

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

I. Li and Na

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Received 14 June 1991; accepted for publication 2 January 1992

UPS and metastable impact electron spectroscopy (MIES) were employed to study the interaction between oxygen and the alkalis Li and Na in the coverage range up to 3 monolayers (in units of the first complete layer) on W(110) at room temperature. Different charge states of atomic and molecular oxygen could be identified at the surface. For small alkali coverages below 0.5 monolayers 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 intermediate coverage range between 0.5 and 1.2 monolayers a considerable charge transfer from the alkali *s*-orbitals to the impinging oxygen takes place as long as the alkali *s*-orbital is filled. Oxygen molecules are then incorporated into the alkali adlayer as O_2^- ions. Beyond 1.2 monolayer alkali coverage the strong charge transfer leads to the formation of O^{2-} ions which appear even on top of the adlayer. The adsorption of oxygen proceeds until the top layer formed by the alkali atoms loses its metallic character; at this point the valence electrons of the alkalis are involved in the binding of the oxygen.

1. Introduction

The study of the oxidation of alkali metals finds its motivation both in its importance for fundamental research and for technological applications: oxygen may adsorb atomically as well as molecularly in a number of different charge states. The technological interest in oxidized alkali layers stems from their application as electron donors and as low work function materials. Very active fields of research are the study of the catalytic action of alkali-containing compounds and their ability to influence the oxidation rate of semiconductors by many orders of magnitude. Detailed discussions of the topics summarized above may be found in ref. [1].

When applying electron spectroscopic techniques such as UPS and MIES to alkali oxygen compounds one is confronted with a multitude of peak structures originating from different charge states of the atomic as well as the molecular oxygen present in the compound. Normally one

has to deal with multiplet structures consisting of three or more peaks. The peak positions as well as the splitting between peaks within the same multiplet may be influenced by the electronic environment of the emitting oxygen species [1–3]. All these facts cause difficulties in the identification of the emitting species.

In the past a large number of studies appeared applying electron spectroscopic techniques to the oxidation of alkali layers or alkali films prepared under UHV conditions [1]; often it was attempted to identify alkali oxides on the basis of results where either the state of the oxidized surface was only poorly characterized or where only a limited range of alkali coverages or oxygen exposures was under study. Some of the problems may be bypassed when studying the oxygenation of thick alkali films, in this case the oxygen induced peak structures are not influenced by the presence of the alkali–substrate interaction which usually gives rise to additional peaks or peak splittings. Two pioneering examples of this approach are

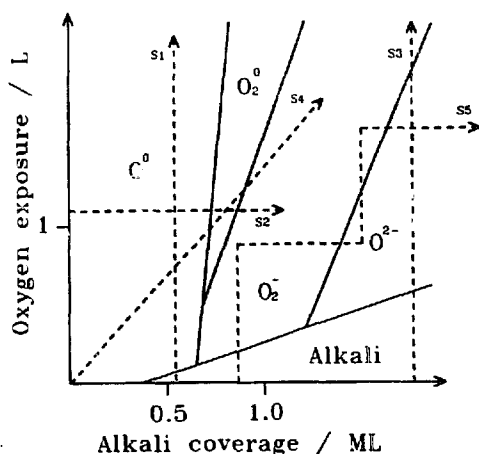


Fig. 1. Coadsorption diagram of Li or Na and oxygen on W(110) at room temperature (see text for details).

the studies of oxidation of Cs films by UPS [3] and by UPS and MIES [4]. The special attraction of MIES arises from its extreme surface sensitivity. The comparison of MIES and UPS results on the other hand offers the possibility to distinguish between contributions from species attached above and below the toplayer formed by the alkali atoms [4].

This study extends the work of ref. [4] to the oxidation of alkali adlayers (Li, Na) in the sub-monolayer coverage range on W(110). Fig. 1 shows a coadsorption diagram for the alkali-oxygen case; it implies that the order of adsorption of the two components is of no importance. The diagram emerges from the results to be reported in this study and also incorporates the large body of information accumulated in earlier studies. At this point its only purpose is to explain the experimental effort which is needed to pin down the essentials of the diagram. Path S3 visualizes the predominant species at the surface when oxygen is offered to the surface precovered by 2 monolayers (ML) of alkali atoms. In order to access as many different regions of the coadsorption diagram as possible the experimental approach included the following procedures:

- (1) study of the oxidation as a function of the alkali precoverage (e.g., path S1 and S3 at various distances from the O_2 -axis in fig. 1),
- (2) alkali exposure to the W(110) surface previously exposed to oxygen (path S2),

- (3) simultaneous exposure of the surface to both alkali and oxygen (path S4), and
- (4) alternate exposure to alkali of the surface (path S5).

The final result of this study is the qualitative coadsorption diagram of fig. 1 which allows one to follow the oxidation process for various possible initial conditions. Corresponding measurements for the oxidation of W(110) precovered by K or Cs are being carried out by us currently.

2. Experimental

The apparatus was already characterized previously [5,6]. Briefly, it consists of a facility to perform MIES and UPS by using the same source to produce either a metastable $He(2^3S; 2^1S)$ (19.8; 20.6 eV) or a He I ($h\nu = 21.25$ eV) UV light beam. According to ref. [7] the triplet/singlet ratio of our metastable beam is about 7:1. This facility enables us to start with the collection of a UP spectrum within less than one minute after the completion of the MIE spectrum without performing any change of surface's position or state. Electron spectra are recorded with a hemispherical electrostatic analyzer of 250 meV resolution. It was positioned under 45° with respect to the surface normal. The direction of incidence of the metastable (photon) beam is also 45° with respect to the surface normal. The change of the surface work function upon oxygenation or alka-lination can be estimated from the shift of the low-energy end of the electron spectra. Structures seen in some of the spectra beyond the low-energy cut-off are due to secondary electrons released in the electrostatic analyzer.

The apparatus is further equipped with AES, LEED and a residual gas analyzer. These tools were essentially employed to monitor the surface cleanliness and to perform work-function (WF) measurements [8]. However, MIES itself is an extremely sensitive technique for the detection of contamination due to residual gases, in particular oxygen which is generated by dissociative adsorption of CO on W(110) [6]. Alkali layers were produced by heating alkali dispenser sources (SAES Getters, Inc.). The cleanliness of the ad-

layers was checked by means of AES and MIES. The thickness of the alkali layers was estimated by the comparison of the ratio of alkali and W(350 eV) Auger peak heights. The onset of the second adlayer produces a kink in the Auger signal curve which defines the completion of the first monolayer. The experimental conditions are described in more detail in refs. [5,6]. All of the present work was done with the sample at room temperature.

3. Results and identification of the peak structures

The measurements were taken in a similar manner as described in ref. [6]. The following procedures were employed (a monolayer (ML) refers to the first complete adlayer at room temperature):

- (1) Continuous oxidation of the W(110) surface partially precovered ($\theta_{\text{Alk}} \leq 3$ ML) by alkalis. O_2 gas is admitted at a slow leak rate usually between 0.1 and 0.2 langmuir (L) per minute. More than ten different alkali precoverages have been investigated for each of the alkalis Li and Na [9].
- (2) Exposure of an oxygen-saturated W(110) surface (10 L oxygen) to alkali atoms. The alkali coverage is estimated under the assumption that the sticking coefficient for alkalis is not altered considerably by the previous exposure to oxygen. Alkali atoms are offered to the surface at a rate of 0.1 ML per minute, typically.
- (3) Alternate exposure to alkali and oxygen of W(110).
- (4) Alkali deposition at a rate of about 0.1 ML per minute in an ambient oxygen atmosphere (about 3×10^{-7} Torr). This procedure was employed for Na only.

The potential energy curves of the various free ion states O_2^{2-} , O_2^- , O_2^0 and O_2^+ can serve as a rough guide for the identification of the multi-peaked UP and MIE spectra (see ref. [3] and references given therein): the Franck-Condon principle demands that the possible ionization energies correspond to vertical transitions from

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

	Alkali	σ_g	π_u	π_g	$E_B(\pi_g)$ (eV)
O_2^-		11.0, 7.8	3.0	0	a)
	Li(E)	8.8, 6.4	2.4	0	4.0 ^{b)}
	Na	10.1, 7.8	3.1	0	4.2 [2]
	Na(E)	9.2, 6.9	3.1	0	3.3 ^{b)}
O_2^{2-}		5.1	3.1	0	a)
	K	6.9	3.1	0	1.1 [15]
	k	4.8	3.1	0	3.1 [14]
	Cs	4.5	3.1	0	3.3 [3]
	Cs	4.2	2.8	0	3.3 [4]
O_2^0		8.2, 6.1	4.0	0	a)
	c)	8.2, 6.0	4.4	0	6.0 [20]
	Na(G)		3.2	0	6.0 ^{b)}
	Li(G)		3.7	0	6.0 ^{b)}

a) Estimates obtained from the potentials of the states of the free ions

b) Values derived from the peak positions of the structures (E, G) with respect to the Fermi level (this work)

c) Values for condensed oxygen.

the respective ground state of the oxygen species at the surface to the possible final states. For adsorbed species there exist various effects, in particular the final state shift, modifying the energy separation between the potentials of the different charge states. But the energetic distance within a given multiplet will be conserved as long as (a) the coupling of the angular momenta, and (b) the internuclear (O-O) equilibrium distance R_e remain the same as in the free ion species [3]. To some extent the multiplet splitting will however be modified by crystal-field effects [2]. Table 1 lists estimates for the energies, E_B (with reference to the Fermi level E_F), required to remove an electron from the indicated lowest 2p-derived molecular orbitals for various oxygen compounds. We present estimates made on the basis of the free ion states (see refs. [3,4]) thereby assuming that the final state multiplet splitting cannot be resolved for the surface adsorbed oxygen complex. Furthermore we give the corresponding experimental values derived from the peak positions with respect to the Fermi level of the various observed structures ((a) values from literature; (b) our values for the oxygen compound in a Li (Na) environment).

3.1. $O_2/W(110)$

He*-induced MIE spectra normally display contributions from inter- and intra-atomic Auger processes: resonance ionization followed by Auger neutralization (RI/AN) and Auger de-excitation (AD) (see ref. [10] for a discussion of these two Auger type processes with respect to MIES) and autodetachment of $He^{-*}(1s2s^2)$ [21]. The MIE spectra shown at the bottom of figs. 9a and 9b are typical examples for AN spectra. UP spectra on the other hand show an oxygen-induced peak at a binding energy (E_B , with respect to the Fermi level in all spectra described below) of $E_B = 6$ eV [10,11]. The results show the well-known behavior for adsorption of oxygen on transition metals: the

oxygen attaches atomically to the substrate. UPS detects the ionization of O 2p while MIES detects electrons from AN involving two electrons from the substrate because the RI process between projectile and metal is not inhibited when oxygen atoms are adsorbed on metal surfaces [10].

3.2. Alkali / W(110) + oxygen

Figs. 2 to 7 show MIE and UP spectra of a W(110) surface precovered by various amounts of Li (Na) when exposed to oxygen. Results for other precoverages ($0 \leq \theta_{Alk} \leq 3$ ML) may be found in ref. [9]. We notice the following features:

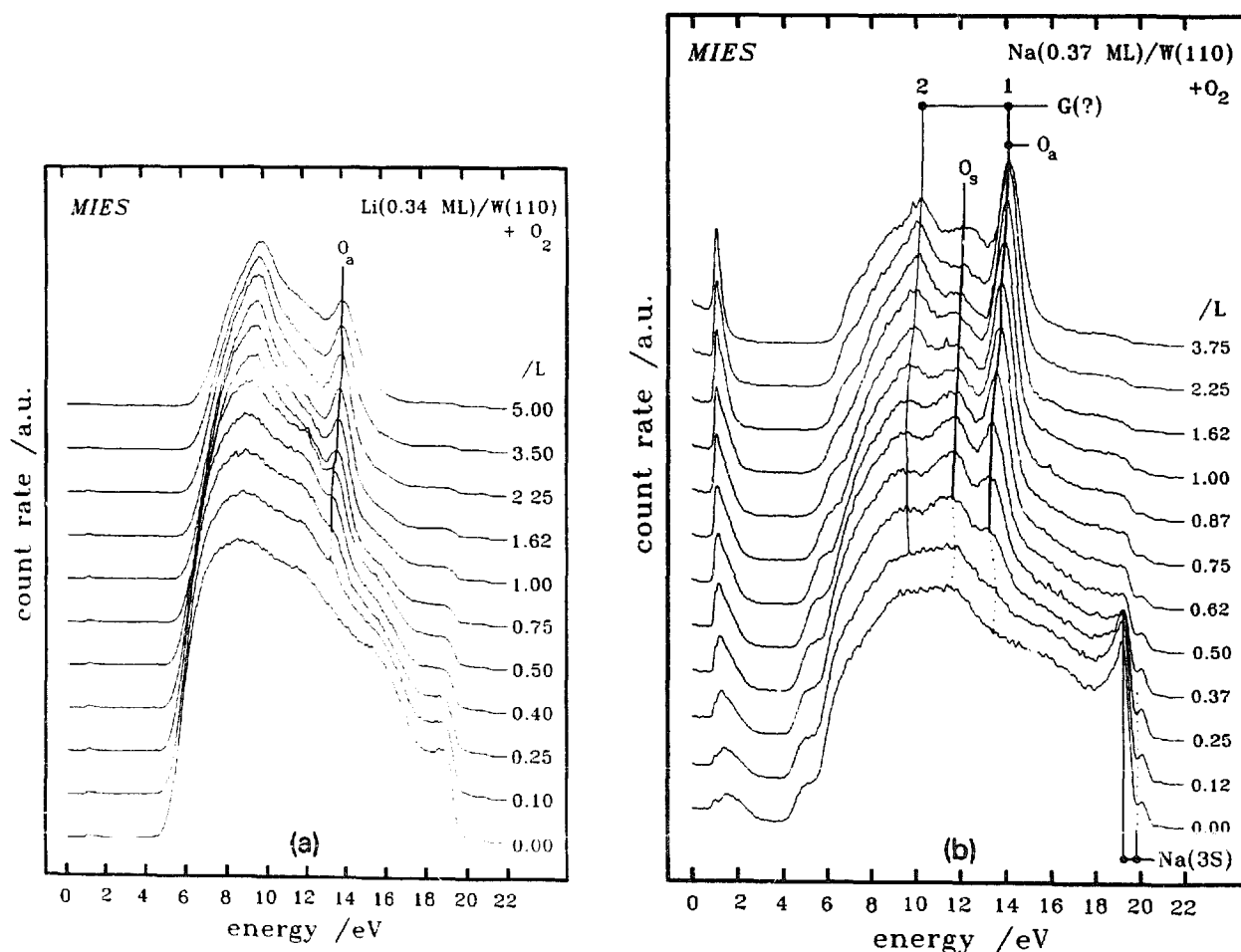


Fig. 2. MIE spectra of a W(110) surface precovered by (a) 0.34 ML Li, and (b) 0.37 ML Na as a function of exposure to oxygen (in langmuir).

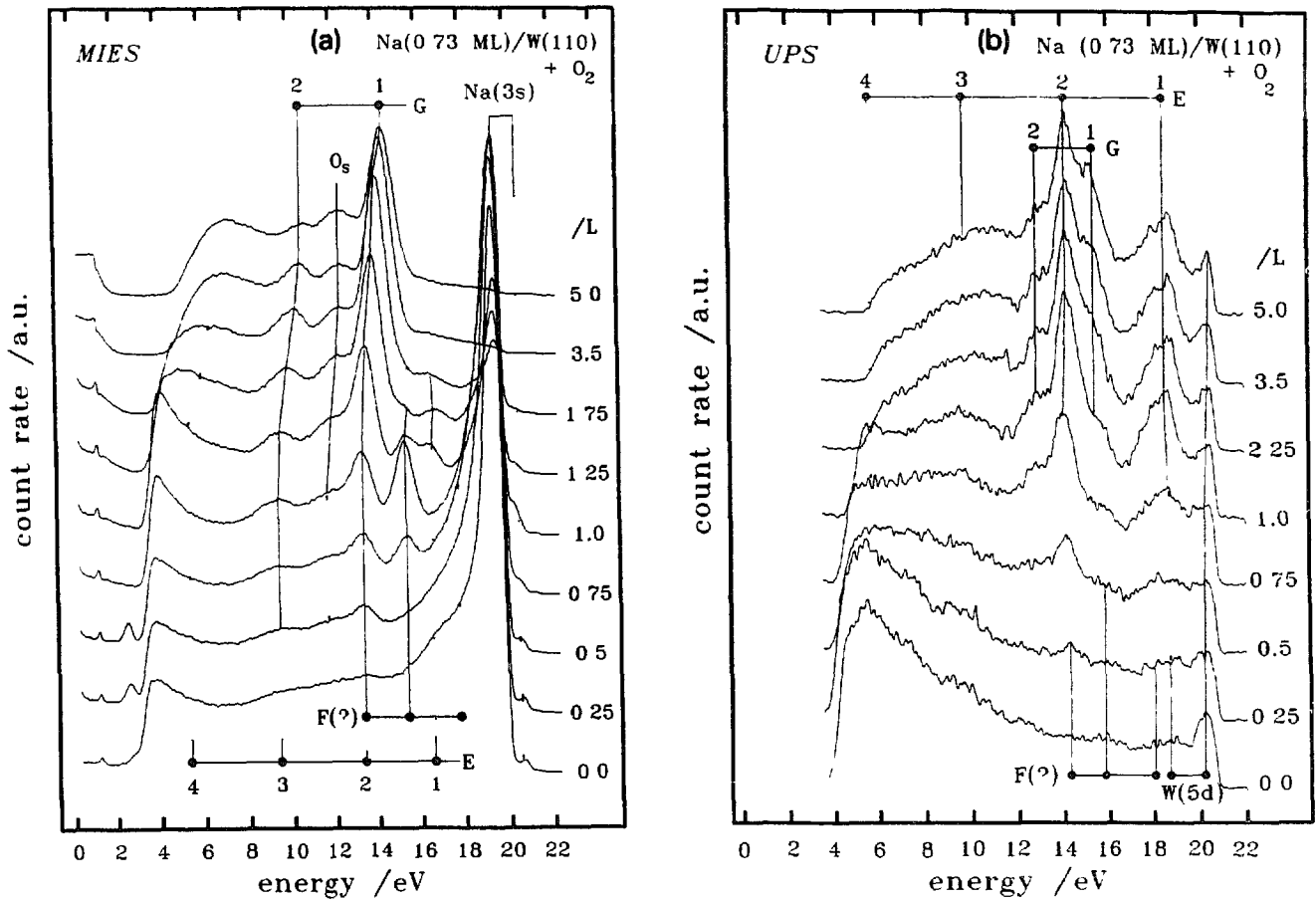


Fig 3 (a) MIE spectra, and (b) UP spectra of a W(110) surface precovered by 0.73 ML of Na as a function of exposure to oxygen

The UP spectra usually show two peaks labeled $W(5d)$ close to the Fermi energy E_F which represent the W d-band emission. Adsorption of alkalis on W(110) produces the strong peak labeled $Li(2s)$ ($Na(3s)$) near E_F in the MIE spectra provided $\theta_{Alk} \geq 0.4$ ML [12]. This peak is due to $He(2^3S)$ de-excitation involving the alkali s-electrons [12,13] and to $He^{-*}(1s2s^2)$ autodetachment [21]. At about 0.8 eV larger kinetic energy a satellite peak can be noticed which is caused by $He(2^1S)$ metastables also present in the beam. The adsorption of alkali atoms (Li, Na, K, Cs) on W(110) has been studied by us in detail in ref. [12]. The decrease in intensity of the alkali s-peak with increasing oxygen exposure may be interpreted as “consumption” of the alkali valence electrons in the binding of the oxygen to the surface [4] and has the following consequence:

the work function (WF) of the surface starts to rise, and the SDOS decreases. The oxygen uptake is essentially completed when the alkali s-peak has disappeared; this depends upon the precoverage, but occurs not later than 2.0 L (1.2 L) for Li (Na) even for the highest precoverages.

For small alkali precoverages ($\theta_{Alk} < 0.5$ ML) (see fig. 2) the oxygen-induced features labeled O_a and O_s are seen both with MIES and UPS (see also figs. 9 and 10). O_a seems to consist of two peaks (1, 2) which are located at $E_B = 5.8$; 9.7 eV and display the same dependence on oxygen exposure. In particular, the oxygen-induced WF changes around 1 L exposure are reflected back into the binding energies of the O_a features indicating that the species which causes C_a is located within or above the adlayer [14]. O_s is seen as soon as the WF decreases sufficiently

in order to inhibit the RI/AN-process [10]. O_s shows a small or negligible shift with WF throughout the entire studied exposure range.

While O_a increases in intensity with increasing alkali precoverage, O_s decreases. UPS shows the same two oxygen-induced features O_a and O_s although their relative intensity is usually different from that in the MIE spectra. The results discussed in section 3.3 prove that O_s and O_a are caused by emission from atomic oxygen chemisorbed at the substrate or bound to alkali atoms, respectively.

In ref. [6] we have studied the coadsorption of CO and alkalis on W(110). It turned out that the CO attaches dissociatively with high probability. For Na we have verified that the resulting spectral features are indeed virtually identical with those seen when coadsorbing O_2 and Na at $\theta_{Na} < 0.5$ ML as in the present case. It appears unlikely that any molecular oxygen formation should occur for small CO exposures at small alkali coverages.

The results for precoverages beyond 0.6 ML will be discussed separately for small (< 1 L) and large oxygen exposures. At least for 0.7 ML Na precoverage molecular oxygen features appear: the four-peaked structure E with binding energies around $E_B = 4.0$ (3.3); 6.4 (6.4); 10.4 (10.2); 12.8 (12.7) eV for Li (Na) is seen both with MIES and UPS (see figs. 3 to 7). Lines are drawn in order to show the exposure dependence of the peaks of the structure; dotted lines in regions where the peak identification seems to be doubtful. In particular E_4 is not always apparent. The results of section 3.3 suggest, that structure E is caused by O_2^- ions (see table 1). The similarity of UP and MIE results suggests that the O_2^- ions are mainly located above or within the alkali layer; this viewpoint is also supported by the fact that structure E shifts with the WF of the surface [14]. It is likely that $E_{2,3}$ contain contributions from structure O_a as well, e.g., molecular as well

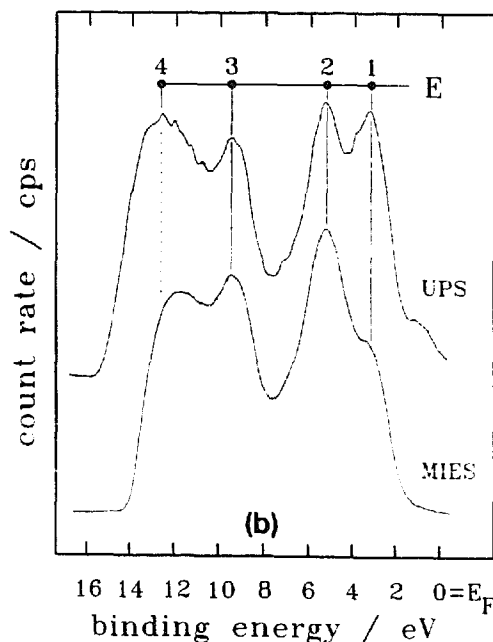
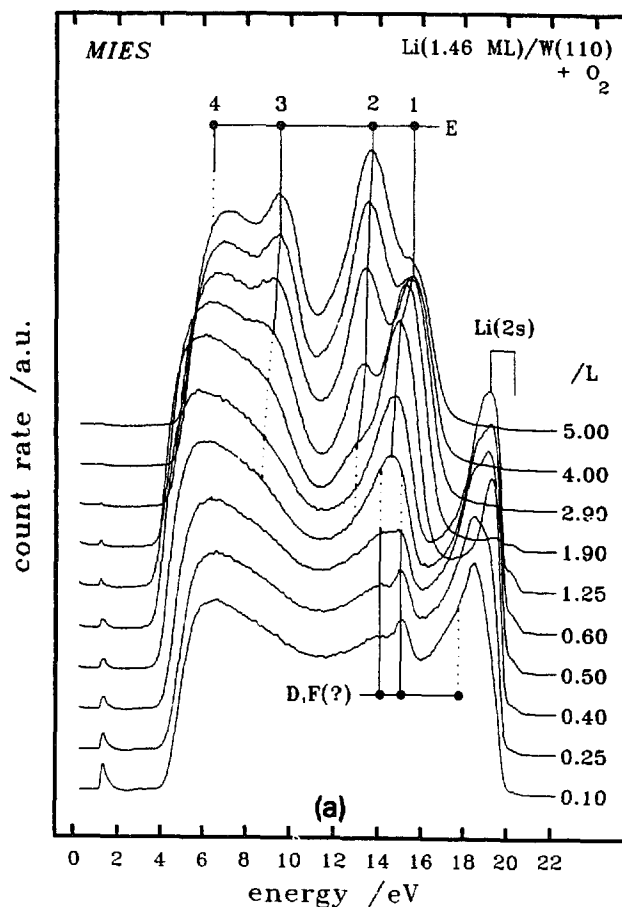


Fig. 4. (a) MIE spectra of a W(110) surface precovered by 1.46 ML of Li as a function of exposure to oxygen. The UP spectrum (b) is measured "simultaneously" with the uppermost MIE spectrum of (a).

as atomic adsorption of oxygen occurs at the surface.

Up to 1.4 ML precoverage we cannot identify definitely the additional oxygen species which are present: additional weak oxygen-induced features are certainly observed at very small exposures both by UPS and MIES. They can be seen rather clearly for the case of Na (see structure F in figs. 3 and 4). On the basis of the observed peak positions and splittings (3 peaks separated by about 2 eV) structure F may belong to O_2^{2-} ; in this case three peaks are expected at about $E_B = 3; 6; 7.5$ eV (see table 1). The energetically lowest peak may well be buried under the strong Na-induced emission near E_F . Alternatively, structure F could be attributed to O^- ionization which would produce three peaks spaced by about 2 eV

each; the energetically lowest peak would be expected around $E_B = 1.5$ eV for the free ion [22].

Around 1.2 ML alkali precoverage (see ref. [9]) an additional single peak labeled D appears (see figs. 4 to 7). D superimposes E_1 to some extent. However, the delayed onset of structure E with oxygen exposure (at around 0.7 L O_2) for the 3 ML precoverage (see figs. 6a and 7a) together with the UP results of figs. 6b and 7b allows the identification and location of D at $E_B = 3.6$ (4.6) eV for Na (Li). Single-peak structures between $E_B = 2.2$ and 2.8 eV are quite commonly observed during the oxidation process of films of the heavy alkalis (K, Cs) and have been identified as emission from the O^{2-} ion [3,4,16] (see table 2). In ref. [17] the presence of O^{2-} ions at the surface was even claimed for the oxidation of

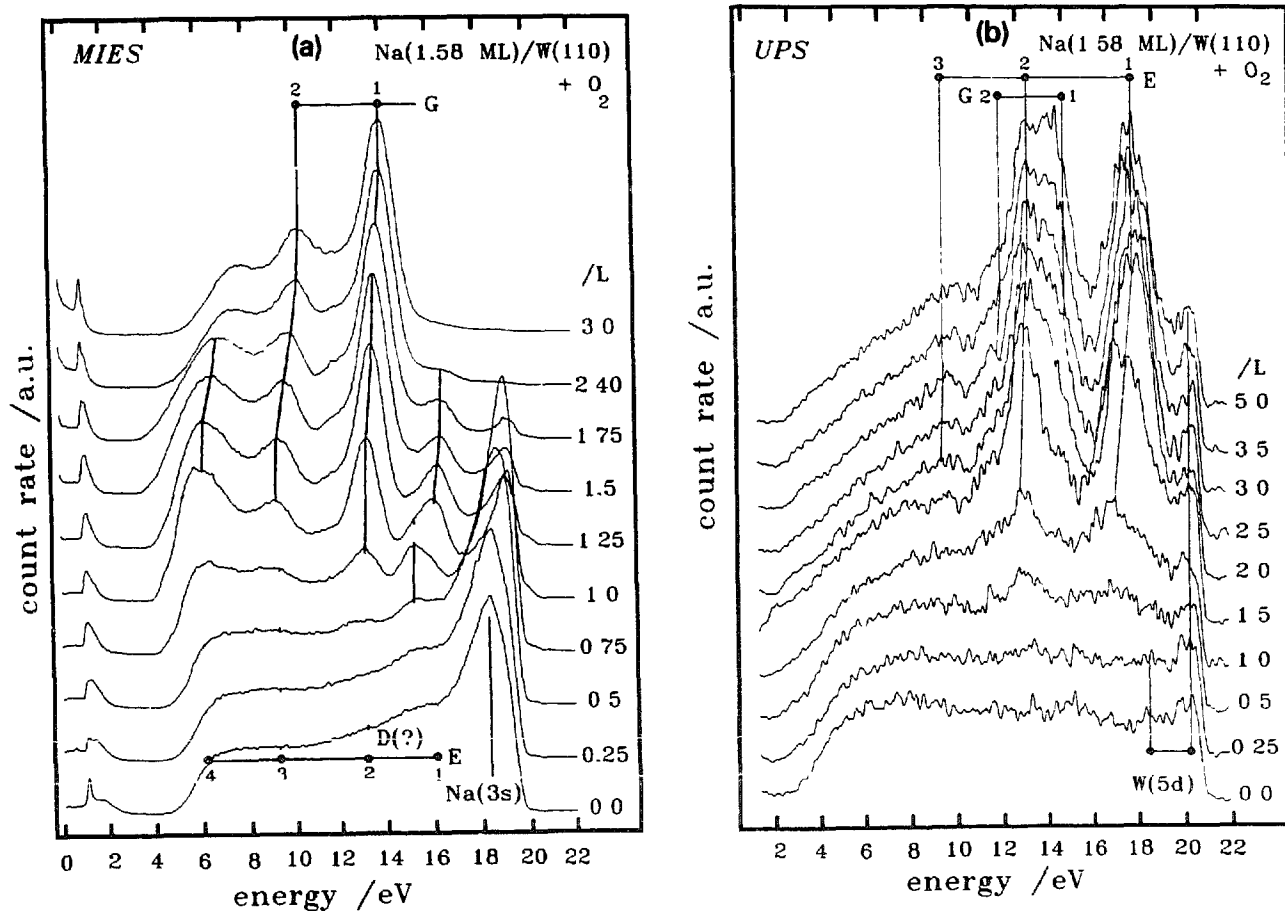


Fig 5 (a) MIE spectra, and (b) UP spectra of a W(110) surface precovered by 1.58 ML of Na as a function of exposure to oxygen

submonolayers of K on silicon. Therefore we attribute structure D to O^{2-} ionization. Because D is also seen by MIES this species must be present on top of the surface for alkali precoverages beyond 1.5 ML. Table 2 lists the ionization energies of O^{2-} when formed in different alkali environments. The presence of O_2^{2-} molecular ions at these precoverages cannot be ruled out definitely from the MIES results (figs. 5a and 6a). However no clear features which could be attributed to O_2^{2-} (see table 1) have been observed by us in the corresponding UPS results.

The weakening of structure E for exposures beyond 2 L is a feature common to most MIE spectra (figs. 3a to 6a) except for alkali precoverages beyond 2 ML. This behavior becomes particularly evident for peak E₁, which disappears almost completely with increasing oxygen exposure,

especially in the case of Na. On the other hand UPS shows structure E still rather clearly (see fig. 4b) indicating that the transformation of E is limited mainly to the outermost surface (which is accessible to MIES). This transformation takes place without appreciable further uptake of oxygen by the surface. The MIES features persisting at large exposure (labeled G₁ and G₂) which are also seen in the UP spectra in addition to structure E can be explained in two ways; additional information (as, e.g., from TDS) is however required for a definite assignment of structure G:

(a) Exposures beyond 2 L lead to a "shrinking" of the size of the Na atoms in the outermost layer of the surface due to the binding of the oxygen. As a consequence the interaction of the oxygen with the W(110) substrate becomes of importance. Most of the oxygen will adsorb atomically

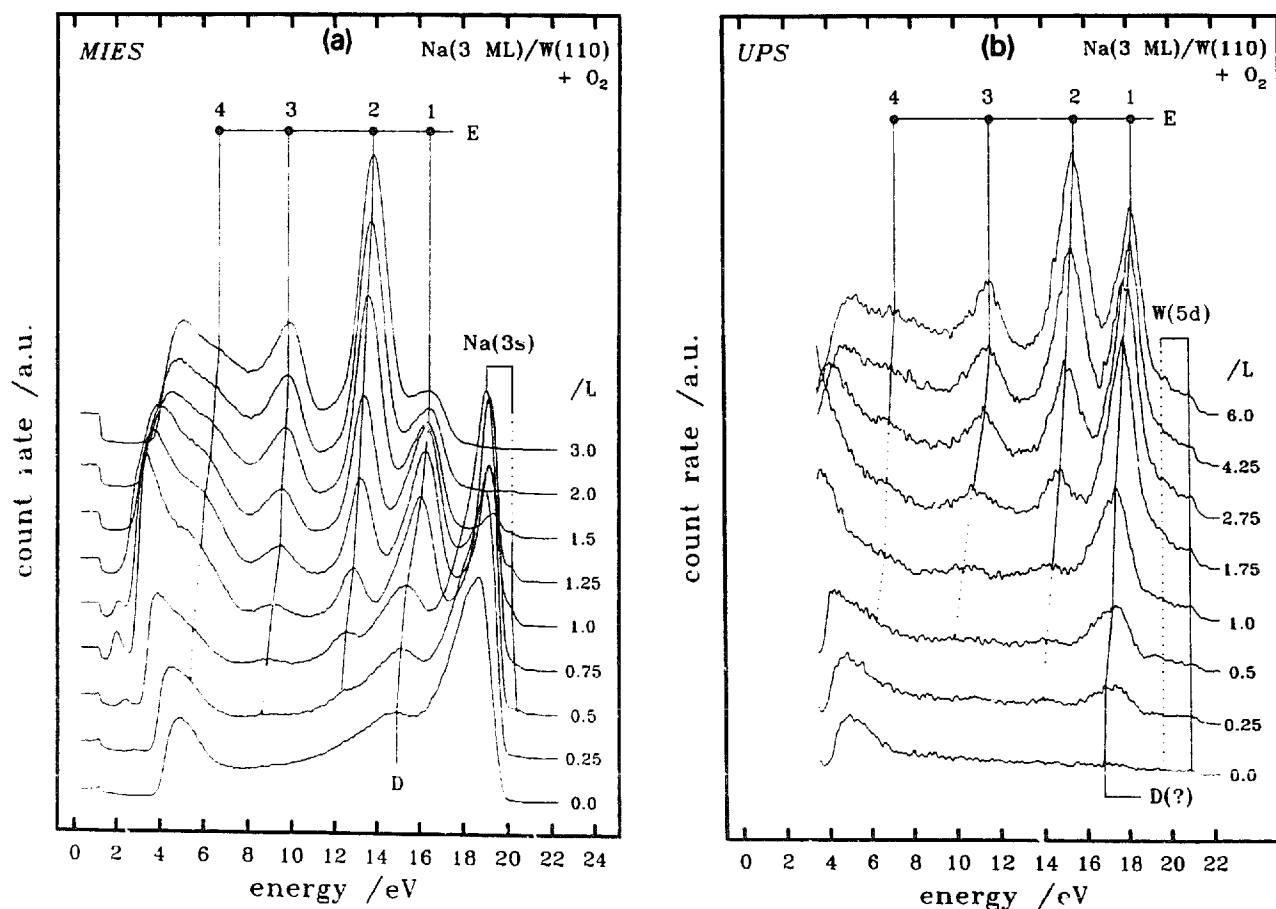


Fig. 6. (a) MIE spectra, and (b) UP spectra of a W(110) surface precovered by 3 ML of Na as a function of exposure to oxygen.

Table 2
Ionization energies of O_2^- in different alkali environments

Alkal ^a	E_B (eV)	Ref
Li	4.5	a)
Na	3.6	a)
K	2.7	[16,17]
Cs	2.7	[3,4]

a) Values derived from position of peak D with respect to the Fermi level (this work)

at two different sites, namely at the substrate far from Na atoms or bond to Na atoms. UPS proves however that some O_2^- ions remain present in the surface layer. In this interpretation G_1 and G_2 would be identical with O_a and O_s , respectively.

(b) At the surface the O_2^- ions turn into neutral oxygen with increasing exposure to oxygen. The spectral features $G_{1,2}$ can then be inter-

preted as ionization of the π_g and π_u O_2 orbitals with $E_B = 5.7; 8.9$ eV, respectively. In order to explain the comparatively small ($\pi_g - \pi_u$) splitting we can argue as follows: the internuclear distance in the O_2 molecule retains the value it had in the O_2^- species produced at small exposures. The spectral features G_1 and G_2 are then caused by a Franck-Condon transition ($O_2^0 \rightarrow O_2^+$) not at the O_2 , but rather at the O_2^- equilibrium distance (at about 1.3 Å instead of 1.2 Å). At this internuclear distance the ($\pi_g - \pi_u$)-splitting is considerably smaller than in the relaxed O_2 molecule.

For the surface precovered by Li the results are basically similar to those for Na (see figs. 4 and 7; measurements for other precoverages in ref. [9]). However, the transition between the different oxidation states occurs already at somewhat smaller precoverages than for Na. The UP results of fig. 4b together with those of section 3.3 are used to identify structure E as caused by O_2^-

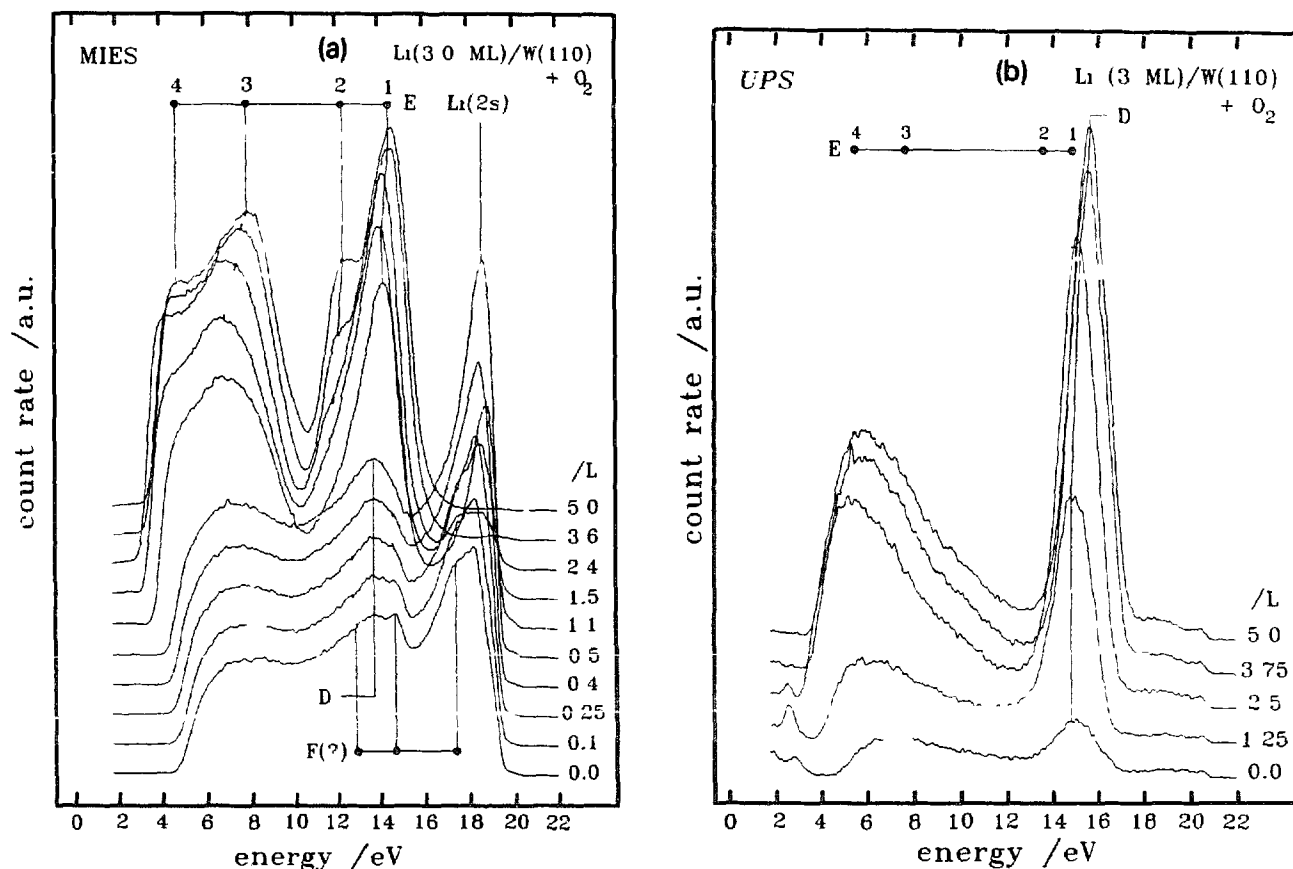


Fig 7 (a) MIE spectra, and (b) UP spectra of a W(110) surface precovered by 3 ML of Li as a function of exposure to oxygen

ionization. Fig. 4a clearly demonstrates the delayed onset of O_2^- formation at the surface which is correlated with the disappearance of the Li (2s) emission. The formation of O_2^- is obviously preceded by formation of some higher charged oxygen complexes as indicated by the features denoted by F. This is confirmed by the results obtained for 3 ML Li precoverage (fig. 7). The UP results (fig. 7b) suggest that in the initial stage of the oxidation O^{2-} ions are the dominating species at least within the surface layer (peak D; $E_B = 4.5$ eV). The MIE results on the other hand show that with increasing exposure the outermost layer of the surface is being transformed into complexes containing O_2^- ions.

Summarizing this section we can state: for an alkali precoverage below 0.6 ML dissociative attachment of oxygen occurs in form of atoms chemisorbed on the substrate (O_s) or bound at the alkalis (O_a). For precoverages between 0.5 and 1.2 ML an alkali adlayer seems to have a passivating action: in this region some of the oxygen, which is integrated into the adlayer, is not dissociated, but appears to form O_2^- ions incorporated into the surface. For precoverages beyond 1.4 ML impinging oxygen is dissociated and integrated as O^{2-} at a small extent even to the surface as long as the oxygen exposure remains sufficiently small. As soon as the electron density at the surface is reduced sufficiently by its "consumption" for binding the oxygen, the surface loses its capability to dissociate O_2 upon further exposure, and top-adsorption occurs as O_2^- ions predominantly. For large exposures to oxygen (> 2 L) the surface layer is at least partially turned into O_2^0 or chemisorbed atomic oxygen while O_2^- ions persist subsurface. The coadsorption diagram of fig. 1 is a convenient way to visualize these conclusions; it indicates the predominant species found in the outermost layer of

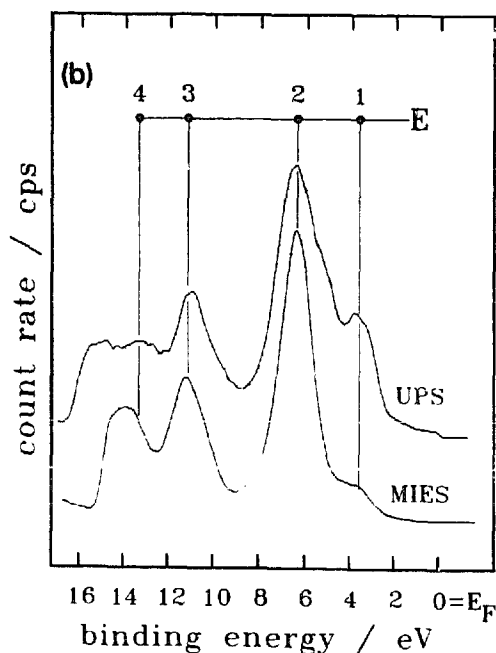
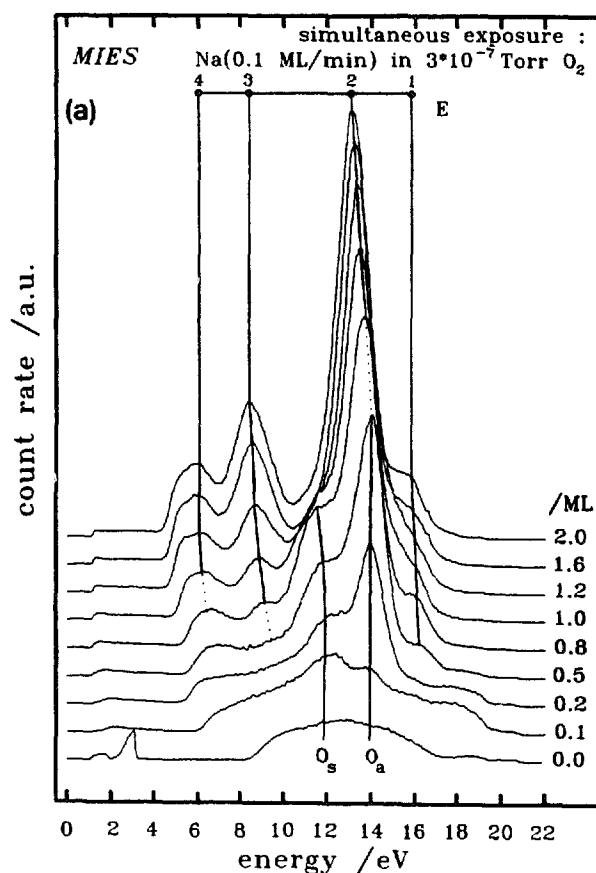


Fig. 8. Simultaneous exposure to Na and oxygen of a W(110) surface. Alkali deposition (0.1 ML per minute) was made in an ambient oxygen atmosphere of 3×10^{-7} Torr, (a) MIES data; Na coverage was estimated under the assumption of unity sticking probability, (b) UPS data for the conditions corresponding to the top MIE spectrum of (a).

the surface for the various combinations of alkali and oxygen exposures.

3.3. Oxidation by simultaneous exposure of the W(110) surface to Na and oxygen

Figs. 8a and 8b show MIES and UPS results obtained when depositing Na at a rate of 0.1 ML/min in an ambient oxygen atmosphere. These particular Na deposition rate and oxygen pressure (3×10^{-7} Torr) were chosen in order to reproduce the (Na-O) film structure of refs. [2,18] where a detailed analysis of the He II UP spectra from the ionization of O_2^- was made. In the coadsorption diagram of fig. 1 this procedure corresponds to pathway S4. Indeed the four-peak structure (labeled E) attributed to O_2^- emission [2,18] appears rather clearly both in UPS and

MIES. E_1 and E_2 are only weakly seen with MIES. The peak splittings and even the absolute peak positions agree also rather well with those obtained in refs. [2,18] except for the (E_1-E_2) splitting which is considerably smaller than expected. As discussed in section 3.2 this could be due to the ionization of an unrelaxed O_2^- species with an internuclear distance which is approximately 0.1 \AA larger than in the free O_2^- ion. MIE spectra of Cs films during the oxidation process were reported in [4]; a four-peak structure with binding energies similar to those in fig. 8 was observed for exposures $> 3 \text{ L}$. Again the peak at $E_B = 3.4 \text{ eV}$ (E_1) appeared rather faint as in our results. We conclude that O_2^- ions are formed at the surface under the conditions of fig. 8. Because the peak positions of structure E in the results of section 3.2 coincide also rather closely

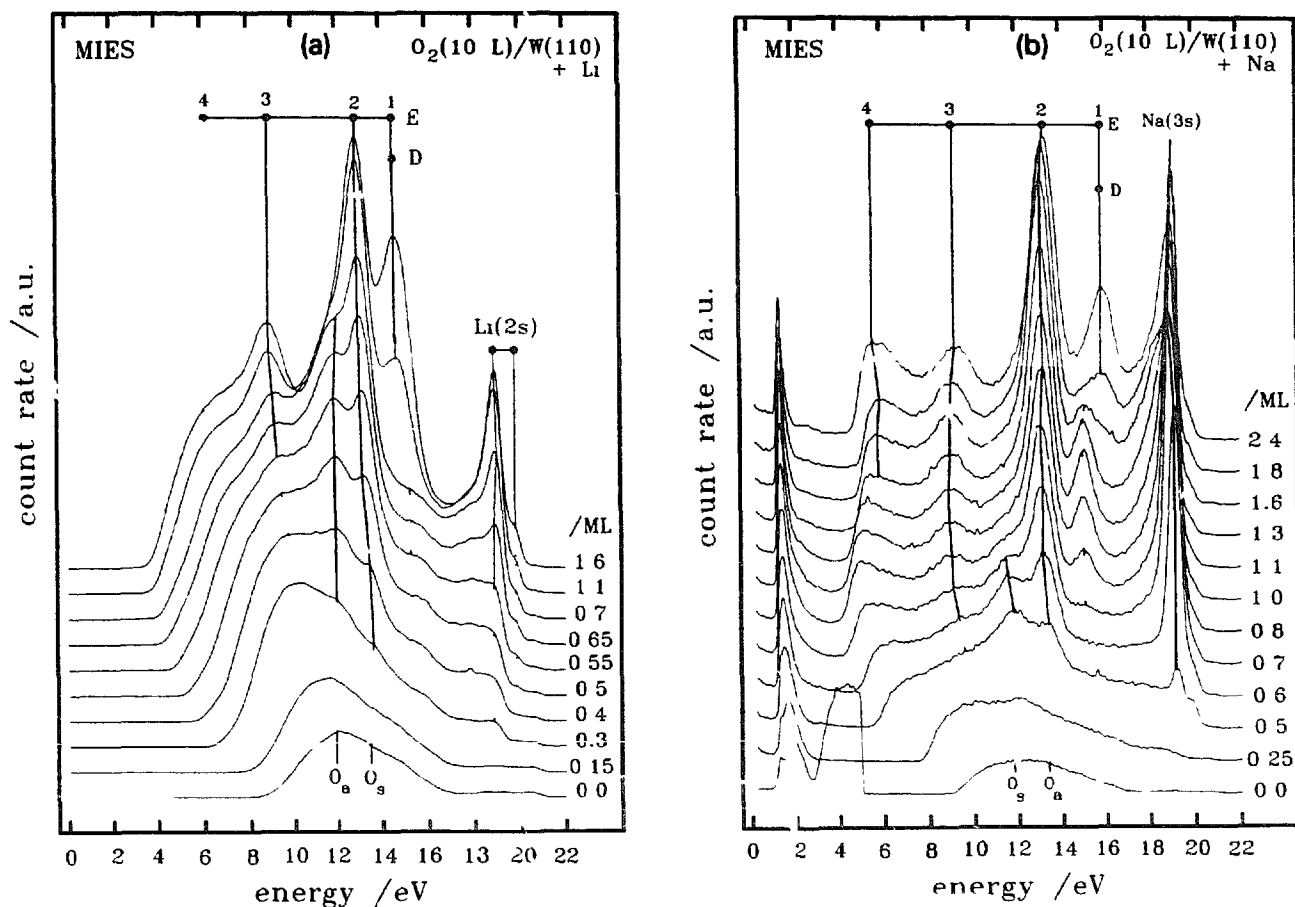


Fig 9 MIE spectra of a W(110) surface exposed to 10 L oxygen. The alkali coverage is estimated under the assumption of unity sticking probability, (a) Li and (b) Na

with those of fig. 8, we also identify the oxygen species which produces structure E under the conditions of section 3.2 with O_2^- ions. The different peak intensities must reflect the different environment felt by the O_2^- ions.

The features O_s and O_a appear at small exposures. We attribute O_s to atomic oxygen on the substrate and O_a bound to the Na, respectively (see also sections 3.2 and 3.4). As expected O_s disappears with ongoing oxygen adsorption.

3.4. O / W(110) + alkali

Figs. 9a and 9b show the MIE spectra obtained when exposing an oxygen-saturated (10 L O_2) W(110) surface to varying amounts of Li or Na. At small alkali exposures the two peaks O_s and O_a are seen again. Their energetic positions agree with those of the corresponding peaks in previous figures. UPS results (not reproduced) show convincingly that the photopeak due to ionization of atomic oxygen on clean W(110) merges into O_s with increasing alkali exposure. It must be remembered that MIES will see atomic oxygen only when the RI/AN process is suppressed with decreasing WF. This proves that O_s is due to the ionization of oxygen atoms adsorbed at substrate sites. On the other hand, O_a must be due to the ionization of oxygen atoms bound to alkali atoms because its intensity increases with the number of adsorbed alkali atoms. Michel et al. [17] give the same interpretation on the basis of UP spectra obtained during the oxidation of silicon partially covered by K atoms ($\theta_K = 0.15$ ML): their conclusion is that the two peaks at $E_B = 7.1, 5.0$ eV are due to oxygen adsorbed on the silicon substrate and close to K atoms, respectively. In addition they could support their interpretation by XPS measurements.

In fig. 9 structure E (except E_4) becomes rather pronounced at alkali exposures where also alkali s-emission is seen clearly. Again we cannot exclude that peak E_2 contains contributions from O_a , e.g., also oxygen atoms are present on top of the surface layer. Over a wide range of the alkali coverage the (E_1 - E_2) splitting is again much smaller than expected for the free O_2^- ion. We

propose that the O_2^- species is strongly distorted by the alkali environment, e.g., the (O-O) distance is larger than in the free molecular ion. In the case of Na the energetic distance between E_1 and E_2 seems to increase suddenly at 1.2 ML Na coverage. However an alternative explanation could be that O^{2-} formation starts at this coverage; peak D superimposes E_1 . For Li, peak D (due to O^{2-} formation) appears at about the same energy as E_1 (see table 1). Therefore no peak shift is expected when O^{2-} ions are formed. Both for Li and Na O^{2-} formation would then set in at about the same alkali coverage as in the results of section 3.2.

3.5. Alternate exposure to alkali and oxygen

MIE spectra of a W(110) surface alternately exposed to alkali and oxygen are presented in fig. 10. The surface was first precovered by about 0.6 ML Na and then exposed to 1 L oxygen. The procedure corresponds to pathway S5 in fig. 1. This procedure was repeated 3 times. The spectra 1, 6 and 10 were measured immediately after depositing again about 0.6 ML Na. The results obtained between the first two cycles roughly correspond to fig. 3a, the atomic feature (O_s) appears somewhat stronger, as expected for the smaller Na precoverage. Structures E and D (due to O_2^- and O^{2-} formation at the surface) which cannot be separated uniquely become prominent after the second cycle. Finally the adlayer generated in this manner was exposed to 10 L oxygen (not shown in fig. 10) with the result that the outermost layer of the surface underwent a partial transformation into O_2^0 as indicated by the considerable weakening of peak E_1 (see section 3.2). We associate the weak peak seen at $E_B = 7$ eV (O_s) tentatively with oxygen atoms chemisorbed to the surface; these atoms probably originate from the decomposition of the chemisorbed O_2^- molecular ions. Under the chosen conditions O_2^{2-} formation – if present at all – is weak. This indicates that at sufficiently large alkali coverages O_2^{2-} dissociates with high probability which leads to O^{2-} formation at the surface.

4. The oxidation process involving Na (Li) atoms

The oxidation process will be discussed on the basis of fig. 1 which summarizes information from previous studies and our results presented in section 3. This qualitative scheme denotes regions of the experimental parameters, oxygen exposure and alkali coverage, in which metallic-like alkali and various ionic oxygen states exist at the outermost edge of the surface as sampled by MIES. It implies that the order of adsorption is of no importance. The calibration of the ordinate should be considered with caution because the exposure needed to achieve a desired oxygen content in the surface will depend on the sticking

coefficient which is a function of the alkali pre-coverage. Dashed lines (S1 to S5) symbolize the coadsorption procedure; the solid lines indicate the regions in which different oxygen species are postulated to dominate. Minor contributions of species from adjacent regions are present as well. There are three key parameters which control the oxidation process [3,4]:

- (1) the electron density in the alkali adlayer,
- (2) the distance between the alkali cores, and
- (3) the lateral interaction between adjacent oxygen atoms relative to their interaction with the alkali/substrate.

It has been demonstrated for Cs that a clean alkali layer of sufficient thickness is capable to lower the activation barrier for dissociation of oxygen molecules considerably [3,4]. The reason is the ease of transferring electrons from the alkalis to antibonding molecular orbitals of the oxygen molecule. On the other hand, once the alkali's valence electron density is reduced to zero by its complete transfer to the oxygen, the alkali cores form an inert layer on top of the W(110) substrate. Consequently the capability of the alkali layer to dissociate additional oxygen is lost. It has been demonstrated in ref. [4] using UPS and MIES (MDS) that this stage is reached when the emission from the alkali s-valence has disappeared. At this stage the distance between the alkali cores in the ionized (oxidized) alkali layer becomes of crucial importance: if their distance is sufficiently large, the substrate itself becomes accessible for the dissociative adsorption of oxygen again. If on the other hand the distance between the alkali cores remains sufficiently small after the oxidation of the toplayer, as in the case of Li and Na, the lateral interaction between neighboring oxygen adatoms and of the oxygen with the alkali cores may dominate their interaction with the substrate. The capability of the surface to dissociate the oxygen will then be reduced or even lost. Provided the sticking coefficient is not zero this will lead to molecular attachment of oxygen on the outermost layer of the surface.

Path S3 in fig. 1 visualizes the remarks made above for the studied cases (Li, Na): by electron transfer from the alkali atom to the oxygen

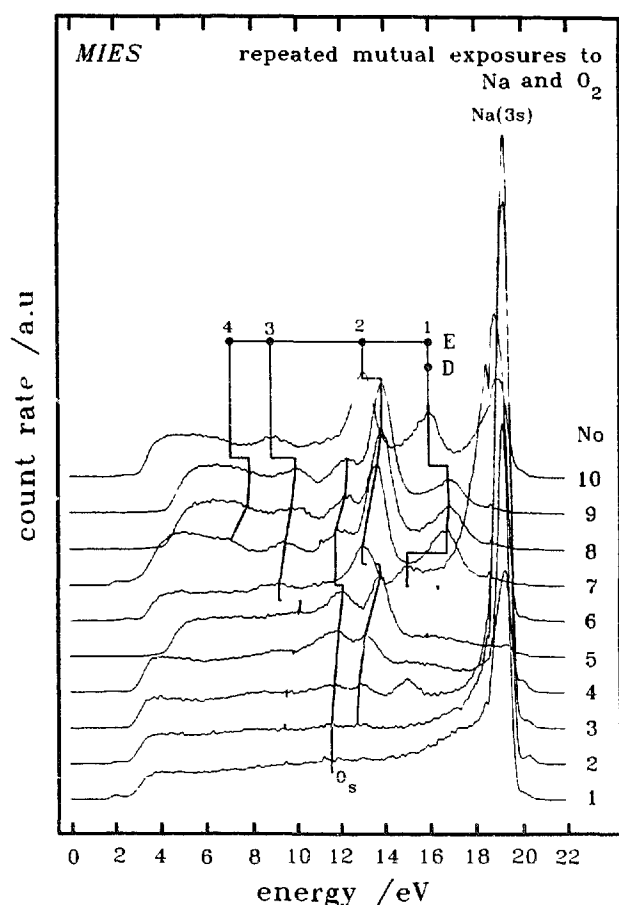


Fig 10 Repeated mutual exposure of a W(110) surface to Na and O_2 (1) 0.6 ML Na, (2) +0.2 L O_2 , (3) +0.2 L O_2 , (4) +0.2 L O_2 , (5) +0.4 L O_2 , (6) 0.6 ML Na, (7) +0.2 L O_2 , (8) 0.4 L O_2 , (9) +0.4 L O_2 , (10) +0.6 ML Na

molecule most likely weakly bound O_2^{2-} is formed, which dissociates immediately and leads to the integration of O^{2-} into the adlayer. For Cs in addition oxygen atoms appear at the surface in the initial stage of the oxygenation [4]. At about 1 L oxygen exposure the capability of the surface to dissociate additional oxygen is lost because no electrons are left which may be transferred to the oxygen. This is reflected by the disappearance of the alkali s-emission at this stage.

Path S1 is also easily understood: the reactive W(110) surface dissociates the oxygen molecules; most of the oxygen atoms bind to the substrate, but some bind to alkali atoms, and at somewhat larger precoverages are probably present also as O^- ions.

Apparently there exists a range of alkali precoverages (< 1.2 ML) where the alkali layer is not dense enough, i.e., its free-electron density not high enough, to dissociate the impinging oxygen molecules via the formation of O^{2-} . Charge transfer from the alkali to the oxygen then leads to the formation of O_2^- molecular ions.

On path S2 oxygen is initially adsorbed atomically mainly on the substrate as expected from the discussion of S1. For sufficiently large exposures to alkalis a metallic-like top layer is formed by the alkali atoms as judged from the appearance of s-emission near the Fermi energy. The oxygen-induced features do not simply disappear, i.e., the alkali atoms are not located on top of the oxygen atoms. Instead the oxygen-induced features become rather more pronounced indicating that the oxygen becomes integrated into the top-layer, thus becoming accessible for MIES. As predicted by fig. 1, O_2^- is formed for sufficiently large exposure to alkalis. Here the oxygen-substrate interaction is not dominating any more over the lateral interaction between two adjacent oxygen atoms which, loosely speaking, are pushed together by the alkali atoms to form molecular oxygen.

Following path S4 one might expect to obtain the same result as for the oxidation of free alkali atoms in an oxygen atmosphere. For Na this should lead to the formation of Na_2O_2 , e.g., to the formation of O_2^{2-} ions [19]. However, fig. 8

demonstrates that S4 – at least under the chosen conditions – leads to predominant formation of O_2^- both in the bulk and on the surface.

5. Summary

UPS and metastable impact electron spectroscopy (MIES) are combined to study the interaction between oxygen and the alkalis Li and Na on W(110), mainly at submonolayer coverages. From the observed structures in the electron spectra a coadsorption diagram is derived which allows one to predict the dominant oxygen species (atomic/molecular and the charge state) at the surface as a function of the exposure to oxygen and the alkali coverage. Briefly, for small alkali precoverages impinging oxygen molecules are dissociated at the W(110) substrate. When a metallic-like alkali toplayer is formed, considerable charge transfer from the adlayer to the attached oxygen takes place initially and leads to the formation of O_2^- ions at the surface and underneath. Beyond 1.4 ML alkali coverage this charge transfer leads to dissociative attachment of the oxygen causing the formation of O^{2-} ions even at the surface. The formation of an O_2^{2-} precursor ion appears likely.

When the metallic character of the top layer is destroyed by the increasing oxidation of this film the surface loses its capability to dissociate additional oxygen. Accommodation of additional oxygen eventually takes place in form of O_2^- ions on top of the inert surface. The final oxidation state is reached when the surface layer is entirely transformed into an inert layer of neutral chemisorbed oxygen (for small alkali precoverages) or O_2^- (for precoverages larger than about 2 ML).

Acknowledgement

Financial support by the Bundesminister für Forschung und Technologie (BMFT) under grant no. 13N5676 is gratefully acknowledged.

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