

Alkali adsorption on W(110) studied by metastable impact electron spectroscopy

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The adsorption of alkali atoms (Li, Na, K, Cs) on W(110) at room temperature has been studied by Metastable Impact Electron Spectroscopy (MIES) and UPS as a function of the alkali coverage.

In the coverage range up to 0.5 ML (in units of the saturation coverage at room temperature) emission via the Auger de-excitation process involving substrate electrons is observed.

Emission which can be associated with the alkali s-levels can be identified only at alkali coverages exceeding 0.4 ML. This conclusion is corroborated by results obtained for the W(110) surface exposed to NaCl and by the oxidation of alkali layers.

An explanation is offered for the fact that the interaction of the He(2^1S) and He(2^3S) metastables with the surface is different. An attempt is made to analyse and interpret the line shapes of the alkali induced features.

1. Introduction

Metastable Impact Electron Spectroscopy (MIES) is uniquely suited to study the electronic structure of the outermost layer of solid surfaces [1]. As has been shown previously MIES is an excellent method for the investigation of the alkali s-valence band [2,3]. The metastable atoms probe the valence band at a distance of a few ångströms in front of the surface. MIES is therefore extremely surface sensitive. Due to the small HeI-photoionization cross section the UPS-features arising from the s-valence band are completely masked by the W(5d) emission near the Fermi level; UPS is therefore not as capable as MIES for the investigation of the alkali valence band [4].

In the last few years the question of the ionicity of an adsorbed alkali atom in the submonolayer range has been discussed in the literature very intensively [5–10,27]. Theoretical work often relies on a MIES study published by Woratschek et al. [2]. The authors interpreted the onset of the electron spectra at the Fermi level for the system K/Cu(110) as the beginning of the 4s-emission. It

was concluded that the structure due to the 4s-emission is discernible even at a coverage as low as 0.02 ML K. This interpretation gave strong evidence for the non-ionic adsorption of alkali atoms even at low coverages. In the following we will show that this interpretation should be treated with caution. An alternative interpretation was given by Lee et al. for analogous structures observed for K/Ni(111) [3]: the emission below the Fermi level observed at the lowest coverages is due to Auger de-excitation involving electrons of the substrate. Although the work of Lee et al. [3] was published at the same time as ref. [2], it has not received the same attention in the literature as the interpretation of Woratschek et al. [2].

We have investigated the adsorption of Li, Na, K, and Cs on W(110) by MIES and UPS. These results are supplemented by MIES data obtained for oxygenated alkali films and from NaCl adsorbed on W(110); the latter system is not capable of forming a valence band near E_F , but nevertheless the electron spectra show essentially the same onset at the Fermi level as those obtained for alkalis on W(110).

2. Experimental

The apparatus has already been described in detail [11]. Briefly, it consists of a source for metastable He with an intensity of 2×10^{10} He*/s at the target (corresponding to 3.2 nA/mm²) and HeI photons of comparable intensity, a 180° analyzer, a CMA, a quadrupole mass spectrometer, and a four-grid LEED optics. The base pressure is about 4×10^{-11} Torr and amounts to 7×10^{-10} Torr when the metastable source is switched on. The He* beam consists of He(2³S) (85%) and He(2¹S) (15%) [12]. Due to the very efficient conversion of the singlet atoms into the triplet state atoms in front of the surface prior to de-excitation [13] the singlet states are removed with high probability.

The alkalis Cs, K, Na and Li are deposited onto the surface using SAES Getters dispensers. The degree of coverage is determined by the ratio of the alkali and W Auger signals and work function (WF) measurements which show the behavior

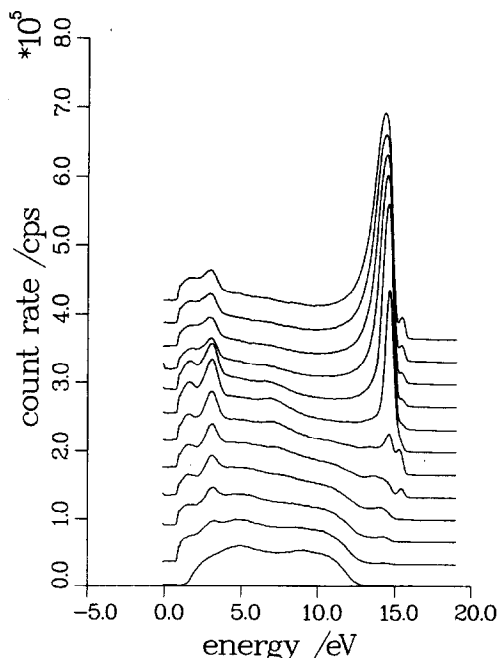


Fig. 1. MIE spectra of the Cs adsorption on W(110). The bottom spectrum corresponds to $\theta_{\text{Cs}} = 0$, the top spectrum represents the complete monolayer. The coverage increases by 0.09 ML Cs per spectrum.

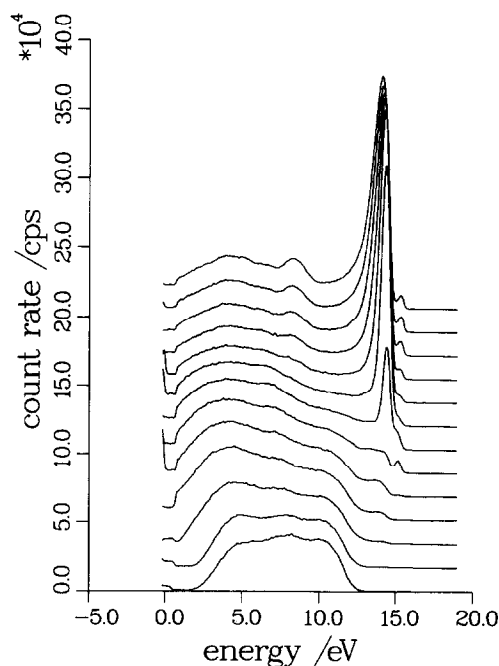


Fig. 2. MIE spectra of the K adsorption on W(110). The bottom spectrum corresponds to $\theta_{\text{K}} = 0$, the top spectrum represents the complete monolayer. The coverage increases by 0.08 ML K per spectrum.

familiar from previous studies [14]. Cs and K form only one complete monolayer on W(110) at room temperature while Na and Li are able to form thick layers. Coverages are given in fractions of the complete first monolayer at room temperature which is denoted by 1 ML. 1 ML corresponds to a surface density of 5.2×10^{14} cm⁻² (Cs), 5.9×10^{14} cm⁻² (K), 8.0×10^{14} cm⁻² (Na) and 1.4×10^{15} (Li) on W(110) (1.42×10^{15} cm⁻²) at room temperature.

All measurements were performed with the target at 45° both with respect to the incoming He*/HeI and the optical axis of the 180° analyzer. When performing UPS measurements the metastables are quenched out of the beam [2,3]; when performing MIES measurements the photoelectrons are ignored due to their small intensity compared to the He* electrons (1:50). Usually UPS contributions to the MIE spectra can only be observed beyond the Fermi energy for He*. The completion of a MIE spectrum requires about 50 s for data collection and storage; UP

spectra require about 3 min. The resolution of the analyzer is 250 meV at a constant pass energy of 10 eV.

For Cs and K the spectra were taken without any target bias and are thus cut-off at the low energy side. For the ionization by He(2^3S) and He(2^1S) the Fermi level is found at $E_{kin} = 14.8$ and 15.6 eV, respectively. The Li and Na spectra are biased by 4.8 V; the Fermi level is found at $E_{kin} = 19.6$ eV and 20.4 eV, respectively. The low-energy onset of the spectra gives a qualitative idea of the work function change as a function of the alkali coverage.

3. Results

The MIE spectra for the adsorption of the alkali atoms Li, Na, K and Cs on W(110) are shown in figs. 1, 2, 4–7. Each bottom curve shows the spectrum of the clean substrate. The electrons are emitted by the Auger Neutralization (AN)

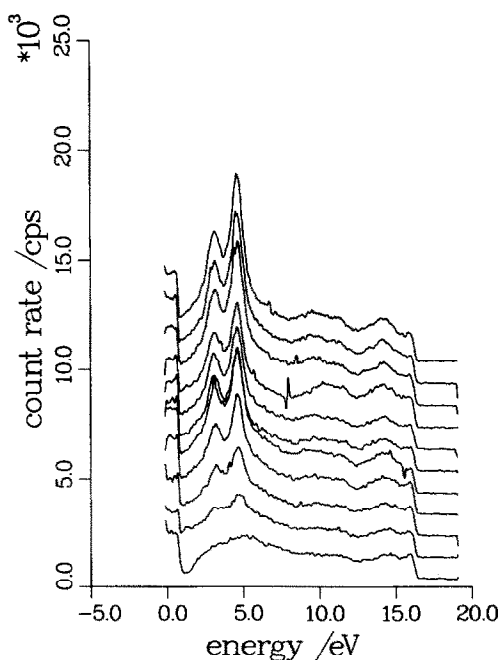


Fig. 3. UP spectra of the Cs adsorption on W(110). The bottom spectrum corresponds to $\theta_{Cs} = 0$, the top spectrum represents the complete monolayer. The coverage increases by 0.1 ML Cs per spectrum.

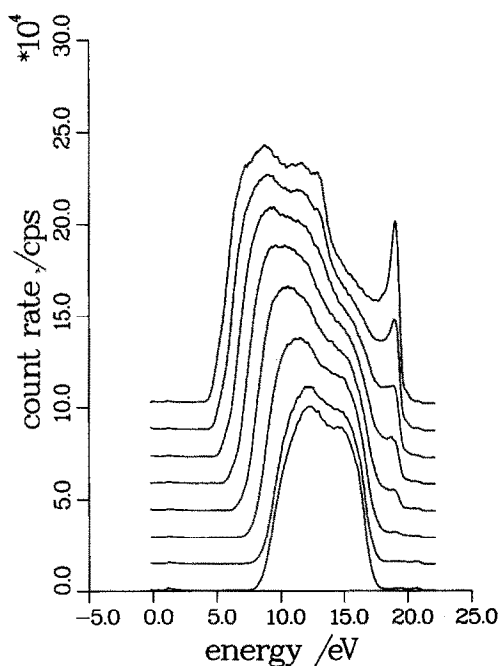


Fig. 4. MIE spectra of the Li adsorption on W(110). The bottom spectrum corresponds to $\theta_{Li} = 0$. The coverage increases by 0.085 ML Li per spectrum.

process which is typical for high work function surfaces [1,11].

With increasing alkali coverage the spectra become broader because the Auger De-excitation (AD) process becomes possible. The first additional feature with increasing alkali coverage is a shoulder at the high kinetic energy end of the spectra. In the case of Cs, in addition, a doublet appears starting with the lowest coverage at a binding energy of $E_B = 11.5/13.0$ eV. The doublet is attributed to ionization of the Cs($5p_{3/2}$)/Cs($5p_{1/2}$) levels which are split due to the spin-orbit interaction [11,13]. The doublet is also visible in the UP spectra which are shown in fig. 3; these spectra are taken under the same conditions as those of fig. 1. Above about 0.4 ML alkali coverage a strong peak located near the Fermi level appears in the spectra which becomes the more pronounced the higher the alkali coverage is. This peak is attributed to the ionization of the alkali s-orbital [2,3,13].

At saturation coverage the Cs(6s) peak dominates the spectrum completely; in the corre-

sponding UP spectra (see fig. 3) it cannot be distinguished at all. The small peak seen in figs. 1, 2, 4 to 7 beyond the Fermi level for He(2^3S) ionization corresponds to s-state ionization induced by the singlet species of the metastable He which are not converted into the triplet state. Some of the spectra (see fig. 5) display a small peak near $E_{\text{kin}} = 0$ which is caused by photoelectrons.

For Li and Na it was impossible to collect the spectra for all coverages up to 1 ML in just one run because oxygen induced features appeared which might influence the height and shape of the s-peaks. Auxiliary measurements taken at coverages larger than those shown in figs. 4 and 5 show, however, that the shape and height of the s-peak changes in the same way as for K and Cs.

Fig. 7 shows a magnification of the region below the Fermi energy for the first six spectra of fig. 1; the center of the structure, which is visible in the low coverage range, shifts from $E_{\text{kin}} = 14.4$ eV at 0.09 ML Cs to $E_{\text{kin}} = 13.4$ eV at 0.45 ML Cs. The Cs(6s) emission starts at 0.45 ML Cs as

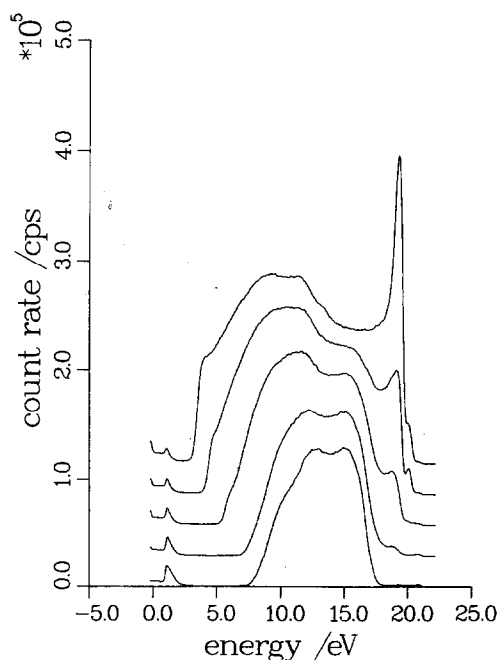


Fig. 5. MIE spectra of the Na adsorption on W(110). The bottom spectrum corresponds to $\theta_{\text{Na}} = 0$. The coverage increases by 0.12 ML Na per spectrum.

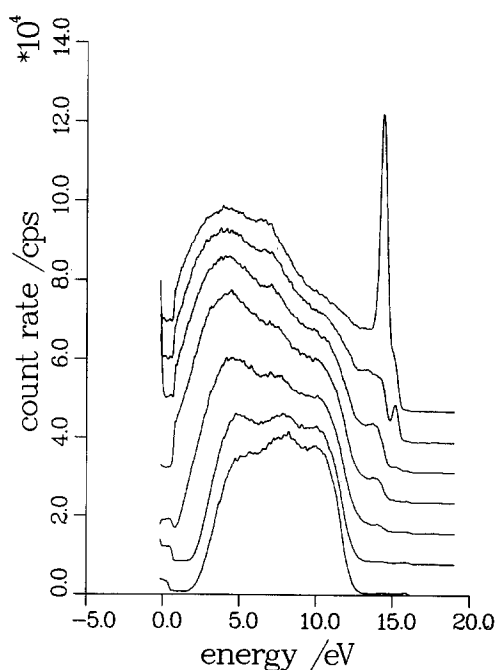


Fig. 6. MIE spectra of the K adsorption on W(110) (coverage range $\theta_{\text{K}} \leq 0.48$ ML). The bottom spectrum corresponds to $\theta_{\text{K}} = 0$. The coverage increases by 0.08 ML K per spectrum.

judged from the appearance of the He(2^1S) induced peak. It is clear from figs. 7, 1, 2 and 6 that for K and Cs the singlet induced emission shows up already at lower coverages than the triplet emission. This behavior was noticed before for K/Ni(111) [3], and can be seen in the ion neutralization spectra using He⁺ projectiles for K/Cu(100) and K/Ni(100) [15].

The electron emission intensity in counts per second, ΔN , in the region of the alkali s-emission is shown in fig. 8 for all alkalis. The location and the width of the energy window are chosen in such a manner that the entire s-peak, which appears beyond 0.4 ML, is included. A separation of the s-peak and other contributions cannot be done unambiguously.

For all alkalis it can be seen clearly that the signal increases rapidly around 0.4 ML. The arrow indicates the first appearance of the s-peak as judged from the singlet induced emission which is not masked by any other contributions. Therefore the position of the onset of the s-emission can easily be estimated. In contrast it has already been

shown in ref. [11] that the Cs(5p) emission increases linearly beginning with the lowest coverage. After passing a maximum the s-emission decreases slightly for all alkalis. The position of the maximum is correlated with the work function minimum.

Fig. 9 displays MIE spectra obtained for the adsorption of NaCl molecules on the W(110) surface at a slow constant rate. Only the region close to E_F at 19.6 eV will be of relevance for the discussion of the results of figs. 4 to 7. The emission seen above 19.6 eV is due to ionization by HeI UV photons. The distinct peak appearing around $E_B = 6.0$ eV is due to the ionization of the Cl(3p) orbital; the transition from the adsorption

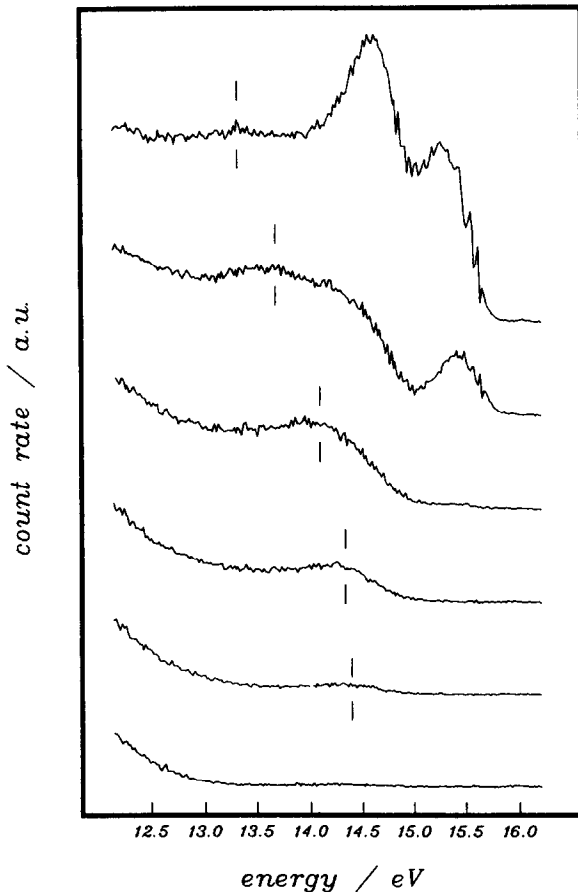


Fig. 7. Magnification of the first six spectra of fig. 1 in the energy range between 12.0 and 16.4 eV. The position of the maximum of substrate emission is marked.

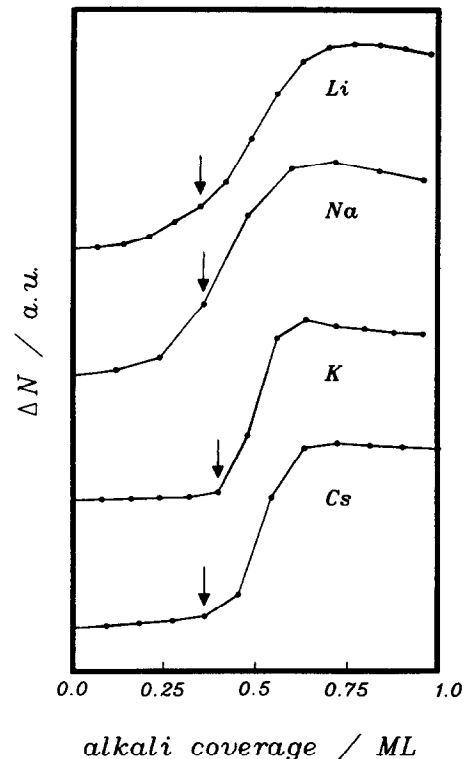


Fig. 8. Number of counts ΔN in an energy interval of 0.5 eV at the position of the s-emission peak for Li, Na, K and Cs.

of single (Na-Cl) adcomplexes to the NaCl-bulk on W(110) will be studied in detail elsewhere [16].

Fig. 10 shows the MIE spectra obtained when 1 ML of K on W(110) is exposed to oxygen; the oxygen exposure increases by 0.125 L per spectrum. Again only the region close to E_F will be discussed in order to identify the emission seen close to E_F at low alkali coverages in the alkali-W(110) data. The features appearing upon oxygen exposure between $E_B = 5.5$ eV and 10 eV will be identified in a forthcoming publication as due to O(2p) atoms chemisorbed on top of the alkali adlayer [17].

Some of the measurements were repeated using a metastable Ne beam, but are not reproduced here. The excitation energy of Ne is 16.6 eV; therefore the spectra are smaller and the Cs(5p) emission cannot be observed. In contrast to He the metastable Ne has a vacancy in a p-orbital. The variation of the electron spectra as a function of the alkali coverage near the Fermi edge is the

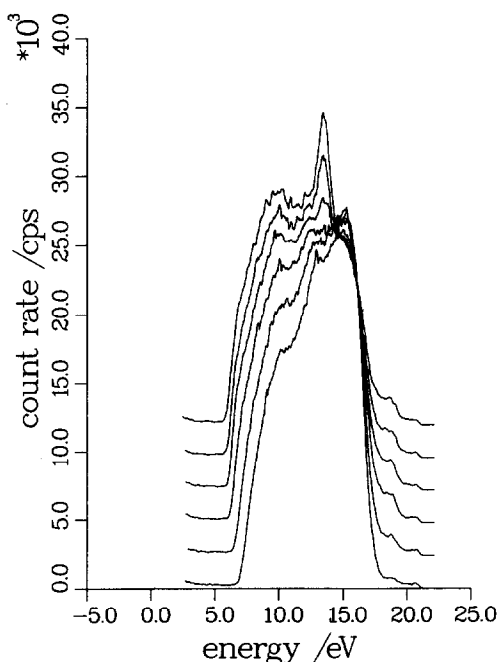


Fig. 9. MIE spectra for NaCl adsorption on W(110). The bottom spectrum corresponds to $\theta_{\text{NaCl}} = 0$. The coverage increases by 0.02 ML NaCl per spectrum.

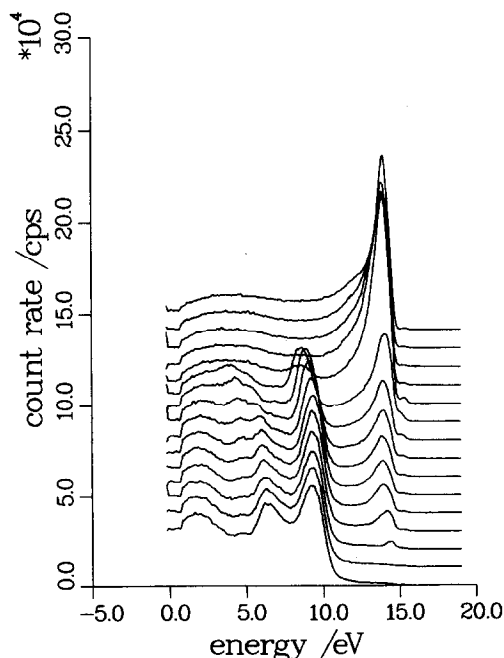


Fig. 10. MIE spectra for the oxidation of 1 ML K on W(110). The top spectrum shows only K. The oxygen exposure increases by 0.125 L per spectrum.

same as observed with He* except for the absence of the He(2^1S) induced emission; in particular the s-peak again appears around 0.4 ML. We can therefore conclude, that the spectra near E_F are not influenced by the particular type of overlap of the wave function of the metastable and the surface.

4. Interpretation

4.1. Alkali adsorption ($\theta_{\text{Alk}} < 0.4 \text{ ML}$)

For the clean surface where the de-excitation occurs via Resonance Ionization (RI)/AN the maximum kinetic energy of the electrons is given by $E_{\text{kin,max}}^{(\text{AN})} = I - \phi - \phi_{\text{loc}}$ where I is the effective ionization potential of the ground state atom, and ϕ_{loc} is the local work function of the surface at the location of the de-excitation [2].

Adsorption of alkali atoms leads to the appearance of spectral features at kinetic energies higher than $E_{\text{kin,max}}^{(\text{AN})}$ because AD becomes possible. The highest kinetic energy is now given by $E_{\text{kin,max}}^{(\text{AD})} = E^* - \phi$ where E^* is the effective excitation energy of the metastable He atom and defines the position of the Fermi level E_F . Up to approximately 0.4 ML a shoulder is seen below E_F becoming the more pronounced the higher the alkali coverage is. Lee et al. [3] have proposed that this spectral feature originates from AD involving the d-electrons of the nickel. We follow this interpretation because for $\theta_{\text{Alk}} > 0.4 \text{ ML}$ there appears an additional, narrow alkali induced feature which must be attributed to emission of s-electrons from the adsorbed alkali atom. More evidence for this interpretation which is at variance with the one given in ref. [2] for K-Cu(110) will be presented in section 4.2.

Fig. 1 proves convincingly that indeed – at least for the case of Cs – alkali atoms are adsorbed starting from the very beginning of the exposure of the W(110) crystal. In ref. [11] we have shown that the Cs($5p_{3/2}$)-intensity increases roughly linearly with Cs exposure. The same result would be obtained from the UP spectra of fig. 3. We wish to point out that – although the emission from the Cs($5p$) level ionization as well as the

alkali induced W d-band ionization can clearly be seen already at low alkali coverages – no features which can be associated unambiguously with the alkali s-valence state ionization can be detected for $\theta_{\text{Alk}} < 0.4$ ML for all alkali adsorbate atoms studied. Two recent UPS studies (K/Al(111) with $h\nu = 25$ eV and Cs/Al(111) with $h\nu = 21$ eV [4] and K/Ag(100) with $h\nu = 3.2; 5.1$ eV [18]) also found emission attributable to s-band ionization for $\theta_{\text{Alk}} \geq 0.4$ ML only.

Our interpretation is furthermore supported by the NaCl–W(110) results presented in fig. 9: in this case the Na adsorption is certainly ionic. As in the case of Na adsorption the work function of the surface is locally decreased close to the adsorbed Na^+ -ions [16]. The emission close to E_F therefore must come from AD of the metastable by W d-band electrons. The MIE spectra close to E_F show the typical shoulder which is observed for all alkali–W(110) combinations.

Further evidence is given by the features shown in fig. 10 for the oxygenation of 1 ML of K on W(110). The charge density of the 4s electrons (top spectrum) is increasingly “consumed” by the binding of the oxygen [13]. Nevertheless electron emission very similar to that seen at low alkali coverages (see fig. 2) occurs up to the Fermi level even after the s-peak has disappeared entirely. This shows once more that the occurrence of emission just below E_F must not necessarily be related to the occupation of the K(4s) valence state as was claimed for K–Cu(110) [2].

4.2. Alkali adsorption ($\theta_{\text{Alk}} > 0.4$ ML)

For $\theta_{\text{Alk}} > 0.4$ ML a narrow spectral feature appears very close to E_F . For K and Cs the feature appears first for the ionization of $\text{He}(2^1\text{S})$ -atoms. At slightly higher θ_{Alk} the same feature, but induced by $\text{He}(2^3\text{S})$ atoms, appears at 0.8 eV lower kinetic energy and grows in intensity rapidly while the singlet induced feature stays rather small or even decreases in intensity. We attribute this narrow feature to AD of the alkali s-valence electrons [3]. It has been proposed in ref. [13] that the strong dominance of the triplet over the singlet induced feature is caused by a rapid singlet–triplet-conversion prior to He^* de-excita-

tion. From fig. 8 we conclude that for all alkali adsorbates on W(110) AD involving the alkali valence electron is not seen for $\theta_{\text{Alk}} < 0.4$ ML with MIES. This is in agreement with recent UPS-studies which also do not show emission from alkali s-states for alkali adsorption.

There are essentially two ways to explain the absence of the s-emission at small coverages ($\theta_{\text{Alk}} < 0.4$ ML) in MIES:

(1) the SDOS at small coverages is modified in such a way as to produce the shoulder just below E_F . This shoulder would be due to AD involving alkali-surface hybrid states. On the basis of the existing calculations for alkali chemisorption it is, however, not obvious how the emergence of the narrow s-peak with increasing coverage should be explained: no drastic changes are observed in the charge distribution near the adatoms as a function of alkali coverage [25].

The energy dispersion of the adlayer band was studied in ref. [27] by calculating the adatom DOS as a function of the momentum of the states, $\delta_a(\mathbf{k}_{\parallel}, E_B, \theta_{\text{Na}})$, for Na layers on semi-infinite jellium. $\delta_a(\mathbf{k}_{\parallel} = 0, E_B, \theta_{\text{Na}})$ displays a peak which crosses E_F at a coverage θ_{Na} roughly corresponding to the minimum of the work function. If for some reason the AD process in MIES would involve surface states with \mathbf{k}_{\parallel} mainly close to zero, the appearance of a distinct peak in MIES for higher coverages could be explained. Such a momentum selection appears plausible because AD occurs mainly with those surface states whose exponentially decaying tails extend the most into the vacuum.

(2) The alkali atoms are adsorbed ionically at small coverages, and the degree of ionicity decreases with increasing coverage; the s-emission will not be seen before the initially unfilled s-resonance is shifted below the Fermi level [26]. This simple picture seems to describe the experimental facts fairly well, even the relative importance of the Cs(5p)- and Cs(6s)-emission (see section 4.1). The observed shoulder in the low coverage regime is due to AD by d-band states which becomes possible in the region of the locally decreased work function. It has been shown that a substantial shift of the electron distribution from the substrate towards the adsorbate (in particular to

its vacuum side) occurs and accounts for the onset of the region with the WF minimum [25]. Because this is the coverage region where MIES becomes able to detect the alkali s-state emission, we suggest that only then the overlap of the He(1s) wavefunction and the adsorbate s-orbital becomes strong enough to cause AD involving the alkali s-orbital. This becomes even more pronounced when the de-excitation by alkali s-emission is in competition with other processes like AD by p-emission for K and Cs (see below).

At present the conclusive explanation of the coverage dependence of the alkali-s-emission in MIES (and UPS) has to wait for additional theoretical work on alkali-metal chemisorption.

Fig. 6 of ref. [11] presents the coverage dependence of the Cs($5p_{3/2}$) peak area versus the Cs coverage; as soon as the Cs(6s)-peak becomes noticeable the Cs(5p) emission intensity starts to decrease. Using the ionicity argument discussed in of section 4.1 we suggest that the 6s- and 5p-electrons are in competition for AD, e.g. in filling the He(1s) vacancy: as soon as the 6s electrons get involved in AD, the AD process via 5p ionization occurs less frequently.

4.3. Influence of the He-surface interaction potential on the de-excitation process

In a first approximation one would expect that He* de-excitation via AD involving alkali s-orbitals should occur at lower alkali exposures for triplet He than for singlet He because the triplet state has the larger binding energy; consequently it should be in resonance with filled states at the surface already at larger work functions. At least for K and Cs adsorption this is certainly not the case: singlet de-excitation is observed before triplet de-excitation occurs.

We offer the following explanation which postulates a different character of the singlet (triplet)-surface interaction: as for the binary He*-alkali interactions [19,20] the He(2^3S)-alkali adsorbate-interaction potentials are considerably less repulsive than the corresponding singlet-alkali adsorbate potentials. Therefore the triplet He atoms will approach the surface more closely than the singlet atoms. At such distances the de-excita-

tion via the s-state ionization is, however, in competition with de-excitation via the alkali p-state ionization provided the He* excitation energy is large enough to ionize these states which is the case for K and Cs (see fig. 1). For K the excitation energy is only sufficient for AD connected with the lifting of the He(2s) electrons into empty states of the substrate above E_F , not with the production of free electrons. For the low s-charge density of the alkali atoms at coverages < 0.5 ML this competing process is efficient (see fig. 1). Consequently, the triplet atoms (which come closer to the surface) will be de-excited more efficiently by p-state ionization than the singlet atoms. As soon as the s-state charge density increases with increasing alkali coverage (> 0.4 ML) the p-state charge density will be more efficiently shielded, and its influence on the He de-excitation process becomes less important. For Li and Na, where de-excitation via core ionization is energetically not possible, the de-excitation via s-valence state ionization should be seen at the same alkali-precoverage for singlet and triplet collisions, which is indeed the case. Further support comes from the fact that we find no indications for AD via p-ionization by singlet atoms which should produce a second peak in the spectra of fig. 1 about 0.8 eV beyond the Cs($5p_{3/2}$) peak.

An alternative explanation for the early appearance of the singlet induced emission has been forwarded in ref. [15]; it is solely based on the variation of the positions of the He* levels with respect to the Fermi energy as a function of the local work function of the alkaliated surface. However, this explanation seems not to be able to cope with the different behavior observed for Li and Na versus K and Cs.

4.4. Lineshapes and linewidths

At first the linewidth of the s-emission will be discussed for the two following limiting cases:

(a) The observed linewidth represents the intrinsic width of the adatom resonance, and the broadening of the line by the finite lifetime of the final s-state hole at the adatom against filling from the substrate may be neglected. The narrow symmetric lineshapes observed at coverages < 0.6 ML

are, however, in conflict with the calculated rather broad and diffuse changes induced in the SDOS by the adsorption of single alkali atoms [25].

(b) The width of the line is essentially determined by the lifetime of the final s-state hole at the adatom, and the intrinsic width of the adatom resonance may be neglected. This would imply that the intrinsic width of the adatom resonance is considerably smaller than 0.6 eV in the low coverage regime, and is again in conflict with the existing calculations [25].

Therefore it is concluded that the difference of the shape of the experimental electron energy distribution to that of the calculated SDOS is due to matrix element effects in the sense described in ref. [23]: the AD process between the He* and the surface in the vicinity of the adatoms occurs essentially with states close to the Fermi level E_F because the exponentially decaying tail of the states at the surface is of relevance for the AD process only. Within the Sommerfeld model the wave function is proportional to $\exp(-\sqrt{E_B}z)$ where E_B is the binding energy of the electron and z is its distance from the surface. States close to the Fermi level contribute more to the overlap with the He(1s)-wavefunction and therefore also the AD rate.

With increasing coverage the valence band of the adatoms develops and the s-peak may be represented by [21]:

$$P_{(E)} \sim \int_0^\infty \frac{dE' |H_{if}|^2 \sigma(E')}{(E - E_0)^2 - \Gamma^2/4}, \quad (1)$$

where $\sigma(E')$ represents the shape and density of the adatom resonance. The final state lifetime $\tau = 1/\Gamma$ will in general be coverage dependent (see $0.45 \text{ ML} < \theta_{\text{Alk}} < 0.7 \text{ ML}$). The low-energy tail of the s-peak observed at $\theta_{\text{Alk}} > 0.7 \text{ ML}$ is due to the convolution of the Lorentzian with the adatom resonance $\sigma(E')$; in principle $\sigma(E')$ may be recovered by an inversion procedure. It has been pointed out in ref. [23] that this requires the knowledge of $H_{if}(E')$, and that matrix element effects have to be taken into account before estimating bandwidths from MIE spectra.

The linewidth of the Cs($5p_{3/2}$) peaks in the MIE spectra (fig. 1) is in general about 200 meV

larger than in the corresponding UP (fig. 3) spectra. Because of the equal lifetime of the final state hole in both situations we attribute this difference to the influence of the He*-metal interaction potential onto the effective excitation energy at the point of the AD: from the broader peaks obtained in MIES (as compared to UPS) we may conclude that the He*-metal potential possesses an attractive well depth D_e^* which is at most $D_e^* = 200 \text{ meV}$ in the case of the He(2^3S)-Cs/W(110) interaction. For binary (He* + Cs) collisions $D_e^* = 533 \text{ meV}$ for He(2^3S) + Cs, and $D_e^* = 277 \text{ meV}$ for He(2^1S) + Cs were measured [19]. Although the interaction of the metastable with the adatom is certainly highly localized, it must be remembered that the charge state of the adsorbed alkali atoms differs considerably from that of the free alkali atoms [10].

One comment is in order concerning a comparison of the linewidth for Cs(5p) and Cs(6s) emission (fig. 1). The $5p_{3/2}$ peaks are wider than the 6s peaks by about 300 meV at low coverages ($\theta_{\text{Cs}} = 0.55 \text{ ML}$). In both situations the potential describing the initial state interaction is the same. The larger 5p linewidth therefore could be due to either one or a combination of the following reasons:

(i) the final state interaction He($1s^2$) + Cs⁺($5p^56s$) possesses a well depth D_e^* which is about 300 meV larger than the one for He($1s^2$) + Cs⁺($5p^6$), or

(ii) the $5p_{3/2}$ emission involves contributions from $|m_j| = \frac{1}{2}$ and $\frac{3}{2}$ of slightly different energy due to the 5p final state splitting caused by the Cs-substrate interaction. Similar results were found for the adsorption of Xe on various transition metals [24].

5. Summary

The adsorption of alkali atoms (Li, Na, K, Cs) on W(110) is studied by Metastable Impact Electron Spectroscopy (MIES) as a function of the alkali coverage up to the monolayer at room temperature. Electron emission which can be associated with the alkali-s-levels can only be identified for alkali coverages $> 0.4 \text{ ML}$ (in units of the

saturation coverage at room temperature). It is found that the interaction of He(2^1S) and He(2^3S) with surfaces partially covered by alkali atoms differs considerably; an attempt is made to explain this behavior on the basis of information available for the binary He*–alkali interaction potentials. An analysis of the lineshapes for the s-emission reveals that considerable matrix element effects must be taken into account before deducing information on the shape and width of the alkali induced s-valence band.

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References

- [1] G. Ertl, Surf. Sci. 80 (1979) 525.
- [2] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl and H. Haberland, Phys. Rev. Lett. 55 (1985) 1231.
- [3] J. Lee, C. Hanrahan, J. Arias, F. Bozso, R.M. Martin and H. Metiu, Phys. Rev. Lett. 54 (1985) 1440.
- [4] K. Horn, J. Somers, T. Lindner and A.M. Bradshaw, in: Physics and Chemistry of Alkali Metal Adsorption, Eds. H.P. Bonzel, A.M. Bradshaw and G. Ertl (Elsevier, Amsterdam, 1989) p. 55.
- [5] H. Ishida and K. Terakura, Phys. Rev. B 38 (1988) 5752.
- [6] H. Ishida, Phys. Rev. B 39 (1989) 5492.
- [7] D.M. Riffe, G.K. Wertheim and P.H. Citrin, Phys. Rev. Lett. 64 (1990) 571.
- [8] E. Wimmer, A.J. Freeman, J.R. Hiskes and A.M. Karo, Phys. Rev. B 28 (1983) 3074.
- [9] H. Ishida, Phys. Rev. B 38 (1988) 8006.
- [10] M. Scheffler, C. Droste, A. Fleszar, F. Máca, G. Wachutka and G. Barzel, Physica (1990).
- [11] W. Maus-Friedrichs, M. Wehrhahn, S. Dieckhoff and V. Kempter, Surf. Sci. 237 (1990) 257.
- [12] H. Hotop, E. Kolb and J. Lorenzen, J. Electron. Spectrosc. Relat. Phenom. 16 (1979) 213.
- [13] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl and H. Haberland, J. Chem. Phys. 86 (1987) 2411.
- [14] H.P. Bonzel, Surf. Sci. Rep. 8 (1988) 43.
- [15] H.D. Hagstrum, P. Petrie and E.E. Chaban, Phys. Rev. B 38 (1988) 10264.
- [16] S. Dieckhoff, W. Maus-Friedrichs, V. Kempter, W. Sesselmann and G. Ertl, in preparation.
- [17] W. Maus-Friedrichs, S. Dieckhoff, M. Wehrhahn, S. Pülm and V. Kempter, to be published.
- [18] H.B. Nielsen, U. Burghaus, G. Broström and E. Matthias, Surf. Sci. Lett. 234 (1990) L271.
- [19] M.-W. Ruf, A.J. Yencha and H. Hotop, Z. Phys. D 5 (1987) 9.
- [20] J. Lorenzen, H. Hotop and M.-W. Ruf, Z. Phys. D 1 (1986) 261.
- [21] E. Merzbacher, Quantum Mechanics (McGraw-Hill, New York, 1961).
- [22] P. Nordlander, in: Desorption Induced by Electronic Transitions, DIET IV, Vol. 19 of Springer Series in Surface Sciences (Springer, Berlin, 1990) p. 12.
- [23] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl and H. Haberland, Surf. Sci. 180 (1987) 187.
- [24] J. Hulse, J. Küppers, K. Wandelt and G. Ertl, Appl. Surf. Sci. 8 (1980) 453.
- [25] N.D. Lang, in: Physics and Chemistry of Alkali Metal Adsorption, Eds. H.P. Bonzel, A.M. Bradshaw and G. Ertl (Elsevier, Amsterdam, 1989) p. 11.
- [26] R.W. Gurney, Phys. Rev. 47 (1935) 2798.
- [27] H. Ishida, Phys. Rev. B 42 (1990) 10899.