Organic molecule adsorption on solid surfaces: chemical bonding, mutual polarisation and dispersion interaction

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ABSTRACT
We discuss some of the most relevant bonding scenarios for the adsorption of organic molecules on solid surfaces from the perspective of first-principles calculations. The adsorption of uracil and phenanthrenequinone on Si(001) and the adsorption of adenine on Cu(110) and graphite(0001) surfaces serve as prototypical examples to highlight relevant molecule–substrate interactions and their consequences for the properties of the adsystem. Covalent bonds formed during organic reactions with semiconductor surfaces significantly modify the structural and electronic properties of both the adsorbed molecules and the substrate. Organic molecule adsorption on metals may be driven by mutual polarisation that leads to substantial charge transfer and rehybridisation, despite small adsorption energies. Subtle effects related to the lowering of the kinetic energy of the valence electrons as well as dispersion forces, finally, govern the interaction between the organic molecules and chemically inert substrates such as graphite.

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1 Introduction

Organic molecules are very promising building blocks for electronic devices due to the possibility of tailoring molecules with particular properties, the tunability of their characteristics and the efficiency and flexibility of deposition methods. Their functionality with respect to molecular electronics [1], nanodevices [2] and molecular recognition [3] has been intensively investigated. For some years already, molecular materials have been used in solar cells, gas sensors, heterojunctions and ultra-fast optical switches. Because they have typically dimensions of a few nanometres, molecules are the ultimate limit of electronic devices.

Self-organisation of organic molecules appears as one of the most promising approaches to the further miniaturisation of electronic devices. This so-called bottom-up approach contrasts with the exponentially increasing fabrication costs of further down-scaling the lithographic processes in the top-down approach for device manufacturing. The latter approach already has led to atomic dimensions (the gate oxide thickness of the presently produced transistors of the 65-nm generation amounts to only 1.2 nm, i.e. about 4–5 atomic SiO2 layers) and is bound to lead soon to fundamental physical limits. The rich variety of living structures that are all based on different combinations of a few molecular building blocks, i.e. amino acids, proves the usefulness and robustness of the bottom-up approach for producing complex structures. However, we are only beginning to understand how the mechanisms of molecular recognition and self-assembly could be exploited for actual device production.

In order to investigate the molecular self-organisation, suitable model systems need to be found that allow us to study the molecular interactions reproducibly and with high accuracy. Surface adsorbed molecules are an obvious choice. They are accessible to sophisticated surface analysis tools such as scanning tunnelling microscopy (STM) as well as electron diffraction techniques, infrared and other optical spectrosocopies. However, suitable substrates must be chosen that ensure that the molecule–molecule interactions are not completely masked by the interactions between the substrate and the molecules. In this context, metal substrates or graphite are often used as static checkerboards for the molecules [4, 5]. In particular in the latter case, the substrate-induced perturbations of the molecular properties are minimal and the molecule seems to swim freely on the substrate, as illustrated in Fig. 1 for the case of adenine adsorbed on graphite(0001) [6]. Highly ordered structures of adenine are also observed on Cu(111) [7–9] and on Cu(110) surfaces [10]. STM images show that in the latter case ordered one-dimensional molecular chains grow along the lateral [±1, 2] directions (given with respect to [110] and [001]). Upon increasing the adenine coverage, the chains order into chiral domains of \( \frac{1}{2}(\frac{2}{6} \cdot \frac{6}{0}) \) periodicity. The interaction of homochiral adenine chains on Cu(110) with inherently chiral molecules may lead to the formation of diastereoisomers due to enantiomeric interactions [11]: while co-adsorption of S-phenylglycine leads to decorations of only those adenine chains that are oriented along the [1, 2] direction in the surface plane (see Fig. 2), the separate adsorption of R-phenylglycine on an adenine-treated Cu surface shows amino acid molecules now decorating chains aligned along [−1, 2].

While metal and chemically inert surfaces are well suited for investigating such fundamental aspects of molecular...
recognition and self-assembly, organic molecule adsorption on semiconductor surfaces seems now to become more relevant for device applications. In fact, the combination of the available and highly sophisticated silicon-based integrated-circuit technology with the rich variety of chemical, electronic and optical properties that can be realised using tailor-made organic molecules is very promising for the development of new semiconductor-based devices [12, 13].

In chemistry, structural theory is an extremely useful method of classifying the enormous number of organic compounds into smaller, more tractable families. It is based on the observation that molecules with similar arrangements of atoms will react similarly. These atomic arrangements are known as functional groups. Polyfunctional organic molecules can react with solid surfaces in a variety of ways, which opens the possibility of purposeful tuning of the surface properties. The adsorption of polyfunctional groups on solid surfaces can also be used to form an ordered array of functional groups available for further reactions [14, 15].

The deoxyribose nucleic acid (DNA) bases adenine, guanine, cytosine and thymine as well as uracil are polyfunctional molecules that are particularly amenable to the synthesis of complex molecular structures, due to their Watson–Crick complementarity. In this brief review, we use the adsorption of uracil and phenanthrenequinone on Si(001) as well as the adsorption of adenine on Cu(110) and graphite(0001) surfaces as prototypical model systems to highlight important aspects of organic molecule adsorption on solid surfaces.

2 Adsorption on semiconductor surfaces

Some functional groups relevant for molecular adsorption on semiconductor surfaces are shown in Fig. 3. They are separated into two categories, see also [16]: the bonding functional groups include alkanes, alkenes and alkynes. Each of these functional groups have all of their valence electrons paired in bonds between neighbouring atoms. Alcohols, amines, carbonyls and nitriles, in contrast, contain non-bonding valence electrons that are not paired with an electron from an adjacent atom. These non-bonding electrons are spin coupled into a single non-bonding orbital also known as a lone pair. This division of organic molecules allows for a rough classification of organic chemistry at the semiconductor surface: molecules with bonding functional groups tend to form pericyclic surface products. The $[2+2]$ cycloaddition reaction of cyclopentene with Si(001) is a well-investigated example [14, 17, 18]. Molecules with non-bonding groups, on the other hand, have a significant cloud of electronic charge that can be donated during electrophilic/nucleophilic reactions, e.g. by forming a dative bond with the ‘down’ Si(001) surface dimer atom. Often this is the precursor for a subsequent proton transfer. The adsorption of pyrrole [19] or butanediol on Si(001) [20] are examples for the latter class of reactions. However, there are examples that are not so easily categorised. Phenanthrenequinone, for example, has two carbonyl groups that allow for the formation of a $[4+2]$ cycloaddition product with the Si(001) surface dimer [21, 22]. However, the donation of the O lone-pair electrons into the empty $p_z$ orbital of the Si down dimer atom is the probable precursor state.

The adsorption in a weakly bound precursor state by dint of lone-pair donation followed by a proton transfer is reminiscent of water adsorption on Si(001) [23, 24]. Upon heating the substrate to around 600 K, the oxygen of the surface bonded hydroxyl group can insert into the silicon to form a Si–O–Si structure. The pathway to oxidation, however, consists of multiple activation barriers [25]. Similarly, the adsorption of organic molecules on the surface may occur in steps, where the formation of the final structure will depend on the preparation conditions. Unlike the relatively simple case of water, however, the complexity of organic molecules allows for exploiting the activation barriers to tune the surface electronic and optical properties. This has been investigated by Seino et al. for the case of uracil adsorption on Si(001) [26, 27] using density functional theory (DFT) calculations within the generalised gradient approximation (GGA).