Intermolecular H-Bonding for Porphyrin Molecules on Surfaces: experimental evidences and theoretical investigation.

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Abstract

The study of the chemical bond of adsorbates on and with surfaces is of particular importance for new widespread developments, from healthcare to electronics or environment. In most cases these interactions are weak and they can be considered in the context of supramolecular chemistry, which studies the organization of systems based on weak and reversible non-covalent interactions. Among them, hydrogen bond is one of the most important. It is defined as *X*-H···*Y* where the H atom is in between another two, *X* and *Y*, and acts like a bridge between them. *X* and *Y* can be the same or different elements and depending on their nature the strength of the bond varies. Thus, bonds of the type C-H···F are one of the weakest interactions whereas it has been demonstrated that the most strongest, ubiquitous and persistent H-bonds are those formed between O and N atoms in the carboxylic acids and pyridine groups (therefore N-H···O-C or C-O-H···N). [1]

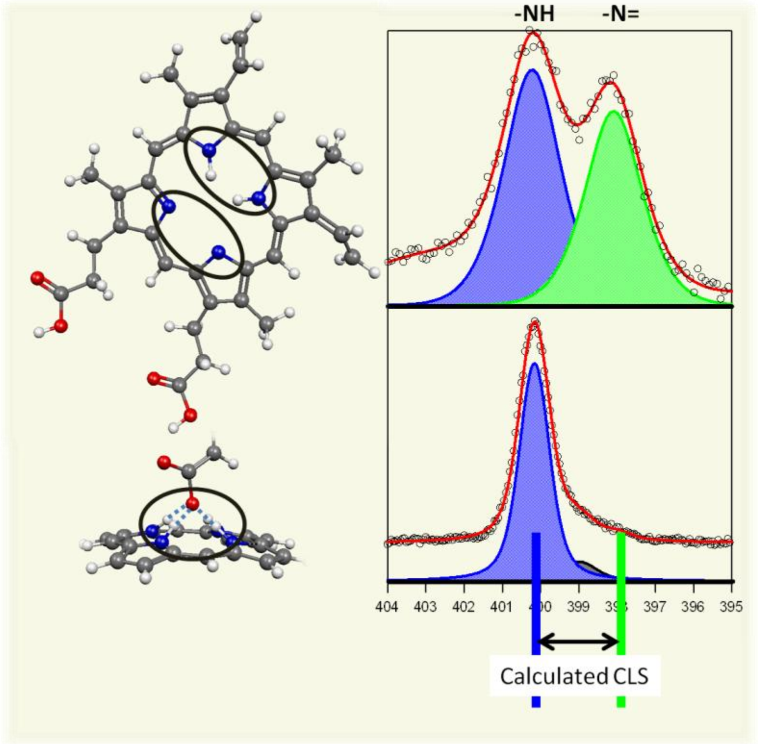

Figure 1 Experimetnal N 1s core levels of the H2PPIX in powder (top) and H2PPIX on Cu(110) (bottom)and the calculated CLS for both different N environments. The molecules adsorved on the surface exhibit the formation of H bonds (covalent H-N H-bonds as well as N-H□O-C H bonding

In the present work we detect the formation of this type of H bond for porphyrin molecules adsorbed on metal surfaces. Particularly, by the comparison of the experimentally observed shifts of the core-levels with first principle calculations, it is possible to identify the nature of the interaction of protoporphyrin IX molecules (H2PPIX) evaporated on Cu surfaces at low-temperature

By X-ray photoelectron spectroscopy (XPS) it was observed that the shape of the N 1s core level of H2PPIX evaporated on Cu surfaces at low temperature (around 200K) was different than the expected one: the component related to the N atoms in a N-H form is higher than expected [2]. Figure 1 illustrate this effect comparing the N1s of the H2PPIX power with the

H2PPIX adsorbed on Cu(110). The ab-initio calculation of the XPS core level shift (CLS) [3] determines the new intermolecular interactions for H2PPIX on Cu surfaces. Calculated values of CLS of the order of 2eV explain the formation of bonds: covalent H-N H-bonds as well as N-H···O-C H bonding between the carboxylic group and the pyrrolic ring of adjacent molecules has been revealed. Moreover, the unexpected high value of the CLS for H-bonding gives a relation between H-bond strength and shifts in the core level position: as higher the core level, stronger the hydrogen bond. Thus, since CLS are strongly affected by the local and chemical environment of each atom, valuable information on the conformation of the system can be extracted by calculating core-level shifts and comparing them to measured XPS spectra.

References

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