

## ELECTRONIC AND STRUCTURAL PROPERTIES OF COMPLEX SURFACES AND NANOSTRUCTURES FROM FIRST-PRINCIPLES

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First, I will briefly introduce some of the work that has been performed recently in the DIPC and the joint CSIC-UPV/EHU Materials Science Research Centre on the physics of surfaces and nanostructures. Particularly, I will present some of the theoretical work in the field of the dynamics of electronic excitations and adsorbates: lifetimes of surface and image states [1], plasmons [2,3], charge transfer from adsorbates [4,5,6], chemical reactions of molecules and catalysis [7,8], etc...

Then I will describe with more detail two particular examples: i) water absorption on the surface of NaCl and the oxygen covered Ru(0001) surface [9,10,11], and ii) the electronic, magnetic and structural properties of Ni substitutional impurities in carbon nanotubes [12].

Thin films of water molecules cover most surfaces under ambient conditions. This phenomenon is crucial in biology, material sciences and chemistry. For example, chemical reactions occurring at the wet surface of sea salt aerosols, which are mainly composed by NaCl particles, play a fundamental role in tropospheric chemistry. Our calculations [9] show that a significant amount of the surface chlorine ions are very likely to emerge in the presence of only one monolayer of water adsorbed on the NaCl(100) surface already at low temperatures. These findings support the AFM measurements that show a strong negative surface dipole along flat NaCl terraces already at this coverage [9]. The energy associated with the Cl<sup>-</sup> rising is governed by electrostatic interactions. Thus, the low energy cost for the anion emergence is a consequence of the efficient screening provided by the highly polarizable water monolayer. This process is important to understand the catalytic activity of the NaCl surfaces at low relative humidity, with implications for surface reactions in salt aerosols, where chloride anions play a key role.

We have also investigated the structure and energetics of the first hydration layer on NaCl(100) at larger coverages [10]. We have analyzed in detail the role of the hydrogen bond between the adsorbed molecules for the determination of the most favourable structures. Using water dimers as basic building blocks two very stable and approximately degenerate structures can be constructed: i) a model with (1x1) periodicity at 2 ML coverage, ii) ice-like bilayers with a c(4x2) unit cell at 1.5 ML. Based on these findings, we propose an interpretation for the experimental observed transition of the periodicity the first hydration layer on NaCl(100) from (1x1) to c(4x2) upon electron irradiation. According to our model, the transition would be driven by the partial desorption of (1x1) bilayer structures corresponding to a local coverage of 2ML and the further rearrangement of the remaining water molecules to form a quasi-hexagonal structure with c(4x2).

We have also studied the adsorption configuration of water on O(2x2)/Ru(0001) combining STM experimental information with first-principles calculations [11]. Substantial differences in the adsorption energies and geometries are found when compared to the clean metallic Ru(0001) surface.

Finally, I will present some of our results for the electronic, magnetic and structural properties of Ni substitutional impurities in carbon nanotubes. Interestingly the magnetic properties of these impurities are shown to strongly depend on the metallic or insulating properties of the

host nanotube and on the Ni concentration. Only for metallic carbon nanotubes and low impurity concentration the Ni atoms develop an appreciable magnetic moment. The interaction between these moments seems to be ferromagnetic.

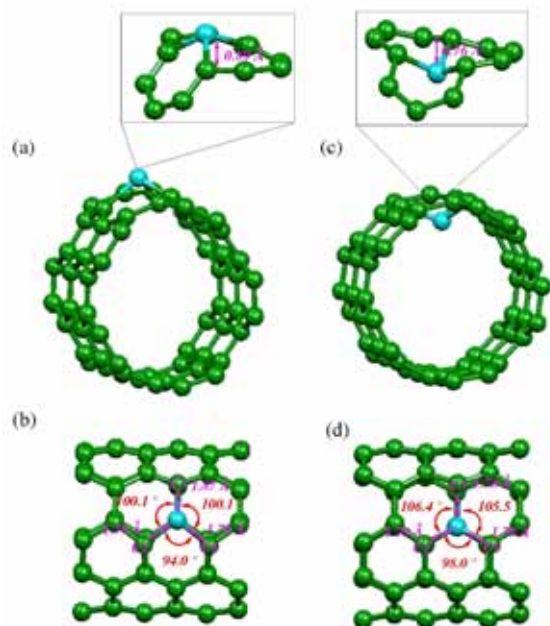


Figure. Two stable geometries for a Ni substitutional impurity in a (5,5) metallic nanotube. *Outward* geometries are always more stable than *inward* relaxed structures.

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