Blue-shifted Hydrogen Bonds with Proton-donors Incapable of Rehybridization

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Blue-shifted hydrogen bonds were found for F–He–H···Y ($Y{=}N_2$, CO, and He) systems where the proton-donor (He) was incapable of rehybridization. This finding indicated that rehybridization is not a generally applicable driving force for the blue shift.

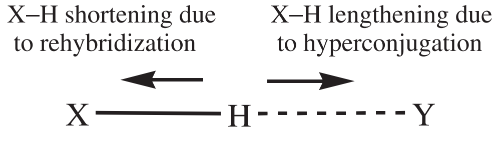
The major driving forces for the hydrogen bond (X–H···Y) are usually believed to include electrostatic and charge-transfer interactions. Both these interactions can weaken the X–H bond and consequently, increase the X–H bond length and decrease the X–H stretching vibration frequency. This effect is called a red shift. It represents the most important, easily detectable manifestation of the formation of a hydrogen bond.[1]

However, it was found recently that some hydrogen bonds (e.g. $F_3CH\cdots OH_2$) exhibit a blue shift of the X–H stretching vibration frequency. The X–H bond length in these systems is accordingly shortened upon the hydrogen bond formation.[2,3] In order to account for these peculiar and fascinating behaviors, a number of theories about the blue shift have been proposed.

Certainly all these theories have contributed a lot to the understanding of the blue shift. Nonetheless, some previous theories about the physical origin of the blue shift may not be generally applicable. For example, Hobza et al. once proposed that the blue shift was caused by the charge transfer from the proton acceptor Y to remote highly electronegative atoms in X (e.g. F in CF_3) instead of the X–H σ* orbitals.[2] Although this insightful theory was applicable to a number of blue-shifted hydrogen bonds, we recently found that a simple conventional N–H···O hydrogen bond might also be blue shifted if sufficient steric effect was introduced.[4] This finding indicated that Hobza's theory about the blue shift is not adequate.

Another interesting theory about the blue shift was recently provided by Alabugin et al.[5] (Scheme 1). According to the theory, the X–H bond length in the X–H···Y complex is controlled by a balance of two main factors acting in opposite directions. "X–H bond lengthening" due to n(Y)→ σ*(H–X) hyperconjugative interaction is balanced by "X–H bond shortening" due to increase in the s-character of the X–H bond.

A central idea in Alabugin's theory is the rehybridization of X. If X is incapable of rehydridization, using the theory one should predict no blue shift because the bond lengthening effect caused by hyperconjugation cannot be balanced by any bond shortening effect under this condition. Although Alabugin et al. showed that some systems incapable of rehybridization (e.g. H–H···Y) indeed can exhibit red shifts only,[5] in the present study, however, we wish to report that some systems incapable of rehydridization can still exhibit a blue shift.



Scheme 1. Alabugin's theory about the blue shift.

The systems we chose to study are $F{-}N_g{-}H\cdots Y$ (N_g=He, Ne, Ar; $Y{=}N_2$, CO, N_g). These complexes are of considerable interest currently because of the recent discovery of the fascinating HArF and HKrF molecules.[6] Strikingly, a large blue shift of the H–Kr stretching frequency of H–Kr–Cl was observed experimentally upon complexation with N_2.[7] Recent excellent theoretical studies by McDowell have clearly demonstrated that $FArH\cdots N_2$, FArH···CO, and $FKrH\cdots N_2$ are linear blue-shifted hydrogen bonds.[8]

We envisioned that F–He–H and F–Ne–H may also form blue-shifted hydrogen bonds. Therefore, we conducted MP2/aug-cc-pVQZ//MP2/cc-pVDZ calculations on their linear hydrogen-bonded complexes with N_2, CO, and N_g.[9] For comparison, we also included F–Ar–H in the study. It is worthy to note that although F–He–H and F–Ne–H have not been observed experimentally, their possible existences have been studied theoretically.[10]

Our results indicated that F–Ne–H and its complexes are not stable species. These observations are consistent with Wong's work because at CCSD/cc-pVTZ level he found that F–Ne–H was not a stable species, either.[10] Nevertheless, H–He–F, H–Ar–F and their linear complexes with N_2, CO, and N_g are all in real minima on the MP2/cc-pVDZ potential surface without any imaginary frequency.

For F–Ar–H, the Ar–H bond length in the free monomer is 1.417 Å (See Table 1). This value is slightly larger than McDowell's value (1.326 Å) at MP2/6-311++G(2d,dp) level. Upon hydrogen bonding with N_2 the Ar–H bond length decreases to 1.397 Å. This means a shortening of 0.020 Å. The Ar–H stretching frequency accordingly increases by $184.6\,cm^{-1}$. McDowell's bond shortening value is 0.012 Å. His frequency blue shift is $+153.0\,cm^{-1}$. The binding energy of the complex is 7.1 kJ/mol.

Table 1. Bond lengths (d: Å), stretching frequencies (ν: cm^{-1}), and binding energies (ΔE: kJ/mol) of $F{-}N_g{-}H\cdots Y$ complexes

Species	d_{H-Ng}	ν_{H-Ng}	d_{Ng-F}	ν_{Ng-F}	ΔE^{a}
F–He–H	0.914	1877.2	1.366	912.6	—
$F{-}He{-}H\cdots N_2$	0.884	2053.2	1.370	1019.0	−8.2
F–He–H···OC	0.895	1972.7	1.363	1004.3	−2.2
F–He–H···He	0.914	1879.2	1.366	915.2	0.1
F–Ar–H	1.417	1631.4	1.974	509.4	—
$F{-}Ar{-}H\cdots N_2$	1.397	1816.0	1.984	500.4	−7.1
F–Ar–H···OC	1.402	1767.5	1.976	507.3	−3.0
F–Ar–H···Ar	1.414	1656.5	1.976	508.3	−1.6

[a] Binding energy is corrected with zero point energy at MP2/cc-pVDZ and basis set superposition error (BSSE) at MP2/aug-cc-pVQZ level.

The F–Ar–H$\cdots$OC complex also shows the blue shift. The Ar–H bond length is reduced by 0.015 Å upon the complexation. The concomitant vibration blue shift is $+136.1\,\text{cm}^{-1}$. The binding energy is 3.0 kJ/mol.

Interestingly, we found that F–Ar–H can also form a stable linear complex with Ar, although the binding energy of this complex is very small (1.6 kJ/mol). The Ar–H bond length also decreases in this complex by 0.003 Å. The concomitant vibration blue shift is $+25.1\,\text{cm}^{-1}$. It is worthy to note that this complex may exist when F–Ar–H is in the Ar matrix.

Ar has 3s and 3p orbitals. Therefore, Ar may be capable of rehybridization. However, He only has 1s orbital (2s and 2p of He are too high in energy). Therefore, He should be incapable of rehybridization. Since the hyperconjugation interaction is always present, according to Alabugin's theory one should predict no blue shift for any He–H hydrogen-bonded complex. Unfortunately, this prediction is not correct for F–He–H$\cdots$$N_2$ (Figure 1).

According to MP2/cc-pVDZ calculations, the He–H bond length in the free monomer is 0.914 Å. Upon complexation with N_2, the He–H bond length becomes 0.884 Å. This means a shortening of 0.030 Å. The concomitant vibration blue shift is $+176.0\,\text{cm}^{-1}$. The binding energy is 8.2 kJ/mol. Clearly, this system has a reasonably stable blue-shifted hydrogen bond.[11]

The He–H bond length in F–He–H$\cdots$OC is also shortened by 0.019 Å. The concomitant vibration blue shift is $+95.5\,\text{cm}^{-1}$. The binding energy is 2.2 kJ/mol. Therefore, this system is also a stable blue-shifted hydrogen-bonded complex.

Finally, F–He–H$\cdots$He does not show any observable change in the He–H bond length. Nevertheless, the He–H stretching is blue shifted by $+2.0\,\text{cm}^{-1}$ in this complex. The binding energy of this complex after zero point energy corrections is slightly positive.

At this point, it is worthy to note that we also tried F–N_g–H complexes with other molecules such as HF and F_2. However, none of these complexes is a stable species. This is clearly caused by the high reactivity of F–N_g–H. Also, although all the complexes in Table 1 are blue shifted, there are, however, red-shifted hydrogen-bonded complexes of F–N_g–H. One good example (i.e. F–Ar–H$\cdots$$P_2$) has been provide by McDowell.[8]

The above results indicate that Alabugin's theory about the blue shift is not generally applicable. Certainly this does not mean that Alabugin's theory is not valuable. A nice point about this theory is the chemical perspective it provides for the blue-shifted hydrogen bonds. Thus possibly a chemist would find that it is easier to use Alabugin's theory to understand the blue-shifted hydrogen bonds of the "common" systems such as C–H, N–H, and O–H. Nevertheless, few "chemistry" theories are fully correct, because they are more from empirical rules than from first-principle physics.

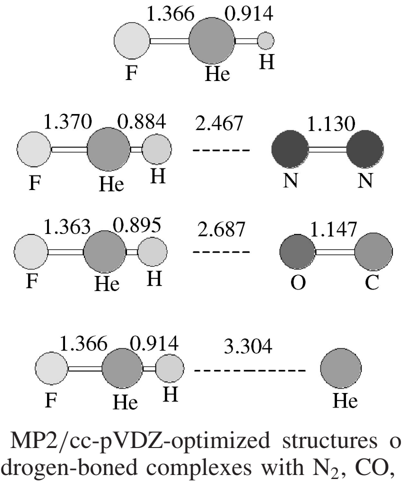


Figure 1. MP2/cc-pVDZ-optimized structures of F–He–H and its hydrogen-boned complexes with N_2, CO, and He.

What is the universal cause of the blue-shifted hydrogen bond? A recent study has provided the answer.[12] According to it, there is a balance between the X–H elongation effect due to the orbital interactions and the X–H contraction effect due to the Pauli and nuclei-nuclei repulsions. In F–He–H$\cdots$$N_2$, He carries significant amount of positive charge.[10] Therefore, in addition to $H^{\delta+}\cdots N_2$ attraction there is considerable $He^{\delta+}\cdots N_2$ attraction. The attraction between $He^{\delta+}\cdots N_2$ is strong enough to force H and N_2 to be too close to each other. At this point, H senses considerable Paul and nuclei repulsion from N_2. Instead of elongation, He–H bond is forced to contract.

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