Electrostatics and Dispersion in X–H···Y (X = C, N, O; Y = N, O) Hydrogen Bonds and Their Role in X–H Vibrational Frequency Shifts

Saumik Sen*‡ and G. Naresh Patwari*§

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

Supporting Information

ABSTRACT: The frequency shifts of donor stretching vibration in X–H···Y (X = C, N, O; Y = N, O) hydrogen-bonded complexes of phenylacetylene, indole, and phenol are linearly correlated with the electrostatic component of the interaction energy. This linear correlation suggests that the electrostatic component, which is the first-order perturbative correction to the stabilization energy, is essentially localized on the X–H group. The linear correlation suggests that the electrostatic tuning rate, which is a measure of the X–H oscillator to undergo shifts upon hydrogen bonding per unit increase in the electrostatic component of the stabilization energy, was found to be in the order of O–H > N–H > C–H. Interestingly, for each of the donor groups, viz., C–H, N–H, and O–H, the vibrational frequency shifts were inversely correlated to the dipole moment of the acceptor separately, which is counterintuitive vis-à-vis the electrostatic component. This implies that extrapolation to zero dipole moment of the acceptor will yield very large shifts in the hydrogen-bonded X–H stretching frequencies. The trends in the variation of the dispersion and exchange-repulsion components and the total interaction energy vis-à-vis frequency shifts of donor stretching vibration are similar for hydrogen-bonded complexes of phenylacetylene, indole, and phenol. Furthermore, it was observed that the vibrational frequency shifts of all of the complexes are linearly correlated with the charge transfer from the filled orbital of the hydrogen acceptor to the vacant antibonding (σ*) orbital of the X–H donor group on the basis of natural bonding orbital calculations.

INTRODUCTION

Hydrogen bonding is one of the most important and ubiquitous noncovalent interactions due its strength and directionality.1−4 Hydrogen bonding involving O–H and N–H groups is common and very prevalent.5−9 The hydrogen bonds involving C–H groups have also been reported in the literature and are also known to influence crystal structures.8−12 Vibrational spectroscopy has been extensively used to probe the donor stretching frequency in the hydrogen-bonded systems.13−16 Mainly due to the fact that the donor being directly involved in the hydrogen bond formation is very susceptible to the nature of hydrogen bonding. The vibrational frequency shift in the donor is a measure of hydrogen bond energy and depends on the molecular properties of the hydrogen donor and acceptor.17 In general, hydrogen bonding leads to a red shift in the donor vibrational frequency; however, examples of hydrogen-bonded complexes wherein the donor stretching frequency shifted to blue have also been reported.18−24 Very early work on hydrogen bonding has led to the formulation of the Badger–Bauer rule, according to which the red shifts in hydrogen donor vibrational frequencies linearly correlate with their enthalpy of formation. Furthermore, several examples of correlation between the red shifts in the donor stretching frequencies and various properties of the donor and/or acceptor have also been reported.25−29

The IUPAC definition of a hydrogen bond suggests that it is an attractive interaction between an X–H group and a suitable acceptor, wherein X is more electronegative than H.3 High-level quantum chemical calculations have established that various interaction energy components, such as electrostatics, polarization, dispersion, charge transfer, and exchange repulsion, contribute to the overall stabilization energy.30−34 The relative contributions from each energy component vary widely depending on the nature of hydrogen bond donor–acceptor characteristics. In recent years, efforts are being made to determine the origin of vibrational frequency shifts in the
donor stretching vibrations. Our group had earlier shown that the red shifts in the acetylenic C–H stretching vibration of C–H···X (X = O, N) hydrogen-bonded complexes of 3-fluoro- and 2,6-difluorophenylacetylenes were linearly correlated with the electrostatic component of stabilization energy but not the total stabilization energy. Moreover, it was also shown that the dispersion energy component modulates the trends observed in total stabilization energy. On the other hand, for a series of ammonia and methylamine complexes of fluorine-substituted phenylacetylenes (PA), the shifts in the acetylenic C–H stretching vibration were linearly correlated with the stabilization energies. For a series of O–H···O hydrogen-bonded water complexes of fluorophenols, based on the correlation between the shifts in the O–H stretching frequencies and the stabilization energies, the complexes were categorized into two sets. However, the energy decomposition analysis (EDA) revealed that the shifts in the O–H stretching frequencies were linearly correlated with the electrostatic component of the stabilization energy. In this case, the interaction energies were decomposed using the localized molecular orbital energy decomposition analysis (LMO-EDA) method. In some cases, the red shift in the donor stretching frequencies was correlated with the exchange-repulsion term, which was obtained by the symmetry-adapted perturbation theory in combination with the density functional theory (DFT-SAPT). Hobza and co-workers have recently shown one-to-one correspondence between DFT-SAPT and the canonical EDA method. Lane et al. have investigated the hydrogen bonding interactions in a series of 15 different complexes of OH donor groups with various acceptor atoms, which exhibit a strong correlation between the red shifts in the O–H stretching frequency and the kinetic energy density integrated within the reduced density gradient volume with $s = 0.5$ au, irrespective of the atom type of the hydrogen bond acceptor.

In the present work, we seek to address a simple question, whether or not the shifts in the X–H stretching frequencies of various donor groups, such as C–H, N–H, and O–H, in their hydrogen-bonded complexes are governed only by the electrostatic component and not by the total stabilization energy, irrespective of their inherent polarity. To this end, investigations on X–H···Y (X = C, N, O) hydrogen-bonded complexes of phenylacetylene (PA), indole (IN), and phenol (PH), respectively, with various Lewis bases (see Scheme 1) such as water, methanol, etc. were carried out using experimentally guided ab initio calculations, and the results are presented in this article.
RESULTS AND DISCUSSION

The structures of several linear X−H···Y (X = C, N, O; Y = N, O) hydrogen-bonded complexes of phenylacetylene, indole, and phenol were optimized at the MP2/aug-cc-pVDZ level of theory. The structural parameters (bond lengths and angles) for all of the hydrogen-bonded complexes are given in Table S1 (see the Supporting Information). The CCSD(T)/CBS interaction energies were not calculated for indole complexes because of paucity of computational resources.

It is well known that hydrogen bonding leads to red shifts in X−H stretching frequencies accompanied by an increase in the anharmonicity in the potential energy function of the donor X−H groups. The increase in anharmonicity with the basicity of the hydrogen bond acceptor eventually leads to double-well potential along the proton-transfer reaction coordinate. To estimate the role of hydrogen bonding in anharmonicity of the X−H bond, anharmonic calculations were carried out using second-order vibrational perturbation theory (VPT2) at the B3LYP-D3/aug-cc-pVDZ level\(^{31,42}\) for the phenylacetylene, indole\(^{43,44}\) and phenol\(^{47,48}\) complexes for which the experimental X−H stretching frequencies are reported in the literature and are listed in Table S3. To evaluate the performance of the anharmonic calculations, the calculated harmonic and anharmonic frequencies were plotted against the experimental frequencies (shown in Figure S1; Supporting information). Figure S1 suggests that even the calculated anharmonic frequencies have to be scaled to match the experimental values, which is in accord with the earlier reports.\(^{31,42}\) On the other hand, Figure S2 (see the Supporting Information) shows the correlation between experimental and harmonic frequencies calculated at the MP2/aug-cc-pVDZ level. It can be observed from Figures S1 and S2 that the quality of fits is much better for the harmonic calculations. Therefore, it can be inferred that scaling of harmonic frequencies is a better approach to anharmonicity at least for the present set of calculations. Based on these results, the calculated frequencies at the MP2/aug-cc-pVDZ level were scaled with 0.852, and to the resulting frequencies, 404.9 cm\(^{-1}\) was added to obtain the final calculated frequencies, which are listed in Table 1, and were used for further analysis. Table 1 lists experimentally observed X−H stretching frequency shifts, wherever available, which enables comparison with the corresponding calculated values.

It has been reported that for the phenol complexes the red shifts in the O−H stretching frequencies were correlated with the proton affinity of the acceptor.\(^{14}\) Figure 1 shows the plot of shifts in the X−H stretching frequencies against the corresponding X−H covalent bond distance, which shows a linear correlation, suggesting that the vibrational frequency shifts due to hydrogen bonding are a measure of bond elongation. Furthermore, Figure 1 also shows the plot of shifts in the X−H stretching frequencies against the proton affinities of the acceptors (see Table S4), and in all of the three cases, the data could be fitted to a second-order polynomial. A comparison with the linear fits for the same set of data is shown in Figure S3 (see the Supporting Information), which clearly suggests a nonlinear correlation between the X−H stretching frequency shifts and the proton affinity of the acceptor and the influence of the second-order effects with the increase in the shifts. This is in contrast to several other examples of hydrogen-bonded systems reported in the literature wherein the shifts in the donor stretching frequencies are linearly correlated to the proton affinity of the acceptor.\(^{4,15,35,38,50}\) On the other hand, Pines et al.\(^ {39}\) suggested the possibility of nonlinear correlation between the X−H stretching frequency shifts in the hydrogen-bonded complexes and proton affinities, especially for the stronger bases, which is related to an increase in the anharmonicity and

![Figure 1](image-url)
indicates the eventuality of formation of double-well potential along the proton-transfer reaction coordinate.\textsuperscript{49,50}

It was earlier reported, by our group, for a series of C–H···X (X = O, N) hydrogen-bonded complexes of 3-fluoro- and 2,6-difluorophenylacetylene, that the red shifts in the C–H stretching frequencies were linearly correlated with the electrostatic component of the interaction energy but not with the overall stabilization energies of the complexes.\textsuperscript{35} Therefore, to probe the role of various energy components in the shifts in X–H stretching frequencies for all of the three sets of complexes (viz., phenylacetylene, indole, and phenol), energy decomposition analysis was carried out using the SAPT2 method, and the results are presented in Table 2. The BSSE- and ZPE-corrected CCSD(T)/CBS stabilization energies and the ZPE-corrected SAPT2 interaction energies for the phenylacetylene and the phenol complexes are presented in Tables 1 and S2. It is observed that these two sets of energies are in excellent agreement with each other and show a maximum deviation of within ±1.3 kJ mol\textsuperscript{−1} with a standard deviation of 0.75 kJ mol\textsuperscript{−1}. Figure 2 shows the plot of shifts in the X–H stretching frequencies for all of the three sets of complexes against the ZPE-corrected SAPT2 interaction energies, which clearly suggests that these two parameters are not correlated (also see Figure S4; Supporting Information). The lack of correlation between X–H frequency shifts and the SAPT2 interaction energies signifies that the Badger–Bauer rule is not valid for the linear X–H···Y hydrogen-bonded complexes of phenylacetylene, indole, and phenol with different bases, even though the hydrogen bonding abilities of C–H, N–H, and O–H groups are relatively different. It must be pointed out that a general trend of the overall increase in the stabilization energies from water complexes to trimethylamine complexes is observed. Furthermore, Figure 2 also shows the plot of shifts in the X–H stretching frequencies against the electrostatic and dispersion components of the interaction energy. Figures S5–S7 (see the Supporting Information) show plots of shifts in the X–H stretching frequencies against various energy components of SAPT analysis. A linear correlation between the X–H stretching frequency shifts and the (i) electrostatic component, (ii) induction component, and (iii) sum of electrostatic, induction, and charge-transfer components was observed in all of the three cases. In SAPT, the electrostatic and induction components correspond to the first- and second-order perturbative correction to the total interaction energy.\textsuperscript{31} The observed linear correlation between the X–H stretching frequency shifts and the electrostatic component as well as the induction component suggests that these perturbative corrections are essentially localized on the X–H group. On the other hand, all of the other energy components show modulation in the frequency shifts. It can be inferred from the plots shown in Figure 2 that the electrostatic component of the interaction energy is responsible for the X–H frequency shifts in the hydrogen-bonded complexes irrespective of the identity of the hydrogen bond donor. Based on the comparison of plots of the X–H stretching frequencies against various components of SAPT2 interaction energy (Figures 2 and S5–S7, see the Supporting Information), it can be inferred that dispersion and exchange-repulsion components are better indicators of the stabilization energy trends vis-à-vis vibrational frequency shifts in hydrogen-bonded complexes.\textsuperscript{32} The dispersion and exchange-repulsion terms

| complex    | $E_{\text{exch}}$ | $E_{\text{disp}}$ | $E_{\text{CT}}$ | $E_{\text{exch}}$ | $E_{\text{disp}}$ | $E_{\text{SAPT0}}$ | $E_{\text{SAPT2}}$ | $E_{\text{exch}}/E_{\text{disp}}$ |
|------------|------------------|-------------------|----------------|------------------|-------------------|-------------------|-------------------|------------------|
| PA–H$_2$O  | −18.0            | −5.1              | −1.1           | −5.7             | 16.6              | −14.4             | −12.2             | 3.16             |
| PA–MeOH    | −21.6            | −6.5              | −1.5           | −9.6             | 23.5              | −16.7             | −14.1             | 2.25             |
| PA–EtOH    | −24.3            | −7.0              | −1.7           | −14.2            | 30.5              | −17.6             | −15.1             | 1.71             |
| PA–MeOME   | −24.5            | −7.7              | −1.9           | −14.3            | 31.7              | −17.5             | −14.9             | 1.71             |
| PA–EtOEt   | −28.8            | −9.4              | −2.3           | −21.2            | 41.4              | −21.1             | −18.0             | 1.36             |
| PA–NH$_3$  | −26.1            | −8.4              | −1.5           | −7.6             | 26.1              | −18.2             | −16.1             | 3.43             |
| PA–NH$_3$Me| −30.5            | −10.5             | −2.0           | −12.2            | 34.6              | −20.9             | −18.6             | 2.50             |
| PA–NH$_3$Me$_2$ | −35.5       | −15.2             | −2.4           | −17.4            | 45.2              | −23.6             | −21.0             | 2.04             |
| PA–NMe$_3$ | −38.8            | −15.2             | −2.4           | −17.4            | 45.2              | −23.6             | −21.0             | 2.04             |
| IN–H$_2$O  | −36.4            | −11.0             | −2.6           | −10.0            | 33.0              | −26.6             | −24.3             | 3.64             |
| IN–MeOH    | −42.7            | −12.7             | −2.8           | −22.2            | 48.2              | −32.7             | −29.4             | 1.92             |
| IN–EtOH    | −48.3            | −15.4             | −3.4           | −28.6            | 59.9              | −35.9             | −32.4             | 1.69             |
| IN–MeOEt   | −48.8            | −18.6             | −4.8           | −33.0            | 61.0              | −33.1             | −29.5             | 2.12             |
| IN–EtOEt   | −56.3            | −21.9             | −5.6           | −35.0            | 79.8              | −37.2             | −33.2             | 1.61             |
| IN–NH$_3$  | −53.9            | −19.0             | −4.2           | −14.1            | 55.0              | −33.5             | −32.1             | 1.62             |
| IN–NH$_3$Me| −60.8            | −23.6             | −5.3           | −20.3            | 69.2              | −37.1             | −35.4             | 3.00             |
| IN–NH$_3$Me$_2$ | −69.6     | −29.7             | −6.3           | −29.9            | 89.2              | −42.2             | −40.0             | 2.33             |
| IN–NMe$_3$ | −74.7            | −33.7             | −6.7           | −32.0            | 99.0              | −43.9             | −41.4             | 2.33             |
| PH–H$_2$O  | −47.7            | −15.8             | −4.6           | −12.7            | 48.2              | −32.6             | −30.0             | 1.63             |
| PH–MeOH    | −57.3            | −20.6             | −5.9           | −23.6            | 68.0              | −39.1             | −33.5             | 2.43             |
| PH–EtOH    | −58.7            | −21.9             | −5.8           | −29.6            | 75.1              | −41.1             | −35.1             | 1.98             |
| PH–MeOEt   | −62.0            | −24.6             | −7.1           | −26.3            | 77.9              | −41.5             | −35.0             | 2.18             |
| PH–EtOEt   | −68.6            | −27.9             | −7.6           | −39.3            | 94.8              | −48.3             | −41.1             | 1.75             |
| PH–NH$_3$  | −69.8            | −27.9             | −7.7           | −17.7            | 76.7              | −43.1             | −38.7             | 3.94             |
| PH–NH$_3$Me| −82.6            | −35.1             | −9.3           | −29.6            | 101.3             | −50.7             | −45.9             | 2.79             |
| PH–NH$_3$Me$_2$ | −87.8       | −39.8             | −10.1          | −32.9            | 111.8             | −53.6             | −48.6             | 2.67             |
| PH–NMe$_3$ | −93.8            | −45.7             | −11.1          | −36.7            | 124.7             | −57.1             | −51.5             | 2.56             |
in SAPT do not have any classical analogues and are governed by the electron correlation between the monomers and the overlap of wave functions of the two monomers, respectively. Evidently, these two components depend on the nature of the interacting molecules and thus regulate the total stabilization energy.

The experimental dipole moments and calculated polarizabilities for the various hydrogen bond acceptors are given in Table S4 (see the Supporting Information). Figure 3 depicts the plots of shifts in the X−H stretching frequencies against the dipole moment of the acceptor for the three sets of donors. Surprisingly, for all of the three donors, viz., C−H, N−H, and O−H groups considered in this study, the shifts in X−H (X = C, N, and O) stretching frequencies decrease with the increase in the dipole moment of the acceptor, separately. A linear correlation with negative slope was observed between the X−H stretching frequency shifts and the dipole moments of the acceptor. It must be pointed out here that in all of the three cases the data points corresponding to hydrogen-bonded complexes with ethers (both dimethyl and diethyl ethers) were found to be outliers, even though they follow the general trend, i.e., dimethylether with a higher dipole moment shows a smaller frequency shift. The linear fits with all of the data points including those corresponding to dimethyl and diethyl ethers, shown in Figure S8 (see the Supporting Information), also suggest a general linear trend but with relatively lower quality fits. The deviation of the ethers from the linear correlation can be attributed to relative orientation of the ethers vis-à-vis other complexes because of geometry constraints (steric effects). In these two cases, the dipole of the acceptor and the X−H bond are not in the same plane, which is in contrast to all of the other cases, thereby leading to suboptimal shifts. The linear correlations in Figure 3 appear to be counterintuitive given that the shifts in the hydrogen-bonded X−H stretching frequencies are linearly correlated with the electrostatic component of the total stabilization energy, as can be seen in Figure 2. The dipole moment, which is an indicator of charge separation, in a classical sense, does not favor the hydrogen bond formation. It is interesting to note that extrapolation of these fits to zero dipole moment yields very large shifts in the hydrogen-bonded X−H stretching vibrations. It can therefore be inferred that if the charge distribution of the lone pair of electrons, which act as hydrogen bond acceptors, is compensated by the charge distribution from the rest of the molecule it would lead to the formation of strongest hydrogen-bonded complexes. It is important to emphasize that the electrostatic component in SAPT corresponds to the first-order perturbation correction to the interaction energy of the complex. The observed inverse correlation between the acceptor dipole moment and the frequency shifts hints that the increased dipole moment of the acceptor molecule results in lower first-order correction to the stabilization energy of the complexes. Furthermore, this also suggests that the trends in the quantum and classical descriptions are opposing.

Figure 3 also shows the plots of shifts in the X−H stretching frequencies against the calculated polarizability of the acceptors, which show clear modulation in the trend (dashed line). However, the shifts for the X−H···O and X−H···N hydrogen-bonded complexes show linear correlation separately. A comparison of Figures 2 and 3 suggests that the electrostatic component of the stabilization energy is a better physical parameter to understand the X−H frequency shifts, as it is independent of geometry constraints and nature of the acceptor.

The natural bonding orbital (NBO) theory suggests that charge transfer between the hydrogen acceptor and donor plays a crucial role in hydrogen bonding complexes. Using NBO calculations at the MP2/aug-cc-pVDZ level of theory, the magnitude of charge transfer from the filled orbital of the hydrogen acceptor to the vacant antibonding (σ*) orbital of the donor group (X−H) and the population changes in the σ*(X−H) orbitals due to the hyperconjugative charge transfer for various X−H···Y (X = C, N, and O; Y = O and N) hydrogen-bonded complexes of phenylacetylene, indole, and phenol complexes, respectively.
against (A) charge transfer to the vacant antibonding ($\sigma^*$) orbital of the donor group (X−H) and (B) population changes in the $\sigma^*(X−H)$ orbitals. It is clearly evident from plots Figure 4 A,B that the frequency shifts are linearly correlated with both the charge transfer and the population changes occurred during the hydrogen bond formation. Moreover, the data from all of the three sets of complexes have shown a single correlation, suggesting that NBO parameters are better descriptors for the vibrational frequency shifts. It must be pointed out that the plots of frequency shifts for each of the three sets of complexes against the charge-transfer component calculated using SAPT do not show any trend (see panel C of Figures S5–S7; Supporting Information), which is completely in contrast to the linear correlation observed in NBO (see panel A of Figure 4). The discrepancy arises due to different treatment of charge-transfer components in SAPT and NBO.54−57

Furthermore, topological parameters were calculated using the atoms-in-molecules (AIM) theory for all of the complexes and are listed in Table S6 (see the Supporting Information). Figure 4 also shows the plots of shifts in the X−H···O and X−H···N (X = C, N, and O) hydrogen bonds was
observed. These results suggest that the topological parameters are dependent on the type of acceptor atom (O vs N), unlike NBO parameters.

Figure 2 shows that the shift in the X–H stretching fundamentals due to hydrogen bonding is linearly correlated to the electrostatic component of the stabilization energy ($E_{\text{elec}}$) and has the functional form given by eq 1

$$\Delta \nu_{\text{HB}} = \gamma E_{\text{elec}} - \kappa$$

Thus, $E_{\text{elec}}$ effectively captures the changes in the potential energy function of the X–H oscillator because of the formation of hydrogen bonds. Furthermore, $\gamma$ can be termed as the electrostatic tuning rate with units of $\text{cm}^{-1} \text{kJ mol}^{-1}$, akin to the stark tuning rate,58,59 which describes the sensitivity of the X–H oscillator to undergo shifts upon hydrogen bonding per unit increase in the electrostatic component of the stabilization energy. The linear correlations in Figure 2 result in electrostatic tuning rates of 8.3, 9.6, and 10.5 $\text{cm}^{-1} \text{kJ mol}^{-1}$ for the hydrogen-bonded complexes of phenylacetylene, indole, and phenol, respectively, indicating that the O–H oscillator is more sensitive to changes in the electrostatic component followed by N–H and C–H oscillators. Furthermore, in the case of zero-shifting hydrogen bond, wherein $\Delta \nu_{\text{HB}} = 0$, the corresponding electrostatic component of the stabilization energy, $E_{\text{elec}}^0 = \kappa/\gamma$, can be termed as critical electrostatic energy and $\kappa$ can be termed as the stopping frequency. Thus, it can be inferred that if $E_{\text{elec}} > E_{\text{elec}}^0$, it will lead to red shifts, whereas $E_{\text{elec}} < E_{\text{elec}}^0$ will lead to blue shifts. One of the artifacts of the linear fitting is that the zero electrostatic component will lead to a blue shift equivalent to $\kappa$, which is physically absurd. This essentially implies that interpretation should be carried out with utmost care on the basis of an appropriate physical model and a single correlation may not work for the entire range. Similar physical models can be built for all of the linear correlations observed for the frequency shifts against dipole moment. On the other hand, in the case of nonlinear correlation as observed in the plot of frequency shifts against proton affinities of the acceptors

$$\Delta \nu_{\text{HB}} = a + b_1 (\text{PA}_a) + b_2 (\text{PA}_a)^2$$

In the fitting function, the parameters $a$, $b_1$, and $b_2$ in eq 2 are mathematical constructs and may not have any physical meaning, as is the present scenario, but capture the behavior of change in the potential energy function. This fitting function shows only the nonlinear dependence on the independent parameter plotted on abscissa. However, if the initial portion of the curve is fitted to a straight line, then the
x-intercept can be interpreted as the value of the proton affinity that will produce zero shift.

CONCLUSIONS

Several linear $X\rightarrow H\rightarrow Y$ ($X = C, N$, and $O$; $Y = O, N$) hydrogen-bonded complexes of phenylacetylene, indole, and phenol were analyzed with various interacting bases using ab initio calculations, and the following inferences can be made:

- The stabilization energies are in the order phenol $>$ indole $>$ phenylacetylene, which can be attributed to the hydrogen bonding ability of the donor ($O\rightarrow H > N\rightarrow H > C\rightarrow H$).
- The SAPT2/cc-pVTZ energy decomposition analysis shows that for all of the three sets of complexes the observed red shifts in the $X\rightarrow H$ stretching frequencies are linearly correlated with the electrostatic component of stabilization energy, whereas the dispersion and exchange-repulsion component plots follow the trend similar to that of the total stabilization energy, irrespective of the hydrogen bonding ability of the donor.
- The linear correlation between the electrostatic component and the $X\rightarrow H$ frequency shifts suggests that the first-order perturbative correction to the total energy is essentially localized on the $X\rightarrow H$ group.
- The shifts in $X\rightarrow H$ stretching frequencies for $C\rightarrow H$, $N\rightarrow H$, and $O\rightarrow H$ donor groups in each case were inversely correlated to the dipole moments of the acceptor, which indicates that the larger the dipole moment, the lower is its ability to perturb the $X\rightarrow H$ oscillator.

COMPUTATIONAL METHODOLOGY

The details of the computational methodology adopted for the present work are given in the Supporting Information. Briefly, geometry optimization was followed by vibrational frequency calculations of hydrogen-bonded complexes using the MP2/aug-cc-pVDZ level of theory and the stabilization energies were calculated incorporating ZPE and BSSE corrections. Furthermore, anharmonic vibrational frequencies were also calculated for selected complexes using the B3LYP-D3/aug-cc-pVDZ level following geometry optimization at the same level of theory. The single-point energies calculations were carried out at the at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ levels. Energies at MP2/aug-cc-pVTZ and MP2/aug-cc-pVDZ levels were extrapolated to estimate MP2/CBS energies using the extrapolation scheme given by Helgaker and co-workers, wherein the electron correlation error is on the order of $N^{-3}$ for the aVNZ basis set. The CCSD(T)/CBS energies were estimated on the basis of the fact that the difference in stabilization energies between MP2/aug-cc-pVDZ and MP2/CBS levels is similar to that between CCSD(T)/aug-cc-pVDZ and CCSD(T)/CBS levels. Furthermore, the energy decomposition analysis of all of the hydrogen-bonded complexes considered in the present study was also carried out using second-order symmetry-adapted perturbation theory (SAPT2). The geometry optimization and vibrational frequency calculations were carried out using the Gaussian 16 suite of programs with the graphical interface GaussView 5. Anharmonic vibrational frequencies were calculated using the second-order vibrational perturbation theory (VPT2) implemented in Gaussian 16. The SAPT calculations were performed using the PS14 program.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01802.

Computational methodology along with plots of vibrational frequency shifts against various parameters, tables containing stabilization energies at various levels of theory, tables of estimated proton affinities, experimental dipole moments and calculated polarizabilities of various hydrogen bond acceptors, NBO and AIM analyses, and coordinates of all optimized structures (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: saumiksen@chem.iitb.ac.in, saumik.sen@mail.huji.ac.il (S.S.).
*E-mail: naresh@chem.iitb.ac.in (G.N.P.).

ORCID
G. Naresh Patwari: 0000-0003-0811-7249

Present Address
1Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel (S.S.).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

G.N.P. is supported by the Board of Research in Nuclear Sciences [Grant No. 2012/34/14] and Department of Science and Technology [Grant No. SB/S1/PC-29/2012]. S.S. thanks the Department of Chemistry, IIT Bombay, for teaching assistantship. The authors wish to thank the reviewers whose comments have improved this manuscript substantially and also enhanced understanding of concepts in hydrogen bonding. They are also grateful to acknowledge the Space-Time-2 supercomputing facility at IIT Bombay for the computing time.

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