

## The electronic structure of CsI adlayers on W(110)

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The electronic structure of thin CsI adlayers deposited on W(110) at room temperature is studied by ion impact electron spectroscopy (IIES) with  $\text{He}^+$  and  $\text{He}^{2+}$  ions, metastable impact electron spectroscopy (MIES) with  $\text{He}^*$  atoms, ultraviolet photoelectron spectroscopy (UPS), work function measurements, and to some extent with electron energy loss spectroscopy (EELS). The transition from the electronic structure of single adsorbed molecules to that of the bulk structure could be studied by following the emergence of bulk properties, in particular the bandgap, as a function of the CsI exposure. The experimental results are consistent with the following conclusions:

The first step in the layer growth is molecular adsorption of CsI perpendicular to the surface with the iodine end of the molecule pointing toward the substrate accompanied by decrease of the surface work function. The next step, starting with the occurrence of a pronounced work function minimum, is the formation of two-dimensional islands formed by CsI molecules. The results are consistent with lateral growth of the islands until the substrate is largely covered by CsI. The electronic structure of the adlayer cannot be distinguished anymore from that of CsI bulk material by means of electron spectroscopic techniques at exposures which are more than three times that of the occurrence of the work function minimum.

The production of vacancies in the  $\text{I}^-$  (5p) and  $\text{Cs}^+$  (5p) orbitals under the influence of the ionizing radiation is studied as a function of the CsI exposure. Their relevance for the desorption processes induced by electronic transitions (DIET) is discussed.

### 1. Introduction

The electronic properties of ionic compounds, in particular the alkali halides, adsorbed on (non-)metallic substrates are of interest in several respects as for

(i) the understanding of the desorption and sputtering of heavy particles induced by ionizing radiation (electrons, photons, ions) [1,2],

(ii) the formation and migration of defects, colour centers in the case of the alkali halides, under the influence of the ionizing radiation [3], and

(iii) the charging of insulators under the bombardment of ionizing radiation [4].

Despite the reasons presented above the emergence of the electronic bulk structure during the deposition of alkali halide adlayers on (non-)metallic substrates has not yet been studied at great detail. So far detailed studies have ap-

peared only for NaCl and KCl on Ge(100) [5,6] and NaCl on W(110) [7,8].

In the present study we have exposed W(110) surfaces to CsI [short notation: CsI/W(110)] at room temperature. The film growth is monitored by ion impact electron spectroscopy (IIES) with singly and doubly charged helium ions, metastable impact electron spectroscopy (MIES) employing thermal helium metastable atoms, ultraviolet photoelectron spectroscopy (UPS), and work function measurements. Some information available from electron energy loss spectroscopy (EELS) and AES is also taken into account.

It was also the aim of this work to supply information on primary processes which could be of relevance for the desorption of heavy particles, primarily iodine in the present case, under the influence of the ionizing radiation. Such processes are thought to be initiated by electronic transitions between the constituents of the ad-

layer and the ionizing projectile. Information on such transitions is obtained from our results by analyzing the structures appearing in the electron spectra.

In general, we follow similar lines as in our previous detailed study concerned with the adsorption of NaCl on W(110) [short notation: NaCl/W(110)] [8].

## 2. Experimental

Two apparatus were employed for the present studies; both were characterized in some detail already in ref. [8]. More details can be found in refs. [9–12]. Briefly, the apparatus for MIES and UPS is equipped with a cold cathode gas discharge capable to produce both an intense He metastable beam and a He I photon flux sufficiently intense to perform UPS. Electron spectra

are now normally recorded at an emission angle of  $90^\circ$  with respect to the surface (except for figs. 1b and 2b where the emission angle is  $45^\circ$ ). The other apparatus employed for IIES (and EELS) features an intense mass/charge analyzed beam of singly and doubly charged He ions as required for IIES studies.

Otherwise the experiments were performed under the same conditions as described in ref. [8]. All spectra were recorded as a function of the CsI exposure at room temperature in the following manner: the substrate is continuously exposed to CsI during the data collection procedure. The times required to collect a complete spectrum is 1 min for MIES and 4 min for UPS. Therefore the bottom spectra figs. 1b and 2b show already some features characteristic for CsI adsorption, as a decrease of the work function [as compared to clean W(110)] and the appearance of the Cs(5p) peaks in fig. 2b. A  $(1/E)$  correction is applied to

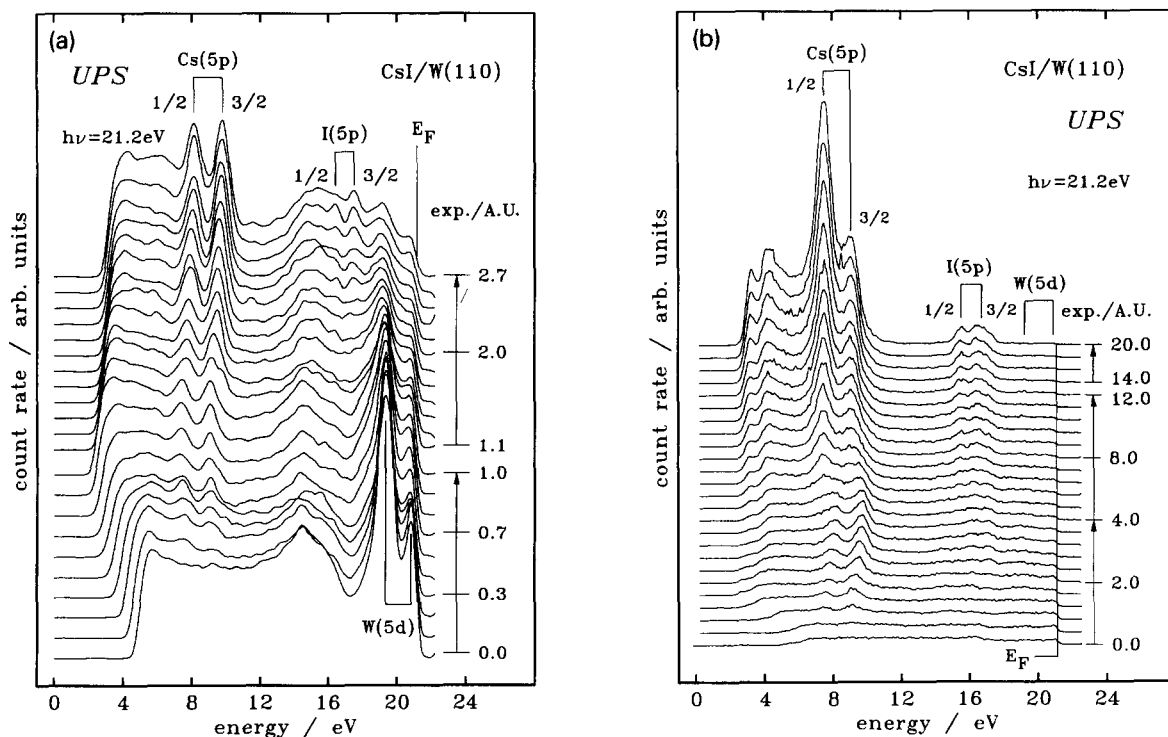


Fig. 1. UP spectra ( $h\nu = 21.2$  eV) obtained during the exposure of W(110) to CsI. The bottom curve corresponds to zero coverage. The coverage is given in arbitrary units (au), see text. (a) Exposure rate: 0.04 au per min, normal emission, (b) exposure rate: 0.2 au per min, emission under  $45^\circ$ .

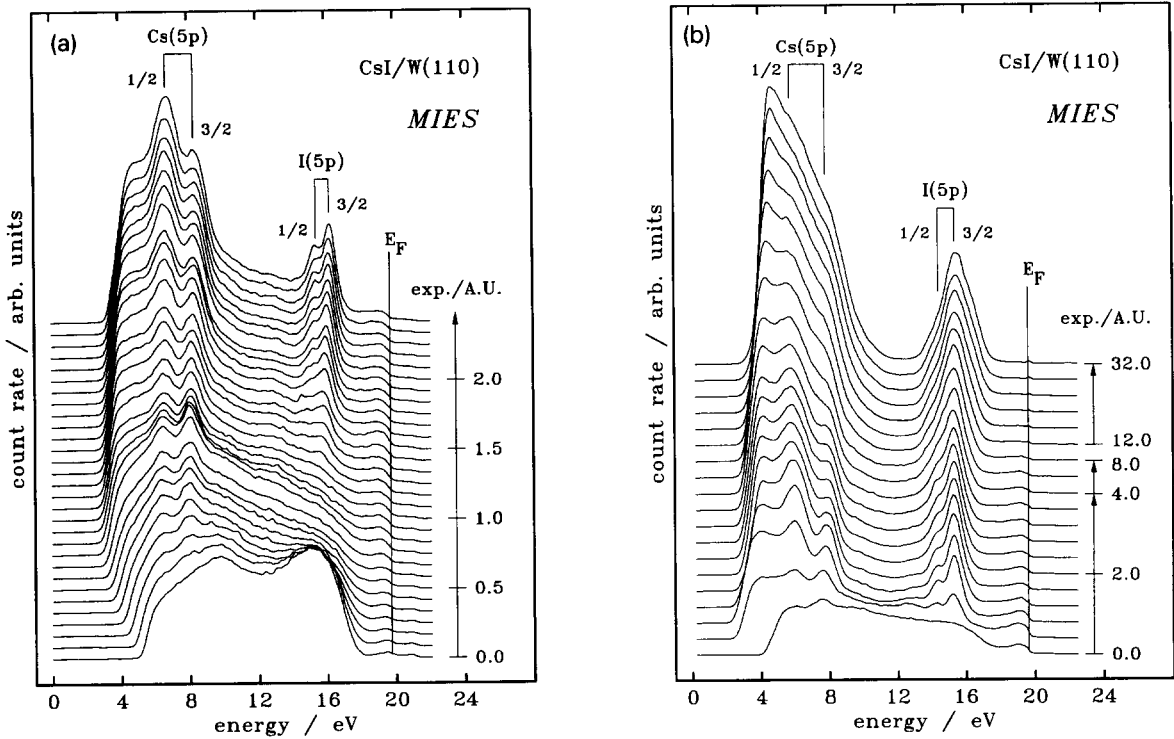


Fig. 2. MIE spectra obtained during the exposure of W(110) to CsI. (a) Exposure rate: as in fig. 1a, normal emission. (b) Exposure rate: as in fig. 1b, emission under  $45^\circ$ . Otherwise as indicated with fig. 2.

all spectra in order to take into account the energy dependence of the electron optical properties of the hemispherical analyzer including its entrance lens system.

IIE, MIE, and UP intensities are presented as a function of the kinetic energy of the emitted electrons. The crystal is biased with respect to the spectrometer in such a way that the Fermi level  $E_F$  (see line) appears at 21.2 eV in the UP spectra. The MIE spectra show also weak emission due to the UV photons ( $h\nu = 21.2$  eV) present in the helium metastable beam [8–10]. In the MIE spectra the Fermi level  $E_F$  (see line) appears close to 19.8 eV which is the excitation energy of an isolated  $\text{He}(2^3\text{S})$  metastable atom. This procedure ensures that the low energy cut-offs of the MIE and UP spectra appear at 5.2 eV when recording emission from clean W(110). The bottom spectra in figs. 1b and 2b show a work function less than 5.2 eV because the exposure to CsI starts with the data collection procedure as

mentioned above. In the IIE spectra induced by  $\text{He}^+$  ions  $E_F$  (see line) is also near 19.8 eV: the  $\text{He}^+$  ions are converted into  $\text{He}^*$  metastables by resonant capture of a surface electron before hitting the surface [24]. Likewise, the onset of the  $\text{He}^{2+}$  induced IEE spectra occurs at 5.2 eV for clean W(110).

CsI molecules are supplied to the surface by thermal evaporation (700 K) of single crystal chips. The exposure  $\Theta$  is given in arbitrary units (au):  $\Theta_0 = 1$  au corresponds to the CsI exposure at which the pronounced minimum of the surface work functions occurs. The variation of the work function with exposure was derived from the corresponding shift of the low-energy cutoff of the energy spectra obtained with either IIES, MIES or UPS.

No attempt has been made to obtain structural information from LEED: it has been shown [26] that CsI exposure of W(110) at room temperature does not produce extra spots. It has been sug-

gested [26] that efficient desorption (ESD) of the iodine component [1] of the adlayer is induced by the low-energy electron bombardment.

Measurements performed with the two different apparatus were linked to each other by work function measurements. AES results, also available with both apparatus, were used very cautiously because they may again be affected by efficient ESD [1]; AES (and work function) results for CsI/W can be found in ref. [26].

None of the ionizing probes (photons, electrons, and He projectiles in different charge and excitation states) produces any detectable change in stoichiometry for doses up to  $5 \times 10^{15} \text{ cm}^{-2}$ .

### 3. Interpretation of the electron spectroscopic results

#### 3.1. Ultraviolet photoelectron spectroscopy (UPS)

The bottom spectra of figs. 1a and 1b are typical for clean W(110) under normal emission: the pronounced structure close to the Fermi level consisting of two peaks at binding energies  $E_B = 1.5$  and  $4.0$  eV with respect to the Fermi level (at  $21.2$  eV) is due to W(5d) band emission. In fig. 1b (emission angle  $45^\circ$ ) the W(5d) band emission is much less pronounced. Upon exposure to CsI a decrease of the surface work function by about  $2$  eV occurs (see also ref. [26]) as is manifested by the shift of the low-energy cutoff of the spectra towards lower energies.

We will first discuss the CsI induced features for exposures which are smaller than the exposure  $\Theta_0$  leading to the pronounced work function minimum (see fig. 1a):

The double peak structure with  $E_B = 11.5$  and  $13$  eV, labeled Cs(5p) in fig. 1, is due to the formation of the two fine structure states  $^2P_{1/2}$  and  $^2P_{3/2}$  of cesium  $p^5, ^2P$  [9,10,17]. The  $p^5, ^2P$  states are populated essentially according to statistical expectation for small exposures. The peak intensities rise roughly linearly with exposure. The UP spectra are very similar to the corresponding ones obtained when exposing W(110) to cesium [9,10] except that, at a given adsorbate induced work function decrease, the attenuation

of the W(5d) features is somewhat stronger for the CsI adsorbate.

Only for  $\Theta > \Theta_0$ , e.g. after passing the work function minimum, the two peaks at  $E_B = 3.9$  and  $4.8$  eV, labeled I(5p), from photoionization of iodine appear: they are due to the formation of the two fine structure states  $^2P_{1/2}$  and  $^2P_{3/2}$  of iodine  $p^5, ^2P$ . This identification can be made on the basis of photoelectron spectroscopy results from gaseous CsI [13,14] and UPS data from CsI bulk material [15]. Adding the work function to the binding energies  $E_B$  we obtain the ionization energies  $6.9$  and  $7.8$  eV with respect to the vacuum level; these values have to be compared with the ionization energies of  $7.2$  and  $8.1$  eV of the free CsI molecule [13,14]. The iodine fine structure splitting agrees with that of the free iodine atom [16]. It was pointed out in refs. [13,14,19] that in order to find the fine structure splitting of the free iodine, any negative charge placed near the iodine must feel a rather weak external field as it is indeed found in the free CsI molecule where the attraction towards  $\text{Cs}^+$  is largely counterbalanced by the electron affinity of iodine [13], or when the iodine is found in an isotropic environment [19].

In the same exposure range  $\Theta \sim \Theta_0$  UPS starts to populate the cesium  $p^5, ^2P$  fine structure states nonstatistically; the  $^2P_{1/2}$  peak does even dominate at sufficiently large exposures (see fig. 1b for  $\Theta > 4\Theta_0$ ). Around  $12\Theta_0$  emission from the substrate has practically disappeared (see fig. 1b), and the spectra appear rather similar to CsI bulk spectra [15].

#### 3.2. Metastable impact electron spectroscopy (MIES)

MIE spectra from alkali halide films on glass and NaCl adlayers on W(110) were reported in refs. [20,8], respectively. Some results for CsI/W(110) can be found in ref. [7].

The bottom spectra in figs. 2a and 2b are typical for Auger neutralization (capture) of  $\text{He}^+$  ions formed by resonant ionization of the impinging He metastables in front of the surface [21,22].

For exposures  $\Theta < \Theta_0$  the double peak structure, labeled Cs(5p), appears at  $E_B = 11.6$  and

13.1 eV with respect to  $E_F$  (at 19.8 eV). As was discussed in the previous section, it is due to the formation of the  $^2P_{1/2}$  and  $^2P_{3/2}$  fine structure states of  $p^5$ ,  $^2P$  of cesium. The same features are found in the MIE spectra for Cs/W(110) (see fig. 3b and refs. [9,10]). These features behave very similar as in UPS as far as their energetic positions, spacing and relative intensity as a function of the exposure are concerned. There is no corresponding  $p^5$ ,  $^2P$  emission of iodine for  $\Theta < \Theta_0$ . Instead, a CsI induced decrease of the intensity from the Auger capture process is observed near the Fermi level  $E_F$  (see fig. 3a). This decrease is much stronger than for Cs/W(110) as the comparison of figs. 3a and 3b reveals, and must therefore be iodine induced mainly. Accordingly we interpret the intensity decrease as caused by an iodine induced decrease in the density of states near  $E_F$  similar to that found for O/W(110) [23]. A complete discussion of the results for Cs/W(110) shown in fig. 3b has been given by us

elsewhere [9,10]; we also discuss there the origin of the weak emission seen beyond  $E_F$  (which is caused by the  $\text{He}^*(2^1S)$  metastables in the beam).

With decreasing work function additional emission appears beyond the high energy end of the Auger capture spectrum located at about 18 eV. It is due to electrons emitted in the Auger deexcitation process (Penning ionization) of  $\text{He}^*$  involving electrons from the surface whose density of states is eventually modified by the adsorbate. The high-energy cutoff occurs at 19.8 eV and corresponds to electrons emitted from the Fermi level (binding energy  $E_B = 0$  eV with respect to  $E_F$ ) by  $\text{He}^*(2^3S)$  metastables (19.8 eV excitation energy).

For  $\Theta > \Theta_0$  two peaks, labeled I(5p), develop which are due to the formation of the two fine structure states  $^2P_{1/2}$  and  $^2P_{3/2}$  of iodine  $p^5$ ,  $^2P$ . This identification follows from the comparison with the UP spectra: the I(5p) features appear at about the same binding energies  $E_B = 3.6$  and 4.4

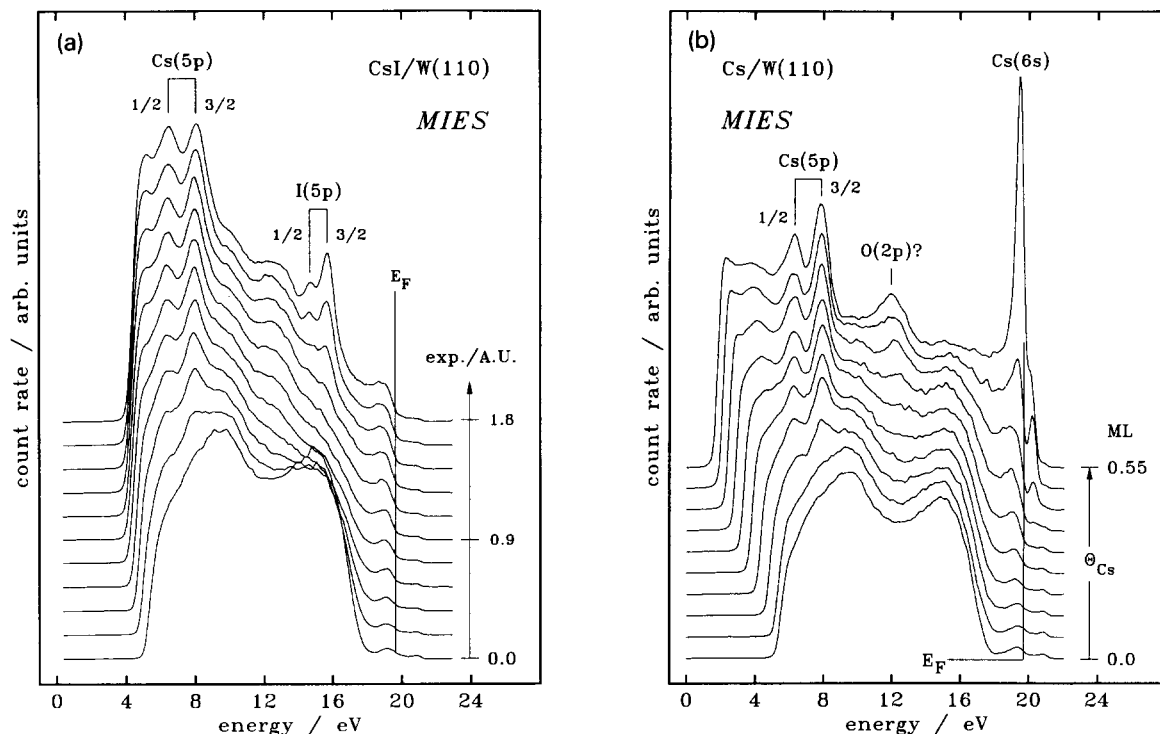


Fig. 3. MIE spectra for small exposures of W(110) (a) to CsI, and (b) to Cs. Cs coverage is given in units of the saturation coverage at room temperature. Otherwise as in fig. 1.

eV with respect to  $E_F$ . Just as in the case of the Cs(5p) features the emission is caused by Auger deexcitation of  $\text{He}^*$ , here involving the I(5p) electrons.

For sufficiently large exposures ( $\theta > 2\theta_0$ ) (see fig. 2b) both the Cs(5p) and I(5p) features lose their twin-peak structure almost entirely. This happens at exposures where EELS results [34] indicate that at least locally the band gap of the CsI bulk material has emerged, and excitonic features can be seen. The identification of the features appearing in the EELS results has been made by comparison with previous EELS data obtained in transmission on evaporated films [24]. At this exposure the MIE spectra appear already rather similar to the CsI bulk UP spectra of fig. 1b indicating that with MIES (which is sensitive to the outermost edge of the surface layer only) the electronic structure of the CsI/W(110) adlayer cannot be distinguished anymore from that of the bulk surface. In particular, any emission between I(5p) and  $E_F$  has almost completely disappeared for  $\theta > 12\theta_0$  (see fig. 2b). This indicates that at this point the substrate is not accessible to MIES, e.g. is completely covered by the adlayer.

One might like to conclude that in the initial phase ( $\theta < \theta_0$ ) CsI adsorbs dissociatively whereby the iodine partner immediately desorbs again; this could indeed explain the absence of the I(5p) features at this point. This is already in contradiction with the results of figs. 3a and 3b which indicate that not only cesium can be present. Fig. 4 presents the MIES results obtained when the W(110) surface, precovered by CsI ( $\theta < \theta_0$ ) (without showing the I(5p) features initially), is exposed to cesium. Upon cesiation the I(5p) features appear very clearly. Fig. 4 (and corresponding results down to  $\theta = 0.2\theta_0$ ) show that iodine is indeed adsorbed to the surface also in the initial phase although not detectable through the formation of iodine 5p,  $^2P$ . In addition a weak feature appears around 13 eV (see dashed line) which is not well understood at present. Longer exposure to cesium produces the strong feature labeled Cs(6s), which is due to intra- and inter-atomic Auger processes involving the Cs(6s) electrons [24,25].

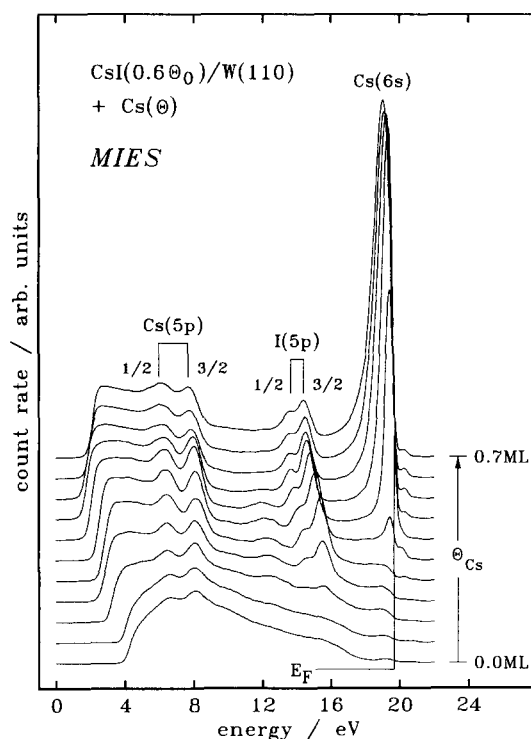


Fig. 4. MIE spectra for the exposure of W(110) (pre-exposed to CsI) to Cs. The coverage scale  $\theta_{\text{Cs}}$  would apply to exposure of clean W(110) to Cs.

As for NaCl/W(110) [7,8] we have made an attempt to study electron stimulated desorption (ESD; 300 eV electrons) with MIES. Some of the results are presented in ref. [7]. In contrary to NaCl/W(110) no metallization of the surface by alkali accumulation can be detected in the present case. It is however known [26] that  $\text{I}^+$  ions desorb, in particular for  $\theta > \theta_0$  where a linear rise of the  $\text{I}^+$  intensity with exposure is found. We conclude that iodine and cesium desorb simultaneously in the present case. Even with electron doses of  $> 5 \times 10^{15} \text{ cm}^{-2}$  (300 eV electrons) we were not able to remove the CsI adlayer completely [18].

### 3.3. Ion impact electron spectroscopy (IIES)

Figs. 5 and 6 present the electron spectra emitted during grazing incidence collisions of 50 eV  $\text{He}^+$  and 100 eV  $\text{He}^{2+}$ , respectively, with

W(110) as a function of the CsI exposure. Corresponding IIE spectra for NaCl/W(110) were reported by us in ref. [8], and their general structure was discussed there in detail.

We concentrate to the  $\text{He}^+$  results first (fig. 5): as in MIES the bottom spectrum is due to Auger capture AC [W(5d)] of the  $\text{He}^+$  ions involving the W(5d) electrons.

For small exposures ( $\theta < \theta_0$ ) the presented spectra are almost identical with the corresponding ones from Cs/W(110) [25] when the comparison is made at the same values of the adsorbate induced work function change [with respect to clean W(110)]. The structure of the spectra for Cs/W(110) was already discussed in detail [25], and could be compared with numerical simulations of the spectra made with the model of refs. [27,28]:

As soon as the Auger deexcitation (AD) pro-

cess dominates, the Cs(5p) electrons are involved mainly. This produces the structure labeled AD [Cs(5p)]. The binding energies of the  $\text{Cs}^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2}$  fine structure states, as detected by IIES, are  $E_B = 11.5$  and  $13.0$  eV with respect to  $E_F$  ( $= 19.8$  eV). Auger capture involving one Cs(5p) and one W substrate electron may also contribute to emission in this spectral region. Very little emission is seen at energies close to  $E_F$ . In particular, as with UPS and MIES no formation of iodine  $p^5$ ,  $^2\text{P}$  is seen for  $\theta < \theta_0$ . The very weak emission beyond the high-energy onset for Auger deexcitation (structure (1) at  $19.8$  eV) is a contribution from the intra-atomic Auger process autodetachment of  $\text{He}^{-*}$  formed by the resonant capture of two electrons from the surface when the surface work function becomes low enough [24,25]. At this stage also the structure of IIE and MIE spectra is rather similar; the MIE results show however a larger contribution from the substrate which is largely hidden to the  $\text{He}^+$  ions impinging under grazing incidence onto the surface.

The comparison of the IIE spectra for CsI/W and Cs/W allows an estimate for the upper limit of the coverage of W(110) by CsI at  $\theta_0$ : we assume that an adsorbed CsI molecule is at least as efficient as Cs in shielding the W substrate. From the adsorbate induced decrease of the Auger capture intensity (involving the W(5d) electrons) we estimate 0.3 as upper limit for the coverage at  $\theta_0$ .

Summarizing, we conclude that only the Cs species is accessible to electronic processes with the  $\text{He}^+$  projectile for exposures  $\theta < \theta_0$ .

For exposures  $\theta > \theta_0$  in addition the formation of the fine structure states of iodine  $p^5$ ,  $^2\text{P}$  ( $E_B = 4.1$  and  $5.0$  eV) is detected via the Auger deexcitation process (structure AD [I(5p)]). At this exposure  $\theta_0$  the IIE and MIE spectra start to become qualitatively different: with IIES the resonant capture of surface electrons becomes increasingly more difficult because the band gap of the CsI bulk emerges. Therefore the IIE spectra start to become governed by Auger capture again (as for clean W(110), but now involving mainly the I(5p) electrons). On the other hand, the MIE spectra remain dominated by the contri-

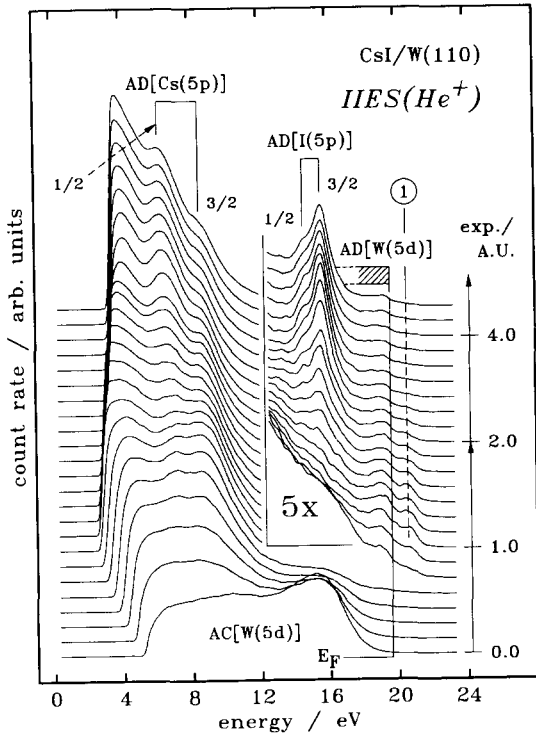


Fig. 5. IIE spectra induced by 50 eV  $\text{He}^+$  ions during the exposure of W(110) to CsI. Ion incidence is under  $5^\circ$  with respect to the surface. Otherwise as in fig. 1.

bution from Auger deexcitation involving iodine and cesium 5p electrons mainly.

The increasing deviations between the IIE and MIE spectra clearly reflect the gradual transition of the surface to an insulating layer starting at exposures around  $\Theta_0$ . We are able to simulate the general structure of the IIE spectra at this stage using the model of refs. [27,28] with rather simple models for the valence band structure of the surface density of states of the CsI adlayer [35].

A detailed discussion of the general structure of IIE spectra from the grazing incidence of slow  $\text{He}^{2+}$  ions on NaCl/W(110) has been presented [8].

For  $\Theta < \Theta_0$  (see fig. 6a) the spectra for slow collisions of  $\text{He}^{2+}$  with CsI/W(110) are as for  $\text{He}^+$  collisions, very similar to the corresponding ones from Cs/W(110) [25] provided the comparison is made at the same value of the adsorbate

induced work function change. A detailed analysis of the spectra from Cs/W(110) was already given [25] together with simulations of the spectra along the lines in refs. [27,28]. The most prominent features can be explained solely on the basis of the cesium induced work function change. In particular, the structure at the high energy end of the spectra is due to autoionization of  $\text{He}^{**}(2121')$  and that at about 7.5 eV is due to Auger deexcitation of  $\text{He}^{+*}(n=3)$  to  $\text{He}^{+*}(n=2)$  [25].

For  $\Theta > \Theta_0$  (see fig. 6b), as for NaCl/W(110) [8], we find a strong dominance of very slow electrons. This was proposed to be a consequence of the electrostatic interaction of the projectile, as long as it is still charged, in particular in the states  $\text{He}^{+*}(n=2)$  and  $\text{He}^+(n=1)$ , with vacancies in the surface layer which were created in previous electronic transitions suffered by the He projectile [8].

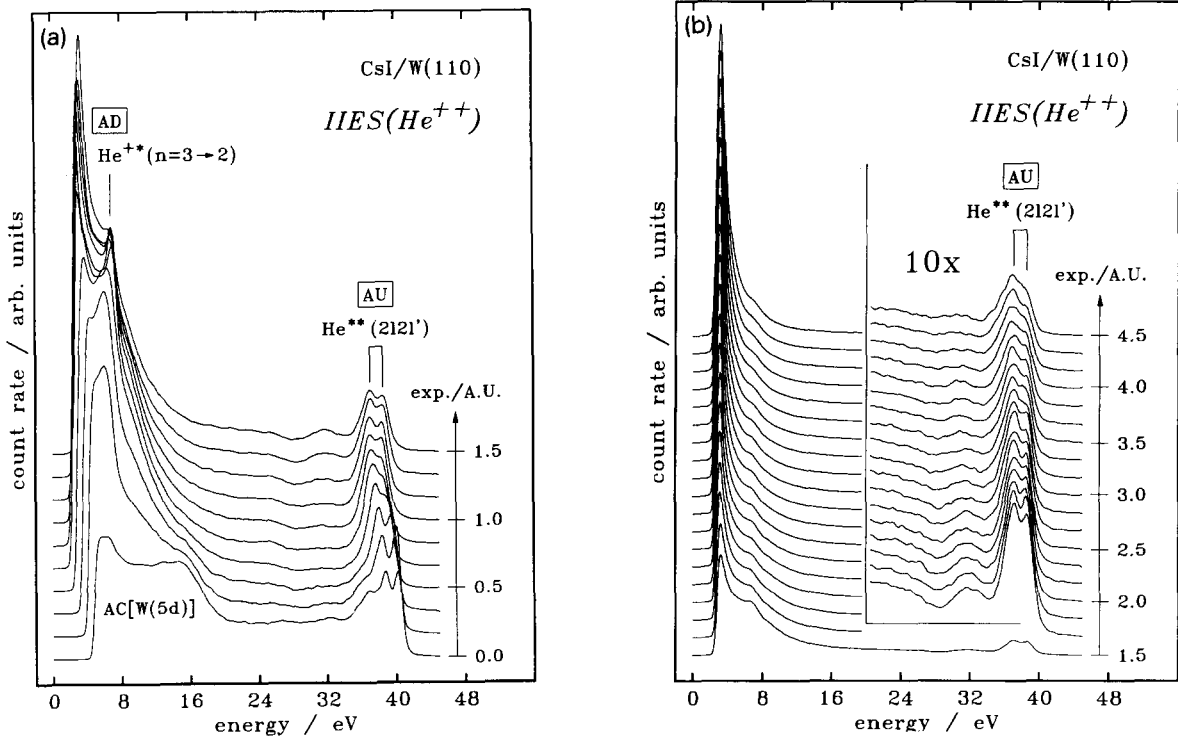


Fig. 6. IIE spectra induced by 100 eV  $\text{He}^{2+}$  collisions during the exposure of W(110) to CsI as in fig. 5. (a) Exposure up to 1.5 au. (b) Exposure above 1.5 au.



Summarizing, two observations are of particular importance for the discussion of the next section: for  $\Theta < \Theta_0$  the surface layer appears like a cesium adlayer to the  $\text{He}^{2+}$  projectile impinging under grazing incidence onto the surface; formation of iodine  $p^5, ^2P$  is not detectable. For  $\Theta > \Theta_0$  the toplayer of the surface starts to develop properties of an insulator.

#### 4. The growth of the CsI adlayer

As a guide in understanding the layer growth we rely on the model developed for NaCl on Ge [5,6] and W(110) [8]. The following conclusions are consistent with the results of the previous sections.

For exposures  $\Theta < \Theta_0$ , i.e. for a coverage  $< 0.3$  (see section 3.3), we propose the adsorption of single undissociated CsI molecules with the iodine end pointing towards the substrate. The large work function change upon exposure excludes dissociation and the adsorption of both Cs and I in contact with the substrate. The results of fig. 4 exclude the formation of a substrate halide on top of which Cs atoms are adsorbed [33]: in this case we would not expect the formation of iodine  $p^5, ^2P$  as a consequence of the supply of additional Cs atoms. Because the iodine species points towards the substrate, MIES and IIES both show only features due to Cs ionization, apart from features originating from the substrate whose surface density of states may eventually be modified by the iodine adsorption (see the MIES results of fig. 3a).

The absence of structures due to the formation of iodine  $p^5, ^2P$  in the UP spectra is most likely a final state effect: the  $I(5p)$  vacancy created in the photoionization process will couple strongly to the substrate as long as the iodine species is in direct contact with the substrate. This leads to a strong separation of the  $5p$  orbital, analogous to a Stark field splitting, into  $\sigma$  and  $\pi$  components according to their projection with respect to the surface normal [13,14]. The  $(\sigma - \pi)$  splitting probably amounts to about 2 eV as in the case of the iodine adsorption on many metals [29–31].

The final state interaction of the iodine  $p^5, ^2P$  in contact with the substrate can therefore lead to a spectral contribution from  $I^-$  ionization which will spread out over several eV's, thus not leading to a distinct structure in the UP spectra.

For  $\Theta \sim \Theta_0$ , i.e. for a coverage  $> 0.3$ , additional CsI molecules become adsorbed near the existing nuclei for condensation – possibly also in contact with the substrate –, but now also with the Cs end of the molecule pointing towards the substrate. This leads to the observed work function increase upon further exposure because the initial surface dipole is partly compensated by those additionally adsorbed molecules which point into the opposite direction. Obviously the iodine species is now accessible to MIES and IIES. Because the iodine species detected by these techniques is not in direct contact with the substrate, we expect to see essentially the photoelectron spectra of the free CsI molecule which are dominated by the fine structure splitting of the iodine  $p^5, ^2P$  final states of neutral iodine [13,14]. Also UPS detects now the formation of the iodine  $p^5, ^2P$  fine structure states, although comparatively weakly.

MIES shows substrate emission until  $\Theta > 12\Theta_0$ ; consequently the surface is not yet fully covered by CsI up to this coverage. On the other hand, typical bulk features are seen long before this exposure, as band gap formation with EELS, IIES, and MIES, exciton formation with EELS, and bulk like IIE and MIE spectra.

Following the discussion in refs. [5,6,8] we propose that in this exposure range the adsorbed CsI forms islands wherein neighbouring molecules have opposite orientation. Island formation is rather likely because of the strong lateral interaction between the neighbouring molecules in adlayers of ionic compounds [32]. The coverage dependence of the intensity of the Cs(5p) features is difficult to determine exactly because the features, labeled Cs(5p), wash out for  $\Theta \sim \Theta_0$ . Nevertheless, the intensity dependence upon exposure seems to be linear up to  $3\Theta_0$  from where on it saturates quickly. The linear rise is compatible with two-dimensional growth of the CsI islands up to  $\Theta = 3\Theta_0$ .

We may speculate that the “washing-out” of

the  $p^5$ ,  $^2P$  fine structure states and the nonstatistical population of the Cs fine structure states observed for  $\Theta > 2\Theta_0$  is related to a rearrangement of the species in the upper half of the double layer in order to produce the bulk structure. Except for  $\Theta < \Theta_0$  the toplayer always contains both I and Cs. This suggests the formation of a film with the [110] direction perpendicular to the substrate.

### 5. Remarks on desorption induced by electronic transitions (DIET)

We have discussed the various electronic transition processes which occur in NaCl adlayers on metals [8]; these considerations do equally well apply to CsI adlayers: in the present case all applied types of ionizing radiation produce vacancies both in the Cs and I(5p) orbitals. For the He projectiles in different charge and excitation states these vacancies are produced exclusively at species of the toplayer. In the studied exposure range none of the ionizing probes – not even electrons as for NaCl/W(110) – produces any detectable stoichiometric changes in the adlayer, in particular no preferential desorption of the iodine species, for doses up to  $5 \times 10^{15} \text{ cm}^{-2}$ . By contrast, for NaCl/W(110) electron stimulated desorption (ESD) leads to preferential desorption of Cl manifesting itself in the metallization of the surface as detected by MIES [8]. On the other hand, it was shown that also for CsI/W(110) efficient ESD of iodine occurs for  $\Theta > \Theta_0$  [26].

The following observations (see section 3.2) suggest that the condensation of the CsI molecules in two-dimensional islands is a necessary requirement for the occurrence of efficient ESD: (i) efficient ESD occurs only after the onset of condensation ( $\Theta > \Theta_0$ ) [26]. A weak ESD signal could be detected for  $\Theta < \Theta_0$  [26] suggesting the small probability for ESD from isolated CsI molecules, and it is not possible to desorb the CsI adlayer completely solely by ESD even after extended bombardment [18]: the MIE spectrum still displays the presence of CsI molecules at the

surface with essentially the photoelectron spectrum of the free molecule.

### 6. Summary

The electron emission from W(110) exposed to CsI at room temperature was studied with ion impact electron spectroscopy (IIES), metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), work function measurements, and to some extent by electron energy loss spectroscopy (EELS) as a function of the CsI exposure. Information is obtained on the growth mode of the adlayer, and on the production of vacancies in the 5p orbitals of both I and Cs under the influence of the ionizing radiation. The following interpretation is consistent with the experimental results.

Initially, CsI molecules adsorb with the iodine end pointing towards the substrate. Around a CsI coverage of about 0.3 the formation of two-dimensional islands of CsI molecules with opposite orientation of neighbouring molecules starts. At this coverage a pronounced minimum in the surface work function occurs.

All types of ionizing radiation lead to the formation of vacancies in the 5p orbitals of both I and Cs. The vacancy formation does however not lead to preferential desorption of the iodine species.

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