

Ionic adsorbate structures on metal electrodes calculated from first principles

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Abstract

¹ The equilibrium coverage of metal electrodes in contact with an electrolyte has been addressed by periodic quantum-chemical calculations based density functional theory. The electrolyte has been treated in a grand-canonical approach using the concept of the computational hydrogen electrode. After briefly reviewing the theory and illustrating it using the co-adsorption of bromide and hydrogen as an example, the interaction of nitrate with a Pb(111) electrode is addressed. A spontaneous reconstruction of the uppermost Pb layer is observed leading to the formation of a salt-like layer.

Introduction

Electrochemistry is concerned with structures and processes at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte.¹ The electrolyte

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is often in the liquid phase, in particular in electrocatalysis, containing ions to make it conductive. Typically, these ions, especially anions, are subject to an attractive interaction with electrodes leading to a concentration of the ions on or near the electrodes that is much higher than their equilibrium concentration in the bulk electrolyte.² These ions are part of the electrical double layer, but their interaction with the electrode can also modify the electronic and chemical and even structural properties of the electrodes significantly.²⁻⁶ Because of this significant effect the presence of ions in the electrolyte can have on electrode properties, it is important to understand and predict the thermodynamically stable structure of adsorbed ions as a function of environmental parameters such as ion concentration in the electrolyte and electrode potential.

The theoretical description of the interfaces of electrodes with liquid electrolytes represents a considerable conceptual and numerical challenge as both the liquid phase of the electrolyte and the presence of electrified surfaces needs to be taken into account⁷⁻⁹ which requires to perform computationally costly statistical averages and consider charged electrodes. Note that at electrochemical interfaces the reference for the adsorption energy has to be determined with respect to the corresponding species in solution. However, in a very elegant grand-canonical approach that is now coined computational hydrogen electrode (CHE)^{10,11} the evaluation of solvation energies can be avoided. It corresponds to the combination of atomistic calculations with a grand-canonical approach to describe the reference energy of the adsorbates.^{12,13} It is particularly useful for electrochemical systems as it is based on the observation that at specific thermodynamic conditions species in solution are in equilibrium with corresponding gas-phase species which are much easier to describe theoretically.^{10,11,14,15} In addition, the dependence of the reference energy on electrochemical parameters such as electrode potential, pH and ion concentration is known. Furthermore, at metal electrodes adsorption energies are often only weakly dependent on the presence of the electrochemical environment.^{10,11,16-19} This concept has been rather successfully used to address electrocatalytic reactions on metal and oxide electrodes.^{10,11,20-23} We have recently used this concept

to derive the equilibrium coverage of halides on metal electrodes,²⁴ furthermore we extended this approach to address the co-adsorption of halides and hydrogen on Pt(111).²⁵ We could successfully reproduce and explain the experimental observation^{26–28} of the competitive adsorption of halides and hydrogen as a function of electrode potential.

In this paper, we will first briefly review the concept to derive the equilibrium coverage of ions on electrode surfaces from first-principles electronic structure calculations based on density functional theory (DFT) and illustrate the findings. We will then extend this approach to address the interaction of nitrate with Pb(111). This system was chosen because it corresponds to the electrochemical setup recently used in a single-atom transistor controlled by the electrode potential^{29–32} as a model for a microscopic quantum device.³³ There we will demonstrate that the presence of anions in the electrolyte can lead to a severe restructuring of metal electrodes, for example leading to the formation of a salt layer.

Computational details

The DFT calculations presented in this paper were done using the periodic electronic structure code VASP,³⁴ employing the Perdew, Burke and Ernzerhof (PBE) functional to account for the exchange and correlation effects.³⁵ For the electron-core interaction the projector augmented wave method was used.^{36,37} The electronic one-particle wave functions were expanded in a plane-wave basis set up to an energy cutoff of 500 eV. Different surface unit cell sizes were employed in these studies. In each case it had been made sure that the special k -points set used to replace the integration of the first Brillouin zone are chosen large enough to yield converged results.

Stable adsorbate phases are characterized by the minimum in the free energy of adsorption per surface area A_S :²⁴

$$\Delta\gamma = \frac{1}{A_S} (G_{\text{surf,ads}} - G_{\text{surf,0}} - \sum_i n_i \mu_i) . \quad (1)$$

Here $G_{\text{surf,ads}}$ and $G_{\text{surf},0}$ are the Gibbs free energies of the adsorbate-covered and the clean surface, n_i is the number of adsorbed atoms of the type i per surface area A_S , and μ is the chemical potential of the adsorbates in their corresponding reservoir. In electrochemical systems, the chemical potential has to be replaced by the electrochemical potential $\tilde{\mu}_i = \mu_i + z_i e U$, where z_i is the charge state of the particle, e the elementary electric charge and U the electrode potential. As mentioned above, in electrochemical situations the electrochemical potential is given with respect to the solvated particle whose energy is hard to calculate as it involves thermodynamic integration scheme. However, one can take advantage of the fact that there are specific thermodynamic conditions in which the solvated particle is in equilibrium with a corresponding particle in the gas phase. For example, the proton in solution is in equilibrium with the hydrogen molecule in gas phase at standard conditions,



In fact, this equilibrium defines the standard hydrogen electrode (SHE). This means that one can use the H_2 molecule in the gas phase as a reference which is much easier to evaluate than the proton in solution. Furthermore, it is known how the electrochemical potential of the proton in solution depends on electrode potential U and pH:

$$\tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{H}_2} - eU_{\text{SHE}} - k_B T \ln(10)\text{pH} . \quad (3)$$

This concept is not restricted to hydrogen, but can be used for any redox couple.³⁸ For example, for halides such as Cl^- , Br^- , and I^- , the corresponding relation for the electrochemical potential reads

$$\tilde{\mu}_{\text{A}^-} - \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{A}_2} + e(U_{\text{SHE}} - U^0) + k_B T \ln(a_{\text{A}^-}), \quad (4)$$

where U^0 is the reduction potential of the corresponding halide, and a is the thermodynamic activity of the anion A^- .

This is the essence of the concept of the computational hydrogen electrode. It still remains the problem that in Eq. 1, the free energies of adsorbate-covered electrode and the uncovered electrode need to be determined. It is common practice in applications of the computational hydrogen electrode to neglect entropic contributions and the influence of the electrochemical environment, namely the presence of the electrolyte and the variation of the electrode potential, in the determination of $G_{\text{surf,ads}}$ and $G_{\text{surf},0}$. As far as metal electrodes is concerned, this approximation seems to be justified^{10,11,16–19} because of the strong chemical interaction with electrodes and the good screening properties of metals. This allows to use DFT total energies instead of free energies so that Eq. 1 can be replaced by

$$\Delta\gamma = \frac{1}{A_{\text{S}}} \left(E_{\text{surf,ads}} - E_{\text{surf},0} - \sum_i n_i \tilde{\mu}_i(T, p, U) \right). \quad (5)$$

Finally we reformulate this expression by referring the electrochemical potentials of the solvated species to the corresponding stable gas-phase species and the electrochemical potential of the electrons²⁵ that corresponds to the Fermi energy of the metal electrode, similar to what is done in *ab initio* thermodynamics,¹³ arriving at

$$\Delta\gamma(T, p, U) = \frac{1}{A_{\text{S}}} \left(E_{\text{ads}}^{\text{tot}} - \sum_i n_i \Delta\tilde{\mu}_i(T, p, U) \right). \quad (6)$$

where the adsorption energies $E_{\text{ads}}^{\text{tot}}$ are taken with respect to the gas-phase species. Note that in this particular formulation the dependence of the free energy of adsorption on entropic contributions entirely enters through the corresponding dependence of the electrochemical potentials of the species in the reservoir on temperature, pressure, and electrode potential.

Results and Discussion

We will illustrate the approach to determine the thermodynamically stable adsorbate structure at electrochemical electrode/electrolyte interfaces using the co-adsorption of hydrogen

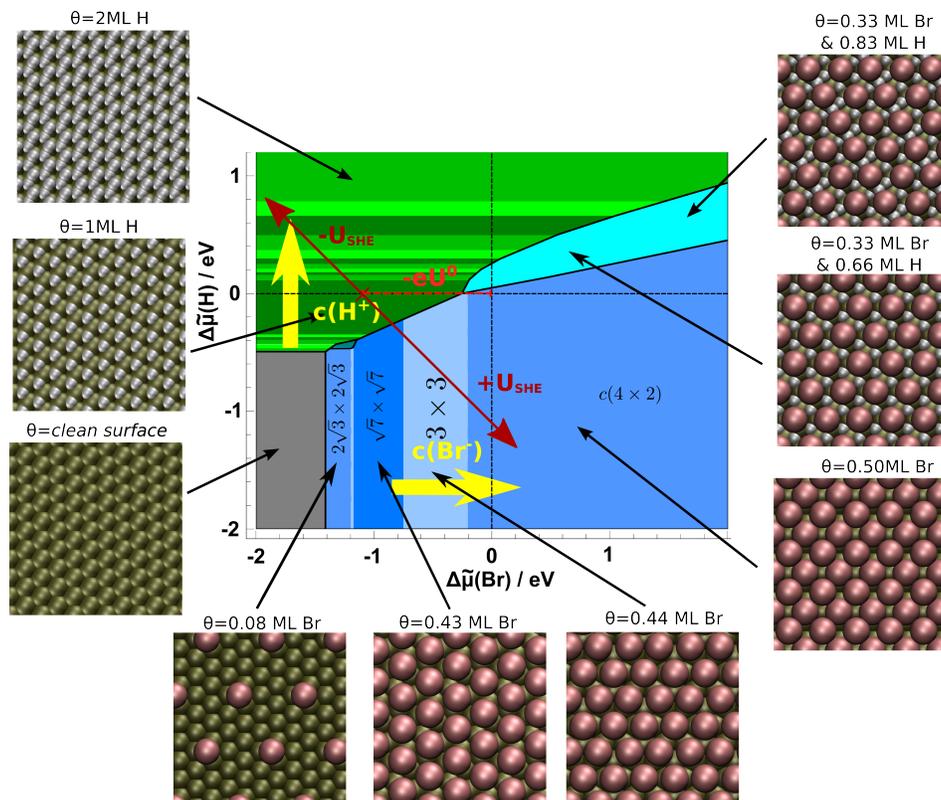


Figure 1: Stable phases of co-adsorbed bromine and hydrogen on Pt(111) as a function of the electrochemical potentials of hydrogen and bromine. Bluish areas denote pure bromine coverages, greenish colors show pure hydrogen coverages and the turquoise area denotes a co-adsorbed structure of both H and Br. Only the most stable structures are illustrated in sub-figures. Especially in the case of hydrogen adsorption are regions where the stable coverage is varying dynamic in between the sub-figures. The red double arrow denoted by $-eU^0$ indicates a variation of the electrode potential with all other parameters kept fixed at standard conditions, whereas the yellow arrows illustrate the influence of the ion concentration.

and bromine on Pt(111) as an example. Experimentally, it has been observed that the substitution of adsorbed hydrogen by bromine on Pt(111) as a function of electrode potential occurs in a very narrow potential range,^{28,39} indicative of competitive adsorption. Cyclic voltammograms further show^{40,41} that on the negative going scan the bromine desorption peaks appear at potentials negative to the hydrogen adsorption peaks on the clean surface, demonstrating that hydrogen is replaced by bromine. This is at first glance surprising because one would expect that there is an attractive electrostatic interaction between an adsorbed cation (proton) and an adsorbed anion (bromide).

As a first step, several adsorbate structures of hydrogen and bromine alone and both adsorbates together within (3×3) , $c(4 \times 2)$ and $(\sqrt{7} \times \sqrt{7}R19.1^\circ)$ surface unit cells were determined and the adsorption energy evaluated. The (3×3) and $(\sqrt{7} \times \sqrt{7}R19.1^\circ)$ structure were observed in experiments^{39,42,43} whereas the $c(4 \times 2)$ structure was seen for a chlorine adlayer on Pt(111).⁴⁴ In these calculations, no electrolyte was present. However, we have recently shown⁴⁵ that for halide coverages above $1/3$ closed water layers form above the halide adsorbate layer, i.e., the water molecules do not penetrate into the halide adsorbate structure.

Note that according to Eq. 6, as a function of the electrochemical potentials of the proton and of bromide each adsorbate structure is represented by a plane in a three-dimensional space spanned by $\Delta\tilde{\mu}_{\text{H}^+}$, $\Delta\tilde{\mu}_{\text{Br}^-}$ and the Gibbs free energy of adsorption $\Delta\gamma$, and for a given set of electrochemical potentials the structure with the lowest $\Delta\gamma$ corresponds to the thermodynamically stable phase.

The resulting phase diagram is plotted in Fig. 1 together with an illustration of the structure of the stable phases. Most of the phase space is characterized by either purely hydrogen-covered (greenish colors) or purely bromine-covered (bluish colors) region. Typically there is an indirect repulsive interaction between adsorbates through adsorption-induced modifications of the metal substrate.⁵ However, one could imagine that this might be compensated by an attractive dipole-dipole interaction between adsorbed anions and cations. However, there is apparently no attractive interaction between adsorbed hydrogen and bromide. This result can be understood considering the fact that the adsorption of bromine on Pt(111) leads to an anomalous work function decrease⁴⁶ caused by the strong polarization upon adsorption.⁴⁷⁻⁴⁹ As a consequence, a dipole-dipole repulsion between adsorbed bromine and hydrogen results.

However, in electrochemistry, the electrochemical potential of solvated species is typically not specified, but rather the concentration and the electrode potential. The variation of the electrode potential at standard conditions is illustrated by the red arrows in Fig. 1.

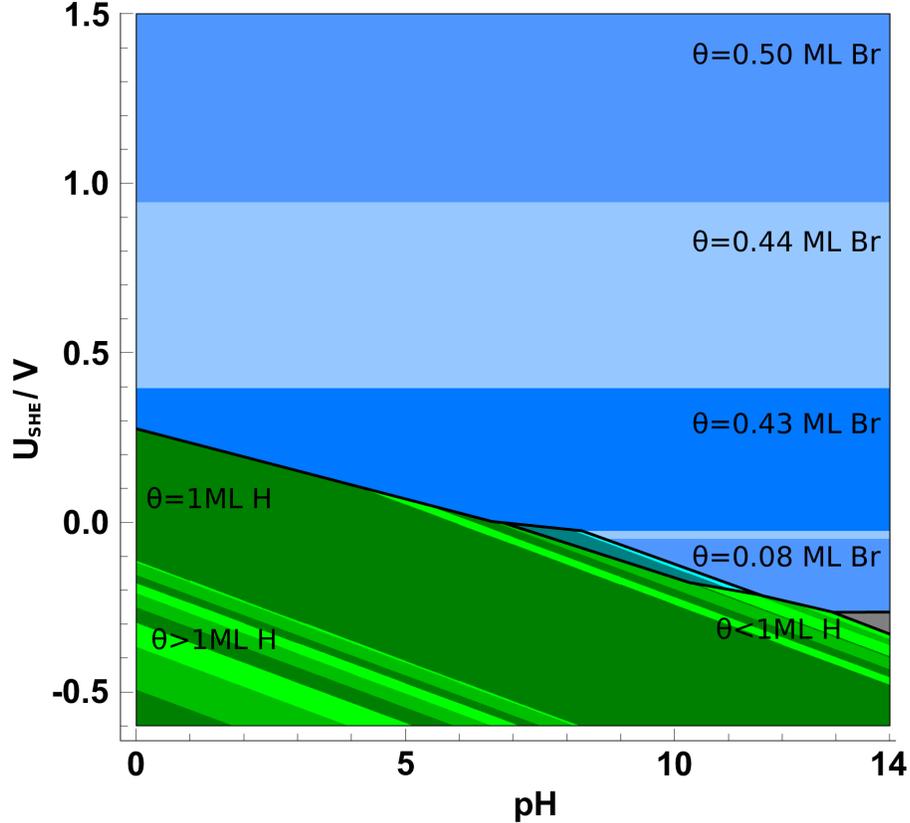


Figure 2: Calculated Pourbaix diagram, i.e., a map of the stable phases of co-adsorbed bromine and hydrogen on Pt(111) as a function of pH and electrode potential for a fixed bromine concentration corresponding to an activity of $a = 0.1$. The color code is the same as in Fig. 1 where also the geometric structures of the corresponding phases are given. Greenish colors denote a pure hydrogen phase, bluish colors a pure bromine phase. In between the hydrogen and bromine phases, there is a thin region, where a co-adsorbate structure with both species is stable. The gray area corresponds to a region where the clean, uncovered electrode is stable.

Hence it is rather helpful to transform the phase diagram into Pourbaix diagram, i.e., into a map of the stable phases as a function of pH and electrode potential. The Pourbaix diagram derived from the phase diagram plotted in Fig. 1 is shown in Fig. 2. For a given pH value, the stable surface structures as a function of the electrode potential can be directly read off, an information, that is directly relevant for the interpretation of cyclic voltammograms. The diagram demonstrates that indeed upon increasing the electrode potential purely hydrogen-covered phases are replaced by purely bromine-covered phases. Due to the presence of bromine, the upper potential edge of the stable hydrogen phases is shifted to

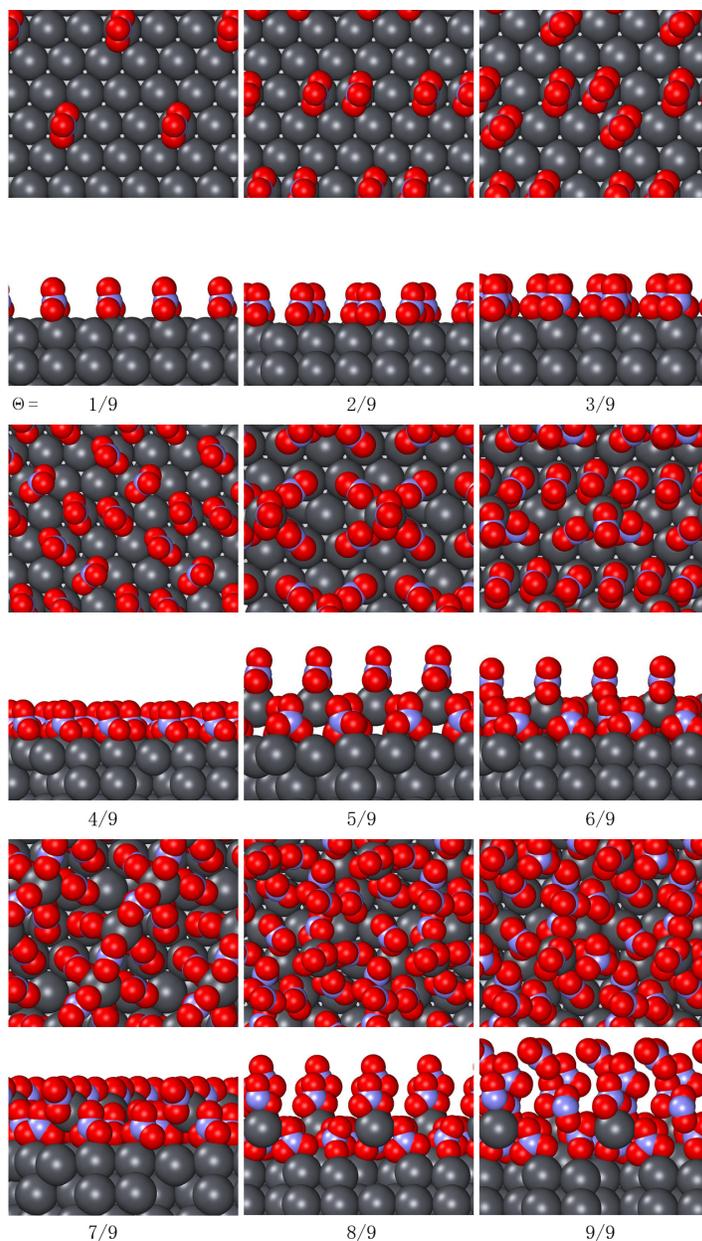


Figure 3: Illustration of the structures of nitrate adsorbed on Pb(111). Pb atoms are colored in dark grey, oxygen in red and nitrogen in blue.

lower potentials, confirming the competitive nature of hydrogen and bromine inferred from the experiment.^{28,39-41} Only at higher pH values there is a small pocket in which hydrogen and bromine co-adsorption structures are stable, but only over a rather narrow potential range, thus confirming experimental findings.^{39,50}

The stable bromine phases correspond either to a $(\sqrt{7} \times \sqrt{7}R19.1^\circ)$ structure with a

coverage of $\Theta = 3/7$ or a 3×3 structure with $\Theta = 4/9$. Both structures have been observed in the experiment^{39,42,43}. The calculated results for the co-adsorption of hydrogen with chlorine and iodine are also all consistent with experimental observations²⁴ indicating the reliability of the approach outlined here based on the computational hydrogen electrode.

This same approach has also been used to evaluate the interaction of nitrate with Pb(111). Pb electrodes have recently been of interest as they are one of the materials used to realize a single-atom transistor in an electrochemical environment²⁹⁻³² which opens attractive perspectives to prepare microscopic quantum devices.³³ It is based on the fact that atomic-scale quantum point contacts can be reversibly switched as a function of the electrode potential. Still, the details of the operation of the single-atom transistor are not understood. Therefore, in a series of first-principles-based studies we have tried to elucidate possible mechanisms to form atomic contacts at Pb electrodes⁵¹ and to determine the water structure at flat and stepped Pb electrodes.^{45,52} We have now extended this project in order to assess the influence of nitrate (NO_3^-) on the structure of Pb electrodes as a nitrate-based electrolyte has been used in the experiments realizing the single-atom transistor.³¹

Again, the first step is to search for minimum energy adsorbate structures for various coverages. To the best of our knowledge, there is no experimental study identifying the structure of nitrate on Pb(111). Therefore we have chosen a 3×3 surface unit cell that should be sufficiently large to allow the formation of different structures. Still it should be admitted that thus we might miss some stable structures. However, without prior knowledge of the periodicity of adsorbate structures a search for all possible arrangements is computationally extremely demanding.

The considered structures within 3×3 surface unit cell are illustrated in Fig. 3, the corresponding adsorption energies are shown in Fig. 4. At low coverages, the molecules arrange on the unreconstructed Pb(111) surface, the adsorption energies become less negative with increasing coverage indicative of a repulsive interaction between the adsorbed nitrate molecules. Interestingly enough, at coverages starting from $\Theta = 5/9$, the Pb(111)

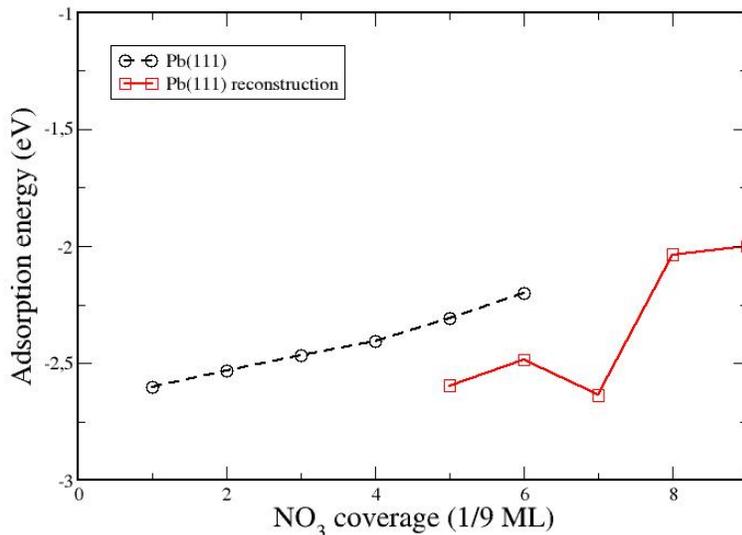
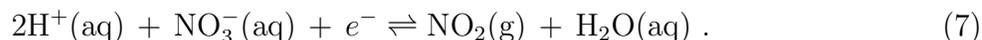


Figure 4: Adsorption energy of NO_3 on Pb(111) per molecule as a function of the coverage. Black circles denote adsorption on the unreconstructed electrode, red boxes correspond to adsorption involving a reconstruction of the Pb(111) electrode.

spontaneously reconstructs upon exposure to nitrate. A lead atom is extracted from the Pb electrode and forms a Pb- NO_3 complex. This is associated with a significant energy gain. The ease to form such a complex involving the extraction of a Pb atom from the surface is obviously a consequence of the relatively low cohesive energy of lead of 2.03 eV/atom.⁵³ Note that in these calculations the presence of the electrolyte was ignored. However, water is relatively weakly interacting with lead. For example, the adsorption energy of water monomers on Pb(111) is only -0.07 eV.⁵² Hence we do not expect that the chemically driven reconstruction of Pb(111) will be strongly modified by the presence of water.

The stable adsorption phases as a function of the electrode potential are plotted in Fig. 5. In order to derive this phase diagram based on the concept of the computational hydrogen electrode, the following redox couple has been used to define a reference for nitrate,



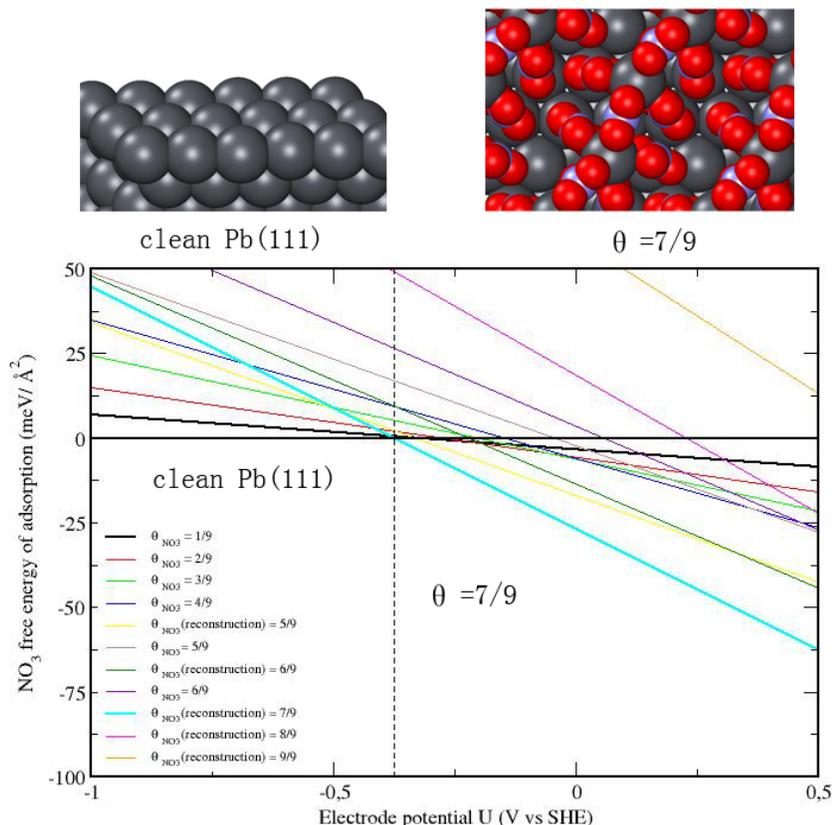


Figure 5: Phase diagram of the stable nitrate structures as a function of electrode potential.

Furthermore, a nitrate activity $a_{\text{NO}_3^-} = 1$ has been assumed. Up to an electrode potential of about -0.4 V vs. SHE , the clean Pb(111) electrode is thermodynamically favored. For higher electrode potentials, the reconstructed Pb(111) electrode at a nitrate coverage of $\Theta = 7/9$ becomes stable over a wide potential window corresponding to the conditions typical for electrochemical experiments in aqueous electrolytes. Inspecting Fig. 3 reveals that for this coverage a complete lead nitrate layer evolves. At lower coverages, this layer is not completed, at higher coverages a new layer starts to grow.

In order to understand the origin of the stability of the reconstructed Pb(111) electrodes at a nitrate coverage of $\Theta = 7/9$ involving the the formation of a Pb-NO₃ complex even further, we compare in Fig. 6 the structure of bulk lead nitrate with the corresponding complex on the Pb(111) surface. Panels a and c show the bulk unit cell of Pb(NO₃)₂ and

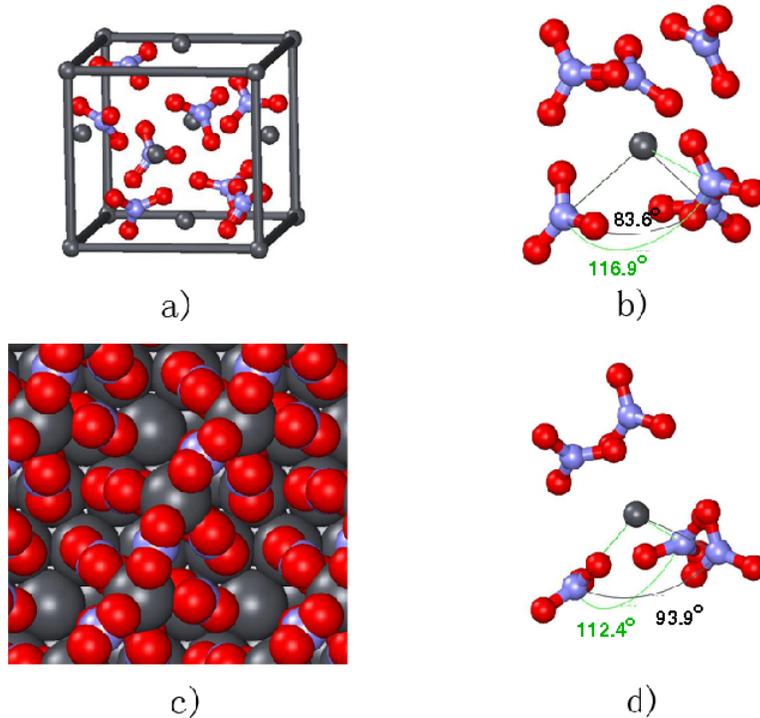


Figure 6: Comparison of the $\text{Pb}(\text{NO}_3)_2$ bulk structure and the structure of the lead nitrate complex formed spontaneously on $\text{Pb}(111)$ at a nitrate coverage of $\Theta = 7/9$. a) Bulk unit cell of $\text{Pb}(\text{NO}_3)_2$, b) arrangement of nitrate around a Pb atom in the bulk, c) top view of reconstructed $\text{Pb}(111)$ surface, d) b) arrangement of nitrate around a Pb atom in the surface complex.

the top view of reconstructed $\text{Pb}(111)$ surface, respectively. The local nitrate arrangements around the lead atom in the bulk and in the surface complex are compared in panels b and d. Due to the lattice mismatch between bulk lead nitrate and $\text{Pb}(111)$, no perfect agreement should be expected. Still the local arrangements are rather similar. We illustrate this by particularly considering the N-Pb-N angles with regard to the NO_3 groups nearest to the Pb atom. In the bulk, these angles have values of 83.6° and 116.9° , as indicated in Fig. 6b. In the case of the reconstructed $\text{Pb}(111)$ surface, these particular angles are only slightly modified to values of 93.9° and 112.4° , respectively, and the local coordination is also hardly changed, as Fig. 6d shows. This indicates that the nitrate-induced surface reconstruction of $\text{Pb}(111)$ can be viewed as the formation of a surface lead nitrate layer or as the initial step of lead nitrate salt formation⁵⁴ inspite of the fact that lead nitrate readily dissolves in water⁵⁵.

Our results show that the exposure of a metal electrode to an aqueous electrolyte can lead to a substantial surface re-structuring. This is of course not the case for any anion-containing electrolyte. However, once such a surface reconstruction occurs, it significantly modifies the structural, electronic and chemical properties of the electrode and should not be neglected.

The results presented in this study show that first-principles calculations using the concept of the computational hydrogen electrode are a powerful tool to determine equilibrium structures of metal electrode/aqueous electrolyte interfaces. In the determination of the adsorption energies entering the formalism, the explicit influence of the electrolyte and of varying electrode potentials has been neglected. This approximation is justified by the good screening properties of metals. However, there is certainly a need to assess the validity of this approximation by including the electrochemical environment explicitly. First steps along this route have already been taken.^{17–19,23,56} For the results presented in this work, explicitly considering the electrochemical environment in the calculations will change the results quantitatively to a certain extent, but it is not expected that any qualitative trends will become modified.

Conclusions

The structure of metal electrode/aqueous electrolyte interfaces has been studied by first-principles calculations treating the electrochemical environment in a grand-canonical approach based on the concept of the computational hydrogen electrode. Phase diagrams of the thermodynamically stable adsorbate structures as a function of electrochemical potentials have been derived which allows, e.g., to derive Pourbaix diagrams that can be directly compared to experiment. Addressing the co-adsorption of hydrogen and bromine on Pt(111), the results were able to reproduce the experimentally observed competitive nature of the co-adsorption. The presence of a nitrate-containing electrolyte over a lead electrode leads to a

significant reconstruction of the lead electrode presenting the first steps of lead nitrate salt formation.

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