The interaction mechanism of cesium with water on the SrTiO$_3$(100) surface at room temperature

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Abstract

The interaction of water with cesium on the strontium titanate surface SrTiO$_3$(100), was studied, mainly by means of work function measurements and thermal desorption spectroscopy. The catalytic role of cesium with respect to the dissociation of water on surface was investigated, by applying two different adsorption processes at room temperature (RT): (1) The adsorption of water on the cesium covered surface (sequential adsorption), and (2) the co-adsorption process (simultaneous adsorption) on surface. Based on the results and by adopting the Lewis acid–base model, we conclude that during the sequential adsorption the water molecules are mostly adsorbs non-dissociatively on surface, without oxidizing the alkaline overlayer. This seems to be due, first to the strong interaction between the alkaline adatoms and the substrate, and secondly to the limited maximum pre-deposited amount of cesium (≤ 0.45 ML). Instead, water dissociation appears to merely occur on defective sites of the substrate in accordance with previous studies. For a full cesium layer covered surface, the adsorbed water retracts the metallicity of cesium due to electrostatic interactions. In contrast to the sequential adsorption, during the co-adsorption process the oxidation of cesium takes place above a critical coverage of cesium (≥ 0.45 ML). It appears that the co-adsorbed cesium with water modifies the surface potential providing an effective template for cesium oxide, Cs$_2$O development. Based on that, we suggest a catalytic reaction of water dissociation according to the Langmuir–Hinshelwood mechanism. Finally, we propose atomistic adsorption models for both processes of cesium with water adsorption.

Keywords Adsorption · Cesium · Strontium titanate · Lewis model · Cesium oxide · Water dissociation · Langmuir–Hinshelwood mechanism

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Introduction

Over the past decades, the interaction of water with solid surfaces has intensively attracted the research interest in several scientific fields, such as corrosion chemistry, heterogeneous catalysis, electrochemistry, solar energy conversation, fuel cells, photocatalysis etc. The so far provided knowledge is well presented in excellent reviews [1–5], by giving information about how the water behaves on different type of surfaces, such as metals, oxides and semiconductors. Basically there are two possibilities for the adsorbed water molecules on a surface: a) the associative or molecular adsorption, and b) the dissociative adsorption. Although the enthalpy change seems to be a rough thermodynamic criterion of what adsorption pathway will be followed [6], kinetic effects cannot be ignored [3, 7, 8]. Furthermore, in some cases the structure as well as the temperature [9], the composition [10] and the morphology of the substrate (steps or terraces) [11], seems also to play a decisive role in determining whether or not dissociation of water will take place on surface. In addition, water-surface bonding can be influenced by the presence of additives and their coverage on surface, thus enhancing the dissociative adsorption [12–14]. Moreover, the surface imperfections like steps [11, 15], edges [16] and defects [17] can also promote water dissociation. On the other hand, additives such as CO, H and Br on metal surfaces, do not favor the dissociative adsorption of water (see Sect. 6.2.1 in [1] and references therein). In contrast, the electronegative adsorbed oxygen, in most of the cases promotes the dissociation of water on surfaces [10, 13, 17–20], although there are cases where preadsorbed O prevents the dissociation process [21, 22]. Concerning the electropositive additives, alkali metals have attracted much of interest mainly because most of them are constituents of many electrochemical cells. In general, alkalis promote the dissociation of water depending on the coverage, temperature of adsorption, the kind of alkali atom and the type of substrate [7, 12, 14, 23–28]. For example, although Li, Na and K enhance the dissociation on nickel surfaces under certain conditions [26], Li and Cs do not allow dissociation on the Ag(110) surface at any instance [29, 30]. Also Cs submonolayer quantity on the Cu(110) surface, does not dissociate but instead increase the adsorption energy of water [31]. In contrast, Shi and Jacobi [27] reported that Cs submonolayers of 0.25 and 0.33 ML on the Ru(001) surface, cause dissociation of water, while for 0.08 ML predeposited cesium, H2O adsorbs molecularly on surface. In addition, Cs on the MgO(100) surface dissociates the adsorbed water too [32]. From the above discussion, it is obvious that there is no a common behavior of alkalis. Differently, it seems that their role in the water-surface interaction strongly depends on the conditions of the adsorption process and the type of the substrate.

Generally speaking, it is widely accepted, that when water molecules are adsorbed on surfaces, they interact mostly through their O atoms. Water-surface interaction through hydrogen bonds is rare. In most of the cases, the interaction occurs with a charge transfer to the surface, resulting in a negative WF change (see [1] and references there in). This makes water to act as an electron donor (Lewis base), whereas the surface as electron acceptor (Lewis acid). The Lewis...
acid–base simple model has been extensively applied to the chemistry of metal surfaces and heterogeneous catalysis [16, 33, 34]. In principle, the oxygen atom in water molecule is electronegative due to the interaction between the O 2s and 2p atomic orbitals with that of the H 1s. This makes water a polar molecule with an electric dipole moment in the gas phase equal to $p = 1.83 \times 10^{-18}$ esu.cm or 1.86 D [35]. Therefore, the adsorbed molecular water (associative adsorption), by inducing negative work function changes, it should orientate its dipole moment “outwards” of the surface. If the water molecule dissociates on surface (dissociative adsorption), then OH and O may be formed. Because of their electronegativity, both of these species can extract electrons from the surface, thus becoming anions and inducing positive WF change.

In general the chemisorbed water shows a relatively weak bonding with surfaces, thus placing the adsorption of water on the borderline of physisorption. The weakness of the water-metal interaction is due to van der Waals forces [36], which act synergistically and promote the intermolecular hydrogen bonding between the adsorbed water molecules. This effect leads to the formation of water clusters on surfaces and affects the WF [31, 37–39]. However, cluster formation inhibits the study of the real H$_2$O-surface interaction, therefore someone needs to work at low coverages and low temperatures (< 100 K).

Regarding the water adsorption on the strontium titanate surface, SrTiO$_3$(100), the so far numerous works have shown that the surface is inert to water adsorption at room temperature (RT) [40–44]. However at low temperature [41, 43, 45], or after ion bombardment (reduced sample) [40–42], or at high exposure pressures [46], water adsorbs non dissociatively on the SrTiO$_3$(100) surface, although dissociation has also been reported in some cases of bombarded [45, 47] and stepped samples [15, 47]. Theoretical studies have also been carried out with some of the results to be in conflict, regards to the dissociation or non-dissociation of the adsorbed water on strontium titanate [48, 49].

Strontium titanate, SrTiO$_3$ (STO) is a perovskite-oxide compound, which has been used for decades as electrode and catalyst for light-assisted water splitting [50–52]. In addition, the interaction of water with catalytic promoters such as alkalis on oxide surfaces, is of great importance in heterogeneous catalysis. For this reason it is intriguing to study any catalytic interference of alkalis (if so) in the water-STO interaction. Therefore in this work we study: (a) the water adsorption on the clean and the cesium covered STO(100) surface, and (b) the co-adsorption of water and Cs on the same perovskite surface. Both adsorption processes carried out in ultra high vacuum (UHV) conditions at RT. Most of the previous studies concerning the water adsorption on cesiated surfaces were performed in sublayer regime and at low temperatures. By this work, our aim is to clarify the role and the possible catalytic behavior of cesium regards to the water dissociation in more realistic conditions such as room temperature defines. In this manner we approach better the real experimental conditions of corrosion, electrochemistry and photocatalysis. Thus, we will hopefully provide useful results for the design and construction of more effective based on the STO electrodes, for photolysis of water in electrochemical cells [53–55].
**Experimental section**

All the experiments were performed in a usual UHV system equipped with basic surface analysis techniques, such as Auger electron spectroscopy (AES), low energy electron diffraction (LEED), electron energy loss spectroscopy (EELS), thermal desorption spectroscopy (TDS), and an electron gun for relative work function (WF) measurements by the diode mode. The base pressure in the UHV chamber during the measurements was of the order of $10^{-10}$ Torr.

A monocrystal SrTiO$_3$(100) doped by Fe acceptors (0.14 wt%) purchased from Crystal GmbH and used as substrate, fixed within a Ta foil case and mounted on a rotated X–Y–Z manipulator. The substrate heating was performed by passing current through a 0.05-mm thick Ta strip, uniformly pressed between the sample and the Ta case. The temperature of the substrate could be measured by a spot welded NiCr–NiAl thermocouple onto the case. The thermocouple was calibrated by an infrared pyrometer within the 250–1100 °C temperature range. The cleaning process of the STO(100) surface was performed by Ar$^+$ ion sputtering with energy $E=2$ keV, at argon gas pressure $\sim 10^{-6}$ Torr, for $\sim 30$ min bombarding time. The restoration of the $1 \times 1$ substrate symmetry checked by LEED, was achieving with post annealing at about 400 °C.

The TDS experiments were carried out by a linear rate of the sample heating $\sim 17$ K/s. The experimental error of the desorption temperature was estimated at about $\pm 20$ K. The changes of the WF of the surface were recorded by measuring the characteristic $I–V$ curve of a diode, with an electron gun playing the role of the cathode and the substrate such of the anode. The accuracy of the relative WF measurements was at about $\pm 0.05$ eV. The AES measurements were performed by utilizing a primary electron beam with energy, $E=2$ keV. The Auger electrons were collecting and analyzing by a Varian cylindrical mirror analyzer (CMA), with an accuracy of 0.1 eV for the O(KLL) Auger transition line. The AES as well as EELS spectra were recorded in the first derivative mode, $dN(E)/dE$, and the signal intensity was measured from the peak to peak height (AP-PH).

Cesium quantities were deposited on the substrate by evaporation from a commercial SAES Getters source. The heating current of the source during the evaporation was 6.0 A. By considering one monolayer (1 ML) of Cs on the STO(100) surface equal to $6.56 \times 10^{14}$ atoms cm$^{-2}$, the deposition rate was estimated $\sim 0.028$ ML/min. Finally the water adsorption was performed by exposing the surface to the pressure of vapors of distilled water through a beakable leak valve. The exposure was counted in Lagmuirs, L ($1 \text{ L} = 10^{-6} \text{ Torr} \times 1 \text{ s}$), while the base pressure was not exceeded $10^{-8}$ Torr during the water adsorption.
Results and discussion

Cs adsorption on the STO(100) surface

Initially we investigated the adsorption of cesium on the clean STO(100) surface. Here we briefly present the main results since a full report has been published elsewhere [56]. AES measurements based on the Auger peak to peak height (AP-PH) of Cs (47 eV), O (510 eV) and Ti (380 eV) Auger transition lines, showed that Cs on the STO at RT develops with constant sticking coefficient up to the completion of an almost physical layer of the absolute coverage ~0.45 ML. This estimated coverage is in agreement with previous studies [30–32]. Above this coverage, the sticking coefficient of Cs decreases drastically almost to zero, preventing the development of a second Cs layer. The cesium overlayer is amorphous, since the 1 × 1 LEED pattern of the clean STO(100) surface was gradually disappeared. No any new order was observed at any Cs submonolayer coverage. In addition, according to the WF and TDS results, the Cs adatoms at low coverages are ionic or strongly polarized, while as the overlayer is getting formed, it becomes metallic with no indication of substrate reduction and any CsₓOᵧ compound formation.

H₂O adsorption on the clean and Cs covered STO(100) surface

The interaction of water with catalytic promoters such as alkalis on oxide surfaces, is of great importance in heterogeneous catalysis. Since work function is a very sensitive physical property to even tiny chemical and structural changes of the surface, we firstly recorded the WF change ΔΦ of the clean as well as the Cs pre-covered STO(100) surfaces versus water exposure. Fig. 1 shows the ΔΦ change as a function of H₂O exposure for the clean and two different cesiated STO surfaces of about 0.28 and 0.45 ML coverage.

Fig. 1 The work function change ΔΦ of the clean and cesiated STO(100) surfaces as a function of the H₂O exposure at room temperature
On the clean surface, the WF increases continuously up to about 0.55 eV for 100 L water exposure. Differently, on the covered with 0.28 ML of cesium STO surface, the WF initially decreases at about ΔΦ = -0.15 eV for ~20 L of H₂O exposure, and then increases up to ΔΦ = 0.45 eV at 150 L. A similar behavior is noticed during water exposure on the pre-covered with almost one single layer of cesium, Cs(0.45 ML)/STO surface. In the latter case, however, the initial decrease ΔΦ of the WF is larger and equal to about -0.35 eV for ~15 L exposure. Further water adsorption gradually leads to less negative ΔΦ resulting to a final WF just ~0.12 eV higher than that of the clean STO (Fig. 1). We observe that the more pre-deposited cesium, the deeper ΔΦ minimum (lower WF) is recorded, while a slower WF increase follows. Finally, it is clear that the water exposure increases the WF of both cesiated surfaces. We note, however, that the higher cesium coverage, the longer water exposure is needed to get a positive ΔΦ (120 L against 35 L). Conclusively, the above described WF changes are strong indications of water adsorption on both type of STO surfaces (cesiated and clean) either with dissociative or associative mode.

In order to investigate the adsorption process further, we recorded the desorption states of water and cesium by performing TDS measurements. Fig. 2 presents the TDS spectra of the Cs QMS signal after H₂O exposure on the Cs(0.45 ML)/STO(100) surface at RT. A first important observation is that as the H₂O exposure increases, the low temperature cesium TD peak, which is attributed to the metallic state [56], shifts to higher temperature. This effect indicates that the binding
energy of the initially participating in the metallic phase Cs adatoms increases with the presence of H$_2$O on the surface. In other words, it seems that water retracts the metallicity of cesium overlayer and increases the bond strength of Cs with the substrate. Regards to the high temperature TD peak at about 1200 K, no substantial change is observed. This desorption state is due to the strong Cs-substrate interaction probably of ionic nature, once almost the half of the Cs overlayer has been thermally removed from the surface.

Fig. 3 shows the QMS signals of Cs, H$_2$O, O and H$_2$ respectively, from the Cs(0.45 ML)/STO(100) surface exposed to 50 L of H$_2$O at RT. As we observe, at desorption temperatures (< 500 K) the TD peaks of H$_2$O and O do not coincide with any TD peak of Cs. This presumably indicates that H$_2$O does not interact chemically with Cs. In the case of chemical interaction, the water dissociation should had been correlated with the formation of CsxOy compounds on surface. However, no any CsO, CsOH or Cs$_2$O compound was detected by the QMS. An additional and quite
impressive observation is that water desorbs from surface within a high temperature range of about 550–1130 K. A possible explanation of this effect could be the recombination of co-adsorbed species as OH, O and/or H. In that case a dissociative water adsorption should be taken place on surface. Regarding the 1050 K water desorption state, we notice simultaneous H₂O, O and H₂ desorption states which may be an indication of such recombination process. However, in order to further investigate the possibility of water dissociation on the cesiated STO surface, we performed TDS measurements with the QMS focused on OH (17 amu). No clear hydroxyl signal was recorded. An additional indication of no water dissociation at RT was given by EELS measurements. In fact H₂O adsorption did not show any substantial change of the EELS spectrum of the 0.24 and 0.45 ML cesiated STO surfaces (not shown). The characteristic EELS features of Cs covered STO surface remained unchanged up to exposure of 120 L. In contrast to our results, OH and O anions have been identified for alkali metal covered Ru(001) surface, indicating water dissociation above a critical alkali’s coverage [24]. Finally, we consider that more detailed measurements are required to elucidate the nature of the peculiar water high temperature desorption states.

We also performed TDS measurements of atomic oxygen for water exposure of 50 L on the clean and cesiated STO(100) surfaces. The results are shown in Fig. 4. The O desorption at ~ 360 K, from the clean STO surface indicates that this desorption state is irrelevant to cesium. Moreover, apart from a reasonable small decrease, this atomic oxygen TD peak remains almost unaffected versus the cesium coverage. Concerning the cesiated surfaces, however, two other O desorption states appear at ~550 K and ~1050 K. Both of them seem to depend on Cs coverage as they

![Graph](image-url)

**Fig. 4** The O (16 amu) QMS signal after H₂O(50 L) adsorption on different cesiated STO(100) surfaces at room temperature. The spectra are shifted along the vertical axis, therefore bear in mind the zero intensity dotted lines.
increase in intensity. Therefore we ascribe these O desorption states to some kind of interaction between water and cesium. On the other hand no QMS signal of molecular oxygen was recorded.

Let us now discuss the adsorption of water based on both of our WF and TDS results. According with the literature, although no or negligible water adsorption is reported on the clean defect-free STO(100) surface at RT [40–44], water can be adsorbed under some particular conditions. More specifically, associative adsorption has been observed at low temperature [41, 43, 45], at high pressure [46] and on reduced STO surfaces [40–42]. Differently, dissociative adsorption has been observed for stepped [15, 47] or defective areas with oxygen vacancies on the STO surface [43, 45, 47]. More recently Becerra-Toledo et al. by comparing experimental and simulated scanning tunnelling microscope (STM) images found that the reconstructed 2×1 and 4×1 STO surfaces can be explained by dissociative water adsorption [57], while other reconstructions such as c(4×2), 2×2 and (\(\sqrt{2} \times \sqrt{2}\)) R45° can adsorb water too [8]. In addition, Hinojosa et al. by performing density functional theory (DFT) calculations, predicted water dissociation on the TiO₂ terminated STO(100) surface at low coverages (< 0.5 ML) and temperatures [49]. In our case, the WF change of the clean STO after water exposure is an indication that water adsorption occurs in some extent. Based on the literature, the reason for that may be a number of surface defects or oxygen vacancies on the surface. Furthermore, in contrary to what happens with the metallic surfaces, our results show that water adsorption causes a WF increase of the STO surface. This can be attributed to a dissociative water adsorption instead of a molecular one, since adsorbed hydroxyls and/or oxygen are electronegative and expect to act as electron acceptors (Lewis acid), thus increasing the WF [58]. On the other hand, it is known that the molecular adsorption of water on surfaces usually causes a WF decrease (see Table 5 in [1]). Therefore the WF increase of the clean STO surface shown in Fig. 1, can be explained with O anions and/or OH⁻ radicals’ adsorption on defect sites after water decomposition. We believe that such kind of defects and O vacancies cites were created in our STO sample after the repeating annealing cycles. This is actually an experimental fact, since we have previously recorded TiO desorbing compound, after heating the clean STO(100) surface above 1100 K [59].

As far as it concerns the initial WF decrease for both cesiated surfaces, this behavior is consistent with the consideration of water as a Lewis base. This can be visualised by adopting a simplified adsorption model of molecular physisorption, where the water molecules initially “relax” on atop site of the Cs adatoms, as Fig. 5a illustrates. Based on DFT calculations, this kind of site seems to be the most stable water adsorption site on several metallic surfaces [36, 60–62]. Moreover, atop site is also suggested as preferable for water monomers by some experimental studies too [37, 63]. In accordance with our adopted adsorption model, the majority of the water molecules should be initially adsorbed on the cesiated STO surface, along with the C₂ᵥ point group molecular coordination by forming an “outwards” initial dipole moment \(p_o\) across the surface, thus explaining the initial WF decrease. The molecular adsorption of water is also preferred to dissociative one on the Na covered STO(100) surfaces, as experimental [44] and theoretical work [64] support too. In contrast, Cs predeposition above a critical coverage on other substrates such as
Ru(0010) [27], Cu(110) [31] and MgO(100) [32], induce water dissociation with hydroxyls formation to cause a WF increase [27, 31]. Based on that, the initial WF decrease is a good argument for molecular adsorption of water on the cesiated STO surfaces. However, we cannot rule out the formation of hydroxyl species on surface, at least in some extent, as the adsorption processes proceeds. We invoke this eventuality because of the final positive measured ΔΦ (WF increase) of both cesiated STO surfaces. We discuss this issue below.

In principle, the experimentally measured WF change after the associative adsorption of a molecule on the first atomic layer of a surface, can be due to two effects: (1) to dipole moment of the adsorbed molecule (permanent or induced), and (2) to the net electron transfer between the adsorbate and the substrate [1, 33]. In our case, apart from the water polarization itself, the initial ΔΦ decrease in Fig. 1 could be due to a modified water polarization induced by the electropositive Cs adatoms through an electrostatic interaction. This interaction probably takes place through the “lone pairs” of the oxygen atom, thus enabling the O to coordinate on the Cs adatoms, which at low alkali coverages, are expected to be positive ions [32, 56]. Similar electrostatic interaction has been reported between water molecules and predeposited Na on the STO(100) surface [44]. Such kind of interaction results in water polarization and clustering around the alkaline adatoms, without cleavage of the internal bonds of water molecules [44]. In that view, the more predeposited Cs adatoms on surface, the larger WF reduction is expected after water adsorption. This

![Fig. 5](image-url)
is in line with the larger initial $\Delta \Phi$ change recorded for water adsorption on the Cs(0.45 ML)/STO surface, compared to that on Cs(0.28 ML)/STO (Fig. 1). Therefore, we mainly attribute the stronger WF lowering to the more extensive water adsorption on the surface. The 0.45 ML of Cs, however, corresponds to a rather metallic state. Based on that, we can not exclude a charge accumulation from the O atom of water to the metallic Cs overlayer, which causes a stronger polarization of the adsorbed molecules of water. Actually, such kind of charge rearrangement has been confirmed by DFT calculations on investigating the geometric structures and electronic properties of the water-gold interface [65]. In fact, the calculations predict a charge accumulation from O to the Au top atoms, leading to polarization of the water molecules, as such as to decrease the WF of the surface. Similar water polarization and WF decrease has been calculated for water adsorption on other metals too [66]. However, as more water molecules nucleate around the cesium adatoms, the acidity of neighboring Cs adatoms is gradually reduced due to inductive effects [51]. These effects in combination with some possible depolarization and clustering effects between neighboring interacting water molecules, may lead to a smaller mean surface dipole moment $p$ for adsorbed water as it is depicted in Fig. 5b. Moreover water clustering may induce a significant tilting of the water polar axis towards the surface level, as previous calculations [60] and experiments [31] indicate. This tilting results in a slower rate of WF decrease. In general, hydrogen bonding between two or more neighboring H$_2$O molecules, is often competitive with the water-substrate bond, leading to water clusters formation even at low coverages [1, 31, 35, 67, 68] or at room temperature, too [44]. In addition, concerning the gradual WF increase after the work function minimum, we can not exclude a partial reorientation of the water molecular dipole moment by the cesium overlayer itself, with the hydrogen atoms pointing towards the surface and forming the so called H-down bilayer [66]. Such kind of water molecules reorientation induced by electropositive additives is supported by previous experiments [31] and calculations too [69, 70]. This eventuality together with that of the hydroxyls formation at the defective substrate sites, is depicted in Fig. 5c.

Finally the gradual WF increase ends up to a positive $\Delta \Phi$ for both cesiated surfaces. Apart from the water clustering, a plausible explanation for the WF increase is the dissociation of water to hydroxyls and O or H at the uncovered defective sites of the STO surface. Since the Cs(0.28 ML)/STO surface is less covered than the Cs(0.45 ML)/STO surface, it leaves more STO defective adsorption sites available for water dissociation. This could be the reason why the final positive $\Delta \Phi$ is much higher for the less covered with cesium STO surface than that with the full layer.

Out of the TDS results (Fig. 2), we noticed that water retracts the metallicity of cesium overlayer. This interpretation is in accordance with the already discussed WF results, where a charge rearrangement between water and Cs adatoms has been reckoned. In this manner, the Cs-water electrostatic interaction removes in some extent the metallicity of the pre-deposited alkaline overlayer, by weakening the Cs-Cs interaction. Analogous behavior has been observed after oxygen exposure on Cs/Si(111) [71] and Na/Si(111) surfaces [72]. The interaction, however, between water and cesium should be in the range of physisorption, as previously denoted for the Na modified STO surface too [44, 64]. This is consistent with the absence of CsO,
CsOH or Cs₂O compounds detection, which normally are expected to be the result of water dissociation. Based on that, the desorbing water at about 350 K should be irrelevant to Cs adatoms. Therefore, we assume that this water desorption state is possibly the recombination product between preformed OH anions on defective STO sites, according to the reaction

$$\text{OH(s)} + \text{OH(s)} \rightarrow \text{H}_2\text{O(g)} + \text{O(g)}$$

This reaction is in line with the atomic O desorption state recorded at the same temperature range in Fig. 4. In fact this desorption state is not energetically affected by the cesium coverage. In addition, previous studies, report that water desorption states above RT are due to OH fragments’ recombination [1, 2, 45, 73, 74]. Furthermore this thermally activated surface reaction has been proposed for water adsorption on alkali metals (K, Na and C) covered Ru(001) surfaces, after annealing up to 300 K and 470 K [24]. Moreover, early experiments of water adsorption on reduced STO samples have confirmed the hydroxyls presence on surface [75, 76].

Finally, concerning the two higher temperature O desorption states at ~550 K and ~1050 K, unfortunately it is not possible to determine their origin for sure out of the present results. Perhaps the oxygen desorption state at 550 K is due to hydrated cesium responsible for the metallicity retraction of cesium overlayer (see Fig. 3). We make this assumption because of the coincidence of this oxygen desorption state with that of cesium at ~550 K (see Fig. 3). Regarding the high temperature O desorption state (~1050 K), it may be due to chemisorption of spurious oxygen from the surroundings, because of the high sticking coefficient of oxygen on the cesiated surfaces [77–79].

**H₂O and Cs co-adsorption on the STO(100) surface**

Apart from the sequential adsorption, we also performed co-adsorption experiments of Cs and H₂O on the STO(100) surface at RT. In these experiments, we provided vapors of water into the vacuum chamber during the deposition of Cs on the STO surface. Note that the Cs deposition took place at water vapor pressure ~ 3.75 × 10⁻⁸ Torr. Under these conditions of co-adsorption, we performed TDS measurements searching mainly for CsₓOᵧ compounds. As Fig. 6 shows, desorbing cesium oxide Cs₂O was recorded at about 900 K. It is quite interesting that Cs₂O was detected, only if the corresponding Cs coverage was ≥ 0.45 ML or equivalently larger than one physical layer. In other words, it seems that a critical quantity of Cs is required, in order a chemical reaction between Cs and water to occur. Moreover, the cesium oxidation probably takes place as long as the reactants are in the gas phase and close to the surface, which presumably is strongly modified by the first cesium layer. Differently, if Cs₂O was formed away from the substrate, it should had been deposited and detected in the TDS measurements for Cs coverages even less than 0.45 ML. However, such eventuality of chemical reaction between cesium and water in the gas phase is unlikely. A second important observation in Fig. 6, is the dramatic increase of the Cs₂O QMS signal recorded for 0.70 and 0.90 ML cesium coverages. Assuming that two atoms of
Cs are required for each reacting molecule of water in order to form a Cs$_2$O molecule, and comparing the recorded QMS signal from the 0.45 and 0.90 ML, we include that the latter is almost 10 times bigger. This means that during the co-adsorption process much more quantity than 0.45 ML of Cs develops on surface, being available to react with water and form cesium oxide. In other words, the growth of at least a second physical layer of Cs on the STO(100) surface seems to be feasible during the co-adsorption process. This process allows the water splitting on surface. The water dissociation probably leads to an almost fully cesium oxidized layer formation above the first pure cesium one. The disproportion between the Cs coverage and the cesium oxide formation is demonstrated in Fig. 7, indicating that the oxide formation is a nonlinear effect. On the other hand, during the sequential adsorption, it is not feasible the growth of more than one layer of Cs, due to the low sublimation energy of cesium [80] and other heavy alkali metals too [81]. This cesium coverage limitation appears to be a serious constrain for developing Cs$_2$O on surface.

From the above description we conclude that the first deposited layer of cesium is not available for oxide formation, even under the co-adsorption process conditions. In contrast, the second layer of cesium seems to become extensively

![Coadsorption of H$_2$O and Cs on STO(100)](image)
oxidized. The reason for this cesium behavior on surface, is the initially strong interaction between Cs and the substrate at low sublayer coverages (see the high temperature TD peak in Fig. 2). It seems that this interaction, does not allow the chemical reaction between Cs and water. Actually, the co-adsorbed water molecules appear to inhibit the metallization of cesium due to electrostatic interactions. This is in line with the sequential adsorption experiments, where we have seen that water retracts the metallicity of the pre-deposited cesium overlayer (see Sect. 3.2 and Fig. 2). When the first layer completes at about 0.45 ML, the next arriving Cs atoms to the surface are available for reaction with the impinging water molecules on the surface, thus the formation of Cs$_2$O set off. The reaction probably takes place through the Cs 6s atomic orbital, with the simultaneous colliding Cs atoms and water molecules on the surface to react with each other. The proposed catalytic mechanism is a Langmuir–Hinshelwood one with the following formula

$$2\text{Cs}(g) + \text{H}_2\text{O}(g) \rightarrow \text{Cs}_2\text{O}(s) + \text{H}_2(g)$$

The negative enthalpy formation $-345.8$ kJ/mol of Cs$_2$O compared to that of water ($-242$ kJ/mol), makes thermodynamically favored the oxidation of Cs [82]. Another possibility is the formation of cesium hydroxide, CsOH, described with the equation

$$2\text{Cs}(g) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{CsOH}(s) + \text{H}_2(g)$$

In our experiments, however, we could not detect desorbing CsOH at any instance. Therefore we should exclude the hydroxylation of cesium (at least in a detectable degree), which may be due to the fact that no abundance of water exists in the gas phase during the co-adsorption experiments (low exposure pressure of water).
Based on the above discussion, a simplified co-adsorption model can be proposed, as Fig. 8 depicts. According to that, initially Cs atoms and water molecules impinge simultaneously on the STO surface (Fig. 8a). During the growth of the first Cs overlayer no cesium oxidation occurs because of the strong interaction between the Cs adatoms and the substrate. This interaction results in a polarization of the Cs adatoms, probably through a charge transfer from the Cs 6s atomic level. As the coverage increases by approaching the first physical layer, the electrostatic interactions between the coadsorbed Cs and water molecules results in a rather non-metallic overlayer (Fig. 8b). This overlayer strongly modifies the surface potential, and provides an effective template for cesium oxidation. In other words, this template seems to catalyze the reaction between H₂O and Cs by dissociating the first and oxidizing the latter. It appears that a Cs coverage of about ≥ 0.45 ML of cesium is required in order the cesium oxidation to set off. In that sense, the next arriving Cs adatoms to the modified STO surface, by having their 6s electron free to react with the simultaneously approaching water molecules, dissociate them and form the cesium oxide layer as it is depicted in Fig. 8c. Out of the present data, however, it is not possible to reveal in more detail the mechanism of cesium oxidation on the STO(100) surface. To give an example,
it is not for sure that no cesium oxide is formed if we alternatively deposit layers of Cs and water on the STO(100) surface. Therefore more detailed measurements are necessary for both adsorption and co-adsorption procedures.

Conclusions

We have studied the interaction of water with cesium on the SrTiO₃(100) surface. Two different adsorption processes were applied. In the first one, we provided water on the pre-covered with cesium STO substrate (sequential adsorption) at RT. By combining mainly WF and TDS results and based on the Lewis acid–base model, we conclude that the water molecules seems to be adsorbed mostly associatively on the Cs covered STO. However, a significant part of the water appears to dissociate on substrate defective sites. During the sequential adsorption, there are no indications of chemical reaction between water and Cs. The main reasons for that seem to be the strong interaction between adatoms and substrate at low coverage, and the confined maximum cesium coverage (≤0.45 ML). Instead of reaction with Cs, water retracts the metallicity of the alkaline overlayer through electrostatic interactions.

In the second adsorption processes, we simultaneously exposed the STO(100) surface at water and cesium vapors at RT. For Cs coverage larger than one physical layer (≥0.45 ML), we recorded the formation of cesium oxide, Cs₂O. We interpret this compound formation by suggesting a catalytic reaction according to the Langmuir–Hinshelwood mechanism. Based on our proposed co-adsorption model, the first deposited physical layer of Cs modifies properly the surface potential, thus providing an effective catalytic template for the dissociation of water.

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