

Theoretical description and modelling of hydrogen bonds at solid surfaces

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Abstract

The formation of self-assembled surface structures based on hydrogen bonding is one of the most active research areas in surface science. This article discusses, mostly from a theoretical point of view, the fundamental aspects of hydrogen bonding interaction and their relationship to the formation of ordered hydrogen-bonded networks on surfaces. First, the basic theoretical concepts about hydrogen bonding and its modelization are presented, outlining the large variety of techniques available for the study of these systems. Second, some relevant research results on this field are reviewed and discussed, describing two important main situations: on one hand, the adsorption of water on both metallic and oxide surfaces; on the other, the formation of ordered networks of hydrogen-bonded organic molecules on various types of surfaces. In the latter case, two main situations are described, involving or not a relevant role of the surface in the formed superstructures.

Keywords

Hydrogen bonds. Surface science. Self-assembly. Nanoarchitectures. Density Functional Theory. Electronic structure. Scanning tunneling microscopy. Water.

Glossary

Density Functional Theory

Computational quantum method used to calculate the ground state electronic structure of many-body systems, by using functionals of the electronic density.

Miller Indices (111), (110)

Set of numbers which identify how a surface plane intersects the main crystallographic axes of a solid crystal, thus labelling the orientation of a given surface.

Scanning Tunneling Microscopy

Microscopy technique for the imaging of surfaces at the atomic level, based on the tunneling of electrons from the surface to a very sharp tip.

Self-assembly

Process in which a disordered set of components (usually atoms or molecules) forms an organized structure or pattern due to specific local interactions, without an external direction.

Nomenclature

AES	Auger electron spectroscopy
eV	Electron-volt
HB	Hydrogen bonding
DFT	Density functional theory
HREELS	High-resolution electron energy loss spectroscopy
IRAS	Infrared reflection-adsorption spectroscopy
LDOS	Local density of states
RAHB	Resonance assisted hydrogen bonding
STM	Scanning tunneling microscopy
TPD	Temperature programmed desorption
UHV	Ultra high vacuum
XC	Exchange-Correlation
XPS	X-Ray photoelectron spectroscopy

Hydrogen bonds: Basic concepts

Hydrogen bonds (HB) form when a hydrogen atom, bound to an electronegative atom (nitrogen, oxygen, fluorine, etc...) interacts with another electronegative atom nearby, which can be part of the same molecule (intramolecular HB) or of other different molecule (intermolecular HB). The atom where hydrogen binds is called donor, and the one which interacts with hydrogen is labelled as acceptor.

Since such hydrogen atoms carry a sizable positive charge, these bonds were traditionally rationalized as weak electrostatic interactions between them and electronegative atoms. While electric interaction certainly plays a major role, today it is generally accepted that H-bonding involves also some covalent and dispersive contributions, making its theoretical study quite a challenge. Such complexity is evident when we consider the large variability in its properties; the strength of HB varies from very weak (less than 0.05 eV) to extremely strong (above 1 eV), with typical values for most organic molecules ranging from 0.10 to 0.30 eV.

Depending on the strength, there exist various types of HB, differing in the way the hydrogen atom interacts with the atom A (the one where hydrogen is bound prior to the HB formation). Figure 1 shows a sketch of the potential energy of the system as a function of the H-A bond distance. For weak or moderate bonds, there is a high energy barrier for hydrogen transfer. In the case of strong bonds, the barrier decreases or even disappears, meaning that hydrogen is actually shared between the atoms which form the bond.

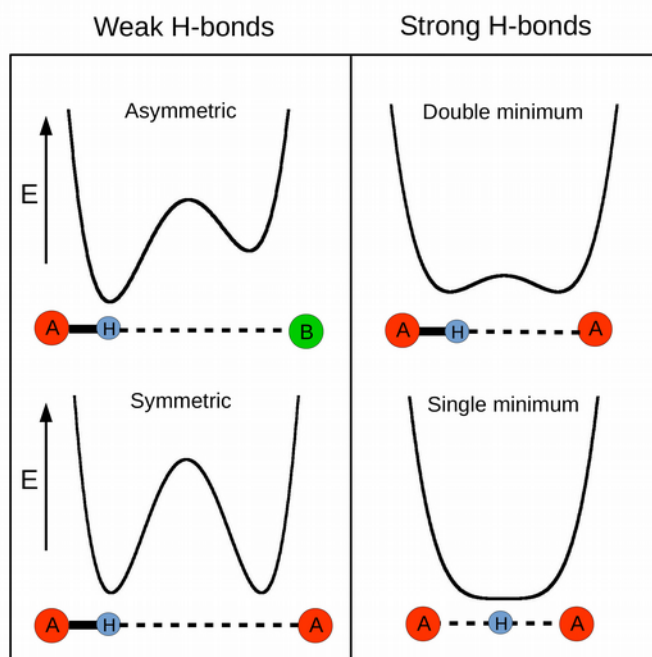


Figure 1: Potential energy curves for various types of hydrogen bonds.

Another feature of HB which adds to the complexity of its description is directionality; frequently, the angle A - H...B is not straight, meaning that the interaction is not purely electrostatic, and that a partial degree of covalency exists. This effect can be understood in terms of partial overlap of molecular orbitals, which are preferentially oriented along specific directions.

Finally, HB have been observed to show cooperative effects, which are essential (as it is further discussed below) for understanding the formation of both biological and artificial self-assembled superstructures. When several molecules are linked together by several HB, the formation of one bond can alter the electronic structure of a molecule in a way which is beneficial to the rest of the bonds. This means that the global binding energy of a collection of bonds is greater than the sum of each individual binding energy.

Theoretical description of hydrogen bonding

There are various ways to describe HB interactions between organic molecules, which can be grouped into the following categories:

1.- High level Coupled Cluster calculations (CCSD(T)), which treat precisely exchange-correlation (XC) effects, so they are able to describe very accurately the various types of interactions (covalent, electrostatic, dispersive, etc..) which

contribute to HB. Unfortunately, because of their high computational cost they can only treat very small systems.

2.- Ab initio Density Functional Theory (DFT), which approximately describes XC effects by using various parametrizations of the XC contribution to the total energy as a functional of the total electron density $E_{xc}[\rho]$. This provides a reasonable description of most features (covalent, electrostatic) of the HB. Although they lack a proper description of dispersive (Van der Waals) interaction, they constitute a good compromise between accuracy and inexpensiveness, and are widely used for systems up to around 500 atoms. In general, this approach works fairly well for medium strength linear A-H ... B bonds, where electrostatic interactions are dominant. In the case of non-linear HB, where dispersive interactions become much more prominent, DFT accuracy sharply decreases. Recently, a partial solution to the problem based on semiempirical corrections to the dispersive interaction (Grimme's DFT-D3 method) has become widely popular.

3.- Semiempirical (MNDO, AM1, PM3, ...) and molecular mechanics (AMBER, CHARMM, ...) calculations. The first make important simplifications for the solution of the quantum problem, while the second completely disregards the electronic structure of the system, by fitting the interaction potential between each type of atoms to a force field based on empirical parameters. While they have serious issues concerning accuracy, they are very inexpensive and become the method of choice for the treatment of very large systems (DNA, proteins, etc...).

Experimental and theoretical techniques for surface studies

To understand the formation of hydrogen-bonded networks on surfaces, a wide variety of experimental surface science techniques can be employed. Among them, the following ones are most important:

1.- Electron spectroscopies, like X-Ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES), probe the electronic structure of molecules adsorbed on a surface, providing valuable information about their chemical state and the interactions with their surroundings.

2.- Vibrational spectroscopies, like Infrared Reflection-Absorption Spectroscopy (IRAS), or High-Resolution Electron Energy Loss Spectroscopy (HREELS), allow the study of the modifications induced in the vibrational modes of molecules upon adsorption.

3.- Desorption spectroscopies, like Temperature Programmed Desorption (TPD), are also valuable tools which are used to obtain information about the binding energies of adsorbates. They also allow identification of adsorbed species, and of their relative amounts.

4.- Scanning Tunneling Microscopy (STM) allows the visualization of adsorbed species with atomic resolution, thus providing an extremely useful tool for direct observation of the way molecules are arranged on the surface. Unfortunately, the images obtained only sample the local density of electronic states (LDOS) at the surface, frequently making difficult identification of the species imaged.

Density Functional Theory simulations are an important complementary tool to precisely identify the arrangement of complex surface networks. Usually, STM images can precisely visualize the substrate underneath adsorbed organic molecules with atomic resolution, but contrast issues result in much poorer resolution of the molecules above, which are imaged as blurred entities with a shape which only approximately resembles the molecular structure. The use of theoretical simulations alongside STM experimental studies allows for the determination of the most stable conformations, and by comparing real with simulated STM images, the exact molecular arrangement can be found among many possible candidates.

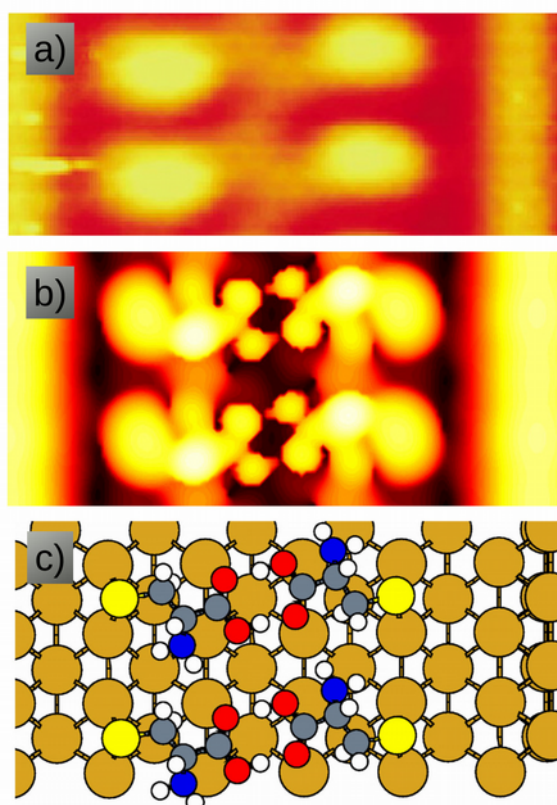


Figure 2: a) STM image of cysteine pairs adsorbed on Au(110). b) Simulated STM image obtained from DFT calculations. c) Candidate structure for the adsorbed cysteine pairs.

Figure 2 shows an example of this procedure. Panel a) shows a STM image of cysteine molecules adsorbed on the Au(110) surface, in a high coverage

situation. Each bright oval corresponds to a cysteine molecule. The image shows how the molecules are arranged into stacked pairs. After testing a few selected candidate structures of adsorbed cysteine, the DFT electronic structure is used to create a simulated STM image of the surface, according to the Tersoff-Hamann theory (which approximates the tunneling current in terms of the local density of states (LDOS) at the surface. Because of thermal effects and the limited resolution, the experimental image shows in general much less detail than the simulated one.

Water on surfaces

Liquid and solid water constitutes the most prominent and widely studied case of a hydrogen-bonded network. For solid ice, water molecules form an average of four hydrogen bonds with their neighbours, a value which decreases to three and a fraction for liquid water. The interaction of this network with various types of surfaces (metals, semiconductor and oxides) is one of the most important topics of current surface science. It is essential to understand water adsorption on surfaces at the molecular level because of its many implications to various problems:

- 1.- Wetting and hydrophilic/hydrophobic character of surfaces.
- 2.- Understanding of corrosive processes
- 3.- Influence of water on catalytic reactions

The first problem to consider when studying water at surfaces is the possibility of water dissociation into adsorbed -H and -OH groups. This is particularly important, because of the implications towards catalytic reactions, in the case of oxide surfaces (TiO_2 , Al_2O_3 , etc...). Depending on the characteristics of the surface (mainly, chemical reactivity), dissociation can be a frequent or rare event. In particular, the presence of surface defects can strongly influence hydroxyl formation. For example, in the case of TiO_2 , water has been observed to readily adsorb on surface oxygen vacancies forming pairs of adsorbed hydroxyls. For this problem, theoretical DFT simulations are a very important tool as they can provide a direct comparison between binding energies of molecular and dissociated water.

If water adsorption takes place mainly in a molecular form, it has been found that the molecule binds to the surface through the oxygen lone pair in a semiparallel conformation, being able to form two hydrogen bonds through its available H atoms. In the case of metals, this can lead to the formation of a double layer of hydrogen-bonded water molecules in an hexagonal arrangement (see Figure 3a). Although the HB interaction is crucial for the formation of such nanostructures, the surface-water interaction, moderately strong, has also a very important role on the type of arrangement of the water molecules. Changes on the metal lattice parameter and on the strength of the water-metal attraction can result on other alternate conformations being more stable.

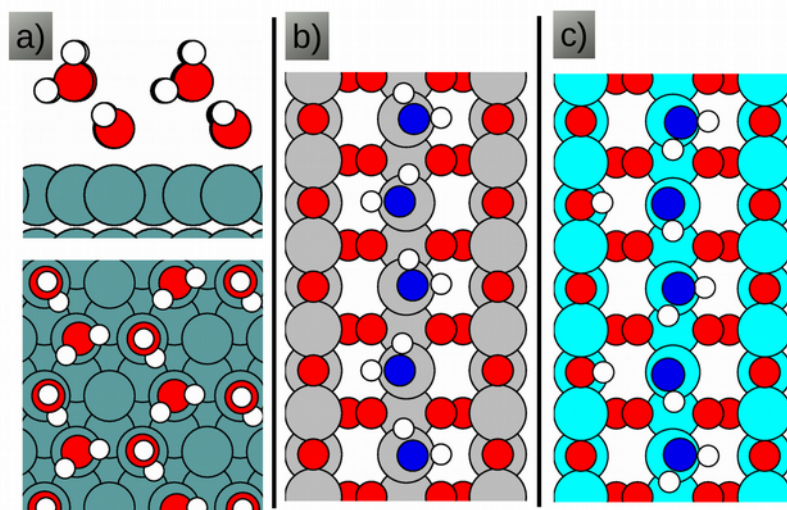


Figure 3: a) Hexagonal water bilayer adsorbed at metal surface. b) Molecular water chain adsorbed at rutile $\text{TiO}_2(110)$. c) Partially dissociated water chain adsorbed at $\text{RuO}_2(110)$. For visual clarity, oxygen atoms in adsorbed water are highlighted blue in (b) and (c).

The problem of water adsorption at metal oxides, and the interaction between adsorbed water molecules, is essential to the understanding of many catalytic and electrocatalytic processes, as for example those taking place at fuel cells. In the case of the rutile $\text{TiO}_2(110)$ surface, the existence of a natural pattern (alternating O and Ti one-dimensional rows) can result in the formation of ordered chains of water molecules linked by hydrogen bonds. The intrinsic characteristics of the substrate, which influence the features of the water-surface interaction, have also in this case an important relation to the type of structures which spontaneously form; in the case of rutile TiO_2 (see Figure 3b) there is a preference for the formation of chains of intact water molecules. Interestingly, for the analogous rutile RuO_2 surface (see Figure 3c) a slightly different structure forms, with half the water molecules dissociated into adsorbed -H and -OH groups.

Hydrogen-bonded self-assembled surface networks

Another example of self-organization processes taking place at surfaces, where hydrogen bonds direct the formation of ordered nanostructures, is the adsorption of organic molecules with various functional groups at metallic surfaces, usually under ultra high vacuum (UHV) conditions. In general, the way these molecules are arranged on the surface is the result of the combination of molecule-surface interactions with molecule-molecule attractive forces, the latter usually determined by hydrogen bonding and dispersive interactions. This allows us to establish a rough classification of self-assembled networks into two main categories:

1.- Self-assembly mainly directed by intermolecular interactions.

This situation takes place when the molecule-surface interaction is relatively weak or uniform, and as a result of this there are not preferential surface sites for the molecules to bind. Therefore, formation of an ordered surface network of physisorbed molecules is completely governed by their mutual molecule-molecule interactions. This is usually the case during adsorption at close-packed noble metal surfaces, with Au(111) being the prototypical case, because of the low reactivity of gold.

In the absence of hydrogen bonds, dispersive van der Waals attraction becomes dominant, and this usually means that the network arrangement tries to optimize packing. If hydrogen bonds are present, they usually direct the network formation, maximizing their number. The way these are located around each molecule usually is strongly related to the symmetry of the network. For example, trimesic acid (a benzene derivative with three COOH groups with mutual angles of 120°), when deposited on Au(111) forms a hexagonal chickenwire network, with each molecule bonded to three neighbours through its carboxylic groups.

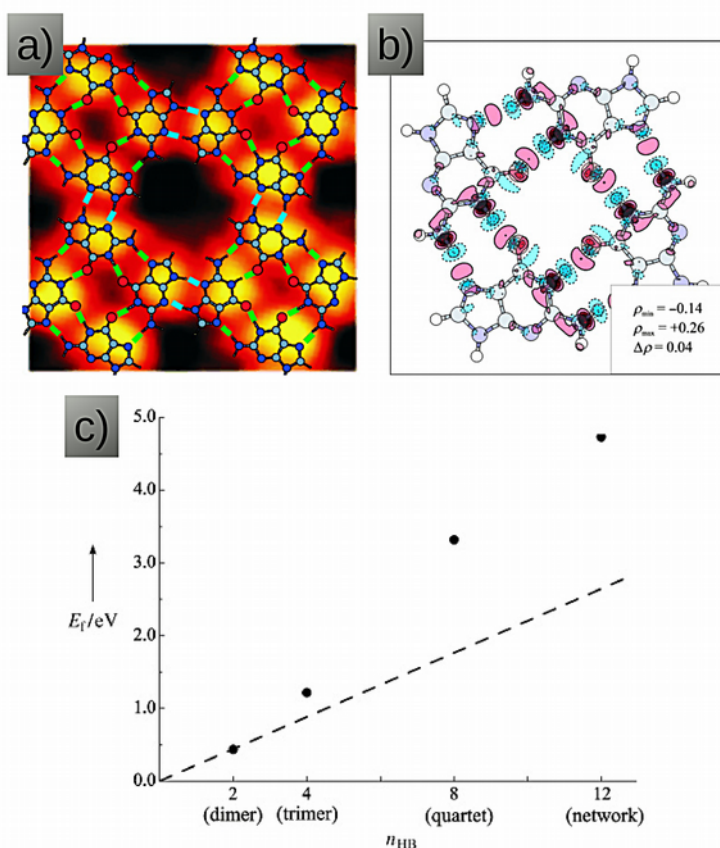


Figure 4: a) STM image of a network of guanine quartets adsorbed on the Au(111) surface. The relaxed DFT structure with the best theoretical fit is

included for comparison. b) Charge density perturbations determined by DFT calculations for the formation of a hydrogen-bonded guanine quartet. c) Formation energy as a function of the number of hydrogen bonds for guanine dimer, trimer, quartet and network structures. The dashed line represents the expected result for hydrogen bonds mutually independent from each other. Reprinted with permission of John Wiley and Sons.

In this circumstances, it has been observed that not only pairwise HB interactions are important during the self-assembly process that leads to an ordered network formation. Cooperative effects (which are closely related to the Resonance Assisted Hydrogen Bonding effect, or RAHB) can have a dramatic effect in the type of arrangement formed on the surface. As it was discussed previously, during multiple HB formation polarization effects are responsible for an enhancement of the bond strength with respect to the single HB case. An interesting example is the formation of a network of guanine quartets upon deposition of this DNA base on the Au(111) surface (see Figure 4).

After adsorption on the Au(111) surface (in a parallel conformation, to maximize dispersive interactions with the surface) the molecules form an ordered network based on hydrogen-bonded guanine quartets (a structure with crucial biological importance during interactions between different DNA chains). DFT simulations of the strength of HB as a function of the number of bond formed show the presence of a marked cooperative effect: guanine quartets bind together (per HB) much more strongly than guanine dimers. The analysis of the DFT electronic structure attributes the origin of such cooperativity to an increasing charge density rearrangement within each molecule as the number of HB formed grows.

2.- Self-assembly controlled by interplay between substrate-molecule and intermolecular interactions.

In many situations, the surface-adsorbate interaction is strong enough or irregular enough to dramatically influence the surface arrangement of a hydrogen-bonded network. We have already seen this situation taking place in the case of water chain formation at the rutile-TiO₂(110) surface: water molecules adsorb preferentially with the oxygen atom on top of Ti⁴⁺ surface sites, which are aligned forming rows; therefore, this template effect results in a preferential growth of the hydrogen-bonded water chains along the Ti rows.

Usually, each substrate has various type of surface sites with different reactivities, meaning that adsorbed molecules will recognize and select the most favourable ones for binding. This will influence the shape of the hydrogen-bonded network formed when molecules adsorbed at neighbouring sites interact with each other. If possible, the molecules will try to form HB between themselves while keeping as intact as possible their surface bonds.

In some cases, the adsorbate-surface interaction is strong enough to drive important structural rearrangements in the surface atoms (called reconstructions in surface science). A well known example of this process is the formation of Self-Assembled Monolayers (SAM) of thiol-terminated hydrocarbon chains on Au(111) surfaces, where there are strong indications of a tendency of the thiol groups to drive Au atoms out of the first layer, for a sufficiently high thiols coverage. Another example, where the role of hydrogen bonds is crucial, is the formation of ordered rows of pairs of cysteine molecules at the Au(110) surface (see Figure 2). These pairs form after strong HB form between the cysteine carboxylic groups. During the adsorption process, whole rows of gold atoms are removed from the surface, to accommodate the binding of the cysteine pairs.

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