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Chemisorption of atomic chlorine on metal surfaces and the interpretation of the induced work function changes

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Abstract

The interaction of Cl on different metal surfaces has been studied by density functional theory. The surface is represented by periodic slab models. It is shown that the change on the surface work function induced by the presence of the adsorbed halide can be either positive or negative, depending on the surface metal. While this has already been pointed out for some particular cases such as Cl on Cu(0 0 1) or N on W(1 0 0), we show that this effect may also appear in the case of having the same adsorbate on different metal surfaces. Therefore, one may conclude that the use of the work function change to extract information about the net charge on the adsorbate should be regarded with extreme caution.
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1. Introduction

Halogens on metal surfaces may be considered as rather simple surface science systems with well defined surface structures [1,2]. At the same time, they may be regarded as typical electrochemical systems since they constitute one of the simplest models for specific adsorption. Therefore, halo-gens on metal surfaces have been studied with some detail both in ultra high vacuum [3–8] and in electrochemical environment [9]. The experimental work has also triggered various theoretical studies aimed at interpreting the experimental findings and determining the oxidation state of the adsorbed species [10–14]. In fact, in spite of the lack of direct experimental evidence for the net charge on the adsorbed halogen, theoretical studies based on the cluster model molecular orbital approach show compelling evidence that the interaction of a halogen with a metal surface involves a

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charge-transfer process in which the halogen is finally adsorbed as halide. Bagus et al. [10] have used several methods of analysis of cluster wave functions to study the nature of the interaction between halogens and a silver surface and concluded that the halogen net charge is essentially -1. Similarly, Rubio et al. [12] have studied the halogen–mercury interaction with similar models and methods and reached the same conclusion. Later on, these results have been confirmed by periodic calculations based on density functional theory (DFT) [15,16]. Hence, it may be safely concluded that chemisorption of halides on metal surfaces constitutes a key example of the formation of an ionic chemisorption bond.

The net charge on the adsorbed halide has several consequences on the observable quantities. In particular, it provokes changes in the metal surface work function (Φ) and also affects the adsorbate and substrate core-level binding energies [17,18]. The jellium model proposed by Lang and Kohn [19] permits one to understand the physical origin of Φ and the changes on it induced by ionic adsorbates. In their seminal paper, Lang and Kohn show that the metal electronic density extends beyond the geometric surface plane creating a surface dipole which hinders the path from a free electron to the vacuum. Therefore, it is almost universally accepted that the presence of a positively charged adsorbate must reduce the surface dipole and hence lead to a decrease of the surface work function. Similarly, a negatively charged adsorbate should lead to an increase in this property. Notice, however, that the real estimate of the net charge on the adsorbate through a change in the surface dipole needs the distance from the adsorbate to the surface plane. The latter is already a tricky quantity as already pointed out by Lang [20] and studied in more detail by García-Hernández et al. [21] (see also Ref. [18]).

Nevertheless, the trend expected from these simple and intuitive arguments is almost always observed although with some exceptions which have been considered as anomalies. The case of N on W(100) is one of the best known in the Surface Science community. N chemisorption on most well defined W crystal faces leads to an increase in Φ; however Φ decreases when the interaction takes place precisely on W(100) and some other faces [22–24]. According to the accepted interpretation this would mean that N takes positive or negative charge depending on the crystal face; this is very counter intuitive. Recently, based on periodic plane wave DFT calculations Michaelides et al. [25] have shown that the work function decrease induced by N adsorption on W(100) is consistent with a negative charge on N and that the reason for the, in principle, unexpected behavior is the overspill electron density into the vacuum. Here it is worth pointing out that an identical interpretation was given in the mid eighties by Pettersson and Bagus [26]. These authors have studied the interaction of Cl on Cu(100) by means of the Hartree-Fock cluster model approach and have shown that a small reduction in the surface dipole moment is compatible with a large negative charge on the adsorbate. Hence, they concluded that changes in the work function are not a measure of the adsorbate ionicity. Here, it is important to stress that, although with some temporal gap, cluster model and slab calculations came to the same conclusion. This is of course rewarding and provides a clear example of the need to avoid oversimplified pictures to interpret complex physical phenomena.

An important aspect of the case of N on W surfaces is that it shows that the same adsorbate can produce increase or decrease of Φ depending on the surface plane. The interpretation of Michaelides et al. [25] suggests that this is due to the particular electronic structure of a given atomic plane. Therefore, one may wonder whether a similar situation may appear when considering always the same surface plane and adsorbate but a different substrate. This is precisely the aim of the present work. To this end periodic DFT based calculations have been carried out for the interaction of chlorine on the (001) surface of Cu, Ag, Au, Rh, Pd, Pt; a series of metal surfaces with a sufficiently large variation of Φ. The surface structure, bonding parameters and work function have been calculated. Depending on the metal, the calculated variations of Φ show positive or negative shifts with respect to the bare surface thus reinforcing the ideas by Bagus and Pettersson [26] and Michelaides et al. [25] that it is not correct to use