

## A Tug-of-War between Electrostatics and Dispersion in Intermolecular Interactions

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**[Abstract]** The red-shifts in the X–H stretching vibration of X–H···Y hydrogen bonded complexes are correlated with the electrostatic component of the stabilization energy, while the dispersion modulates the stabilization energy. In the case of  $\pi$ -stacked complexes, marginal red shifts indicate the minimally perturbation relative to monomers. The observed red shift in the homo-dimers suggests that the antiparallel  $\pi$ -stacked structures contribute predominantly based on a simple coupled dipole model. While dispersion plays a pivotal role in  $\pi$ -stacking electrostatics contributes through the effect of dipole moment which enhances the ability to form  $\pi$ -stacked structures. Further, it is demonstrated that switching of electrostatic dominated regime to dispersion dominated regime leads to folding and unfolding of squaramide based foldamers.

**[Introduction]** Intermolecular interactions such as hydrogen bonding is primarily considered as an electrostatic interaction between the permanent multipoles located at the donor and acceptor molecules. However, the interaction energy calculated using higher level quantum mechanical calculations shows that various components such as electrostatics, polarization, dispersion, charge transfer and exchange-repulsion, contribute to the overall stabilization energy [1]. In a recent article Hoja et al. [2] 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.” On the other hand infrared spectroscopy has been primary choice of experimental method to investigate hydrogen bonding and other intermolecular interactions. The question that we seek to address is what part of the intermolecular interaction does infrared spectroscopy probe? Further taking cues from the gas-phase experiments, new squaramide based foldamers were designed and their structures were elucidated in solution and in the solid state.

**[Methods]** Experiments were carried out in the gas-phase with resonant multi photon ionization (REMPI) method and monitoring the mass ion using a two-stage Wiley-McLaren time-of-flight mass spectrometer. IR-UV double resonance spectroscopic method was used to record the infrared spectra using ion detection method [3]. The experimental results were supplemented with ab initio / DFT calculations to interpret the spectra. Further, squaramide based foldamers were synthesized and their structure were characterized using single crystal x-ray crystallography and two-dimensional NMR in solution.

**[Results and Discussion]** The infrared spectra of several linear X–H···Y (X = C, N, O; Y = O, N) hydrogen-bonded complexes of phenylacetylene, indole and phenol were analyzed using ab-initio calculations. The stabilization energies are in the order phenol > indole > phenylacetylene, which can be attributed to the stronger hydrogen donor ability of the O–H bond in phenol over N–H bond in indole and C–H bond in phenylacetylene. The SAPT2/cc-pVTZ energy decomposition analysis shows that for all the three sets of complexes observed red-shifts in the X–H stretching frequencies are linearly correlated with the

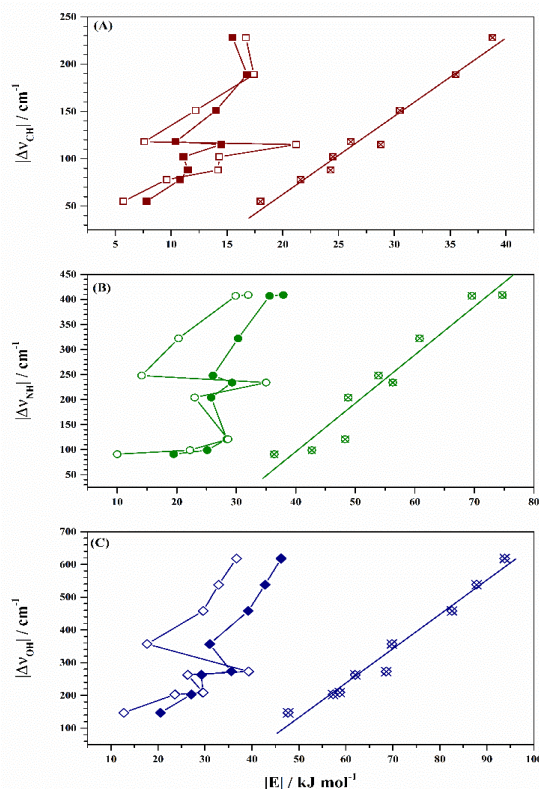
electrostatic component of stabilization energy [4]. Further, the ratio of dispersion for all the three sets of complexes the electrostatic components depends predominantly of the nature of the acceptor with very limited contribution for the donor. The shifts in X–H stretching frequencies were inversely correlated to the dipole moments of the acceptor, whereas X–H stretching frequencies against the calculated polarizability of the acceptors show a linear correlation for the X–H···O and X–H···N hydrogen-bonded complexes separately.

Comparison of IR spectra of the homo-dimers of phenylacetylene and single fluorine substituted phenylacetylenes with the corresponding monomers reveals marginal perturbation of the acetylenic C–H group with red-shifts of the order of 3-5  $\text{cm}^{-1}$ . Such small shifts rule out the possibility of formation of structures involving C–H··· $\pi$  interaction. On the basis of minimal perturbation of the acetylenic C–H groups it was inferred that all the homo-dimers form  $\pi$ -stacked structures, which was amply supported by electronic structure calculations. Further, the observed red shift in the acetylenic C–H stretching vibration were analyzed using coupled dipoles model which suggest the formation of antiparallel  $\pi$ -stacked structures. Partitioning of the interaction energy using SAPT0 scheme reveals that  $\pi$ -stacking in the dimers is dispersion-dominated with reasonable contribution from electrostatics. The stability trends indicate that the dipole moment enhances the ability to form  $\pi$ -stacked structures [5].

Foldamers incorporating squaramide rings fold due dispersion dominated  $\pi$ -stacking between two squaramide rings and are energetically favorable over unfolded structure. The variation of relative energies with respect to dihedral angle strain for these foldamers reveal that the two rings behave differently when it comes to secondary structure formation and there is asymmetry in the folding potential even in the absence of chiral elements. However, in the solid state these foldamers adapt unfolded structure due to extensive hydrogen bonding network, which is dominated by electrostatics.

## [References]

- [1] B. Jeziorski, R. Moszynski, K. Szalewicz. *Chem. Rev.* **94**, 1887 (1994).
- [2] J. Hoja, A.F. Sax, K. Szalewicz. *Chem. - A Eur. J.* **20**, 2292 (2014).
- [3] S. Tanabe, T. Ebata, M. Fujii, N. Mikami. *Chem. Phys. Lett.* **215**, 347 (1993).
- [4] A. Dey, S.I. Mondal, S. Sen, D. Ghosh, G.N. Patwari. *Phys. Chem. Chem. Phys.* **16**, 25247 (2014).
- [5] S.I. Mondal, S. Sen, A. Hazra, G.N. Patwari. *J. Phys. Chem. A* (2014), 3383 (2017).



**Fig. 1.** Plot of shifts in the donor stretching frequency of (A) phenylacetylene (squares), (B) indole (circles) and (C) phenol (diamonds) in their hydrogen-bonded complexes against the corresponding ZPE corrected SAPT2 interaction energies (solid), electrostatic component (crossed) and dispersion component (open). The straight lines are the linear fits to the shifts vs electrostatic component