Research Article **Available online** www.ijsrr.org **ISSN: 2279–0543**

International Journal of Scientific Research and Reviews

An Insight into Hydrogen Bonding

Sarkar Sumana*

Department of Chemistry, Dum Dum Motijheel College, Kolkata – 700 074, India
Email: sumana1206@gmail.com

ABSTRACT:

This work makes an attempt to explore the different aspects of hydrogen bonding, taking into consideration the data available in the literature. Water clusters, dimolecular systems, hydrogen bonding incorporating π-electron systems investigated by either experimental or theoretical techniques have been given special attention. Geometrical features and structural parameters that lead to known and lesser known manifestations in chemistry, have also been discussed.

KEY WORDS: Hydrogen bonding, donor, acceptor, energy

***Corresponding Author;**

Dr. Sumana Sarkar

Department of Chemistry, Dum Dum Motijheel College,

Kolkata – 700 074, India

Email: sumana1206@gmail.com

INTRODUCTION:

An understanding of the nature of chemical bond forms the basis of modern chemistry. Covalent interaction describes a molecule in free space (isolated from surrounding). There are interactions between molecules or between molecules and solvent, which are ascribed as non-covalent interaction. Suchnon-covalent interactions were recognized in the 19th century by J. D. van der Waals, which aided him to modify the equation of state for real gases. These types of interactions are comparatively weaker, though they influence the properties of the system.Hydrogen bonding illustrates one of the most common forms of such interaction. Nucleic acids, proteins possibly stabilize their self-assembly throughhydrogen bonding.

Hydrogen bond represents a weak non-covalent interaction between an electron-deficient H-atom and a high-electron density area. Commonly H-bond is denoted as X-H···Y with hydrogen atom flanked by electronegative element X and region of high-electron density, Y. The elements X, Y studied extensively, are F, O and N sites. More recently, C-H···O systems, frequently encountered in biomolecules,[1-3] along with X-H···π systems,[4,5] have received considerable attention.

WATER CLUSTERS:

Water clusters have been a subject of interest because it provides insight into ice and cloud formation.[6] The investigations commence with O-H (0.959 Å) and ∠HOH (105°) for isolated H_2O molecule.[7]In $(H_2O)_7$ cube like structure, the O-H bond lengthwith H-atom not involved in H-bondis 0.943 Å, while O-H bond (0.955 Å) with bridged H-atom is slightly elongated, as expected. The separation of ~2 Å between a covalently bound H-atom and O-atom of an adjacent H_2O moleculefalls in the range 1.7 – 2.45 Å.[1,8]The O···O distance of 2.8Å, has been attributed to non-linear H-bond (∠OHO 160 - 170°). They found that the stable form of heptamer assumed cube like structure, which is in conformity with previous DFT/HF/MP2 studies.[9-13]Kim *et al* performed ab initio calculations on 12 possible $(H_2O)_7$cluters to explore the conformation and spectroscopic properties of water cluster. Two 3-D cage-like structures comprising seven-membered rings with three additional H-bonds were found to be lowest energy conformations, 0.5 kcal/mol lower than other.[11]

The cluster of eight water molecules,$(H_2O)_8$ adopted the most stable configuration with cubic geometry (having twelve hydrogen bonds). The D_{2d} cubic geometry is in good agreement with experiments performed by Buck *et al*[12], Janzen *et al*.[14] Buck *et al*showed that $(H_2O)_9$ cluster consisted of a 9thwater molecule H-bonded to the cubic $(H_2O)_8$ cluster, thus comprising of 13H-bonds. Their experiments suggested a fused pentameric structure for $(H_2O)_{10}$ cluster to be energetically most stable configuration. Computations by Maheshwary*et al*[15] depicted a fused structure of two cubes to be the most stable with $D_{2d}D_{2d}$ symmetryfor $(H_2O)_{12}$ cluster. The stable structure for $(H_2O)_{13}$ cluster is an extension of cuboid having 21 H-bonds. The cluster of $14H_2O$ molecules is a combination of a cube with a fused pentamer, is found to most stable one. A $(H_2O)_{15}$ cluster is expected to be a fused pentamer with 26 hydrogen bonds, taking into consideration the geometries of $(H_2O)_5$ and $(H_2O)_{10}$ clusters. $(H_2O)_{16}$ clusteradopted a linear fused cube in its most stable configuration, on the basis of $(H_2O)_8$ and $(H_2O)_{12}$ cluster, which is a cube and a fused cube, respectively.It is symmetrical with 28H-bonds. The cluster of 17 water molecules, in its most stable form consists of one water H-bonded to one of the corners of linear cuboid $(H_2O)_{16}$ cluster, having 29 hydrogen bonds in all.$(H_2O)_{18}$ cluster, in its most stable configuration assumed an extended linear cuboidstructure, with a total of 31 H-bonds. In this form, two H_2O molecules are each two-coordinated and linked to two adjacent corners of the linear cuboid by hydrogen bonds. The most stable form of the cluster of19 water molecules, is related to the stability of $(H_2O)_{20}$ cluster. It takes up pentagonoid form with one corner missing, and incorporates 33 H-bonds. The structure of $(H_2O)_{20}$ cluster was computed, taking into consideration the studiesof clathrates undertaken by Pauling.[16] The cage-like structure from fusion of pentameric rings including 36 hydrogen bonds was found to stable one.

HYDROGEN BONDING IN DIMOLECULAR SYSTEM:

Quantum mechanical computations of 1:1 complexes between H_2O and X^-species indicated that only one H-atom of water participated in hydrogen bonding. IR stretching frequencyin $HOH\cdots Cl^-$ ($H\cdots Cl^-$, 2.151Å) and $HOH\cdots I^-$ ($H\cdots I^-$, 2.805 Å)[17,18] also supported this observation. The IR spectrum of ionic $I^-(H_2O)$ cluster was recorded from 3170 – 3800 cm^{-1} by vibrational predissociation spectroscopy.[18] A strong multiplet was observed at 3415cm^{-1} accompanied by a narrow band at 3710 cm^{-1} that were assigned as H-bonded OH stretch and freeOH stretch respectively. This indicated a single H-bond between H_2O and I^- ion. A significant difference between $F^-(H_2O)_n$ and $X^-(H_2O)_n$ [X^- = Cl-, Br-, I^-] was noted, the former preferred structures with negligible hydrogen bonding between H_2O molecules, while the latter favoured surface structures with distinctive hydrogen bonding between H_2O molecules.[19]McMahon and Bogdanov[20] further showed that $H\cdots X^-$ separation in CH_3OH - X^- complexes were shorter than similar complexes with water, implying stronger H-bonded interaction (Table 1).

Table 1.Hydrogen bond distances (Å) of selected hydrogen bonded complexes.

Complex / X^-	F^-	Cl^-	Br^-	I^-
$H_2O\cdots X^-$	1.365[a]	2.151[b]	2.378[c]	2.805[d]
CH_3OH - X^-	1.339[e]	2.079[e]	2.42[f]	2.588[g]

[a] Computations at MP2/aug-cc-pVTZ level [21]

[b] Computations at MP2/6-311++G(d,p) level [17]

[c] Computations at MP2/6-311++G(d,p) level [19]

[d] Computations at MP2/6-311++G(d,p) level using relativistic ECP[22] for I [18]

[e] Computations at MP2/6-311+G** level on CH_3OH complexes [20]

[f] Computations at MP2/D95 level [23]

[g] Computations at MP2/6-311++G(d,p) level using quasi-relativistic ECP for Br and I [24, 25]

Minikis and Jensen undertook the theoretical study of hydrogen bonding in $H_2O\cdots HOH$ and $H_2O\cdots HF$.[26]They utilized MP2 theory within frozen-core approximation[27] for computing the electron-correlation energy. They came forward with some interesting predictions on strength of hydrogen bonds. They studied the H-bond strength by substituting the hydrogen acceptor in $H_2O\cdots HOH$ with HF (in$HF\cdots HOH$). Qualitatively, since F has a larger nuclear charge than O, it exerts stronger pull on the surrounding electrons, suggesting a weaker H-bond than in water dimer. If the HF molecule is in the role of hydrogen donor,*i.e.* $H_2O\cdots HF$, it leads to a stronger H-bond than in water dimer, with a more polar H-F bond and lone pair of H_2O interacting with additional lone pair on HF.This was verified by calculations on MP2/6-311++G(2d,2p) sets.[28,29]It was observed that with HF as the donor, the separation between the heavy atoms is decreased by 0.253Å; with concomitant change in monomer structures upon complexation. The O-H and F-H bonds that directly participated in hydrogen bonding were lengthened by 0.007Å and 0.016Å, respectively. It was suggested that primary effects of changing the donor molecule and the decrease inheavy atom separation (from 2.917Å in O···O to 2.664Å in O···F), are separated from secondary effects due to slight change in internal structures. A change in the position of lone pair of electrons, in going from$H_2O\cdots HOH$ (-28.90kcal/mol) to $HF\cdots HOH$ (-32.77kcal/mol), may have some effect in – 3.87 kcal/mol difference in intermolecular energies. This decrease in intermolecular energy is negated by an enhanced repulsive interaction(2.66kcal/mol) between additional lone pair on F atom and lone pair on O atomof water.Thus, reorganization of lone pairs is only partially effective in eliminating the net repulsive interaction.

The change in internal energy of each monomer in the dimer ($H_2O\cdots HOH$) relative to free H_2O molecules and an intermolecular energy comprised the interaction energy, according to Jensen and Gordon.[30] The intermolecular energy is dominant till the equilibrium separation is reached; when internal energies start increasing and the bond strength represents summation of all energies at this point. The difference between the hydrogen donor tendency of HF and H_2O is mainly from increase ininternal energy of HF, leading to increase in H-bond strength. Relatively smaller decrease in intermolecular energy contributes to a lesser extent to the increased H-bond strength. This study inspired further investigations with NH_3 and CH_4 as hydrogen donor. NH_3 is predicted to be a better acceptor of hydrogen, than water, due to absence of additional lone pair.

Another aspect of looking into hydrogen bond formation was its correlation to proton transfer process. Proton transfer in O-H···O type of H-bonds were analysed,[31-33] taking into consideration –C=O···H-O-C- fragments of organic molecules (neutron diffraction geometries were taken from Cambridge Structural Database).[34,35] Configuration with H-atom located somewhat midway throughO···O separation wasthought of as transition state in proton transfer processes. The observed O···O distances were ~ 2.4 – 2.5 Å apart. For larger O···O separation, the hydrogen atom was placed in the vicinity of one of the oxygen atoms. It was summarized that the hydrogen bonded moiety, particularly in case of strong O-H···O interactions may be considered to be a step towards proton transfer mechanism. Similar correlation was shown for N-H···N interactions.[36]

H-BONDING WITH π - ELECTRON CLOUD:

System with π electron cloud acting as proton acceptors has also been studied.[37]A N-H···π interaction exists in a benzene···indole complex system, with the N-H group (of indole) directed towards the centre of the π electron cloud in benzene. The distances from the centre of mass (in benzene) to the H and N atoms (in theN-H bond of indole) are 2.153 and 3.160 Å, respectively.[5] This is substantiated by an elongation in the N-H bond by ~ 0.0030 Å, shown by computation at RI-MP2/TZVPP level, carried out by Braun et al [JPC-A, 2003]. Stacked and N-H···π hydrogen bonded structures of the neutral dimer were optimized using the approximate resolution of identity (RI-MP2) method together with extended basis sets. This method displayed preferential stability for stacked form. On the other hand, CCSD(T) computations showed theN-H···π hydrogen bonded structure to be favourable one. Estimation of stabilization enthalpy (5.3 kcal/mol) indicated the formation ofN-H···π bounded structure of the complex. Similar O-H bond lengthening of ~ 0.0070 Å in a water dimer was calculated at the same level, for comparison. These interactions possibly exist in nucleic acid and amino acid complexes.

Tsuzuki and Lüthi;[38] explored the extent to which density functional theory helps in prediction of interaction energies of twelve H-bonded systems. The geometries of five of such complexes were from earlier studies[39] and remaining complexes were optimized based on same line of computation.[39]The studies showed that a large basis set and consideration of an appropriate correlation are essential to study interactions of H-bonded complexes by ab initio molecular orbital calculation. The HF interaction energies were found to be considerably lower than that of MP2, which was dependent on basis set. They observed that dispersion formed a significant part of the interaction for H-bonded systems. The increase in size of basis set from cc-pVDZ to cc-pV5Z led to increased calculated HF interaction energies of H_2O-dimethyl ether, H_2O-HCHO, HCN-HF, formic acid and formamide dimers. On the other hand, H_2O-methanol and HF dimer exhibited reverse trend. The calculated charge distributions of the monomers and consequent electrostatic interaction, was dependent on basis set. This is one of the possible reasons on the basis dependence of HF interaction energies.

Plumley and Dannenberg[40]demonstrated a comparative study of the behavior of functional/basis set combinations for hydrogen bonding in water dimer. They showed that optimization using larger basis sets gave qualitatively correct geometry for H_2O dimer. Certain combinations of functions andbasis sets resulted in configurations having two H-bonds. The O···O separation increases upon optimization on the CP-corrected potential energy surfaces,[41] for those combinations that gave qualitatively correct geometry.However, the MP2 surface was so flat that the distortions of the O···O separations needed to make the calculations agree with the experimental value required less than 0.1 kcal/mol. They made a comparative study of their results with that of high level MO calculations exclusive of DFT as well as with experimental findings. The O···O distance computed with aug-cc-pV5Z was found to be in the range 2.893 – 2.922 Å with CP-OPT and within 2.883– 2.919 Å without CP-OPT, when compared to that of 2.886 – 2.925 Å, for optimized geometries for same set of calculations. They found no correlation between interaction energies and O···O separation.

Comparison of the calculated dimer structure and dipole moment, determined from microwave spectrocopy, with experimental results, showed that three out of four measured O···O distances[42-44] in cluster is ~ 2.98 Å, while the remaining distance is 2.94 ± 0.03 Å. The O···O separation, quite shorter than 2.95 Å was predicted for high level MO optimized geometries. The water dimer structure incorporated a symmetry plane, a trans configuration, and a linear H-bond within quoted error limits.[44] Similarly, calculations using CP-OPT and aug-cc-pV5Z basis set with almost all functional exhibited O···O distances (~ 2.924 Å) that is much less than 2.95 Å. The distances were found to still shorter for calculations without CP-OPT.

CONCLUSION:

In this presentation, different aspects of hydrogen bonding have been discussed from theoretical and experimental data available in the literature. An overview of different types of hydrogen bond acceptors has been presented. The effect on separation between atoms linked by H-bond following changes in donor / acceptor atoms or groups have been examined. The most probable structure and geometry of hydrogen bonded complexes have also been discussed.

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