lope, etc. will remain unsure if consumers of *cashmere* continue to be ignorant regarding the source of the products purchased by them. Scientists hope that working in league with the local herders, representatives of the fabric industry and also the government officials will provide them with suitable solutions to implement a sustainable conservation plan that works for all.

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RESEARCH NEWS

Hydrogen bond seen, halogen bond defined and carbon bond proposed: intermolecular bonding, a field that is maturing!

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I wrote my first research news in *Current Science* in 1999, when some results questioning the conventional wisdom on hydrogen bonding were published[1]. The news item discussed three topics, namely blue shifting in X–H infrared stretching frequency in an X–H•••Y hydrogen bond, the experimental evidence for partial covalency in H•••Y bond and the studies on halogen bonds similar to hydrogen bonds. Experimental evidence for partial covalency (chemical bond) was making waves in the field as hydrogen 'bonding' was thought to be just an electrostatic 'physical' interaction between two dipoles. Despite the popular use of the terms 'hydrogen bond' in the literature for close to a century, there were continuous murmurs that 'hydrogen bond' was a misnomer. Eventually I proposed to IUPAC that the hydrogen bond should be redefined and following IUPAC's procedure formed a task group of experts from all over the world to actually do the same[2]. Fourteen years later, three more recent results have prompted me to write again. IUPAC has now defined 'halogen bonding' through another task group, with Gautam R. Desiraju and Anthony (Tony) C. Legon being members common to both task groups[3]. High-resolution atomic force microscope (AFM) has shown images of hydrogen bonds formed by OH and also CH groups as donors[4]. We have recently proposed a 'carbon bond' analogous to hydrogen and halogen bonds[5].

In 2009, stunning images of a pentacene molecule including the bonds (electrons in between the atoms) were revealed by AFM[6]. It was only a matter of time before someone visualized hydrogen bonds using AFM. Somewhat fittingly, a team led by a chemist (Xiaohui Qiu) and a physicist (Zhihai Cheng) has succeeded in recording the AFM images of 8-hydroxyquinoline assembled on Cu(111) surface (Figure 1)[4]. This image has been called a 'stunner' by Kemsley[7] in a research news published by *Chemical and Engineering News*, coinciding with the web release of the article by *Science*. What is stunning about this image is the fact that it not only shows the O–H•••O hydrogen bonds accepted by everyone, but also the C–H•••O and C–H•••N hydrogen bonds questioned and ridiculed by some in the not so distant past[8]. The opposition to call these 'hydrogen bonds' was so prevalent that Desiraju and Steiner had titled their book discussing C–H•••O hydrogen bonds as *The Weak Hydrogen Bond*[9]. A covalent bond could be a covalent bond, no matter how strong or weak it is. Of course, these arbitrary borders in hydrogen bonds vanished with the recent IUPAC definition which only insisted that some evidence be provided that there is bond formation between H already bonded to a more electronegative atom and any other atom or a group of atoms[2]. As the founder, chairman of the IUPAC task group, it is indeed personally pleasing to see the first image showing evidence for O–H•••O, C–H•••O and C–H•••N hydrogen bonds, all in the same molecular system.

With the hydrogen bond well established, chemists started wondering if other atoms could have such interactions. Alkali and halogen group atoms were of course the first targets as H used to top these two groups in older version of the periodic table. Many started working on lithium bonding and halogen bonding. For the first group elements all expected to have a valency of 1, it was simpler to see the presence or lack of lithium bonding. For the halogens it would be difficult as the halogen atoms, except F, were known to exhibit multiple valency with ClF_3 and IF_5 known as stable molecules. Hence, halogen atoms bonded to more than one atom could not constitute a halogen bond analogous to a hydrogen bond. Even with this complexity, halogen bonds similar to hydrogen bonds were seen both in the gas phase molecular complexes[10] and in condensed phase[11]. The definition of the halogen bond proposed by the IUPAC task group, chaired by P. Metrangolo and G. Resnati, reads as follows: 'A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.' One can see the similarity with the hydrogen bond definition. The definition still avoids the use of the term 'electronegativity' commonly used by many chemists and biologists, but detested by purists.

The word 'occurs' right at the beginning of the definition makes one wonder 'what occurs?' Clearly the task group has stayed clear from getting into a debate about what is a 'bond'? Even to an eminent theoretician such as Coulson[12] who wrote a popular book on valence, 'bond' has been a source of confusion. He said: 'Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination.'[13] Of course, Coulson did not have the stunning images to help him visualize the bonds and perhaps could not even imagine that it would become a reality in future. It was always clear to me that the chemical bonds are made of electrons and we can 'see' electrons today. There is no need any more for chemists to shy away from boldly claiming to see the 'bond' between two atoms. Electrons between two atoms can combine to produce an attractive potential between them forming a bond between the two atoms. (We will leave the question of why two electrons having equal negative charge combine, for the beginners course on quantum chemistry.)

One can also see that the proposed definition would lead to the conclusion that a simple molecule such as ClF_3 has a 'halogen bond'. Any definition written for such terms is bound to lead to some anomalies and this is one of the reasons for both the definitions of 'hydrogen bond' and 'halogen bond' to list down some criteria and characteristics running to two pages following the short definition. The task group lists common donors and acceptors and clearly ClF_3 has no 'halogen bond'. Some purists are of the opinion that because of these anomalies, one should refrain from defining terms like 'bond', 'hydrogen bond' and 'halogen bond', but I beg to differ. I indeed like what Hoffman says about bonding: 'Push the concept to its limits. Be aware of the different experimental and theoretical measures out there. Accept that at the limits a bond will be a bond by some criteria, maybe not others. Respect chemical tradition, relax, and instead of wringing your hands about how terrible it is that this concept cannot be unambiguously defined, have fun with the fuzzy richness of the idea.'[13] Perhaps with images like what is shown in Figure 1, it is not that fuzzy anymore. It is not a surprise than that we have now proposed a 'carbon bond' analogous to a hydrogen bond and a halogen bond.

If we look at typical hydrogen and halogen bonds, one thing is common. The hydrogen and halogen atoms involved in these bonding are 'electrophilic' and have partial 'positive charge' or regions of electron deficiency termed recently as a sigma hole by Politzer, one of the members of the task group to define halogen bond[14]. Hence, these atoms already part of a molecule can and do have attractive interactions with other molecules having nucleophilic regions in them. For a gas phase chemist, things are simpler as there are no other complications that cloud interpretation for a condensed phase chemist. Do we have two atoms in close vicinity because they were forced to be so due to their surrounding or do these two atoms really have any attractive interaction that can lead to a bond formation? One molecule of HF can form a hydrogen bond with one molecule of H_2O as the electron-deficient H atom in HF 'bonds' with the lone-pair of electrons in the O atom of H_2O molecule. Similarly, one molecule of ClF can form a halogen bond with one molecule of H_2O as the partially positive Cl in ClF can form a bond with the partially negative O in H_2O. Can one molecule of CH_3F interact with one molecule of H_2O in a similar fashion to form a 'carbon bond'? Figure 2 shows that it can. Prior to AFM, electron density topological analysis, both theoretical and experimental, could identify bond paths and bonds through what are known as 'bond critical points'[5].

Carbon is perhaps the most important element on earth and much of life as we know is based on carbon compounds. Of course, this led to a branch of 'organic chemistry' as chemistry of carbon compounds leaving the periodic table with more than hundred other elements for 'inorganic chemistry'. Carbon has a valence of four and is usually combined with four other atoms forming a three-dimensional structure protecting it from attack or approach by other atoms from any direction. This led to the stability of carbonaceous molecules. One can see that HF and ClF are vulnerable to approach from the direction opposite to the F atoms. Even then, in a molecule like CH_3F, thanks to the most electronegative F atom, the carbon atom becomes somewhat positive and there is a sigma hole behind it. The three H atoms are of course light and they can open their arms for attack by another nucleophilic atom such as O in H_2O. A 'carbon bond' is born[5].

The CH_3 face of CH_3OH is usually characterized as hydrophobic and the OH

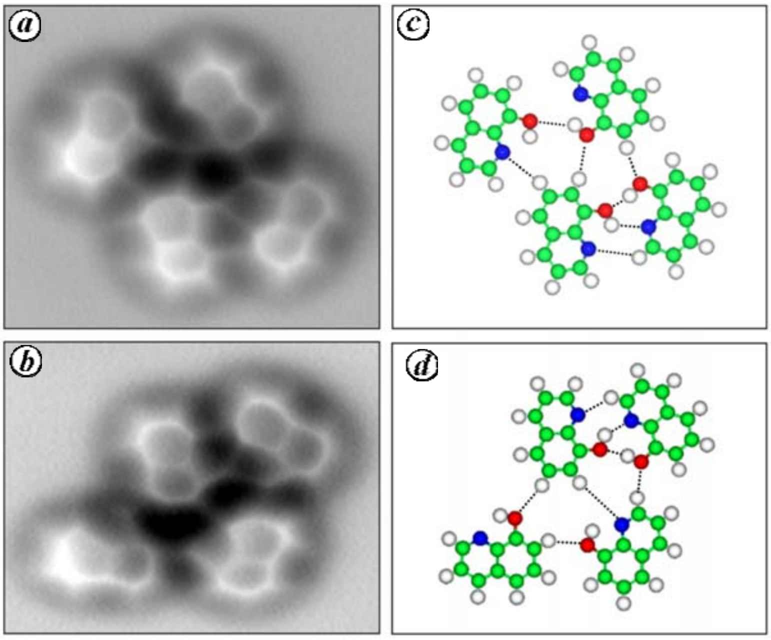

Figure 1. AFM measurements of 8-hq assembled clusters on Cu(111). (***a***, ***b***) Constant-height frequency shift images of typical molecule-assembled clusters, and their corresponding structure models (***c***, ***d***). Imaging parameters: $V = 0$ V, $A = 100$ p.m., $\Delta z = +10$ pm. Image size: (***a***) 2.3 nm × 2.0 nm, (***b***) 2.5 nm × 1.8 nm. The dashed lines in (***c***) and (***d***) indicate likely H bonds between 8-hq molecules (figure reproduced with permission from *Science*[4] ©.)

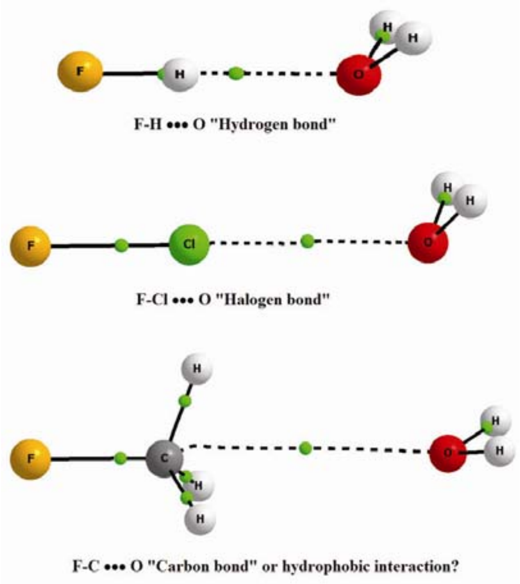

Figure 2. Examples of hydrogen bond, halogen bond and carbon bond formed by FH•••OH_2, FCl•••OH_2 and H_3FC•••OH_2 complexes respectively. The green dots represent a bond critical point. See Mani and Arunan[5] for details. Reproduced with permission from the Royal Society of Chemistry ©.

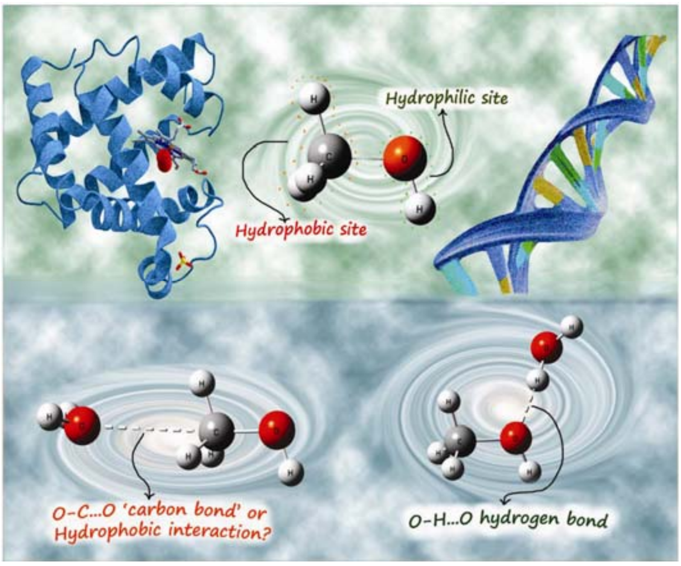

Figure 3. Cartoon representation of the hydrogen bond and the carbon bond formed by $CH_3OH–H_2O$ complex in two different structures. Hydrogen bonding controls the double helix structure of DNA and hydrophobic interactions (carbon bonding?) are important in protein folding[5]. Reproduced with permission from Royal Society of Chemistry ©.

side is called hydrophilic as the O atom in OH can accept a hydrogen bond, i.e. bond with the H of a H_2O molecule. The CH_3 face is hydrophobic and typically H atoms of H_2O turn their face and of course now the O atom has to show its face. This was called 'hydrophobic interaction'. Now, what is hydrophobic interaction? Chemists and physicists thought for long and concluded that there is no such interaction and it is an entropic effect and 'hydrophobic effect' would be a better term. Our work on these isolated complexes has helped identify a part of the hydrophobic interaction as 'carbon bond'. Figure 3 has both hydrophilic (hydrogen bonding) and hydrophobic (carbon bonding) interactions of one CH_3OH molecule with one H_2O molecule. When my colleague S. Ramakrishnan, a polymer chemist, looked at this structure he immediately identified it as an intermediate of SN_2 reactions in organic chemistry. Hydrogen bonding has been an intermediate in proton transfer reactions and clearly carbon bonding is an intermediate in SN_2 reactions. Perhaps 'carbon bonds' have already existed as there have been reports[15] of C atoms interacting with nucleophilic carbonyl groups. In the last few years, beryllium bonding[16], chalcogen bonding[17] and pnicogen bonding[18] have all been proposed. Chemists love naming. For a physicist, it is all part of the electrostatic interactions, after taking covalency and dispersion into proper account.

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