaker bands. The two strong

bands have been assigned to be originating from Fermi resonance coupling and other weaker bands to the higher-order anharmonic coupling terms [25]. The IDIR spectrum of PHA-H_2O (W1) complex (Fig 2B) shows a strong band at 3334 cm^{-1}) accompanied by a weaker band at 3312 cm^{-1}). The appearance of the 3334 cm^{-1} band which is almost at the average position of the 3325 and 3343 cm^{-1}) bands of bare PHA indicates weakening of Fermi resonance coupling [13]. This spectrum is marginally different than the spectrum we had reported earlier [10], wherein the 3312 cm^{-1}) band was much weaker but was noticeable. The IDIR spectrum of PHA-H_2O (W2) complex, depicted in Fig 2C, is almost identical with the spectrum of bare PHA, with the presence of two strong bands at 3325 and 3343 cm^{-1}).

The IDIR spectra of PHA-H_2O complexes were also recorded in the O–H stretching region and the results are shown in Fig 3. The IDIR spectrum of the PHA-H_2O W1 complex (Fig 3A) shows two bands at 3614 and 3709 cm^{-1}, while the corresponding spectrum of the PHA-H_2O W2 complex (Fig 3B) also shows two bands at 3622 and 3730 cm^{-1}). In both cases the higher frequency bands (3709 and 3730 cm^{-1}) can be assigned to the free O–H stretch while the lower frequency band (3614 and 3622 cm^{-1}) can be assigned to the hydrogen-bonded O–H stretch of the water molecule.
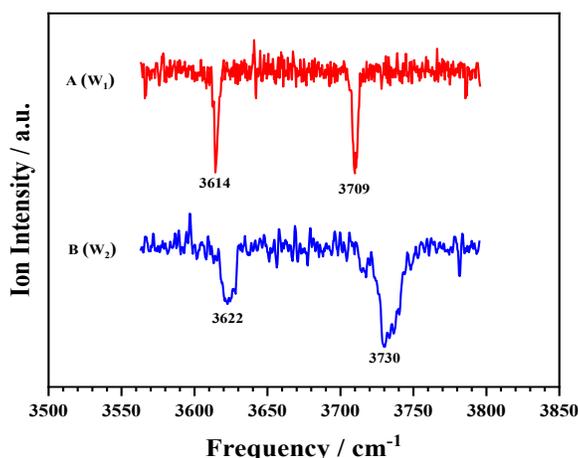

Fig 3. IDIR spectrum of (A) PHA-H_2O W1 and (B) PHA-H_2O W2 complexes in the O−H stretching region.

The MP2/aug-cc-pVDZ level optimized structures of the PHA-H_2O complex are shown in Fig 4. The structure PHAW1 is a linear hydrogen-bonded complex between the acetylenic C–H group and the lone pair of electrons on the oxygen atom of water molecule leading to the formation of a C–H⋯O hydrogen-bonded complex. The next structure PHAW2 is a quasi-planar cyclic complex wherein water molecule acts as both hydrogen bond donor and acceptor. In this structure, one of the O–H groups of the water molecule interacts with the π electron density of the C≡C bond while oxygen atom forms a hydrogen-bonded interaction with the aromatic C–H group present in the ortho position to the acetylenic moiety. The third PHAW3 and the fourth PHAW4 structures are characterized by the formation of an O–H⋯π hydrogen bonding. In the case of PHAW3, a single O–H group of water points towards the benzene ring while in the case of PHAW4 both the O–H groups of water are hydrogen-bonded one each with benzene and acetylene π electron densities. We have earlier reported three structures for the PHA-H_2O complex and PHAW4 is a newer structure [10]. The stabilization energies of various structures of the complexes were calculated at different levels of theory using the structure optimized at MP2/aug-cc-pVDZ level and are listed in Table 1. All the stabilization energies reported in Table 1 are corrected for zero-point vibrational energy (ZPE) and BSSE. The PHAW2 structure is the global minimum at all levels of theory except at the MP2/aug-cc-pVDZ level, wherein the PHAW3 structure is marginally more stable. This observation can be attributed to the overestimation of

dispersion contribution by the MP2 level. The ZPE and BSSE corrected CCSD(T)/CBS stabilization energy ordering of the four structures (optimized at MP2/aug-cc-pVDZ level of theory) is PHAW2 (-11.1 kJ mol^{-1}) > PHAW3 (-9.5 kJ mol^{-1}) > PHAW4 (-8.0 kJ mol^{-1}) > PHAW1 (-7.2 kJ mol^{-1}).

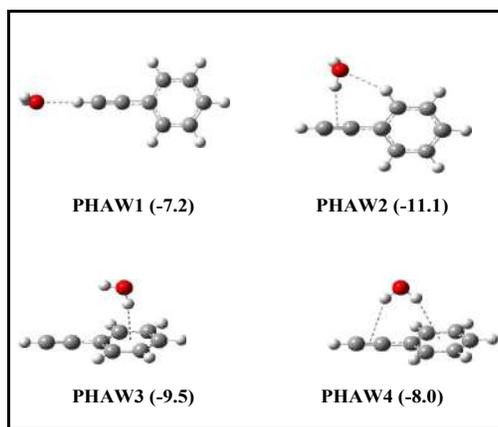**PHAW1 (-7.2)**   **PHAW2 (-11.1)**

PHAW3 (-9.5)   **PHAW4 (-8.0)**

Fig 4. Optimized structures of PHA-H$_2$O complex at MP2/aug-cc-pVDZ level of theory. CCDS(T)/CBS stabilization energies (kJ mol^{-1}) are given in parenthesis.

Table 1. ZPE and BSSE corrected stabilization energies (kJ mol^{-1}) of low energy structures for the PHA-H$_2$O complex.

Structure	MP2/aVDZ	MP2/aVTZ	MP2/CBS	CCSD(T)/aVDZ	CCSD(T)/CBS
PHAW1	-6.2	-7.1	-7.5	-6.0	-7.2
PHAW2	-8.0	-10.5	-11.6	-7.5	-11.1
PHAW3	-8.2	-10.3	-11.1	-6.6	-9.5
PHAW4	-7.6	-9.4	-9.4	-6.2	-8.0

The structures of the observed two isomers of the PHA-H$_2$O complex can be assigned based on the IDIR spectra in the acetylenic C$-$H and the O$-$H stretching regions and with the aid of quantum mechanical calculations. Table 2 lists the vibrational frequencies of the monomers and various complexes calculated at MP2/aug-cc-pVDZ level of theory along with the shifts in the acetylenic C$-$H and the O$-$H stretching vibrations. The IDIR spectrum of bare PHA in the acetylenic C$-$H stretching region (Fig 2A) shows multiple bands of which the two strong bands at 3325 and 3343 cm^{-1} have been assigned to Fermi resonance coupling between acetylenic C–H stretching vibration and a combination band arising out of one quantum of C≡C stretching and two quanta of C≡C$-$H out-of-plane bending modes **19**. A two-state decoupling model places the unperturbed acetylenic C$-$H oscillator of PHA at 3334 cm^{-12} .**7**. The IDIR spectrum of the PHA-H$_2$O W1 complex (Fig 2B) shows a strong band at the position close to the unperturbed acetylenic C$-$H oscillator of bare PHA which indicates that the Fermi resonance coupling is substantially weakened due to interaction of water molecule with PHA. Since the Fermi resonance coupling is exclusively localized on the acetylenic moiety, this spectrum indicates that the water molecule interacts with the acetylenic group of PHA. Further, the corresponding spectrum in the O$-$H stretching region (Fig 3B) shows the presence of free and hydrogen-bonded O$-$H stretching vibrations. Since the water interacts with the acetylene moiety in the W1 complex, the probable structures are PHAW1, PHAW2, and PHAW4. The structure PHAW1 can be ruled out as it would have led to a lowering of the acetylenic C–H stretching frequency by about 60 cm^{-1}. Figure 3 shows the comparison between the experimentally observed IR spectra and the simulated spectra for various structures of the PHA-H$_2$O complex in the O$-$H stretching region. 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 (v_1) and asymmetric (v_3) stretching vibrations, respectively. In the event of hydrogen bond formation to one of the O−H groups of the water moiety, the two frequencies will now correspond to the hydrogen-bonded and free O−H stretching vibrations. Although only one of the O−H group is involved in hydrogen bond formation, both stretching frequencies are lowered due to the partial decoupling of the two O−H oscillators. The vibrational frequencies corresponding to the hydrogen-bonded and free O−H stretching vibrations both of which are lower than the symmetric and asymmetric stretching vibrations, respectively. Since both O−H stretching frequencies are lowered due to hydrogen bond formation, the total shift in the O−H stretching frequencies [$\Sigma(\Delta v_{O-H}) = (\Delta v_1 + \Delta v_3)$] can be used as a tool to assign the intermolecular structures [26,27]. The calculated $\Sigma(\Delta v_{O-H})$ for the PHAW2 is –93 (see Table 2), which is in good agreement with the experimentally observed value of is –90 cm^{-1} for the W1 complex. At the CCSD(T)/CBS level the PHAW2 structure is about 3 kJ mol^{-1} more stable than the PHAW4 structure (see Table 1). Therefore, based on the energetics we assign the observed W1 complex to the PHAW2 structure. This assignment is in line with our earlier assignment [10], and others [9,11].

Table 2. Scaled vibrational frequencies and their shifts (cm^{-1}) for the PHA-H$_2$O complex.

Structure	ΔE / kJ mol^{-1}	v_{C-H}	$\Delta v_{(C-H)}$	$N_{(O-H)}$ (s, as)	$\Delta v_{(O-H)}$	$\Sigma \Delta v_{(O-H)}$
PHA	–	3334	–	–	–	–
Water	–	–	–	3642, 3771	–	–
PHAW1	–7.2	3272	–62	3640, 3767	–02, –04	–06
PHAW2	–1.1	3326	–8	3586, 3734	–56, –37	–93
PHAW3	–9.5	3333	–1	3621, 3744	–21, –27	–48
PHAW4	–8.0	3329	–5	3619, 3729	–23, –43	–66

The IDIR spectrum of the PHA-H$_2$O W2 complex in the O−H stretching region (Fig 3C) also shows the presence of free and hydrogen-bonded O−H stretching vibrations. The IDIR spectrum in the acetylenic C−H stretching region of the W2 complex (Fig 2C) is almost identical to the bare PHA, which indicates that in this case water molecule does not interact with the acetylenic moiety of PHA. Therefore, only the PHAW3 is the possible structure of the W2 complex (Fig 2C). The PHAW3 is the second most energetically stable structure (see Table 1). Further, the simulated IR spectrum of the PHAW3 structure is in good agreement with the IDIR spectrum of the W2 complex in the O−H stretching region. Furthermore, the two transitions in the IDIR spectrum appear at 3627 and 3734 cm^{-1} representing a total shift in the O–H stretching frequencies $\Sigma(Dn_{O-H})$ of –61 cm^{-1}, which is in good agreement with the calculated value of –48 cm^{-1} for the PHAW3 structure. Therefore, we assign the observed W2 complex to the PHAW3 structure. The experimental observation and structural assignment of the W2 complex was carried out for the first time. The intermolecular structure of this complex is similar to that of styrene-water [26] and PHA-H$_2$S [28], complexes.

The SAPT interaction energy decomposition was carried out for all the water complexes of PHA using cc-pVTZ basis set and the results are presented in Table 3. The SAPT0/cc-pVTZ method overestimates the stabilization energies relative to the CCSD(T)/CBS level, even though the relative energies for all the structures of PHA-H$_2$O complex follows almost the same trend. For the PHA-H$_2$O complexes, the W1 complex (assigned to PHAW2) which is the global maximizes both electrostatic and dispersion interactions, even though the dispersion component is about one-half of the electrostatic component. The second PHA-H$_2$O W2 complex (assigned to PHAW3), which is characterized by the presence of the O–H$\cdots \pi_{bz}$ hydrogen bond has almost equal contribution from electrostatics and dispersion. Moreover, the W1 and W1 complexes

both have almost equal contribution from the dispersion component, the difference in the stabilization energies is primarily due to the electrostatic (both first and second-order) components.

Table 3. SAPT interaction energy decomposition (kJ mol^{-1}) for PHA-H$_2$O complex.

	E_{Elec}	E_{Ind}	E_{Disp}	E_{Exch}	E_{SAPT0}	$E_{\text{CCSD(T)/CBS}}$
PHAW1	−18.8	−4.9	−5.7	15.0	−14.4	−7.2
PHAW2	−27.6	−8.6	−13.2	30.6	−18.7	−11.1
PHAW3	−12.9	−4.3	−13.9	17.0	−14.1	−9.5
PHAW4	−17.0	−4.3	−14.0	20.4	−14.8	−8.0

4 Conclusion

Two isomers of the water complex with PHA were observed in the IC-R2PI spectrum, which were assigned to specific structures using IDIR spectroscopic technique with the aid of high-level *ab initio* calculations. The structural assignment of the water complexes is based on the agreement between the experimental and the computed spectra and the total shift in the O–H stretching frequencies. The global minimum for the water complex of PHA is a quasi-planar cyclic complex characterized by the presence of incorporating C_{bz}–H···O and O–H···π_{ac} hydrogen bonds. Additional water also forms a single O–H···π_{bz} hydrogen-bonded complex with the PHA. The stabilization energy of the newly observed complex is about 1.5 kJ mol^{-1} higher than the global minimum.

Acknowledgments

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