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Electrostatics Determine Vibrational Frequency Shifts in Hydrogen Bonded Complexes!

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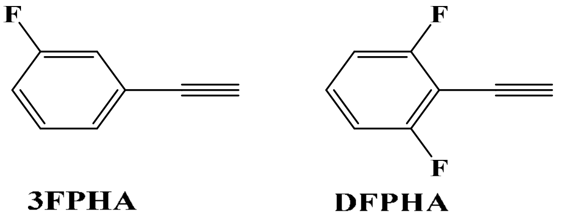
The red-shifts in the acetylenic C–H stretching vibration of C–H···X (X = O, N) hydrogen-bonded complexes increase with increase in the basicity of the Lewis base. Analysis of various components of stabilization energy suggests that the observed red-shifts are correlated with the electrostatic component of the stabilization energy, while the dispersion modulates the stabilization energy.

Hydrogen bonding is central to chemistry, biology and material science and its role cannot be overemphasized. Among several experimental techniques used for probing the formation of A–H···B hydrogen bond, vibrational spectroscopy of hydrogen bond donor group (A–H) has long been identified as an important spectroscopic tool. This is due to the fact that the A–H bond is sensitive to the nature of the hydrogen bond since it is directly involved in the hydrogen bond formation. In general the formation of A–H···B hydrogen bond leads to lengthening of the A–H covalent bond, and consequently the A–H stretching frequency exhibits a characteristic red-shift accompanied by enhanced infrared intensity. Examples of hydrogen bonds which show blue-shift and no-shift in the A–H stretching frequency have also been reported.[1,2] A unified explanation about the nature of shift in the A–H stretching frequency was provided by Joseph and Jemmis.[3] In their classic book, Pimentel and McClellan state that the stretching frequency of the hydrogen bond donor provides a qualitative marker for hydrogen bond formation and quantitative index of hydrogen bond energy and other physical properties.[4] Several examples of correlation between red-shift in the donor (A–H) stretching frequency to various properties of donor and acceptor have been reported.[5] Further, the correlations between red-shift in the donor stretching frequency and the enthalpy of hydrogen bond formation (Badger−Bauer rule) have also been reported.[4,6]

In a recent article Hoja *et al.*[7] raised a simple, yet fundamental, question "is electrostatics sufficient to describe hydrogen-bonding interaction?" and concluded that "electrostatics alone are a poor predictor of the hydrogen-bond stability trends and in fact, dispersion interactions predict these trends better." The question we want to pose is: "Does this imply that the shift in the vibrational frequency of the hydrogen bond donor follow the same trend?" In an attempt to address this question we have carried out investigations on a series of C–H···X (X = O, N) hydrogen-bonded complexes of 3-fluorophenylacetylene (3FPHA) and 2,6-difluorophenylacetylene (DFPHA) (see Scheme 1) with several Lewis bases such as water, methanol, diethylether, ammonia, methylamine, dimethylamine and trimethylamine. Herein, we have demonstrated that the red-shift in the hydrogen bond donor frequency is linearly correlated with the electrostatics component of the total energy and on the other hand, the dispersion component modulates the total energy and therefore, the stabilization.



Scheme 1. Structures of 3-fluorophenylacetylene and 2,6-difluorophenylacetylene used in the present investigation.

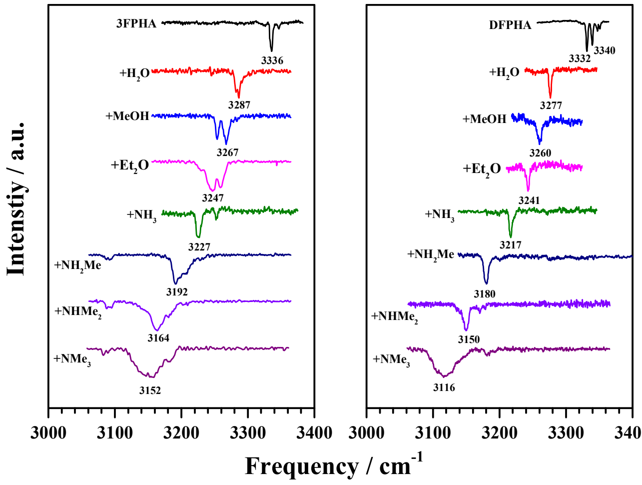


Fig. 1. The IR spectra in the acetylenic C–H stretching region for 3FPHA and its hydrogen-bonded complexes with various bases (left panel) and for DFPHA and its hydrogen-bonded complexes (right panel).

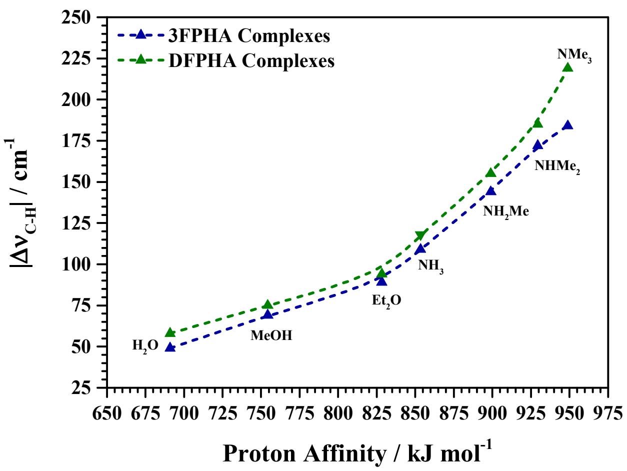


Fig. 2. Plot of the red-shift in the acetylenic C–H stretching frequency in several hydrogen-bonded complexes of 3FPHA and DFPHA versus the proton affinity of the interacting base. The dashed lines are trend lines.

The IR spectra in the acetylenic C–H stretching region of the monomers and their hydrogen-bonded complexes were selectively recorded using IR-UV double resonance spectroscopic method,[8] and the results are presented in Fig. 1. The acetylenic C–H stretching vibration of 3FPHA monomer occurs at 3336 cm^{-1}. In the case of DFPHA, the IR spectrum shows multiple band due to state Fermi resonance and higher order anharmonic couplings, similar to phenylacetylene,[9] which can be analysed to identify the nascent acetylenic C–H stretching vibration at 3335 cm^{-1}.[10] The IR spectra of all the complexes of both 3FPHA and DFPHA show a red-shift in the acetylenic C–H stretching (with respect to the monomers), which increases with increasing basicity of the hydrogen bonding acceptor.

Fig. 2 shows the plot of red-shift in the acetylenic C–H stretching frequency as a function of proton affinity of the base.[11] Even though a qualitative trend of increase in the red-shift with increase in the basicity can be seen, it is clear that the red-shifts are not linearly correlated over the entire range of proton affinities that are considered. Since it is perceived that the red-shift in the donor stretching frequency is an indicator to the hydrogen bond strength, the stabilization energies of all the C–H···X complexes were calculated at the CCSD(T)/CBS level of theory using the geometries optimized at MP2/aug-cc-pVDZ level, which are listed in Table 1. These calculations were carried out using Gaussian-09.[12,13] We observe that the stabilization energy of ammonia complexes are lower than the diethylether complexes, in both the cases (3FPHA and DFPHA), even though ammonia is a stronger base than diethylether. This trend in the calculated stabilization energies is rather surprising, *vide infra*.

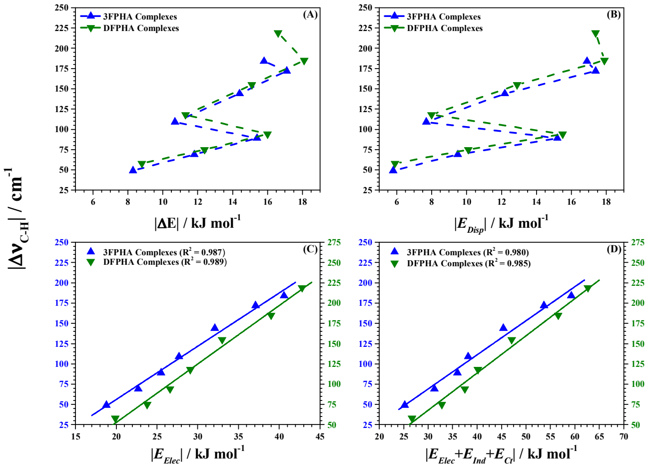


Fig. 3. Plot of red-shift in the acetylenic C–H stretching frequency in several hydrogen-bonded complexes of 3FPHA and DFPHA with (A) ZPE and BSSE corrected CCSD(T)/CBS stabilization energy, (B) dispersion energy, (C) electrostatic energy and (D) sum of electrostatic, induction and charge-transfer energies. In (A) and (B) dashed are trend lines, while in (C) and (D) the solid lines are linear fits to the data points. In (C) and (D) the y-scales for the 3FPHA (▲) and DFPHA (▲) are shifted relative to each other for clarity.

The plot of the red-shifts in the C–H stretching frequencies versus the CCSD(T)/CBS stabilization energies (ΔE) is shown in Fig. 3(A). The absence of any correlation between the two is rather startling given the fact that the hydrogen bond donors and acceptors in the present study are simple and form linear C–H···X hydrogen bonds. This observations question the very basic premise that shifts in the donor stretching frequency are a quantitative index of hydrogen bond energies. To decipher the reason behind this lack of correlation in the observed trend, we have carried out energy decomposition with Symmetry Adapted Perturbation Theory (SAPT), which provides a recipe for the separation of interaction energy into physically well-defined components, such as those arising from the electrostatics or Coulomb interactions (E_{Elec}), induction (E_{Ind}), dispersion (E_{Disp}) and exchange (E_{Exch}).[14] All SAPT calculations were performed with PSI4.[15] The energy decomposition for all the C–H···X complexes was carried out using cc-pVTZ basis set and excerpts of the SATP2 calculations are listed in Table 1 (see Tables S3 and S4 for more details; ESI). The zero point energy corrected SAPT2 energies are comparable to CCSD(T)/CBS stabilization energies within 1 kJ mol^{-1}.

Fig. 3 also shows plots of red-shifts in the C–H stretching frequency versus (i) dispersion component (E_{Disp}) of the stabilization energy, (ii) electrostatic component (E_{Elec}) of the stabilization energy, and (iii) sum of electrostatic, induction and charge-transfer energies ($E_{Elec} + E_{Ind} + E_{CT}$). The appearance of red-shift vs. E_{Disp} plot [Fig. 3(B)] is very similar to the red-shift vs. ΔE plot [Fig. 3(A)] and lacks any correlation. On the other hand the plots of red-shift vs. E_{Elec} [Fig. 3(C)] and ($E_{Elec} + E_{Ind} + E_{CT}$) [Fig. 3(D)] are linearly correlated.

Table 1. ZPE and BSSE corrected CCSD(T)/CBS stabilization energies, ZPE corrected SAPT2 interaction energies, electrostatic and dispersion components of SAPT2 interaction energies (kJ mol^{-1}) and experimentally observed shifts in the acetylenic C–H stretching frequency (cm^{-1}).

Complex	ΔE	E_{SAPT2}	E_{Disp}	E_{Elec}	$\lvert\Delta\nu_{C\text{-}H}\rvert$
3FPHA-H_2O	-8.3	*-8.5*	-5.8	-18.6	49
3FPHA-MeOH	-11.8	-11.7	-9.5	-22.7	69
3FPHA-Et_2O	-15.4	-14.9	-15.2	-25.5	89
3FPHA-NH_3	-10.7	-11.5	-7.7	-27.7	109
3FPHA-NH_2Me	-14.4	-15.3	-12.2	-32.1	144
3FPHA-$NHMe_2$	-17.1	-18.0	-17.4	-37.1	172
3FPHA-NMe_3	-15.8	-16.9	-16.9	-40.6	184
DFPHA-H_2O	-8.8	-9.3	-5.9	-19.9	58
DFPHA-MeOH	-12.4	-12.3	-10.1	-23.8	75
DFPHA-Et_2O	-16.0	-15.4	-15.5	-26.6	94
DFPHA-NH_3	-11.3	-12.1	-8.0	-29.1	118
DFPHA-NH_2Me	-15.1	-15.9	-12.9	-33.9	155
DFPHA-$NHMe_2$	-18.1	-18.9	-17.9	-39.0	185
DFPHA-NMe_3	-16.8	-17.8	-17.4	-42.8	219

As noted earlier, the stabilization energies of the ammonia complexes (in both 3FPHA and DFPHA) are lower than those of the diethylether complexes, even though ammonia is a stronger base than diethylether. The SAPT analysis indicates that the electrostatic components of the ammonia complexes are higher than the diethylether complexes, which is a direct effect of the higher basicity of ammonia. However, the dispersion components for the diethylether complexes overwhelm the higher electrostatic components, and this is an effect of the relatively bulkier alkyl groups of diethylether. Therefore, a better comparison would be between the complexes of two bases with equal number of methyl (alkyl) groups.

The lack of correlation between the observed red-shifts in the acetylenic C–H stretching frequencies versus the CCSD(T)/CBS stabilization energies and the observed linear correlation between red-shifts versus the electrostatic components of the stabilization energies clearly demonstrate the fact that electrostatics regulate the shifts in the donor stretching frequencies in the C–H···X hydrogen bonded systems. Further, induction energy (E_{Ind}) and charge-transfer (E_{Ct}) are second-order electrostatic effects, therefore it is expected that even these energy components would be linearly correlated with red-shifts, which indeed is the case [Fig. 3(D)]. Comparison of plots shown in Figs. 3(A) and 3(B) indicates that dispersion component modulates the total stabilization energy and is in agreement with the observations made by Hoja *et al.*[7] that dispersion interactions predict the stabilization energy trends better.

In summary, the IR spectra in the acetylenic C–H stretching vibration of several C–H···X (X = N, O) hydrogen bonded complexes of 3-fluorophenylacetylene and 2,6-difluoropphenylacetylene were recorded. The red-shifts in the C–H stretching frequency increase with increase in the proton affinity of the interacting base. The red-shifts are linearly correlated with the electrostatic components of the total energies. The stabilization energy on the other hand is modulated by the dispersion component.

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Notes and references

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[†] Equal experimental contribution.

Author Contributions: The problem was formulated by GNP. AD and SIM carried out experiments and some initial calculations on DFPHA and 3FPHA, respectively, in consultation with GNP. Most of the calculations were carried out by SS in consultation with DG. The results were interpreted jointly by GNP and DG along with AD, SIM and SS.

Electronic Supplementary Information (ESI) available: Experimental and computational methodology along with tables containing stabilization energies, SAPT decomposition analysis and various correlation plots. See DOI: 10.1039/c000000x/

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TOC Graphic

The shifts in the acetylenic C–H stretching vibration in the C–H···X hydrogen-bonded complexes correlate with the electrostatic component of the stabilization energy.