TẠP CHÍ KHOA HỌC
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Liên kết hydrogen không cổ điển: Tổng quan chính về sự chuyển dời xanh hoặc đỏ của tần số dao động hóa trị liên kết C-H

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TÓM TẮT

Tổng quan hiện tại hướng tới một cái nhìn tổng quan về sự chuyển dời xanh hoặc đỏ của tần số dao động hóa trị liên kết C-H với nguyên tử carbon ở các trạng thái lai hóa khác nhau (C_{sp}, C_{sp2}, C_{sp3}). Các đặc điểm của liên kết hydrogen không cổ điển bao gồm sự thay đổi độ dài và tần số dao động hóa trị liên kết C-H khi tạo phức đã được xem xét kỹ lưỡng với C-H có độ phân cực khác nhau đóng vai trò phần tử cho proton và các nguyên tử O, S, Se, Te, N hoặc electron π đóng vai trò phần tử nhận proton. Kết quả cho thấy, so với các nguyên tử S, Se và Te, nguyên tử O đóng vai trò quan trọng đối với sự chuyển dời xanh tần số dao động hóa trị C-H tham gia liên kết hydrogen. Mức độ chuyển dời đỏ hoặc xanh của tần số dao động hóa trị C-H chủ yếu được quyết định bởi độ phân cực (DPE) của liên kết C-H và độ base pha khí (PA) của phần tử nhận proton trong monomer ban đầu, bên cạnh tương tác yếu có liên quan và dạng cấu trúc hình học của phức tạo thành. Hơn nữa, tỉ số DPE/PA có thể được đề xuất để phân loại liên kết hydrogen cổ điển và không cổ điển.

**Tác giả liên hệ chính.*

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Non-conventional hydrogen bonds: A brief review of blue shift or red shift of C-H stretching frequency

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ABSTRACT

The present work is geared towards having an overview of the blue shift or red shift of C-H stretching vibration with various hybridized carbon atoms (C_{sp}, C_{sp2}, C_{sp3}). The features of the non-conventional hydrogen bond, including changes in length and stretching frequency of the C-H bond upon complexation, were thoroughly reviewed based on C-H proton donors with different polarity and various proton acceptors such as O, S, Se, Te, N atoms or π electrons. The results show that the O atom, as compared to the S, Se, and Te ones acting as proton acceptors, plays a peculiar role in the C-H blue shift of stretching frequencies involving hydrogen bonds. It is found that the magnitude of red- or blue-shift of the C-H stretching frequency in the hydrogen bond is mainly determined by the C-H polarity (DPE) and gas phase basicity (PA) of the proton acceptor in the isolated isomer, besides relevant weak interactions and the geometrical structure of the formed complex. Furthermore, for the categorization of conventional and non-conventional hydrogen bonding, an intriguing DPE/PA index should be suggested.

1. INTRODUCTION

Understanding non-covalent interactions is critical for unraveling the mysteries of cellular processes in health concerns and developing novel treatment protocols/methods, medicines, and materials.[1] Among them, a hydrogen bond A–H···B is a unique interaction that is important in many fields of research, including molecular recognition, protein folding, structural organization of nucleic acids, crystal and polymer packing, self-assembly, supramolecular chemistry, solvation, and even organic synthesis.[2-5] In a conventional hydrogen bond, A and B are highly electronegative elements, and the hydrogen atom which is strongly electropositive, plays a bridging.[4,6] For example, the conventional hydrogen bonds including N-H···O, N-H···N, O-H···O, and O-H···N, which play the most important role in supramolecular chemistry and structural biology, are strong and mostly driven by the electronegativity differences between the proton donor and acceptor atoms.[7-13] The characteristics of a conventional hydrogen bond are the A–H bond elongation along with a decrease in stretching frequency, which is called a red-shifting

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hydrogen bond (abbreviated as RSHB). It is well known that a lower strength of the A-H bond in the hydrogen bond in comparison with that in the isolated monomer results from a primarily electrostatic force of attraction between the H atom and B atom in the complex.[14] For the non-conventional hydrogen bond, an A-H elongation, and its stretching frequency red shift are suggested by a n(B)→σ*(A–H) intermolecular hyperconjugation overcoming an increase in the s-character and polarization of the A–H bond.[15]

Since the 1980s, however, the non-conventional hydrogen bond with the opposing features including of a shortening in the A-H bond length and a concomitant increase in stretching vibration following complexation has been found, and named the blue-shifting hydrogen bond (abbreviated hereafter as BSHB).[16] Nowadays, the BSHB's characteristics are well observed and have been studied by both accurate quantum calculations and high-resolution experiments. Although the characteristics of the blue shift phenomenon in hydrogen bonds are known clearly, the nature of this new hydrogen bond type is still questionable.

Numerous hypotheses/theorems have been proposed to explain the physical origin of the blue-shifting or red-shifting of non-conventional hydrogen bonds, however, no general explanation has been effectively applied. Among the available rationalizations for the BSHB, some schemes have attracted the most attention, including (*i*) The first explanation proposes a two-step mechanism in which electron density is mainly transferred from B to the remote atoms related to A rather than to the σ*(A–H) orbital, and therefore the A–H bond is shortened as a result of structural re-organization of the proton donor framework.[17-19] (*ii*) The second theorem attributes the short-range repulsive forces encountered by the complex's H atom as the complex attempts to stabilize itself, which would be the reason for the contraction of the A–H bond length.[20,21] (*iii*) The third scheme is that the observed contraction is due in part to the impact of the electric field around B, because an electric field is detected after the A–H bond length is reduced.[22,23] (*iv*) The fourth theory is based on two opposite factors: the A atom's *s*-character percentage and the polarity of the A–H bond on one side, and the intermolecular hyperconjugative interaction on the other, which transfers electron density from the *n*(B) lone pair to the σ*(A–H) orbital on the other side. The A–H bond is shortened when the former prevails. When the latter surpasses the former, the A–H bond is lengthened.[15,24] (*v*) The fifth scheme of the A–H bond contraction along with the increase in stretching frequency proposes that an electron density transfer comes from the presence of B on the right-hand side of the H atom to the A–H bond in the A–H···B hydrogen bond.[25]

Other explanations of BSHB in the non-conventional complexes have been continuously presented. For instance, according to Wei Wu *et al.*, the rivalry between the long-range electrostatic interaction between the A-H bond and the B atom and the short-range hyperconjugative interaction causes the direction of shift in the A-H stretching frequency.[26] Based on the Valance Bond Self-Consistent Field (VBSCF) approach, the authors proposed that the covalent state of the A-H bond tends to shift to blue, whereas its ionic state causes a red shift of stretching frequency.[27] The competition between the two properties induces changes in the A-H stretching frequency. Very recently, the Head-Gordon group from UC Berkeley suggested that Pauli repulsion leads to a contraction of the A-H bond accompanied by an increase in its stretching frequency, whereas electrostatic and dispersion forces cause the A-H bond to lengthen and decrease its stretching frequency.[28] Long-range electrostatic and Pauli exchange interactions overcome the overall impact of polarization and charge transfer interactions, causing the A-H bond to shorten and its stretching frequency to increase.[29] In general, each scheme has benefits and disadvantages, but they all explain the BSHB phenomenon using the features of the hydrogen-bonded complex.

Among conventional and non-conventional hydrogen bonds, the hydrogen bond involving the C-H bond as the proton donor is extremely important because of its prevalence and diversity in nature. Although their binding energies are typically less than 5÷6 kcal mol^{-1} (~21÷25 kJ mol^{-1}), their cumulative contributions prove to be considerable in many cases. Weak hydrogen bonds are a decisive factor in the structure, conformation, and tautomeric preferences of many organic compounds in their crystalline phases, as well as the functional structures of biological macromolecules in living systems.[5,30-33] For instance, the presence of hydrogen bonds C-H···O/S, C-H···N, C-H···π, C-H···X (X = F, Cl, Br) has been observed in molecular clusters, enzymatic mechanisms, proteins, DNA, RNA, crystal packing, etc.[34-38] Every protein contains a huge number of C–H···O/N hydrogen bonds which can occur in thousands of large proteins. Experimentally and theoretically, a wide range of non-conventional hydrogen bonds involving the C-H bond in C-H···O/N/halogen/π hydrogen bonds were found, in which the C-H···O/N hydrogen bonds are most frequently seen utilizing IR and Raman spectroscopy.[36,39-53,57,61] Trudeau *et al.* established the first experimental proof for the blue shift of C-H stretching frequency by investigating complexes of fluoroparaffins and several proton acceptors.[16] Since the 1980s, evidence of an increase in the C-H stretching frequency in hydrogen bonds has been detected in several complexes.[54-56] Due to the vast quantity and rich diversity of C-H bonds in organic chemistry, the organic synthesis approach based on activation and functionalization of C-H bonds is the primary strategy at the moment.[57-59] The existence of hydrogen bonds comprising C-H bonds as proton donors in the intermediates is seen in this approach, which helps the creation of desirable products.[2,60] Remarkably, the vibrational spectral parameters of the hydrogen bond (blue-shift or red-shift) have been recently applied as direct spectroscopy evidence for addressing several matters of concern such as environmental problems[126-128] or the shortage of valuable materials.[129-130]

Nowadays, characteristics of red or blue shifting stretching frequencies in non-conventional hydrogen bonds, particularly the participation of the C_{sp3}-H covalent bond as a proton donor, have received a lot of theoretical and experimental attention. A variety of hydrogen-bonded binary complexes of various haloforms were studied in a variety of physical environments, including supersonic jet expansion, inert gas matrix, cryoliquid, and gas phase at room temperature.[61-69,86] In most situations, the C_{sp3}-H covalent bond exhibits a red-shift of stretching frequency in addition to a blue-shift in certain cases, implying its weakening, similar to the characteristics of conventional hydrogen bonds. However, the underlying reason for the C_{sp3}-H bond shortening or lengthening and its corresponding frequency change remains a subject of debate. Apart from the initial results which are derived primarily from the physicochemical properties of hydrogen bonds with the C_{sp3}-H moiety and numerous proton acceptors, many investigations into various polarizations of the C_{sp3}-H bond were conducted to unravel the origin of BSHB and the classification of the hydrogen bond. The medium polarity of the C_{sp2}-H covalent bond between C_{sp3}-H and C_{sp}-H bonds makes its stretching frequency shift more sensitive when interacting with different proton acceptors. As a result, the significant stretching frequency blue shifts have recently been found in the C_{sp2}-H bond upon the formation of hydrogen-bonded complexes.[70-71] Our recent findings indicate that it is more appropriate to consider the C-H blue or red shift of non-conventional hydrogen bonds from a different perspective, which is based on inherent properties such as the polarity of the C-H bond by deprotonation enthalpy (DPE) and gas phase

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basicity of the B counterpart by proton affinity (PA) in the isolated monomers acting as proton donors and acceptors.[72,73,108] We also propose that the DPE/PA ratio in an isolated monomer be used to predict the type of hydrogen bond that would be found upon complexation.[100,108]

The primary purpose of the present review is to give insight into the characteristics of non-conventional hydrogen bonds involving the different hybridized C-H covalent bonds, which include changes in length and stretching frequency of the C-H bond, as well as give a clearer explanation for the formation of blue or red shifting hydrogen bonds. The effect of the gas phase basicity of the proton acceptor on the characteristics of non-conventional hydrogen bonds is also another purpose of this overview. It is noted worthy that our recent results about hydrogen bonds are also used for discussion and comparison with several authors in this work.

2. THEORETICAL METHODS

The quantum chemical methods available in the packages GAUSSIAN (09), AIMALL, GenNBO 5.G, Psi4, SAPT2012.2, NCIPlot, VMD 1.9.3, Gnuplot, Multiwfn… were used for relevant calculations.[74-82] Methods with high accuracy such as perturbation theory method (MP2), coupled cluster method (CCSD(T)) and density functional theory (DFT) including ωB97XD, M06-2X, B3LYP-D3… in combination with suitable basis sets depending on investigated systems were employed. The MP2 method, in conjunction with the basis sets aug-cc-pVDZ, aug-cc-pVDZ-pp, aug-cc-pVTZ, aug-cc-pVTZ-pp, 6-311++G(3df,2pd), def2-TZVPD… was utilized to optimize the geometries of monomers and complexes. Geometries of the monomer and complex are optimized without symmetry constraints at the chosen suitable level of theory. The infrared spectrum is subsequently calculated for stable structures on the potential energy surfaces in order to determine the stretching vibration modes of the monomer and complex. Deprotonation enthalpies (DPE) and proton affinity (PA) of monomers in investigated systems were calculated at the coupled cluster level CCSD(T) with large basis sets such as 6-311++G(3df,2pd), aug-cc-pVTZ, aug-cc-pVQZ… to obtain more accurate energetic values.

3. DISCUSSION

With a strong electron donor (B) like O, S, Se, Te atoms or others such as N or even π electrons, the question arises whether the influence of different hybridization from the C atom to the magnitude of changes in length and stretching frequency of the C-H bond. To answer this question, several complexes with C-H···chalcogen (O, S, Se, Te)/N/π hydrogen bonds were investigated, and relevant discussion is mentioned as follows.

3.1. C-H···O/S/Se/Te hydrogen bonds

A large blue shift of 30 cm^{-1} upon complexation was first found for C_{sp3}-H···O contacts in fluoroform···oxirane complex.[46] Chung *et al*. reported a C_{sp3}-H blue shift by 7 cm^{-1} and 5 cm^{-1} for the C_{sp3}-H···O non-conventional hydrogen bonds in the gas phase for the complexes between $CHCl_3$/$CDCl_3$ and SO_2. The C_{sp3}-H···O interactions between CF_nH_{4-n} (n= 1,2,3) and H_2O, CH_3OH, or H_2CO were studied at several levels of theory, which show a C_{sp3}-H contraction and a blue shift of its stretching vibration (5-47 cm^{-1}).[21] Similarly, a blue shift of 47 cm^{-1} was theoretically predicted for the $F_3CH···OHCH_3$ complex at the MP2/6-311+G(d,p) level.[83] In a computational study, the complex between triformylmethane and $CHCl_3$ was considered at the MP2/SDD level with the blue shift of C_{sp3}-H stretching frequency in $CHCl_3$ by 19 cm^{-1}.[17] The experimental blue shift of C_{sp3}-H stretching frequency in triformylmethane in liquid $CHCl_3$ is 7 cm^{-1}.[54] In the gas phase at room temperature, the C-D blue-shifted stretching frequency of $CDCl_3$ was detected at 7.1, 4.0, and 3.2 cm^{-1} in complexation with CH_3HCO, $(CH_3)_2CO$, and $C_2H_5(CH_3)CO$, respectively.[69] Through ab initio calculation, the blue shift for C_{sp3}-H bond is also found for the C_{sp3}-H···O hydrogen bonds in complexes formed from the interaction of CHX_3

(X = F, Cl, Br) with HNO. Notably, the low polarity of the C_{sp3}-H bond causes the shortening of the C_{sp3}-H bond and the blue shift of its stretching frequency (Δr_{CH} = -0.0009÷-0.0025 Å and $\Delta\nu_{CH}$ = 18÷41 cm^{-1}). The C_{sp3}-H red-shifting stretching frequency of C_{sp3}-H···Se hydrogen bond was observed for Q_3C-H···SeH_2 (Q = Cl, F, and H) at the MP2/aug-cc-pVTZ level, while the small blue shift was proposed in F_3CH···SeH_2 at a nonlinear structure ($\Delta\nu$ = -15 cm^{-1}).[84] In general, for the same proton donor of C_{sp3}-H, the magnitude of C_{sp3}-H stretching frequency blue shift in C_{sp3}-H···O hydrogen bond is much larger than that in C_{sp3}-H···Se bond.

Besides, some reports indicate that the medium is important in determining the category as well as the magnitude of the C_{sp3}-H stretching frequency shift.[85,86] Indeed, in solution, blue-shifted complexes of $CHCl_3$ and small cyclic ketones were suggested ($\Delta\nu_{CH}$ = 1÷5 cm^{-1}), and as the size of the ketone decreased, the C-H blue shift was enhanced.[87] In complexes of $HCClF_2$ and $HCCl_2F$ with $(CH_3)_2O$ in liquid krypton and liquid argon, a blue-shifted C_{sp3}-H···O bond was reported.[66] The C-H bond in the F_3CH···OH_2 complex is blue-shifted by 20.3 and 32.3 cm^{-1} in argon and neon matrix, respectively.[88] The C-H stretching frequency decreases by 38 and 14 cm^{-1} in the binary complexes of $CHCl_3$ with acetone-d_6 and H_2O prepared in a matrix.[46] Ito *et al*. reported a C-H red shift of 14 cm^{-1} in the $CHCl_3$···H_2O complex in argon matrix at 20 K.[85] Very recently, a C_{sp3}-H red shift of 21.9 cm^{-1} in C_{sp3}-H···O hydrogen bond was reported for the $CHCl_3$···CH_3OH complex in N_2 matrix using experimental IR spectra.[89] In general, the theoretical calculations are in good accordance with the observed IR data.[61,90,91] Moreover, using ab initio calculations and Monte Carlo simulations, the formation of the C_{sp3}-H···S hydrogen bond upon complexation of halothane ($CHBrClCF_3$) with dimethyl sulfide was investigated in solutions of liquid krypton using IR and Raman spectroscopy. In the dimethyl sulfide complex, the halothane C_{sp3}-H stretching mode was found to be red-shifted by 43 cm^{-1}.[92] It can be found that a decrease of C_{sp3}-H stretching frequency blue shift as well as an increase in its stretching frequency red shift detected in the medium were proposed, especially in a noble gas matrix (N_2, Ar, Ne, Kr,…), within which the noble gas is used as an unreactive host material to trap guest particles (atoms, molecules, ions, etc) being diluted in the gas phase.

Considering C_{sp2}-H stretching vibration, the hydrogen-bonded interaction of formic acid-, formaldehyde-, formylfluoride-nitrosyl hydride complexes were studied at 6-311++G(2d,2p) basis set. In which, C_{sp2}-H···O blue-shifted hydrogen bonds were found in the complexes by 19÷27 cm^{-1}.[93] The blue-shifted C_{sp2}-H···O interactions of benzene, phenol, and indole with water were calculated at the MP2/6-31+G(d,p) theory of level ($\Delta r(C_{sp2}$-H) = -0.1÷-0.8 mÅ; $\Delta\nu(C_{sp2}$-H) = 17÷33 cm^{-1}).[94] Notably, the very small red-shifted C_{sp3}-H···O hydrogen bonds (Δr_{CH} = 0.0003÷0.0011 Å; $\Delta\nu_{CH}$ = -2÷-8 cm^{-1}) and large blue-shifted C_{sp2}-H···O hydrogen bonds (Δr_{CH} = -0.0041÷-0.0069 Å; $\Delta\nu_{CH}$ = 55÷85 cm^{-1}) were observed in complexes of CH_3CHO with HNO at different levels of theory.[95]

Tri *et al.* conducted a high-level theoretical investigation of the stable structures of interactions between aldehydes RCHO (R = CH_3, NH_2, F, Cl, Br) and cyanides XCN (X = H, F).[73] The result shows that the C_{sp2}-H···O hydrogen bond plays an important role in the stabilization of RCHO···HCN complexes. Furthermore, the results suggest that the blue shift is affected by both the polarity of the C_{sp2}-H bond in the proton donor and the gas-phase basicity of the proton acceptor. The blue shift of the C_{sp2}-H bond in the C_{sp2}-H···O hydrogen bond is also observed in interactions of ethylene and its 1,2-dihalogenated form with CO_2, in which the magnitude of C_{sp2}-H distance contraction depends on the polarization of the C_{sp2}-H bond. Notably, a contraction of C-H bond length and a blue shift of its stretching frequency were obtained at a high theoretical level for gas phase complexes between XCHZ and CO_2 (X = H, F, Cl, Br, CH_3; Z = O, S) (with $\Delta r_{C\text{-}H}$ = -0.4÷-1.8 mÅ and $\Delta \nu_{C\text{-}H}$ = 10÷27 cm^{-1}).[96]

Remarkably, at the B3LYP/6-311++G(d,p) level, the findings revealed that when a CH_3CHO molecule interacts with two H_2O molecules, the stretching frequency of the C_{sp2}-H bond increases by around 93 cm^{-1}.[70] The blue shifts of ν(C_{sp2}-H) stretching vibration were found to be 45 and 66 cm^{-1} as HCHO complexed with one and two waters, respectively.[97] A considerable C_{sp2}-H blue shift, up to 81÷96 cm^{-1} was seen in the C_{sp2}-H···O hydrogen bond formed by the interactions of RCHZ (R = H, F, Cl, Br, CH_3, NH_2; Z = O, S) with HCOOH.[71] A study using ab initio calculations by Cuc *et al*. shows a large C_{sp2}-H blue shift in the C_{sp2}-H···O hydrogen bonds (92 cm^{-1} in CH_3CHO···$2H_2O$), which is compared to smaller blue shifts in C_{sp2}-H···S/Se/Te ones detected for the first time.[98] This result implies a predominant role of water in enhancing the significant C_{sp2}-H blue shift of stretching vibration upon complexation, which is also reported by Trung *et al*. of the significance of water and intramolecular interaction with a significant blue shift of C_{sp2}-H stretching frequency in binary complexes between the chalcogenoaldehydes and water ($\Delta \nu_{CH}$ = 109 cm^{-1}).[99] Recently, a significant C_{sp2}-H blue shift up to 104.5 cm^{-1} was reported by An *et al*. in binary complexes between CH_3CHO and CH_3CHS with substituted carboxylic and thiocarboxylic acids.[100] These suggested that the large magnitude of C_{sp2}-H blue shift in C_{sp2}-H···O bond is mainly supported by the presence of a strong O-H···O hydrogen bond. Remarkably, the C_{sp2}-H blue shifts in the C_{sp2}-H···O hydrogen bonds are substantially larger than those in the C_{sp2}-H···S/Se/Te ones, while electronegativity of O atom is higher than that of S, Se, and Te one.

The C_{sp}-H···O red-shifted hydrogen bond in HNO···C_2H_2 binary complex was studied by Ying *et al*. through ab initio MO and DFT with different basis sets ($\Delta \nu_{CH}$ = -6 ÷ -22 cm^{-1} with the standard method and $\Delta \nu_{CH}$ = -6 ÷ -19 cm^{-1} with the counterpoise-corrected method).[101] Ying *et al*. suggested that the red-shifted vibrational frequencies for C_{sp}-H stretch in C_{sp}-H···O hydrogen bonds. The red shift of C_{sp}-H stretching vibration was also reported by Andersen *et al*. in the complexes formed by hydrogen-bonded interaction between C_2H_2 and H_2O ($\Delta \nu_{CH}$ = -7.7 cm^{-1}).[102]

It can be seen that in most cases when the proton donor is a sp^2/sp^3-hybridized C atom, its interaction with a proton acceptor results in the blue- or red-shift of C-H stretching frequency, while the red shift is a feature of hydrogen bond with sp-hybridized C atom. The red or blue shift in C_{sp}-H/C_{sp2}-H/C_{sp3}-H···O hydrogen bonds is strongly associated with the different polarity of the C-H bond in the isolated monomer, which is caused by the difference of the electronegativity of C atom based on hybridization state. In short, it is found that the blue shift is larger for the C_{sp2}-H/C_{sp3}-H···O non-conventional hydrogen bonds than for the C_{sp2}-H/C_{sp3}-H···S/S/Te ones in spite of the larger electronegativity of the O atom relative to S, Se and Te one. Besides, it is noted worthy that a remarkable role of water and O-H···O bond generates a considerable blue shift in C_{sp2}-H stretching frequency in the binary or ternary complexes.

3.2. C-H···N hydrogen bond

The C_{sp3}-H···N BSHB with a calculated blue shift of the C-H stretching frequency of 30 cm^{-1} in the CHF_3···$NH_2C_6H_5$ complex was reported first by Fan *et al*. [103] Herrebout *et al*. [51] observed a C_{sp3}-H blue shift of 7.6 cm^{-1} or 3 cm^{-1} in the complexes of CHF_3 with NH_3 or pyridine at low temperature (188 K).[51] The C_{sp3}-H blue shift in the C_{sp3}-H···N hydrogen bond between proton donors of FH_2CH, F_2HCH and proton acceptors of CH_3NH_2, CH_2NH (with N acceptor) was found at MP2/6-31+G(d,p) level ($\Delta \nu_{CH}$ = 6÷25 cm^{-1}).[104] A modest blue shift of around 3 cm^{-1} was reported by Rutkowski *et al*. when $CHCl_3$ was introduced to CD_3CN in liquefied Kr at ~120 K.[65] In 2019, the slight C_{sp3}-H blue shifts of 8.7 cm^{-1}

and 8.6 cm^{-1} for the C_{sp3}-H···N hydrogen bonds in the $Cl_3CH···NCCH_3$ and $Cl_3CH···NCCD_3$ were observed by Fourier transform infrared spectroscopy, while the C_{sp3}-H red shift was reported for both complexes in the Ar matrix.[86] The C_{sp3}-H blue shift was observed for the C_{sp3}-H···N hydrogen bond in complexes formed by the interaction of trihalomethanes CHX_3 (X = F, Cl, Br) with HNO (nitrosyl hydride) at MP2/6-311++G(d,p).[105] Furthermore, Behra *et al*. reported a C_{sp3}-H blue shift of 9 cm^{-1} in the vapor phase at room temperature for the binary complex of $CHCl_3$ and CH_3CN, although Ito suggested a red shift of 25 cm^{-1} in an argon matrix earlier.[85-86]

Hippler reported a C_{sp3}-H···N hydrogen-bonded binary complex of $CHCl_3$ with NH_3 in the gas phase at room temperature with a C_{sp3}-H red shift of 17.5 cm^{-1}.[61] However, the magnitude of its red shift was risen to 38 cm^{-1} in a supersonic jet expansion,[61] and in an argon matrix, the red shift was still larger, *ca.* 45 cm^{-1}.[61,106] The complex of halothane with NH_3 exhibited similar shifting behavior of C_{sp3}-H spectra.[107] The observed red shift of C_{sp3}-H stretching frequency in the gas phase was found to be substantially less at room temperature (30.5 cm^{-1}) than in cryoliquids (55 cm^{-1} in liquid argon at 128 K, 49 cm^{-1} in liquid krypton at 173 K, and 42 cm^{-1} in liquid xenon at 228 K). The red shift of C_{sp3}-H stretching vibration by 4÷11 cm^{-1} in the $CH_3CHO···NH_3$ complex was determined at the high theory of level.[110]

Man *et al*. indicated that there are distinct tendencies toward a blue or red shift of the C_{sp3}-H stretching frequency in the C_{sp3}-H···N hydrogen bond in complexes formed by haloforms with NH_3 and its monohaloge nated derivatives (blue-shift: $\Delta\nu_{CH}$ = 7.0 ÷ 36.3 cm^{-1}; red-shift: $\Delta\nu_{CH}$ = -2.0 ÷ -92.6 cm^{-1}). In this work, Man's research reports that blue- or red shift tendency depends on the polarity of the C_{sp3}-H covalent bond and the proton affinity of the N site in the isolated monomers.[108] Significantly, Man *et al*. proposed using the DPE/PA ratio to predict the type of hydrogen bond following complexation. Accordingly, these authors suggested that the C-H···N hydrogen bonded interaction between a C-H bond and a proton acceptor at N atom with DPE/PA of over 2.0 is expected to form a blue-shifting hydrogen bonding, and a red-shifting hydrogen bond will be formed if this ratio is lower than 2.0. In many cases, for the same proton donor (methane and its derivatives), the gas phase basicity at the N site of the proton acceptor is proportional to an elongation of C_{sp3}-H bond length accompanied by a decrease of its stretching frequency upon binary complexation.

While the hydrogen-bonded complexes with the participation of C_{sp3}-H covalent bond show the blue-shift or in some above cases, a red shift of stretching vibration, the complexes with the C_{sp2}-H bond acting as a proton donor present the blue shift to a much larger extent although the polarity is lower for the C_{sp3}-H than for C_{sp2}-H covalent bond.[109] Indeed, the blue-shifted C_{sp2}-H···N hydrogen bonds were observed in the $CH_3CHO···NH_3$ complexes at the MP2/6-31G(d), MP2/6-311+G(d,p) and MP2/6-311++G(2d,2p) levels ($\Delta\nu_{CH}$ = 46÷71 cm^{-1}).[110] In the complexes of HCN with RCHO (R = H, Cl, Br, NH_2, CH_3), the C_{sp2}-H···N blue-shifting hydrogen bonds were detected, which were inversely proportional to its polarity in the RCHO monomer.[111] Similarly, a theoretical study at high level for stable structures of aldehydes RCHO (R = CH_3, NH_2, F, Cl, Br) and cyanides XCN (X = H, F) was investigated by Tri *et al*., which indicated the blue shift of C_{sp2}–H stretching frequency in the C_{sp2}–H···N hydrogen bond ($\Delta\nu_{CH}$ = 6.2÷41.9 cm^{-1}).[73] Tri *et al*. proposed that replacing one H atom in HCHO with an electron-donating group (CH_3, NH_2) enhances the C_{sp2}-H blue shift in the C_{sp2}-H···N bond, while having a slight effect on the blue shift of the C_{sp2}-H stretching vibration in the case of the halogenated complexes, as compared to that in HCHO···HCN complex and HCHO···FCN complex. This result was considered to depend on the polarity of C_{sp2}-H bond. It is also remarkable that the blue shift of C_{sp2}-H stretching vibration involved in the C_{sp2}-H···N hydrogen bond is generally weaker for RCHO···HCN complex than for RCHO···FCN complex, owing to the larger gas-phase Lewis basicity at the N site of HCN compared to FCN.

The weakly red shift in stretching vibration of C_{sp}-H bond was observed for C_{sp}-H···N hydrogen bond in the complex of acetylene and HSN at MP2/6-311++G(2d,2p) and MP2/aug-cc-pVTZ levels (Δr_{CH} = 1.7 Å; $\Delta \nu_{CH}$ = -12 cm^{-1}).[112] The obtained results at various levels of theory show the red shift of C_{sp}-H stretching frequency in C_{sp}-H···N hydrogen bond in the complex between acetylene (C_2H_2) and NH_3 ($\Delta \nu_{CH}$ = -170 cm^{-1}), which agrees well with experimental measurements ($\Delta \nu_{CH}$ = -97.3 cm^{-1}).[113] Additionally, the C_{sp}-H···N hydrogen-bonded complexes of NH_3 and CH_3NH_2 with several fluorine-substituted phenylacetylenes investigated by Dey *et al*. were characterized by a red shift in acetylenic C_{sp}-H stretching vibration ($\Delta \nu_{Csp\text{-}H}$ = -103 ÷ -157 cm^{-1}).[114] The obtained results in complexes of 3-fluorophenylacetylene and 2,6-difluorophenylacetylene with some Lewis bases such as ammonia, methylamine, dimethylamine and trimethylamine designate that the red-shifts of the acetylenic C–H stretching vibration in the C_{sp}-H···N hydrogen-bonded complexes rise as the Lewis gas phase basicity increases ($\Delta \nu_{CH}$ = -49 ÷ -219 cm^{-1}).[115] It can be seen that all C_{sp}-H covalent bonds as proton donors in the hydrogen bonds in the above-mentioned complexes are the typical red-shifted irrespective of proton acceptor.

3.3. C-H···π hydrogen bond

In 1999, Hobza *et al*. revealed the first experimental evidence for the blue-shifted hydrogen bond in the $CHCl_3$···C_6H_5F complexes using double-resonance IR ion-depletion spectroscopy ($\Delta \nu_{CH}$ = 14 cm^{-1}), which agrees with the ab initio calculation ($\Delta \nu_{CH}$ = 12 cm^{-1}).[90] The agreement of blue shift for both experimental result and theoretical investigation was later also detected in the complex of CHF_3 and fluorobenzene ($\Delta \nu$ = 12 cm^{-1}).[44] Some theoretical investigations into the complexes between proton donors (CH_4, CHF_3, $CHCl_3$, $CHBr_3$, CHI_3) and π-systems acting as proton acceptors (benzene, fluorobenzene, acetylene, and ethylene) proposed a contraction of the C_{sp3}-H bond length and an increase in its stretching frequency.[116-118] Weak C_{sp3}-H···π blue shifting hydrogen bond in C_2H_2···$CHCl_3$ ($\Delta \nu_{CH}$ = 20 cm^{-1}) and C_2H_2···CHF_3 ($\Delta \nu_{CH}$ = 23 cm^{-1}) complexes using matrix-isolation IR spectroscopy and ab initio computations were reported.[119,120] Ab initio investigations on the 1:1 and 1:2 complexes of C_2H_2 with CH_3Cl, CH_2Cl_2 and $CHCl_3$ also predicted a blue shift of the C_{sp3}-H stretching frequency.[121] Some complexes of benzene with proton donors (CH_4, $CHCl_3$) were studied with the contraction of the C_{sp3}-H bond (-0.0009÷-0.0023 Å) and the blue shift of its stretching frequency (15÷52 cm^{-1}).[17] The blue shifting hydrogen bond was detected in the complexes of 3-methylindole and $CHCl_3$/CHF_3 by 2 and 16 cm^{-1} in the cases of $CHCl_3$ and CHF_3, respectively.[49] Similarly, Shirhatti *et al*. suggested that for the complexes between p-cresol/p-cyanophenyl and CHX_3 (X = F, Cl) at MP2/aug-cc-pVDZ, the C_{sp3}-H stretching frequency in the C_{sp3}–H···π hydrogen bond was blue-shifted by 17.2÷65 cm^{-1}.[122] Reimann *et al*. observed the blue shift of the C_{sp3}-H stretching vibration in C_6H_5F···CHF_3 (21 cm^{-1}).[44] While all complexes of CHX_3 (X = H, F, Cl, Br) with benzene have the C_{sp3}-H blue-shifting stretching frequency of *ca.* 9÷50 cm^{-1}), it was observed that the CHX_3···C_6F_6 complexes all have small C_{sp3}-H···π blue-shifts of C_{sp3}-H stretching frequency and a slight contraction of C_{sp3}-H bond in CHX_3 ($\Delta \nu$ = 2÷27 cm^{-1}) at MP2/6-31G(d) level.[123] Notably, matrix isolation IR spectroscopy and ab initio computations were used to examine the blue-shifted hydrogen-bonded complexes of CHF_3 with benzene (C_6H_6) and acetylene (C_2H_2).[64] The red shift of supersonic jet expansion was found to be 55 cm^{-1}. When benzene was utilized as an acceptor, a slight blue shift of

7.7 cm^{-1} and an insignificant red shift of 1.1 cm^{-1} were detected under supersonic jet expansion and liquid krypton at 119 K, respectively.[64] It can be seen that, the C_{sp3}-H···π hydrogen bond is weak and moderately blue-shifted.

For the C_{sp2}-H···π hydrogen bond, the blue-shifting intramolecular C_{sp2}-H···π bonds in conformer of 1,3-hexadien-5-yne and its halogen-substituted derivatives were observed at MP2/6-31G(d,p) level. In which, the polarization of the C_{sp2}-H bond is considered as one of the reasons for the stretching frequency blue shifting in the hydrogen bonds.[124] The complex of benzene with a strong proton donor (HCN) was examined with the elongation of the C_{sp}-H bond and the red shift of its stretching frequency (Δr_{CH} = 0.0017Å and $\Delta\nu_{CH}$ = -18 cm^{-1}).[17] Hydrogen-bonded complexes of acetylene and benzene with HCN, acetylene and trihalomethanes HCX_3 (X = F, Cl, Br) were investigated at MP2/6-311+G(2d,2p) and MP2/aug-cc-pVTZ levels.[112] The red-shift of C_{sp}-H stretching frequency was observed in complexes between acetylene/benzene with proton donors like HCN or acetylene, while with the C_{sp3}-H bond, HCF_3 is a weakly blue-shifting donor, $HCCl_3$ is much weaker, and $HCBr_3$ has no discernible red or blue shift. Our theoretical calculations at the MP2/aug-cc-pVDZ level suggested the C_{sp}–H red shift of 5.7÷24.9 cm^{-1} in the C_{sp}–H···π hydrogen bond for binary complexes of C_2HX (X = H, F, Cl, Br, CH_3, NH_2) with C_6H_6 and $B_3N_3H_6$.[125] As discussed above, from the computational and experimental results in the complexes, it is found that the C–H···π hydrogen bond with a sp3-hybridized C atom shows a larger magnitude of stretching frequency blue shift as compared to that of C_{sp2} atom, and the hydrogen bond involving the C_{sp2}-H bond tends to the red shifting.

4. CONCLUSION

Results on the characteristics of non-conventional hydrogen bonds involving the C-H covalent bond as a proton donor are summarized in this work. This review is hoped to contribute to a more thorough understanding of hydrogen bonding features, including changes in bond length and its corresponding stretching frequencies upon complexation, from a theoretical viewpoint. The non-conventional hydrogen bonds involving the $C_{sp3/sp2}$–H covalent bond in the $C_{sp3/sp2}$–H···O/S/Se/Te/N/π hydrogen bond show both red-shifting and blue-shifting of stretching frequency, however, the C_{sp}–H red shift is observed in most hydrogen-bonded complexes. It is proposed that the polarity of the proton donor and the gas phase basicity of the proton acceptor play a key role in the red- or blue-shift of the C-H stretching vibration. The results also demonstrate that the ratio of deprotonation enthalpy to proton affinity (DPE/PA) might be used to classify non-conventional hydrogen bonds as an indicator. For a clearer understanding on the nature of non-conventional hydrogen bonds, it should be suggested that we need focus on energetic components such as dispersion, induction, electrostatics, etc… to find out the trend of their different contributions for each kind of non-conventional hydrogen bond.

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