

# The interaction of alkali atoms with oxygen on W(110) as studied by UPS and metastable impact electron spectroscopy

II. K and Cs

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UPS and metastable impact electron spectroscopy (MIES) were employed to study the interaction between oxygen and K (Cs) in the coverage range up to one monolayer on W(110) (in units of the first complete adlayer at room temperature) at room temperature. For small alkali coverages below 0.5 ML the oxygen molecules are dissociated at the reactive W(110) surface and adsorbed atomically on two different adsorption sites for all oxygen exposures. In the coverage range between 0.6 and 1 ML efficient charge transfer from the alkali  $s$  orbitals to the impinging oxygen takes place as long as the  $s$  orbital is filled. Molecules are then incorporated into the alkali adlayer as  $O_2^{q-}$  ( $q \leq 1$ ) ions. Beyond the work function minimum (induced by the oxygen coadsorption) most of the adsorbed oxygen is dissociated; the oxygen atoms are then bound at the same two adsorption sites as for the oxidation below 0.5 ML alkali precoverage. The results are compared with previous results for the oxygenation of Li and Na layers on W(110) and for the oxidation of Cs films. A coadsorption diagram is constructed which allows the prediction of the oxidation stage of the surface as a function of the exposures to K (Cs) and oxygen.

## 1. Introduction

We complete the investigation of the coadsorption of alkali atoms and oxygen on W(110) at room temperature (RT) with the results obtained for K and Cs; the results for Li and Na were published previously [1]. The motivation of our work is described in detail in ref. [1]: The coadsorption of alkali and oxygen plays an important role in technological applications as for example in the oxidation of semiconductors [2]. Its importance for fundamental research is the possibility to study the oxidation states of various alkali-oxygen complexes. At present the oxidation process especially in the alkali submonolayer range is not well understood. A major problem in the investigation is the influence of the substrate and the separation of the contributions from the underlying bulk and the surface which are both

present when using UPS. Metastable impact electron spectroscopy (MIES) provides a tool with absolute surface sensitivity: electrons are emitted in collisions of metastable atoms with surfaces. Thereby the impinging metastables (here He) are deexcited by various inter- and intra-atomic Auger processes at a distance of 3–5 Å in front of the surface [3,17]. The comparison of UPS and MIES results is obviously a powerful tool to distinguish between contributions from species attached above and below the toplayer formed by the alkali atoms.

A number of studies has appeared recently in which MIES, UPS, XPS and HREELS (or a combination of these electron spectroscopic techniques) was applied to the interaction of K (Cs) and oxygen on metal and semiconductor surfaces [2,4–9,18–20,22,24]. However most of the studies were either concerned with films of several mono-

layer thickness [4,5] or have avoided to vary the alkali coverage interacting with oxygen in a systematic manner.

We present a study of the alkali–oxygen coadsorption on W(110) by combining MIES and UPS. Both the alkali coverage and the exposure to oxygen are varied systematically over a wide range. The final result of this study is a qualitative coadsorption diagram which allows one to follow the oxidation process for various initial conditions.

## 2. Experimental

The apparatus was already characterized at several occasions [1,10,11]. Briefly, it consists of a source capable of producing both metastable helium ( $\text{He}(2^3\text{S})$ ;  $\text{He}(2^1\text{S})$ ) atoms with a triplet/singlet ratio of 7:1 [12] and He I photons. The fluxes are about  $2 \times 10^{10} \text{ mm}^{-2} \text{ s}^{-1}$  both for  $\text{He}^*$  and He I. AES, LEED and residual gas analysis were employed to monitor the surface cleanliness and to analyze the residual gas composition. The base pressure is about  $7 \times 10^{-11}$  Torr without and  $8 \times 10^{-10}$  Torr with the He source switched on. Alkali layers were produced by heating a dispenser source (SAES Getters, Inc.). The preparation and calibration procedures are described in refs. [1,10,11]. In contrast to Li and Na [1] K and Cs do not form more than one complete adlayer on W(110) at room temperature (RT), corresponding to  $5.9 \times 10^{14} \text{ atoms cm}^{-2}$  for K and  $5.2 \times 10^{14} \text{ atoms cm}^{-2}$  for Cs [13]. We denote the saturation coverage at room temperature with 1 monolayer (ML).

Electron spectra were recorded with an hemispherical electrostatic analyzer of 250 meV (FWHM) fixed energy resolution. It was positioned under  $45^\circ$  with respect to the surface normal. The direction of incidence of the metastable (photon) beam is also  $45^\circ$  with respect to the surface normal. In most of the spectra presented no bias voltage was applied to the electrostatic analyzer in order to compensate the difference in the work functions of analyzer and crystal (typically partially alkaliated). These spectra show an artificial cut-off at 1 eV electron energy.

## 3. Results and identification of the peak structures

The measurements were taken in the same way as described in more detail in refs. [1,11]. The following procedures were employed:

(1) Continuous oxidation of the W(110) surface partially precovered ( $\theta_{\text{Alk}} \leq 1 \text{ ML}$ ) by alkali atoms.  $\text{O}_2$  gas is admitted at a slow leak rate usually between 0.1 and 0.2 L per minute (1 L =  $10^{-6}$  Torr · s). About ten different precoverages have been investigated for both K and Cs [14].

(2) Exposure of an oxygen loaded W(110) surface (10 L oxygen) to alkali atoms. The alkali coverage is estimated under the assumption that the sticking coefficient for alkali atoms is not altered considerably by the previous exposure to oxygen.

(3) Alternate exposure of the surface to alkali atoms and oxygen.

(4) Simultaneous exposure to alkali atoms and oxygen molecules.

### 3.1. Alkali / W(110) + oxygen

Figs. 1 to 6 present MIE and UP spectra of a W(110) surface partially covered by K (Cs) and exposed to oxygen. Results for other precoverages may be found in ref. [14]. The following features should be noticed:

The UP spectra show two peaks labeled W(5d) close to the Fermi energy  $E_F$  which represent the W d-band emission. For precoverages  $\theta_{\text{Alk}} \leq 0.4 \text{ ML}$  the presence of alkali atoms manifests itself by the 2 eV wide shoulder which appears near the Fermi level  $E_F$  (see shaded region in fig. 1). A strong peak labeled K(4s) (Cs(6s)) appears near  $E_F$  in the MIE spectra provided  $\theta_{\text{Alk}} \geq 0.4 \text{ ML}$  [15]. This peak consists of contributions from  $\text{He}^*(2^3\text{S})$  deexcitation via interatomic Auger processes involving the alkali s electrons [14,16], and autodetachment of the resonance  $\text{He}^{-*}(1s2s^2\text{S})$  [17]; its intensity strongly depends upon the surface's work function and the density of states below the Fermi level. It is accompanied by a small peak at the high-energy side which represents the same processes, but induced by  $\text{He} 2^1\text{S}$  atoms. The decrease of the intensity of the alkali

induced peak K(4s) (Cs(6s)) with increasing oxygen exposure was already interpreted as the consumption of the alkali valence electrons in the binding of the oxygen to the surface [5]. For Cs the presence of surface adsorbed alkali atoms manifests itself also by electron emission due to the ionization of the Cs(5p<sub>1/2,3/2</sub>) core levels [4,5,10,15].

For small precoverages by K (Cs) (below 0.55 ML) the oxygen induced features O<sub>a</sub> (E<sub>B</sub> = 5.8 eV) and O<sub>s</sub> (E<sub>B</sub> = 7.5 eV) appear both in the MIE and UP spectra (see figs. 1 and 2). The oxygen uptake is essentially completed when the s peak has disappeared; this depends upon the precoverage, but occurs not later than 1.5 L in the precoverage regime up to 1 ML. As for Li and Na we suggest that O<sub>s</sub> and O<sub>a</sub> are caused by the ionization of atomic oxygen chemisorbed at the substrate and bound to alkali atoms, respectively [1]. Michel et al. [7] propose the same interpretation for the two peaks at binding ener-

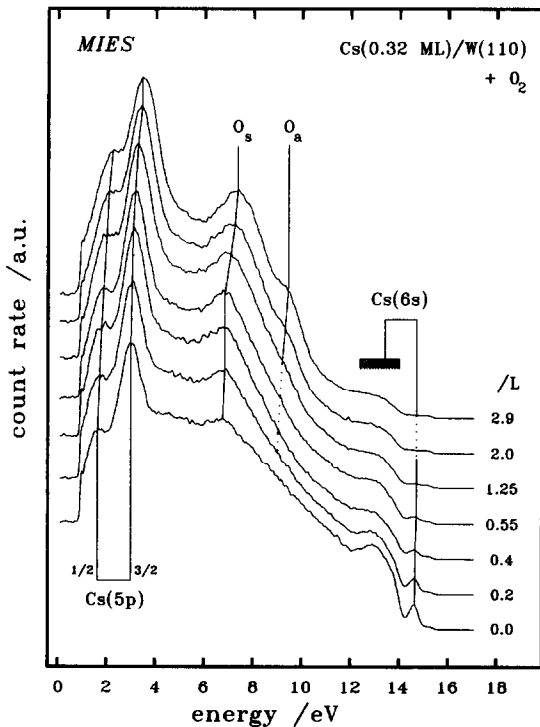


Fig. 1. MIE spectra of a W(110) surface precovered by 0.32 ML Cs as a function of exposure to oxygen.

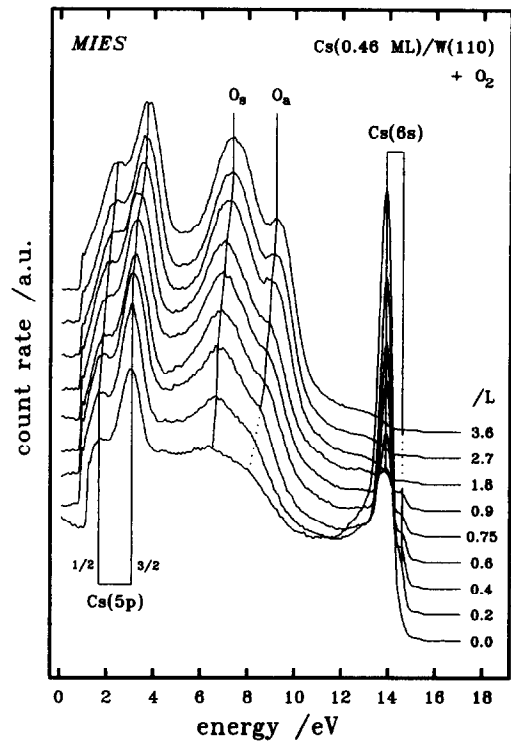


Fig. 2. MIE spectra of a W(110) surface precovered by 0.46 ML Cs as a function of exposure to oxygen.

gies  $E_B = 7.1$  and  $5.0$  eV (O<sub>s</sub> and O<sub>a</sub> respectively) obtained during the oxidation of Si partially covered by K ( $\theta_K = 0.15$  ML relative to the substrate density). They could support their interpretation also by XPS measurements. Interestingly enough, for Ru(001) partially covered by K, only one peak which must correspond to O<sub>a</sub> is seen by MIES when the surface is exposed to oxygen (peak  $\beta$  at  $E_B \approx 4.8$  eV) [9]. This can be understood when the oxygen atoms on Ru(001) are adsorbed below the Ru surface plane, and consequently are not seen by MIES.

The results for precoverages beyond 0.6 ML will be discussed separately for small (below 1 L) and large oxygen exposures: Beyond 0.6 ML Cs precoverage a three-peak structure labeled A ( $E_B = 6.3, 8.0, 10.0$  eV) appears in MIES for small exposures (see figs. 3 and 4). Similar features although less pronounced and at slightly different energetic positions are found for K (see fig. 6a). In the same coverage range UPS detects the

four-peak structure labeled E with peaks at binding energies  $E_B = 2.6, 5.3, 6.6, 8.7$  eV both with K and Cs (see figs. 5 to 7).  $E_1$  can be seen more clearly in the difference spectra (not shown) when the contribution from the W(5d) emission is subtracted. The binding energies of the electrons in the uppermost orbitals of several molecular oxygen species are listed in table 1 as far as they could be identified in previous work involving K or Cs. The energetic positions of the peaks of structure E (also given in table 1) agree well with those attributed to the ionization of the  $O_2^-$  species formed after exposing K and Cs films to oxygen (exposure beyond 10 L) [8,18,19]. A recent critical discussion of UPS results attributed to the ionization of  $O_2^-$  formed during the oxidation of various types of alkali adlayers (Na, K and Cs) can be found in [18,19]. The relative peak intensities found here differ from those in refs. [18,19]; this may be due to the different environment felt by the  $O_2^-$  species (see also ref. [1]). For Li and

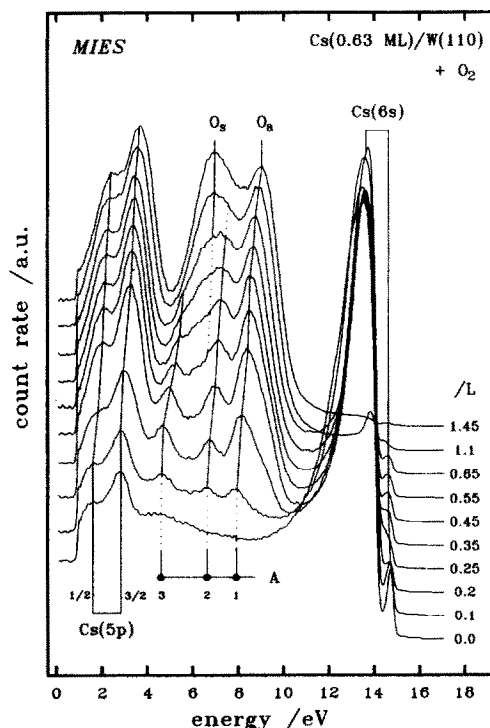


Fig. 3. MIE spectra of a W(110) surface precovered by 0.63 ML Cs as a function of exposure to oxygen.

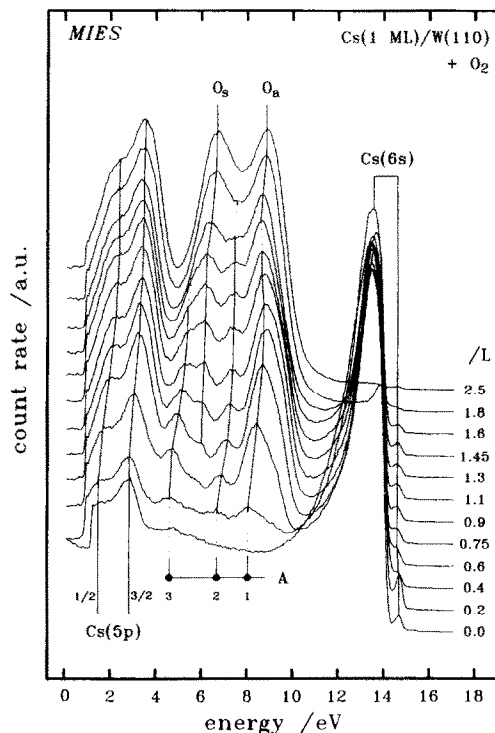


Fig. 4. MIE spectra of a W(110) surface precovered by 1 ML Cs as a function of exposure to oxygen.

Na structure E is also seen by MIES at moderate oxygen exposures indicating that the  $O_2^-$  species is formed even on top of the adlayer. As for Li (Na) we assign structure E to an  $O_2^-$  species embedded into the alkali adlayer.

The features seen by MIES are most likely a superposition of structure E and the additional structure A which dominates the MIE spectra. Structure A originates from the ionization of an oxygen species which is adsorbed on top of the alkali layer while the  $O_2^-$  species responsible for E is rather embedded into it. We conclude that the species which is sampled by MIES differs considerably from that seen by UPS. For a tentative assignment of structure A the following observations may serve as guidance:

- (1) For Li and Na a molecular species is detected on top of the adlayer [1].
- (2) Dissociation of the adsorbed oxygen molecules is caused by charge transfer into anti-bonding orbitals of the molecule. Although the

free-electron density is higher inside the alkali adlayer, UPS shows that some fraction of the oxygen molecules embedded is not dissociated. With the lower electron density on top of the adlayer the probability for dissociation should be even lower.

(3) The only atomic oxygen species which would yield three peaks, equally spaced by about 2 eV, would be  $O^-$ . However the binding energy of the energetically lowest peak in the gas phase is only about 1.5 eV [8,23]; it seems therefore doubtful whether the species can be stabilized by the surrounding alkali atoms to such an extent that the structure shifts by more than 4.5 eV towards larger binding energies.

We propose that the top-adsorbed oxygen species still resembles the free  $O_2$  molecule. Its equilibrium distance has however increased, partly due to charge transfer and partly due to the interaction with the adatoms. Thus we may imagine that structure A is due to Franck-Con-

don transitions  $O_2^0 \Rightarrow O_2^+$  at an internuclear distance enlarged by about 0.2 Å as indicated in fig. 9. This would possibly yield three or four peaks from the transition of  $X^3\Sigma_g^-$  to the final states  $X^2\Pi_g$ ;  $a^4\Pi_u$ ;  $A^2\Pi_u$ ;  $b^4\Sigma_g^-$ ;  $B^2\Sigma_g^-$ . The symbols in brackets denote the molecular orbitals which are involved in the transition. Final state effects may change the energetic separation of the  $O_2^+$  potentials with respect to those for  $O_2$  considerably for surface adsorbed oxygen [1,4,8]. At present we cannot decide whether the peaks detected arise from the ionization of  $\pi_g$ ,  $\pi_u$  and  $\sigma_g$  or only from  $\pi_u$  and  $\sigma_g$  because the lowest energetic peak may still be buried under the strong alkali induced emission near the Fermi level.

Several studies of the oxidation of K (Cs) monolayers on metals [9,24] and semiconductors [7] come to the conclusion that at least some fraction of the oxygen is bonded atomically to the alkali in the initial stage of the exposure to oxygen. Without additional information, as for instance from XPS and/or HREELS, we cannot definitively exclude contributions from the ionization of chemisorbed atomic oxygen in particular to the strong peak which is observed at  $E_B = 5.5$  to 6.5 eV (see figs. 4, 6a, 7a).

At exposures beyond 2 L, the oxygen induced structures in MIES develop into the two peaks denoted by  $O_s$  and  $O_a$ ; UPS very likely sees a superposition of these features and structure E (see figs. 6a and 6b). Their energetic distance as well as their energetic positions agree rather well with those of the two features  $O_s$  and  $O_a$  (and denoted in the same way) which are found at small precoverages at all oxygen exposures. The increasing exposure to oxygen leads to a "shrinking" of the size of the alkali atoms in the surface adlayer due to the binding of the oxygen [5]. As a consequence the interaction of the oxygen with the reactive W(110) substrate increases in importance as in the case for precoverages below 0.5 ML in general. The oxygen will again be adsorbed atomically at substrate sites far from ( $O_s$ ) or bound to the alkali adatom ( $O_a$ ).

There is obviously a correlation between the onset of the substrate oxidation as manifested by the occurrence of peak  $O_s$ , the minimum of the

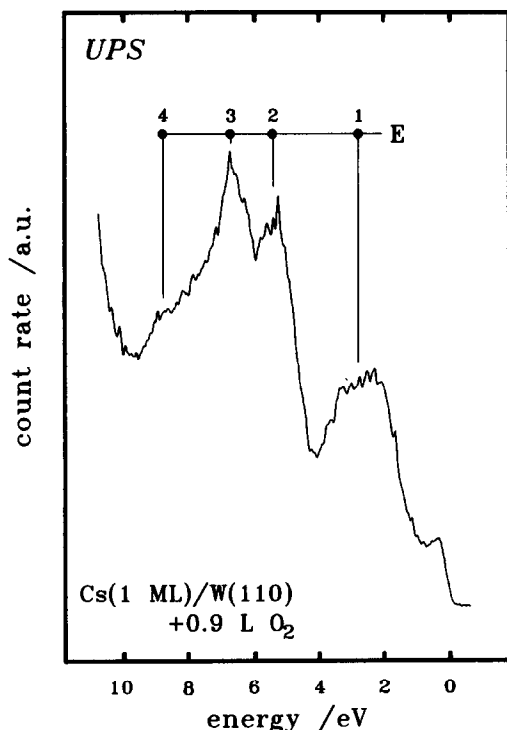


Fig. 5. UP spectrum of a W(110) surface precovered by 1 ML Cs and subsequently exposed to 0.9 L oxygen.

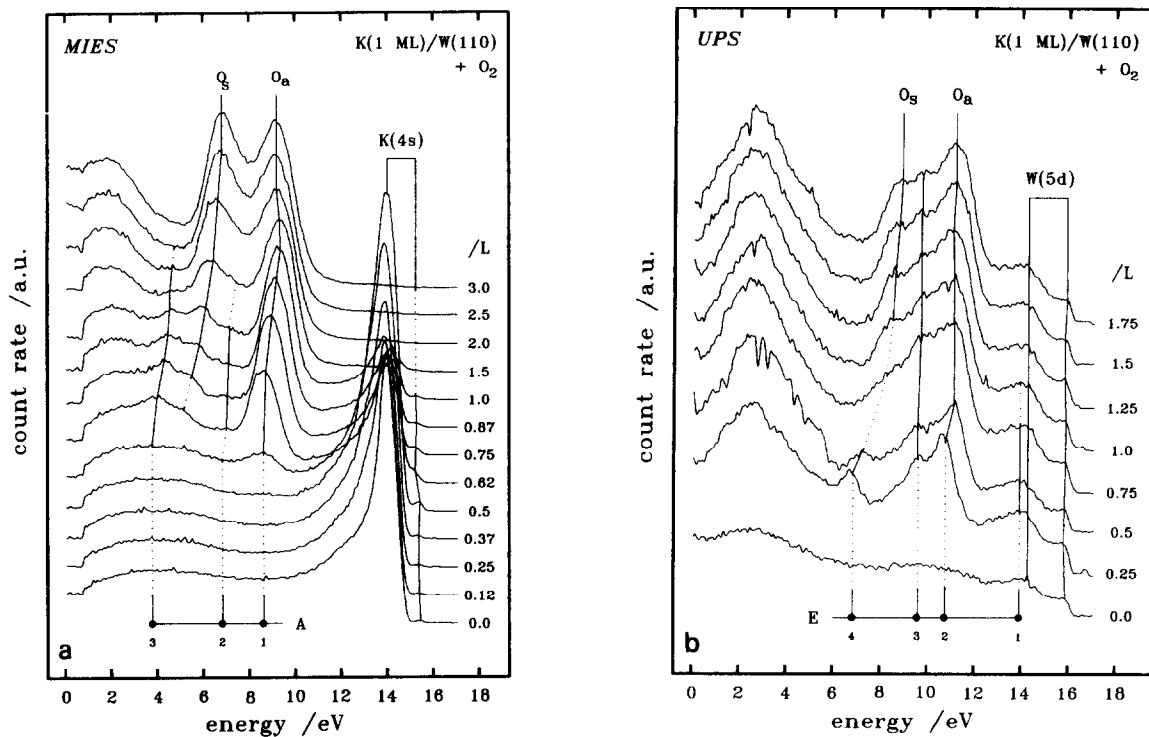


Fig. 6. MIE (a) and UP (b) spectra of a W(110) surface precovered by 1 ML K and subsequently exposed to oxygen.

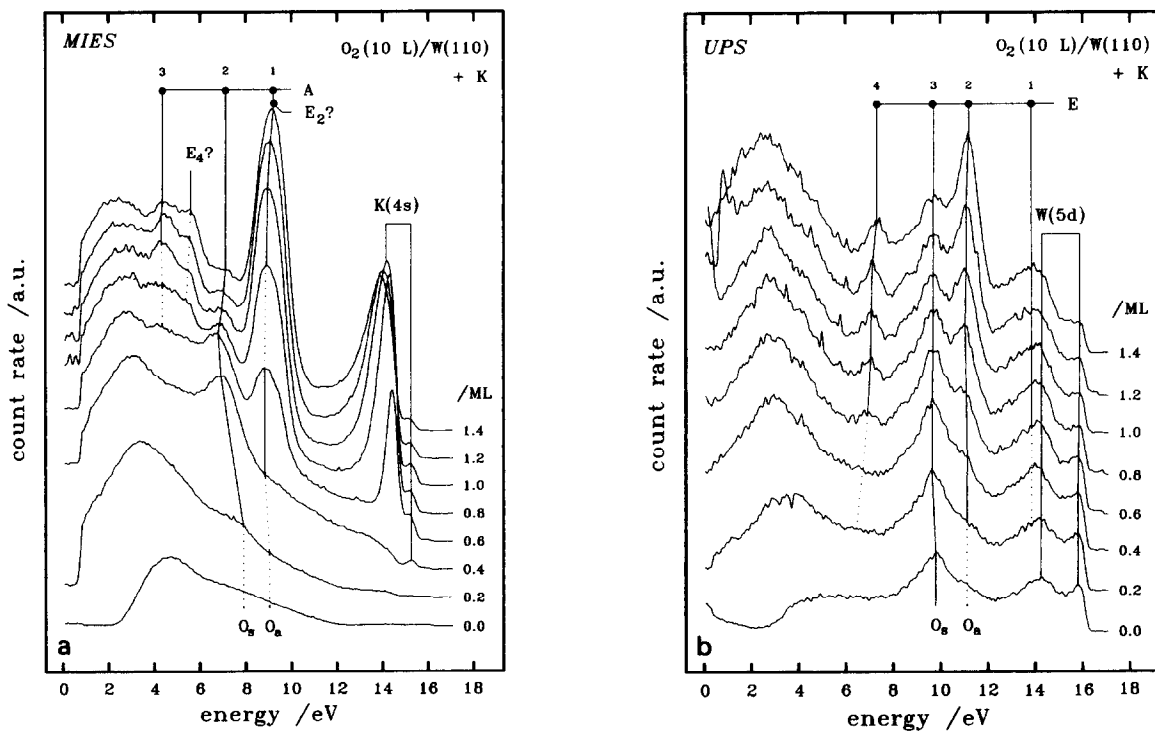


Fig. 7. MIE (a) and UP (b) spectra of a W(110) surface dosed by 10 L oxygen as a function of the subsequent K adsorption.

Table 1  
Binding energies in the 2p derived molecular orbitals for various molecular oxygen compounds

Oxygen	Alkali	$\sigma_g$	$\pi_u$	$\pi_g$	$E_B(\pi_g)$
$O_2^-$	K	6.9; 4.5	3.1	0	2.4 [18]
		5.6; 3.5	2.6	0	2.3 <sup>b)</sup>
	Cs	6.2; 4.4	2.8	0	2.9 [8]
		6.0; 4.0	2.6	0	2.9 <sup>b)</sup>
$O_2^{2-}$	Cs	4.5	3.1	0	3.1 [4]
		4.2	2.8	0	3.3 [5]
		4.3	2.6	0	3.9 <sup>b)</sup>
	K	6.9	3.1	0	1.1 [21]
		4.8	3.1	0	3.1 [22]
		3.0	1.5	0	3.3 <sup>b)</sup>
$O_2^0$	K	8.2; 6.0	4.2	0	5.8 [21]
		8.3; 5.1	3.7	0	6.3 <sup>c)</sup>
		8.0; 6.1	4.4	0	6.0 <sup>a)</sup>

<sup>a)</sup> Condensed oxygen [18].

<sup>b)</sup> Values derived from the positions of structure E with respect to the Fermi level.

<sup>c)</sup> Values derived from fig. 8 and analogous results with K.

work function as a function of the oxygen exposure, and the disappearance of the K (Cs) s emission around about 1 L  $O_2$  exposure. This delayed onset of the enhancement of the oxidation rate in the presence of alkali atoms is also found for semiconductor surfaces [20].

When Ru(001) covered by 1 ML K is exposed to oxygen at 100 K the three-peak structure labeled  $\beta$ ,  $\gamma$ ,  $\delta$  occurs beyond 0.3 L [9]. The energetic positions and in particular the peak splittings are very similar to those of our structure A. However in contrast to our present results the three-peak structure persists at least up to 10 L oxygen exposure, and is not transformed into peaks  $O_a$  and  $O_s$ .

Finally we may summarize the observations of this section as follows:

Up to 0.5 ML precoverage dissociative attachment of oxygen mediated by the strong oxygen-substrate interaction occurs on the substrate either far from any alkali adatoms (peak  $O_s$ ) or bound near to it (peak  $O_a$ ). For precoverages beyond 0.6 ML the impinging oxygen is at least partly not dissociated, but incorporated in form

of  $O_2^-$  ions; the charge transfer from the adlayer to the oxygen molecule appears rather incomplete for those molecules which are top-adsorbed as sampled by MIES. For sufficiently large exposures to oxygen (beyond 2 L for precoverages below 1 ML) the alkali's valence electron density is reduced to zero by its complete transfer to the oxygen, i.e. by its "consumption" in binding the oxygen. Under the combined interaction of the oxygen with the W(110) substrate and the alkali adatoms, molecularly attached oxygen is again dissociated; the oxygen adsorption at the top of the surface takes again place in atomic form giving rise to the peaks  $O_a$  and  $O_s$ ; some molecular oxygen in form of  $O_2^-$  is however still present within the surface layer as suggested by UPS.

### 3.2. Auxiliary measurements

Additional measurements were performed in order to consolidate the conclusions arrived at in section 3.1:

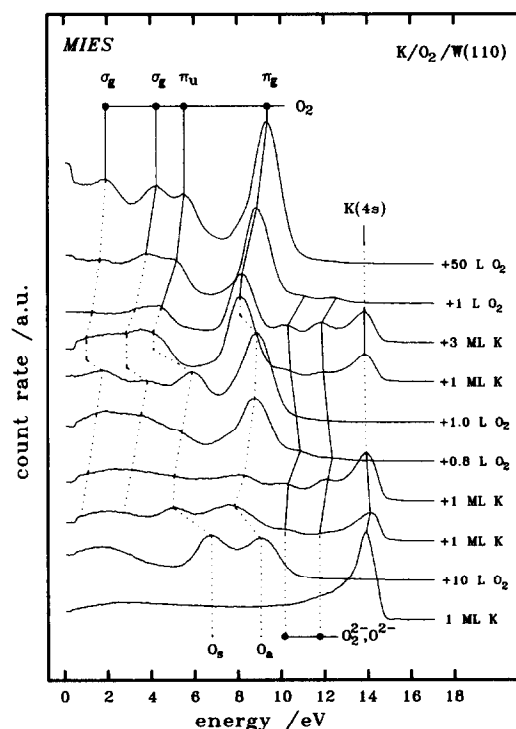


Fig. 8. Alternate exposure of a W(110) surface to K and  $O_2$ .

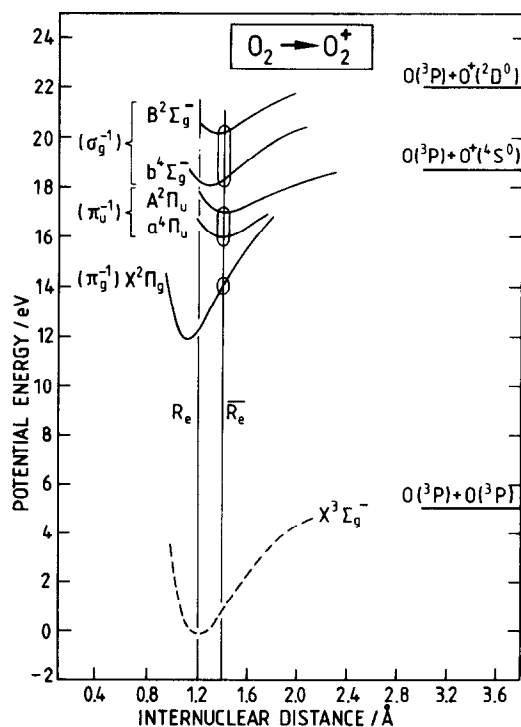


Fig. 9. Potential curves for the free  $O_2$  molecule and the  $O_2^+$  molecular ion (adapted from ref. [23]). Indicated by vertical lines are the Franck-Condon transitions at an internuclear distance extended by  $0.2 \text{ \AA}$  as compared to the free ion.

(1) exposure to alkali atoms of the W(110) surface previously exposed to oxygen,

(2) simultaneous exposure of the surface to both alkali atoms and oxygen, and

(3) alternate exposure of the surface to alkali atoms and oxygen.

Here we reproduce only the results obtained with procedure (1) and (3) for K (figs. 7 and 8); similar results were obtained for Cs. These and additional results can be found in ref. [14].

Figs. 7a and 7b were obtained in the following manner: each UP spectrum was followed by a MIES measurement which was completed within less than 1 min after the completion of the UPS measurement. The UPS results document the transition from purely atomic adsorption on clean W(110) ( $O_s$ ) to molecular adsorption as manifested by the appearance of structure E with increasing exposure to alkali atoms. The formation of molecular oxygen has also been observed when a Ru(001) surface was first exposed to a saturation dose of  $O_2$  at 100 K and then dosed by K [9]. MIES shows indications of structure E as well which remain however comparatively weak; peak  $E_3$  is practically missing, and  $E_1$  may be buried under the strong emission due to K(4s)

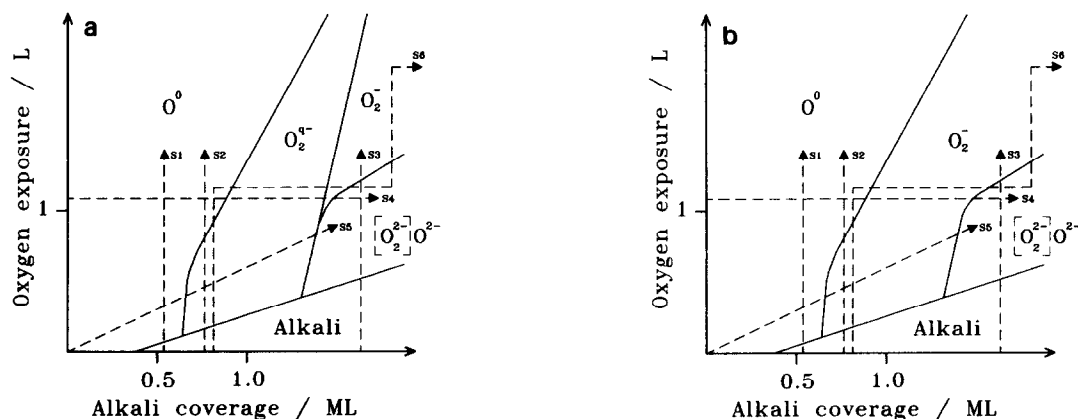


Fig. 10. Coadsorption diagram for the exposure of a W(110) surface to K (Cs) atoms and oxygen molecules, (a) applies to the outermost edge of the surface, (b) to the interior of the surface layer.



ionization. The energetic positions of the remaining features agree with those of structure A in figs. 3, 4 and 6. The oxygen species located on top of the adlayer accessible to MIES differs considerably from that seen by UPS which is located further inside the adlayer. As in section 3.1 we propose that the species seen by MIES is molecular oxygen with an internuclear distance about 0.2 Å larger than in the free O<sub>2</sub> molecule.

Detailed studies with UPS and/or MIES have been performed on Cs films (thickness several adlayers) exposed to oxygen [4–6,8,9]. The MIE results of fig. 8 demonstrate that we obtain similar oxygen induced structures at RT when applying procedure (3). In particular we observe higher charged oxygen complexes, O<sup>2-</sup> and/or O<sub>2</sub><sup>2-</sup> [4–6] when the K (Cs) density is larger than that corresponding to 1 ML. These structures are obviously if at all only very weakly present in the submonolayer regime (see section 3.1). In addition formation of O<sub>2</sub><sup>0</sup> appears at the surface when performing procedure (3). The identification of the species can be made by the comparison with the results obtained in ref. [21]. These results moreover confirm the conclusions of section 3.1 that features O<sub>a</sub> and O<sub>s</sub> are not due to molecular oxygen.

#### 4. The oxidation process

The oxidation process will be discussed on the basis of the coadsorption diagrams shown in figs. 10a and 10b [1] which summarize our results discussed in section 3 and also include results obtained for the oxidation of films [4,5]. Dashed lines indicate the coadsorption procedure. Heavy lines enclose regions in which the indicated oxygen species dominates although species from adjacent regions may also be present to some extent.

Path S3 summarizes the results obtained by refs. [4,5] for the oxidation of thick Cs layers (films): by electron transfer from the alkali adatoms to the impinging O<sub>2</sub> molecule presumably weakly bound O<sub>2</sub><sup>2-</sup> is formed which dissociates and leads to integration of O<sup>2-</sup> into the adlayer (fig. 10a) and attachment of O atoms on top of it. At about 1 L oxygen exposure the

capability of the surface to dissociate additional oxygen is lost because there are no electrons left to be transferred to newly impinging oxygen molecules; this is reflected by the disappearance of the alkali s emission at this stage. In the final stage of the oxidation the surface consists of O<sub>2</sub><sup>-</sup> molecular ions [4,5].

Path S1 visualizes that the reactive W(110) surface dissociates O<sub>2</sub> molecules. Most of the oxygen binds atomically to the substrate; some of it also to alkali adatoms.

Above 0.6 ML and at least up to 1 ML precoverage a K (Cs) adlayer has a passivating action: on the one side it weakens the oxygen–substrate interaction, and on the other side its free-electron density is not high enough to dissociate the arriving O<sub>2</sub> molecules by charge transfer into antibonding oxygen orbitals (see path S2). Charge transfer leads to the formation of O<sub>2</sub><sup>-</sup> molecular ions embedded into the adlayer (fig. 10b) and to the formation of an oxygen species with enlarged internuclear distance (O<sub>2</sub><sup>q-</sup> with  $q < 1$ ) on top of the surface (fig. 10a). Atomic oxygen may also be present on top of the surface. The consumption of the valence electrons in the binding of the oxygen gives rise to a shrinking of the size of the alkali adatoms, thereby exposing at least part of the substrate to the attack of additional oxygen molecules. Path S2 visualizes that in the initial stage the oxygen is attached molecularly while for larger exposures most of the oxygen is again incorporated atomically under the combined interaction with alkali adatoms and the substrate.

On path S4 oxygen is initially adsorbed atomically mainly on the substrate as expected from the discussion of S1. For sufficiently large exposures to K (Cs) a metallic-like top layer is formed by the alkali adatoms as judged from the appearance of the s emission near the Fermi edge. However, the oxygen-induced features become now more pronounced indicating that the oxygen becomes integrated into the top layer rather than being buried under it. For sufficiently large exposures to K (Cs) molecular oxygen is formed as indicated in figs. 10a and 10b.

Path S5 and S6 lead to the formation of higher charged oxygen complexes, not obtainable in the regime up to 1 ML.

In ref. [1] we have studied the oxygenation of Li and Na adlayers on W(110). Compared to the present results there are essentially two major differences:

(1) For Li and Na structure A is not detected; instead structure E appears at moderate exposures even in MIES. Therefore  $O_2^-$  ions are formed in the outermost layer of the surface at moderate oxygen exposures in the coverage region beyond 0.6 ML.

(2) At large oxygen exposures the oxidation process for Li and Na ends with the attachment of neutral molecular oxygen on top of the surface layer (for Li (Na) precoverages beyond 0.6 ML) while under the same conditions for K and Cs atomic oxygen appears at the surface (see section 3.2).

Both facts can possibly be explained by the higher density and the larger free-electron density in the alkali adlayer for Li (Na): this enables a more efficient charge transfer to the oxygen on the one side, and prevents the exposure of the substrate to the oxygen after the free-electron density has decreased to zero (because the inter-nuclear distance between neighboring alkali cores is too small to accommodate an oxygen molecule).

The passivating action of an alkali adlayer, namely its tendency to make oxygen dissociation less likely, is however found both for light and heavy alkalis up to the monolayer precoverage.

## 5. Summary

UPS and metastable impact electron spectroscopy (MIES) are combined to study the interaction between oxygen and K on W(110) mainly for coverages up to the saturation coverage at room temperature. A coadsorption diagram is derived which allows to predict the dominant oxygen species (atomic/molecular and its charge state) within and above the top layer as a function of the exposure to oxygen and the alkali coverage. For small alkali precoverages impinging  $O_2$  molecules are dissociated at the W(110) substrate. When a metallic-like toplayer is formed (beyond 0.6 ML precoverage) charge transfer to the attached oxygen leads to the integration of

$O_2^-$  molecular ions into the top layer. The metallic character of this top layer is destroyed by its forthcoming oxidation because the alkali valence electrons are “consumed” in the binding of the oxygen. This leads to a considerable shrinking of the size of the alkali centers and exposes part of the W(110) substrate to oxygenation. In this stage the oxygen at the top of the surface is accommodated atomically.

## Acknowledgement

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