



Matrix isolation infrared spectra of O–H ··· π Hydrogen bonded complexes of Acetic acid and Trifluoroacetic acid with Benzene

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MS received 6 May 2016; revised 19 August 2016; accepted 19 August 2016

Abstract. Mid infrared spectra of two O–H ··· π hydrogen-bonded binary complexes of acetic acid (AA) and trifluoroacetic acid (F₃AA) with benzene (Bz) have been measured by isolating the complexes in an argon matrix at ~8 K. In a matrix isolation condition, the O–H stretching fundamentals ($\nu_{\text{O–H}}$) of the carboxylic acid groups of the two molecules are observed to have almost the same value. However, the spectral red-shifts of $\nu_{\text{O–H}}$ bands of the two acids on complexation with Bz are largely different, 90 and 150 cm⁻¹ for AA and F₃AA, respectively. Thus, the O–H bond weakening of the two acids upon binding with Bz in a non-interacting environment follows the sequence of their ionic dissociation tendencies ($\text{p}K_a$) in aqueous media. Furthermore, $\Delta\nu_{\text{O–H}}$ of the latter complex is the largest among the known π -hydrogen bonded binary complexes of prototypical O–H donors reported so far with respect to Bz as acceptor. It is also observed that the spectral shifts ($\Delta\nu_{\text{O–H}}$) of phenol-Bz and carboxylic acid-Bz complexes show similar dependence on the acidity factor ($\text{p}K_a$). Electronic structure theory has been used to suggest suitable geometries of the complexes that are consistent with the measured IR spectral changes. Calculation at MP2/6-311++G (d, p) level predicts a T-shaped geometry for both AA-Bz and F₃AA-Bz complexes, and the corresponding binding energies are 3.0 and 4.5 kcal/mol, respectively. Natural Bond Orbital (NBO) analysis has been performed to correlate the observed spectral behavior of the complexes with the electronic structure parameters.

Keywords. Matrix isolation; pi-hydrogen bonding; infrared spectroscopy; spectral shifts; charge transfer.

1. Introduction

OH ··· π interaction is an important variant of non-conventional hydrogen bonds, where the filled π -molecular orbitals of alkene, alkyne or arene moieties are the common hydrogen bond acceptors.^{1–20} Energetically, the hydrogen bonds of this class are much weaker in comparison to their classical counterparts, and in most of the cases reported so far, the binding energies of isolated binary complexes involving small organic molecules are less than 5 kcal/mol, the accepted lower limit of hydrogen bond energy in conventional cases.¹ Nevertheless, OH ··· π hydrogen bonds have been suggested to be significant for stabilities of numerous organic molecular crystals, and structures of biological macromolecules and industrially important polymeric materials.^{1,9,17,20,21} The present article is concerned with mid-infrared spectra and structure of a model binary complex between acetic acid (AA) and benzene (Bz) stabilized by OH ··· π hydrogen bonding. We have

also explored how the OH ··· π binding interaction and structure of the complex are altered if a tri-fluoro substituted variant of AA, trifluoroacetic acid (F₃AA), is used to bind with a Bz molecule. In an aqueous medium, F₃AA is a much stronger acid ($\text{p}K_a \sim 0.0$) compared to AA ($\text{p}K_a = 4.73$).²²

Since the early work of Engdahl and Nelander, a binary complex between Bz and water has been used a popular prototype to investigate the fundamental attributes of OH ··· π interactions.^{2–7,18} Using different spectroscopic methods this binary complex has been studied extensively in a cold supersonic jet expansion,^{3–6} and also in inert gas matrixes.² Electronic structure calculation predicts that the complex prefers a T-shaped structure, where one of the O–H bonds of water preferentially points toward the benzene π -cloud.⁴ The binding results in a shallow intermolecular potential of binding energy ~3.2 kcal/mol according to calculation by CCSD(T) method,¹⁸ and this energy value is somewhat smaller compared to the binding energy of water dimer (5.02 kcal/mol) for calculations performed at the same level.²³ As a consequence of such shallow intermolecular potential, the facile exchange of the complex

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among equivalent structures results in splitting of the O–H stretching fundamentals of water as revealed in an ion-dip infrared spectrum.⁴

Recently, our group measured the infrared spectra of a series of OH $\cdots\pi$ hydrogen bonded phenol-Bz complexes by isolating them in an argon matrix. The goal of the measurements was to see how acidity of the phenols, which increases on fluorine substitutions at different aromatic sites, affects the spectral shifts of the O–H stretching fundamentals ($\Delta\nu_{\text{O-H}}$) of the phenolic donors on complexation with Bz. For the complex with unsubstituted phenol, the measured value of $\Delta\nu_{\text{O-H}}$ is -78 cm^{-1} , and it is much larger compared to that for the water-Bz complex (-18 to -26 cm^{-1} for the ν_1 mode and -18 to -29 cm^{-1} for the ν_3 mode).^{2,8,19} Furthermore, a linear correlation was observed on plotting $\Delta\nu_{\text{O-H}}$ values of different fluorophenols against their macroscopic acidity parameter, $\text{p}K_{\text{a}}$.¹⁹

Amongst the organic O–H donor family, the acidity of carboxylic acids being largest,²² their interactions with benzene π -molecular orbitals are also expected to be comparable to that of phenol-benzene system. These interactions of carboxylic acids with aromatic residues are the determining factors in physicochemical properties of many pigments and polymeric materials like resins.¹⁷ However, reports on spectroscopic as well as electronic structure studies of model carboxylic acid-aromatic complexes are rather scarce in literature. Recently, Zhao *et al.*, have reported an electronic structure theory study of a binary complex of formic acid with Bz.¹⁷ A T-shaped π -hydrogen bonded structure was found to be the most favored conformer with a binding energy of 4.79 kcal/mol for calculation at CCSD(T) level. This energy is comparable with the binding energy of the water dimer, (5.02 kcal/mol)²³ but somewhat larger than that of the water-Bz complex (3.16 kcal/mol).¹⁸ Infrared spectrum of the complex has been measured by our group for the first time.²⁴ Apart from a much larger value of the observed spectral shift ($\Delta\nu_{\text{O-H}} = -120\text{ cm}^{-1}$), the complex displayed some apparently unusual behavior when theoretical methods were employed for predictions of the spectral shift. In electronic structure calculations, spectral shift values ($\Delta\nu_{\text{O-H}}$) were found to be seriously underestimated when basis sets with diffused functions were used. In this paper, presenting the findings of AA-Bz and F₃AA-Bz complexes, we show that the experimental manifestations of OH $\cdots\pi$ interactions of these complexes in terms of $\nu_{\text{O-H}}$ shifts are consistent with those of phenol-Bz complexes. However, the predicted electronic structure parameters are somewhat dependent on the theoretical methods used.

2. Experimental and Computational methodologies

The samples, Bz (99.9%) and AA (98%) were procured from Spectrochem India Pvt. Ltd. and used after vacuum distillation. F₃AA was purchased from Sigma-Aldrich and used as supplied. The apparatus used to record the matrix isolation FTIR spectra of hydrogen bonded complexes has been described elsewhere.^{19,25} Briefly, argon of purity 99.99%, used here as matrix gas, was premixed with Bz and carboxylic acid vapors in different proportions in a stainless steel chamber. The gaseous mixture was deposited through an effusive nozzle of diameter ~ 500 micron onto a cold and polished KBr window maintained at a temperature of ~ 8 K by a closed cycle helium refrigerator (Advanced Research Systems, Inc., Model No. DE202). The partial pressures of carboxylic acids and Bz vapors in the gas-mixing cell were monitored using a high-pressure capacitive diaphragm gauge (Model: CMR 361, Pfeiffer Vacuum). Extreme care was taken to avoid dimerization of the carboxylic acids in the initially deposited matrix, and this was done by maintaining very low partial pressures of the acids in the matrix gas mixture. Typical mixing ratio of carboxylic acid and argon was kept at $\sim 1:2000$. Furthermore, for preparation of uniform matrix, deposition rate was kept very slow (at $< 10^{-5}$ mbar). The effusive nozzle used for deposition was heated to promote thermal dissociation of dimeric species if present in the pre-deposited gas mixture at room temperature. A temperature controller (Lake Shore Model 331) was used to monitor and control the temperature of the cold finger of the cryostat. To prepare the acid-Bz complexes, the initially deposited matrix was annealed by gradually increasing its temperature to ~ 28 K. This condition was maintained for about 15 minutes, and the matrix was then re-cooled to 8 K for recording the infrared spectra. The Fourier transformed infrared (FTIR) spectrometer used in the measurement [Bruker Optics (Model: Tensor 27)] was equipped with a DTGS detector and a ZnSe beam splitter. The spectra reported here were recorded with an instrumental resolution of 1 cm^{-1} . The sample chamber was purged continuously with dry nitrogen to minimize interferences from atmospheric water vapor and carbon dioxide.

Geometry optimizations of AA, F₃AA and Bz monomers and the 1:1 acid-Bz complexes were performed using Gaussian 09 program package by MP2 and DFT/wB97XD methods in conjunction with different basis sets.^{26,27} Basis set superposition errors (BSSE) in calculated binding energies of the complexes were corrected using the counterpoise method of Boys and Bernardi.²⁸ The vibrational frequencies were computed

by the same methods at a harmonic approximation to determine minima on the potential energy surfaces of the monomers and complexes. Natural bond orbital (NBO) analysis was performed in order to obtain populations in different bonding and anti-bonding orbitals, and hyperconjugation interaction energies of different D-A pairs.²⁹ These analyses have been performed on optimized structures predicted by all the methods mentioned above. Furthermore, the binding energies of the complexes were partitioned into their components following the Localized Molecular Orbital-Energy Decomposition Analysis (LMO-EDA) method as implemented in the Gamess US program.^{30,31}

3. Results and Discussion

3.1 Matrix isolation FTIR spectra of the two complexes

Three vibrational bands of the carboxylic acids, O–H str near 3500 cm^{-1} , C–O str near 1100 cm^{-1} and C=O str near 1700 cm^{-1} were tried as probes to observe the complex formation effects with Bz. However, the most discernable changes were observed only in the O–H stretching region. Therefore, only this spectral region of the two acids is depicted in Figure 1. The top two traces are the spectral segments of the matrix isolated AA and F₃AA acids. In order to record these two spectra, the ratio of AA/F₃AA to argon in the deposited matrix was maintained at $\sim 1:2000$. The third panel (trace-c) depicts the segment of the FTIR spectrum of Bz recorded under the same matrix isolation condition, and for this the ratio of Bz to argon in the vapor mixture was kept at $\sim 1:400$. The spectral traces for panels –d and –e depict the annealed matrices of co-deposited vapor mixtures containing AA/F₃AA, Bz and argon in a 1:5:2000 ratio. New bands appear in the spectra as indication of complex formation, and are indicated by arrows in Figure 1.

The ν_{OH} band of AA monomer in the argon matrix (trace-a) appears at 3564 cm^{-1} ,³² while that of F₃AA (trace-b) is positioned at 3553 cm^{-1} .³³ Thus, substitutions of three methyl H atoms by F has only a little effect on the frequency of this mode under isolated condition, although the same chemical substitution has a very pronounced effect on acidity in the aqueous medium, and the respective $\text{p}K_{\text{a}}$ values of AA and F₃AA are 4.7 and 0.0.²² A similar observation had earlier been observed in case of phenol, whose O–H stretching vibrational frequency was found to remain nearly same despite varying degrees of fluorine substitutions at different aromatic ring sites,¹⁹ and the findings are also supported by electronic structure calculations.

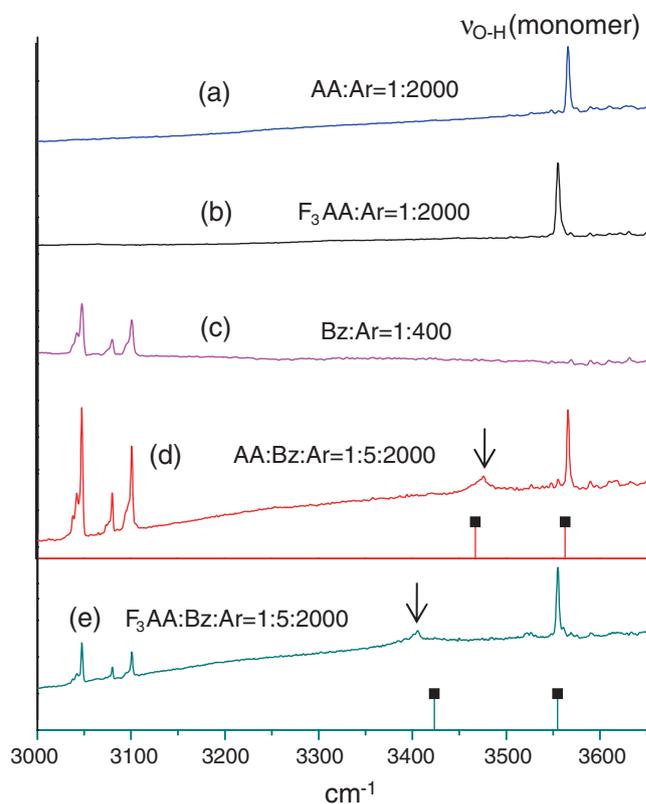


Figure 1. Matrix isolation IR spectra showing bands in the ν_{OH} region of carboxylic acids. The bands corresponding to formation of the O–H $\cdots\pi$ hydrogen bonded complexes of AA [trace (d)] and F₃AA [trace (e)] with Bz are shown by vertical arrows. Traces (a)–(c) correspond to spectra of matrix isolated AA, F₃AA and Bz, respectively, in the same region. The computed ν_{OH} frequencies [at wB97XD/6-311++G(d,p) level, scaling factor: 0.927] of the monomers and complexes of AA and F₃AA are depicted below traces (d) and (e), respectively.

A comparison of the two monomer spectra (traces –a and –b) with those of the spectra of mixed vapors (traces –d and –e) reveals that the new bands due to complexation of the acids AA and F₃AA with Bz appear at red shifts of 90 and 150 cm^{-1} , respectively, (indicated by vertical arrows) from the corresponding monomer bands. The intensities of these bands were found to increase with increasing concentration of Bz in the pre-deposited gas mixture and also with the duration of annealing. We have thus attributed the bands to 1:1 complexes of the two acids with benzene. It is notable that the spectral red shift of the $\nu_{\text{O–H}}$ band of F₃AA is $\sim 66\%$ larger compared to that of AA. This implies that the O–H bond (donor) of the carboxylic acid group of F₃AA experiences much more weakening effect on binding with Bz compared to that of AA, although the O–H oscillators of the two molecules have nearly same frequency when they are isolated. Thus, the bearing of the larger acidity of F₃AA is manifested only on binding of the acid group with a polarizable entity.

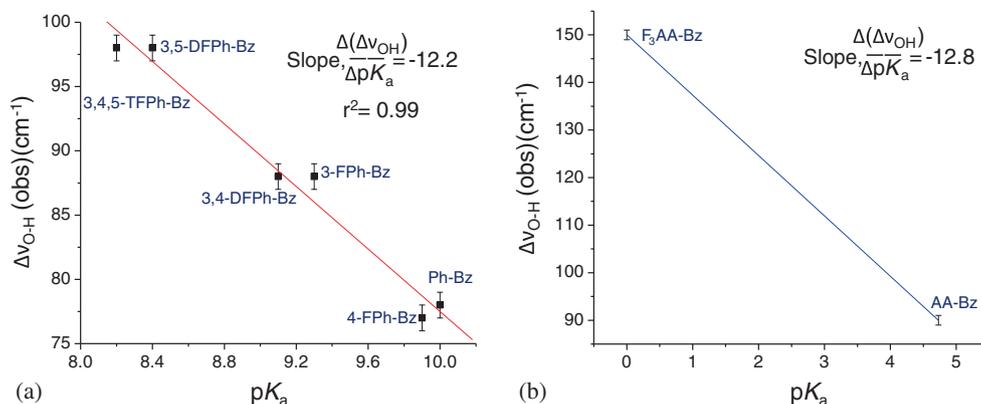


Figure 2. The plot (a) shows a linear variation of the measured infrared spectral shifts ($\Delta\nu_{\text{OH}}$, taken from Ref ¹⁹) of a series of different fluorophenol-benzene complexes with respective pK_a values of the fluorophenols. Here Ph=phenol, 4-FPh=4-fluorophenol, 3-FPh=3-fluorophenol, 3,4-DFPh=3,4-difluorophenol, 3,5-DFPh=3,5-difluorophenol, 3,4,5-TFPh=3,4,5-trifluorophenol and Bz=benzene. Part (b) depicts graphically the change in spectral shift of the $\nu_{\text{O-H}}$ mode from acetic to trifluoroacetic acid upon complexation with benzene observed in the present study. It is noteworthy that the slope is the same for both types of O-H $\cdots\pi$ complexes.

It has been mentioned before that a similar behavior with respect to spectral shifts was observed also for 1:1 Bz complexes of a number of fluorophenol derivatives.¹⁹ The spectra of the fluorophenol-Bz complexes have been depicted in Ref¹⁹, Figure 2. It has been shown below that the $\nu_{\text{O-H}}$ spectral shifts of those complexes display a linear correlation with the acidity parameter (pK_a) of the fluorophenols (Figure 2(a)). The slope of the linear plot $\Delta(\Delta\nu_{\text{O-H}})/\Delta(pK_a)$ provides the measure of the increase in spectral shift ($\Delta\nu_{\text{O-H}}$) for unit lowering of pK_a value of the phenols, and its value for fluorophenol-Bz complexes was estimated as -12.2 cm^{-1} . The question that we address now is whether the same linear correlation is also applicable in the case of carboxylic acid-Bz complexes. An affirmative answer to this question would mean that the interaction primarily responsible for spectral shifts of $\nu_{\text{O-H}}$ transition in OH $\cdots\pi$ bonding must be the same in both carboxylic acid-Bz and phenol-Bz complexes. For the present systems, although we have only two data points, the value of $\Delta(\Delta\nu_{\text{O-H}})/\Delta(pK_a)$ obtained is -12.8 cm^{-1} (Figure 2(b)), which is nearly the same as that for the fluorophenol-Bz complexes. The observation implies that the underlying factors responsible for spectral shifts in O-H $\cdots\pi$ interactions are similar both for aromatic alcohols and aliphatic acids.

3.2 Predictions of electronic structure calculations

3.2.1 Structure: The structures of the 1:1 complexes of the two acids, predicted by calculation at MP2/6-311++G(d, p) level are shown in Figure 3. The complexes assume a T-shaped geometry, with the O-H donor of the carboxylic acid group resting vertically

above benzene and pointing nearly to the center of one of the C=C bonds of the latter. Here, the O-H $\cdots\pi$ hydrogen bond lengths of the complexes can be expressed in terms of the distance of H5 from the nearest C=C bond of Bz, which for AA-Bz and F₃AA-Bz complexes are 2.44 and 2.41 Å, respectively (Figure 3). Similar shapes for the two complexes are predicted also by other theoretical methods employed, and the corresponding geometric parameters are presented in Table 1. In general, according to theoretical predictions, the O-H $\cdots\pi$ hydrogen bond length parameters of the complex of F₃AA are a little shorter compared to those of AA. The DFT-D method used predicts relatively stronger binding resulting in smaller values of the hydrogen bond distance parameters for the two complexes. Furthermore, inclusion of diffused functions in the basis set of calculations results in relatively larger hydrogen bond distance parameters. For example, at the wB97XD/6-31G(d, p) level, the H5 \cdots C6 and H5 \cdots C11 distances for AA-Bz are 2.36 and 2.37 Å, respectively, while the same for calculations at the 6-311++G(d, p) level are predicted to be 2.41 and 2.43 Å, respectively. The same is true for the MP2 calculations.

3.2.2 Binding energies: The BSSE-corrected binding energies of the two complexes AA-Bz and F₃AA-Bz, corresponding to the geometries shown in Figure 3, are 3.0 and 4.5 kcal/mol, respectively, for calculations performed at MP2/6-311++G(d, p) level, and the energy values predicted by other methods of calculations used are shown in Table 2. In general, the binding energies of F₃AA-Bz complex are larger compared to AA-Bz, and for the structure shown in Figure 3 the increase is 50%.

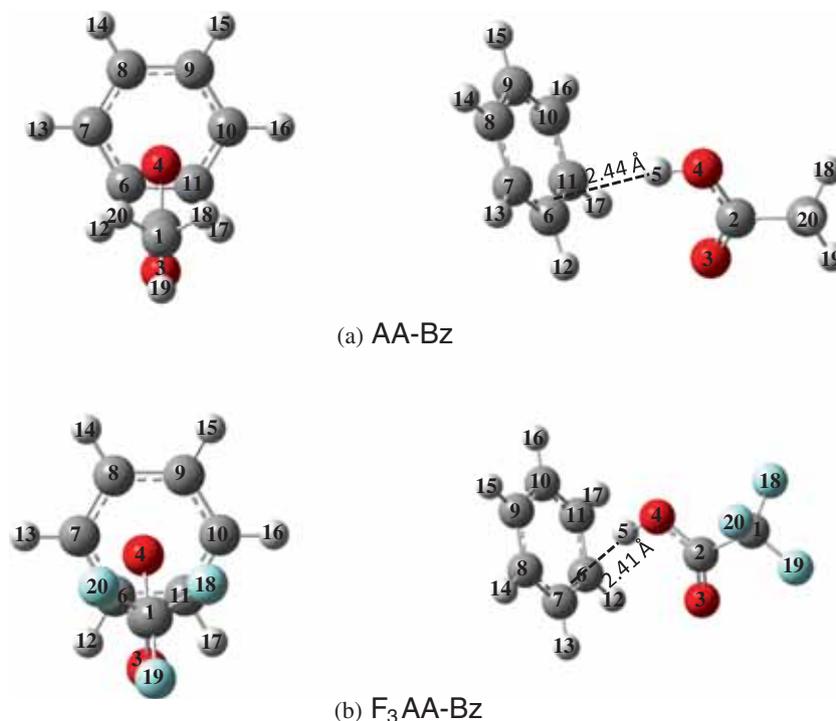


Figure 3. Two different views of optimized geometries of AA-Bz(a) and F₃AA-Bz(b) complexes for calculations at MP2/6-311++G(d, p) level of theory.

Table 1. Hydrogen bond distances of AA-Bz and F₃AA-Bz complexes optimized at different levels of theory.

Carboxylic acid	O4-H5...C6, O4-H5...C11 (Å)			
	wB97XD/ 6-31G(d,p)	wB97XD/ 6-311++G(d,p)	MP2/ 6-31G(d,p)	MP2/6-311 ++G(d,p)
AA	2.36, 2.37	2.41, 2.43	2.45, 2.51	2.54, 2.54
F ₃ AA	2.28, 2.29	2.37, 2.45	2.40, 2.57	2.46, 2.55

The predictions of other levels of calculations are also similar, and thus the energy difference is partly consistent with the 66% larger shift ($\Delta\nu_{\text{O-H}}$) observed for the F₃AA-Bz complex.

The binding energy of a binary complex is the net result of different categories of underlying interactions, which have different physical origins that contribute

collectively to it in various extents. Therefore, in order to interpret the observed 66% increase of the spectral shift from AA-Bz to F₃AA-Bz in terms of energetic factors, the total binding energies are partitioned into components using the LMO-EDA method. At MP2/6-311++G (d, p) level, the predicted contributions of different energy components are depicted in Table 3.

Table 2. Binding energies (BSSE corrected) of the AA-Bz and F₃AA-Bz complexes for calculations at different levels of theory, as well as corresponding percentage variations from AA to F₃AA.

Carboxylic acid	Binding energy (kcal/mol)				$\Delta\nu_{\text{O-H}}$ (obs) (cm ⁻¹)
	wB97XD/ 6-31G(d,p)	wB97XD/ 6-311++G(d,p)	MP2/6-31 G(d,p)	MP2/6-311 ++G(d,p)	
AA	4.5	4.7	2.48	3.0	-90
F ₃ AA	5.8	6.3	4.04	4.5	-150
% change	28.9	34.0	62.9	50	66.6

Table 3. Components of the total binding energies of AA-Bz and F₃AA-Bz complexes obtained from energy partitioning by LMO-EDA method at MP2/6-311++G(d, p) level of theory. The last column gives the percentage variations of the energy components from AA-Bz to F₃AA-Bz.

Energy component (kcal/mol)	AA-benz	F ₃ AA-Bz	% energy change
Electrostatic energy	-4.39	-5.84	33.0
Exchange-repulsion energy	+6.2	+7.25	16.9
Polarization energy	-1.88	-2.84	51.1
MP2 dispersion energy	-3.24	-3.36	3.7

For weak π -hydrogen bonded binary complexes, dispersion contributions to overall energy are expected to be considerable, and the same has been predicted here. The contributions of the electrostatic and dispersion terms appear comparable. However, it is seen that the increase in dispersion contribution to total binding energies from AA-Bz to F₃AA-Bz is only $\sim 4\%$, and obviously this term is correlated poorly with the observed spectral variation. The change in electrostatic contribution is higher, $\sim 33\%$, but it is still inconsistent with the observed increase of $\Delta\nu_{\text{O-H}}$ from a quantitative viewpoint. It is worth mentioning that the significance of the electrostatic parameter to observed $\nu_{\text{O-H}}$ shifting has been stressed recently by some authors in the case of weak hydrogen-bonded complexes.³⁴ However, the contribution of the electrostatic term, shown in Table 3 for the present two complexes, corresponds to interactions involving all atoms on the two molecular moieties. On the other hand, the occurrence of spectral shifting of $\nu_{\text{O-H}}$ mode is likely to be due to local interactions at the binding site, since the same has been revealed in the measured spectra where no significant changes of the vibrational modes that involve remote atoms are seen to occur. Therefore, in the following section we discuss the spectral shifting effect in terms of an interaction that operates primarily at the H-bonding site.

3.2.3 Spectral Shifts and Charge-transfer interactions: A vital interaction that is commonly used to explain the H-bonding effects is the hyperconjugative

charge-transfer (CT) between the filled orbitals of HB acceptor and higher-lying vacant anti-bonding orbitals of the donor.²⁹ In a recent series of experiments involving phenol-Bz and phenol-water complexes,^{19,35} we had shown that such CT effects relate linearly with observed $\nu_{\text{O-H}}$ shifts, and the CT interaction energies are also quantitatively consistent with the spectral variations. In the present study, we have calculated similarly the interaction energies corresponding to $\pi(\text{Bz}) \rightarrow \sigma^*(\text{O-H})$ CT by performing Natural Bond Orbital (NBO) analysis, and the results are shown in Table 4. It is seen that at the MP2/6-311++G (d, p) level, CT energies vary from 1.44 in AA-Bz to 2.36 kcal/mol in F₃AA-Bz, i.e., the change is $\sim 64\%$, which is quantitatively consistent with the $\sim 66\%$ variation of spectral shifting observed. Predictions of other electronic structure methods also suggest higher hyperconjugative CT in F₃AA-Bz compared to AA-Bz, although the extent of enhancement is different. For example, at the wB97XD/6-31G (d, p) level, the change in the CT term is $\sim 36\%$ from AA-Bz (6.0 kcal/mol) to F₃AA-Bz (8.2 kcal/mol). It is well-known that the efficiency of orbital overlap between the donor-acceptor moieties depends on their relative orientation i.e., on the geometry of the complex. It is likely therefore that the small differences in optimized geometrical parameters predicted by different methods of calculation are responsible for the aforementioned differences in CT interaction energies.

4. Conclusions

In this paper, we have reported $\nu_{\text{O-H}}$ segment of the FTIR spectra of O-H $\cdots\pi$ hydrogen-bonded binary complexes of AA and F₃AA with Bz for the first time. The spectra have been measured by isolating the two complexes in an argon matrix at ~ 8 K. The $\nu_{\text{O-H}}$ bands of the two carboxylic acid monomers appear at almost the same frequency, 3564 and 3553 cm^{-1} for AA and F₃AA, respectively. However, the spectral shifts of the $\nu_{\text{O-H}}$ band of the two acids on complex formation with Bz turn out to be significantly different, 90 and 150 cm^{-1} for AA and F₃AA, respectively. It is noteworthy

Table 4. Predicted magnitudes of $\pi(\text{Bz}) \rightarrow \sigma^*(\text{O-H})$ hyperconjugative charge transfer energies for different methods of calculation, as well as their percentage variation from AA-Bz to F₃AA-Bz.

Carboxylic acid	$\pi(\text{Bz}) \rightarrow \sigma^*(\text{O-H})$ (kcal/mol)			
	wB97XD/6-31G(d,p)	wB97XD/6-311++G(d,p)	MP2/6-31G(d,p)	MP2/6-311++G(d,p)
AA	6.01	3.46	3.80	1.44
F ₃ AA	8.19	3.34	5.27	2.36
% change	36.3	-3.4	38.7	63.9

that the IR spectral shift of the O–H stretching mode of F₃AA-Bz complex is the largest among all the binary O–H... π H-bonded complexes reported so far.

Electronic structure calculations suggest a T-shaped geometry for both the complexes, where the O–H bond of the two carboxylic acids points towards the middle of one of the C=C double bonds of benzene. NBO analysis and energy partitioning approaches were employed to understand quantitatively the origin of the spectral shift differences of the two complexes. At a certain MP2 level of theory, the charge transfer terms at the binding site of the complexes appear to correspond best with the observed differences in spectral shifts.

Acknowledgements

The authors acknowledge the financial support received from the Council of Scientific and Industrial Research (CSIR), Govt. of India. IB also acknowledges CSIR for receiving Junior Research Fellowship.

References

- Desiraju G R and Steiner T 1999 In *The Weak Hydrogen Bond* (New York: Oxford University Press)
- Engdahl A and Nelander B A 1985 *J. Phys. Chem.* **89** 2860
- Gutowsky H S, Emilsson T and Arunan E 1993 *J. Chem. Phys.* **99** 4883
- Pribble R N, Garrett A W, Haber K and Zwier T S 1995 *J. Chem. Phys.* **103** 531
- Cheng B M, Grover J R and Walters E A 1995 *Chem. Phys. Lett.* **232** 364
- Zwier T S 1996 *Annu. Rev. Phys. Chem.* **47** 205
- Prakash M, Gopalsamy K and Subramanian V 2009 *J. Phys. Chem. A* **113** 13845
- Fujii A, Ebata T and Mikami N 2002 *J. Phys. Chem. A* **106** 8554
- Meyer E A, Castellano R K and Diederich F 2003 *Angew. Chem. Int. Ed.* **42** 1210
- Panja S S and Chakraborty T 2003 *J. Chem. Phys.* **118** 6200
- Das A, Mahato K K, Panja S S and Chakraborty T 2003 *J. Chem. Phys.* **119** 2523
- George L, Sanchez-García E and Sander W 2003 *J. Phys. Chem. A* **107** 6850
- Panja S S, Biswas P and Chakraborty T 2005 *Chem. Phys. Lett.* **411** 128
- Vaupel S, Brutschy B, Tarakeshwar P and Kim K S 2006 *J. Am. Chem. Soc.* **128** 5416
- Jose K V J, Gadre S R, Sundararajan K and Viswanathan K S 2007 *J. Chem. Phys.* **127** 104501
- Biswal H S and Wategaonkar S 2009 *J. Phys. Chem. A* **113** 12774
- Zhao Y, Ng H T and Hanson E 2009 *J. Chem. Theory Comput.* **5** 2726
- Crittenden D L 2009 *J. Phys. Chem. A* **113** 1663
- Banerjee P and Chakraborty T 2014 *J. Phys. Chem. A* **118** 7074
- Jeffrey G A and Saenger W 1991 In *Hydrogen Bonding in Biological Structures* (Berlin: Springer)
- Grabowski S J (Ed.) 2006 In *Hydrogen Bonding: New Insights* (Dordrecht: Springer)
- Serjeant E P and Dempsey B 1979 In *Ionization Constants of Organic Acids in Aqueous Solution* (Oxford: Pergamon)
- Tschumper G S, Leininger M L, Hoffman B C, Valeev E F, Schaefer III H F and Quack M 2002 *J. Chem. Phys.* **116** 690
- Banerjee P, Bhattacharya I and Chakraborty T 2016 *J. Phys. Chem. A* **120** 3731
- Samanta A K, Pandey P, Bandyopadhyay B and Chakraborty T 2010 *J. Phys. Chem. A* **114** 1650
- Frisch *et al.* 2010 *Gaussian 09*, Revision C.01 (Gaussian, Inc.: Wallingford, CT)
- Grimme S 2011 *WIREs Comput. Mol. Sci.* **1** 211
- Boys S F and Bernardi F 1970 *Mol. Phys.* **19** 553
- Reed A E, Curtiss L A and Weinhold F 1988 *Chem. Rev.* **88** 899
- Schmidt M W *et al.* 1993 *J. Comput. Chem.* **14** 1347
- Su P, Jiang Z, Chen Z and Wu W 2009 *J. Chem. Phys.* **131** 014102
- Macoas E M S, Khriachtchev L, Fausto R and Rasanen M 2004 *J. Phys. Chem. A* **108** 3380
- Ito F 2011 *Chem. Phys.* **382** 52
- Saggu M, Levinson N M and Boxer S G 2011 *J. Am. Chem. Soc.* **133** 17414
- Banerjee P, Mukhopadhyay D P and Chakraborty T 2015 *J. Chem. Phys.* **143** 204306