# Electron solvation by polar molecules: The interaction of Na atoms with solid methanol films studied with MIES and density functional theory calculations

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The interaction of Na atoms with $CH_3OH$ films was studied with metastable impact electron spectroscopy (MIES) under UHV conditions. The films were grown at $90(+/-10)$ K on tungsten substrates and exposed to Na. Na-induced formation of methoxy ($CH_3O$) species takes place, and Na atoms become ionized. At small Na exposures the outermost solvent layer remains largely intact as concluded from the absence of MIES signals caused by the reaction products. However, emission from $CH_3O$, located at the film surface, occurs at larger exposures. In the same exposure range also Na species can be detected at the surface. The spectral feature from $3s$ Na ionization occurs at an energetic position different from that found for metals or semiconductors. The results are compared with density functional theory calculations [see Y. Ferro, A. Allouche, and V. Kempter, J. Chem. Phys. **120**, 8683 (2004), preceding paper]. Experiment and theory agree in the energetic positions of the main spectral features from the methanol and sodium ionization. The calculations suggest that the $3s$ Na emission observed experimentally originates from solvated $3s$ electrons which are located far from the Na core and become stabilized by solvent molecules. The simultaneous emergence of emission from $CH_3O$ and from solvated $3s$ electrons suggests that the delocalization and, consequently, the solvation play an important role in the Na-induced formation of $CH_3O$ from $CH_3OH$. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1690237]

## I. INTRODUCTION

Although the exothermic reaction of Na atoms with liquid methanol, yielding Na ions and methoxy, $CH_3O$, species, is well known, the underlying mechanism for this simple-looking process is not well understood. One particular reason is that it is not easy to obtain direct detailed information on the $3s$ Na electron which plays an active role in this process. Methoxy species have found considerable interest because of their role in the methanol conversion into dimethyl ether (DME) or formaldehyde which represent important routes to nonpollutant fuel production.[1–3] It is generally accepted that the first step in the conversion of methanol to gasoline (MTG) is the dehydration of $CH_3OH$ to DME. Although the MTG process has been studied extensively, few studies exist on low-temperature routes to $CH_3OH$ dehydration.

Methoxy species can be created as a stable intermediate in heterogeneous reactions of methanol on surfaces; they have been characterized by a variety of surface-analytical techniques including photoemission.[4–9] As an example, the $CH_3O$ species can be formed on copper surfaces by deprotonation of methanol with preadsorbed atomic oxygen.[5,6] Furthermore, when adsorbed onto Cu(111), partially covered

by Na, or onto closely packed Na films, $CH_3OH$ reacts to $CH_3O$; the species is stable up to 450 K (Ref. 8).

Previously, we have studied the interaction of Na with films of amorphous solid water by combining the metastable impact electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS).[10–15] As compared to UPS, MIES possesses a rather large sensitivity for the detection of the $3s$ Na electron; consequently, it allows, in combination with UPS, to distinguish between species located atop and underneath the surface under study. In these studies we have concentrated on the role played by the $3s$ Na electron for the water dissociation process. First-principles density functional theory (DFT) cluster calculations suggest that the $3s$ Na electron becomes solvated[16]—i.e., is delocalized from its $Na^+$ core and trapped between the $Na^+$ and surrounding water molecules. Indeed, by combining MIES with first-principle calculations we arrive at the conclusion that the peculiar structure seen in the spectra near the Fermi level is characteristic for solvated $3s$ Na electrons.[14,15] Furthermore, the calculations indicate that the solvated electron plays a key role in the water dissociation reaction.

In the present paper we apply MIES to the study of the interaction of Na with films of solid methanol held at $T = 90$ and 120 K. By confronting the experimental results with those from DFT cluster calculations (preceding paper[17]), we conclude that the $3s$ Na becomes solvated and initiates $CH_3O$ formation. The calculations shed light on the

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underlying mechanism for this process. Two reaction channels were considered: the Na-induced dehydrogenation of methanol and the dehydration of methanol by (C–O) bond breaking. Moreover, the calculations seem to explain the Na-induced dissociation of the $CH_3O–H$ bond reported in Ref. 8.

## II. EXPERIMENTAL REMARKS

The experiments, described in detail elsewhere,[18,19] were carried out under ultrahigh-vacuum (UHV) conditions (base pressure $< 2 \times 10^{-10}$ Torr). Auger electron spectroscopy (AES) and x-ray photoemission spectroscopy (XPS) are used to characterize the chemical composition of the tungsten substrate employed for the deposition of the molecular films. With low-energy electron diffraction (LEED) it was checked that the molecular films are amorphous. The electronic structure of the molecular films was studied by applying MIES and UPS (HeI and II). In MIES metastable helium atoms $(2\,^3S/2\,^1S)$ eject electrons from the edge of the surface under study. The application of MIES to surface spectroscopy is well documented.[20,21] If the Na adsorbate is not fully ionized, a spectral feature is expected from the presence of $3s$ charge density at the Na core. With UPS (HeI) the partially occupied $3s$ orbital is practically not seen due to its low photoionization cross section.[22] However, in MIES it causes a prominent feature $Na(3s)$ close to $E_F$ which is clearly seen on metals and semiconductors for coverages larger than about 0.5 ML (monolayer).[20,21] This underlines the power of MIES for investigating the chemistry between Na and molecular films, which can be expected to be driven by the $3s$ valence electron. For the study of the Na-induced changes in the electronic structure of the molecular films we have confined ourselves to MIES because the UPS (HeI and II) spectra give no information on the $3s$ Na electron.

The primary results of the experiments are energy spectra of the emitted electrons versus their kinetic energy. By choosing a suitable bias voltage between the target and electron energy analyzer, the energy scales in the figures are adjusted in such a way that electrons emitted from the Fermi level (denoted by $E_F$)—i.e., electrons with the maximal kinetic energy—appear at 19.8 eV (which is the potential energy of the metastable He atoms employed for MIES). With this particular choice of bias voltage, the low-energy cutoff in the spectra gives directly the surface work function (WF), irrespective of the actual interaction process which produces the electrons. For a convenient comparison with theory we present our data as a function of the binding energy of the emitted electrons prior to their ejection. Electrons emitted from the Fermi level appear then at binding energy $E_B = 0$ eV.

Na atoms were dosed employing carefully outgassed commercial dispenser sources (SAES Getters). They operate at a rate of 0.05 ML/min, typically. The procedure for the calibration of the alkali coverage is described elsewhere.[23] The exposure is given in units of monolayer equivalents (MLE); at 1 MLE the surface would be covered by one Na monolayer if penetration of the Na into the molecular films could be neglected.

The surface temperature can be varied between about 90 and 700 K; at present, the accuracy of the temperature calibration is 10 K. The surface was exposed to $CH_3OH$ by backfilling the chamber at a substrate temperature of 90 K. The amount of surface-adsorbed methanol can be estimated on the basis of earlier work with MIES on $CH_3OH$ multilayers.[10,19] Prior to Na exposure, the surface prepared as described above was brought to the desired temperature.

## III. THEORETICAL CONSIDERATIONS

The method of computation was fully exposed in Ref. 16 (see also Ref. 17). A DFT calculation was carried out at the B3LYP/6-31+g(d,p) level of approximation. This was performed on several cluster models in order to investigate the potential energy surfaces associated with neutral sodium ionization by solvation. The solvation of the sodium atom by methanol has been studied by an analogous strategy.[17] It is demonstrated that Na is solvated by six methanol molecules and that its $3s$ electron is trapped and solvated between the sodium core and two solvent molecules. This process induces a large mixing of the nonbonding oxygen and OH energy levels. Two reactive pathways were proposed in the preceding paper: dehydrogenation by (O–H) bond breaking and dehydration by (C–O) bond breaking:

(i) The dehydrogenation reaction involves one single methanol molecule, its OH bond breaking, and the capture of the solvated $3s$ Na electron by the ejected proton. The associated activation energy is 56.1 kJ mol$^{-1}$, uncorrected for the zero-point energy.

(ii) The dehydration reaction is associated with the (C–O) methanol bond breaking. The final products are $CH_3O$, the methyl radical $CH_3$, and a water molecule. The (C–O) breaking is therefore equivalent to the dehydration process. The corresponding calculated barrier of activation is 62.6 kJ mol$^{-1}$.

At the present level of approximation, these two reactions are equally probable, not taking into consideration the dynamical and entropic aspects, outside the possibilities of this study. It must be underlined that $CH_3O$ is among the final products of both proposed reactions, but the second one could be the precursor reaction for DME formation because $CH_3$ radical formation occurs.

It was established previously that the interaction of He* with clean and Na-covered $CH_3OH$ films is via the Auger deexcitation process.[11] This implies that the MIES spectra image the surface density of states (SDOS) directly.[20,21] The SDOS, needed for the comparison with the MIES spectra, have been obtained by dressing the DFT molecular energy level distributions, obtained in Ref. 17, with Lorentzian functions of arbitrary height and an half width of 0.25 eV.

## IV. RESULTS AND DISCUSSION

Figure 1 presents MIES results for the interaction of Na with a $CH_3OH$ film held at 120 K. The top spectrum is for the methanol film (four layers thick) prior to Na exposure. The upper set of spectra is obtained during the Na exposure of the film. According to Refs. 11, 24, and 25, $M_1–M_5$ have $n_{O\perp}$, $n_{O\parallel}$, $\sigma_{CO}$, $\pi_{CO}$, and $\sigma_{OH}$ character, respectively. Dur-
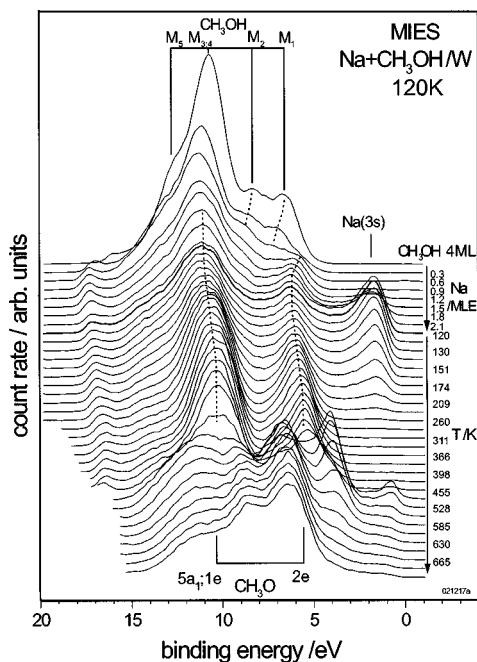
FIG. 1. MIES spectra for the adsorption of Na on solid methanol (three layers) prepared on tungsten (120 K) (upper set of spectra) and the spectral changes resulting from annealing over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

ing Na exposure $M_1$–$M_5$ shift to larger $E_B$'s; simultaneously, a decrease of the WF by 1.3 eV is noticed. The methanol features $M_1$–$M_5$ become weaker during the Na exposure and disappear around 0.5 MLE. Instead, a two-peaked structure, labeled $2e$ and $5a_1;1e$, appears. The identification of the species responsible for this structure can be made on the basis of previous photoemission studies and first-principles calculations carried out on surface-adsorbed $CH_3O$.[4,5,8] According to Ref. 8, $CH_3O$ is formed when coadsorbing Na and $CH_3OH$ on Cu(111). The photoelectron spectra attributed to Na-stabilized $CH_3O$ consist of two peaks at (4.6–5.7) and (9.3–10.5) eV binding energy, their exact peak energy depending on the Na precoverage. Based on Hartree–Fock calculations for the molecular orbitals (MOs) of small clusters simulating the Na-bound $CH_3O$, they can be attributed to the ionization of the $2e$ and $5a_1;1e$ $CH_3O$ MOs, respectively. The contributions from $5a_1$ and $1e$ cannot be resolved. In Ref. 6, $CH_3O$ species were prepared by first exposing a Cu(111) surface to oxygen and subsequently to methanol. The resulting photoemission spectra show three adsorbate-induced features at $E_B = 5.3$, 9.5, and 15.5 eV. The feature at 15.5 eV is seen for special geometries only. First-principles calculations indicate that the adsorbate induced features at $E_B = 5.3$ and 9.5 eV are due to the ionization of the $2e$, $5a_1;1e$ MOs of $CH_3O$ species.[6] Again, the contributions from $5a_1$ and $1e$ cannot be resolved. We note that the formation of a Na–$CH_3O$ complex[8] appears to enlarge the distance between $2e$ and $5a_1/1e$ by about 0.5 eV (energy separation 4.7 eV) as compared to the interaction with bare copper.[6] The identification of the spectral features made in Refs. 6 and 9 is supported by a comparison with the UPS (HeI) spectra for $CH_3F$ (which is isoelectronic with the $CH_3O^-$ anion). Indeed, the photoemission spectra for $CH_3F$

and $CH_3O$ are very similar, both as far as the position and shape of the spectral features are concerned. In the present work the two Na-induced features from the reaction with $CH_3OH$ appear at $E_B = (5.5–6.1)$ and (10.3–10.8) eV (energy separation 4.7 eV). Summarizing, there is ample evidence that Na–$CH_3O$ complexes are the primary result of the interaction of Na with solid methanol at 120 K.

The lower set of spectra (heating from 120 to 665 K) shows that, as a consequence of the heating, the $CH_3O$ structure becomes more pronounced up to 260 K while Na($3s$) decreases monotonously and disappears around 260 K. This implies that above this temperature no neutral Na species are present at the surface. Around 450 K the $CH_3O$ structure disappears. The close agreement of the temperature for the disappearance of the species attributed to $CH_3O$ in Ref. 8 and the present work is further support for our identification of the Na–$CH_3OH$ reaction product as $CH_3O$ species. For $CH_3O$ on Cu, formaldehyde is formed during $CH_3O$ dissociation.[6] However, in the present case the new structure emerging at 450 K, consisting of the three peaks at $E_B = 3.8$, 6.5, and 8.5 eV, cannot be attributed convincingly to formaldehyde species because the distance between the first two peaks is about 1 eV smaller than expected (3.7 eV). Moreover, the three peaks display a different temperature dependence. Neither can the observed structure be attributed convincingly to carbon monoxide formation, observed during the thermal composition of $CH_3O$ on Ni(100) (Ref. 7). The spectrum reminds to the UPS (HeI) spectrum for Na–W–bronze, $Na_xWO_3$ with $x > 0.4$, consisting of peaks at $E_F$, 4, 6.5, and (weakly) 9 eV (Ref. 26). This would imply that the observed $CH_3O$ dissociation yields atomic oxygen that becomes stabilized at the tungsten surface by the available Na species. The geometric configuration could indeed resemble to that of the $Na_xWO_3$ surface.

The results obtained for Na deposition on a $CH_3OH$ film held at 90 K (Fig. 2) differ in some respects: Na($3s$) appears considerably more narrow and, upon heating, disappears already at 110 K, instead at 260 K, for deposition at 120 K. The surface cannot be converted completely into a $CH_3O$ film, because methanol species remain visible throughout the Na exposure. As for the interaction of Na with water ice,[13,14] Na($3s$) occurs at about $E_B = 2.3$ eV, at about 1 eV larger binding energy than on metals, and the reaction product in both cases results from dehydrogenation of the film molecules.

In order to mimic the interaction of Na with liquid $CH_3OH$ we have coadsorbed Na and $CH_3OH$ on tungsten at room temperature (Fig. 3). An equivalent of 1.5 MLE Na and 6 MLE $CH_3OH$ were offered. As the inspection of Fig. 1 shows, the resulting spectrum (top spectrum in Fig. 3) is very similar to the spectra in Fig. 1 when all surplus $CH_3OH$ species have desorbed (above 260 K). Also the change with temperature seen in Fig. 3 is practically identical with that in Fig. 1. This suggests that during codeposition at room temperature Na and $CH_3O$ indeed react under the formation of (Na–$CH_3OH$) complexes.

A detailed discussion of the DFT results for the interaction of Na with $CH_3OH$ clusters can be found in the preceding paper.[17] Here only a short summary will be present-
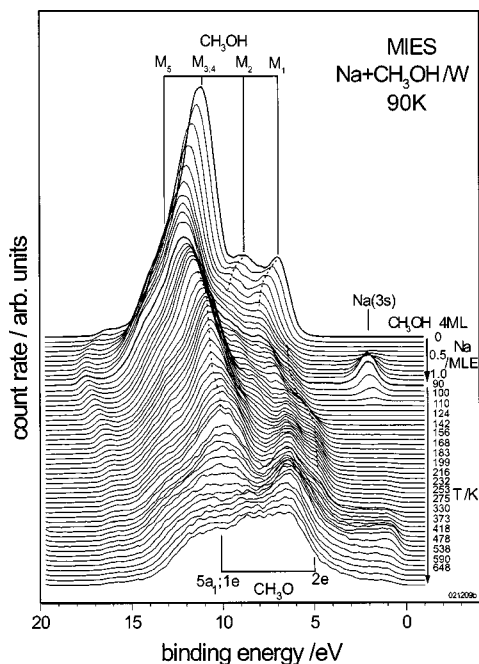
FIG. 2. MIES spectra for the Na-exposed film of solid $CH_3OH$ (four layers prepared on tungsten (90 K) (upper set of spectra) and the spectral changes resulting from annealing over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

ed: the $3s$ Na becomes solvated, both in the $Na(CH_3OH)_6$ and the $Na_2(CH_3OH)_{10}$ clusters modeling Na solvation. As compared to a free Na atom, the ionization energy of $3s$ Na when solvated in $CH_3OH$ is reduced by 1.62 and 1.0 eV, respectively. As Figs. 5(a) and 5(b) of Ref. 17 show, the corresponding MO is delocalized far from the $Na^+$ core and
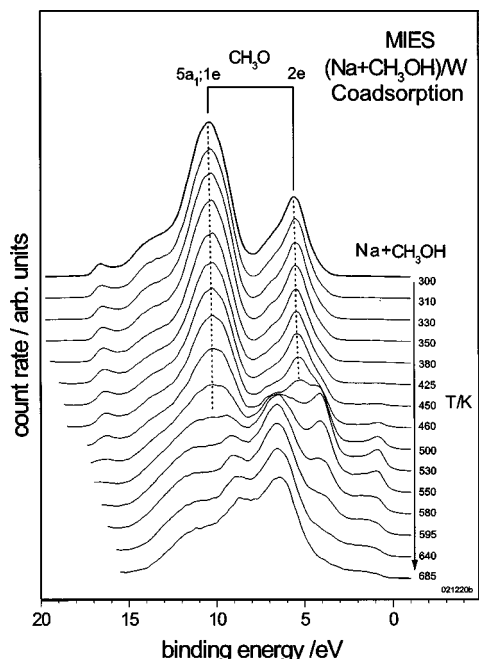


FIG. 3. Codeposition of Na and $CH_3OH$ on tungsten held at room temperature (top spectrum) and the spectral changes during annealing over the indicated temperature range (see text for the acronyms employed in the figure).

is stabilized by $CH_3OH$ molecules; a significant charge fraction is located on the OH bonds pointing towards the solvated electron.

In the dehydrogenation reaction, studied for the $Na(CH_3OH)_6$ cluster, the reaction coordinate is the (O–H) bond distance in the OH group pointing toward the solvated electron [Fig. 5(a) of Ref. 17]. When this distance increases, the proton departs from its original location at the $CH_3OH$ molecule, taking with itself the complete electron spin density. The process under discussion involves only one particular methanol molecule. However, the $CH_3OH$ molecules of the cluster are involved through the H-bonded network. In particular, the amount of energy lost during OH bond breaking is overcompensated by a rearrangement of the H bonds within the solvent medium. The Na atom acts as provider for the electron required for the electron transfer and, in addition, contributes to the electrostatic field responsible for electron solvation and the organization of the H-bonded network. The barrier associated with the reaction is 56 kJ mol$^{-1}$.

In the dehydration reaction, having an activation energy of 63 kJ mol$^{-1}$, all spin density prior to the reaction is on the Na atom.[17] After passing the reaction barrier, the spin density is at the C atom only. This implies that the (C–O) bond breaking takes place as $(CH_3^+-OH^-)$ dissociation. The $CH_3^+$ ion captures the solvated electron, forming $CH_3\cdot$. On the other hand, the $OH^-$ ion captures a proton from a neighboring $CH_3OH$ molecule, thereby producing a $H_2O$ molecule and a $CH_3O^-$ ion. Obviously, the Na atom acts as donator, while the H-bonded network is responsible for the transfer of energy and charge. As shown in Refs. 16 and 17, $H_2O$ molecules, being part of the molecular network, undergo Na-induced hydrolysis when close to a solvated Na species. Therefore, it appears possible that in the final step of the reaction the $H_2O$ molecule from the dehydration of $CH_3OH$ can give $OH^-$ and H.

Figure 4 compares appropriate MIES spectra with the DOS of (a) the Na–$CH_3OH$ cluster prior to the reaction and (b) with that after the dehydrogenation and dehydration reactions have taken place. For the comparison shown in Fig. 4(a) we have assumed that the MIES spectra for about 0.75 MLE Na exposure at 90 K film temperature, to a first approximation, represent the system prior to the reaction between Na and methanol. This is suggested by the comparatively weak signal from $2e$, attributed to $CH_3O$ formation. Thus we can compare these results with the density of states in the Na–methanol cluster prior to the reaction. If necessary, the DFT-DOS was shifted slightly (0.2 eV) in order to align its main peak to the structure $M_{3;4}$. The good agreement with experiment suggests that signal $Na(3s)$ is due to solvated electrons and not simply caused by surface-adsorbed Na atoms.

The comparison with the predictions of theory for the reacted system is shown in Fig. 4(b). It compares the DOS of the reacted $Na-(CH_3OH)_6$ cluster with the spectrum obtained for 0.6 MLE Na exposure from Fig. 1. We choose this spectrum for comparison because the absence of the feature $Na(3s)$ indicates that all Na species take part in the $CH_3O$ formation, manifesting themselves in the shoulder $2e$. For larger exposures the entire surface layer is converted into
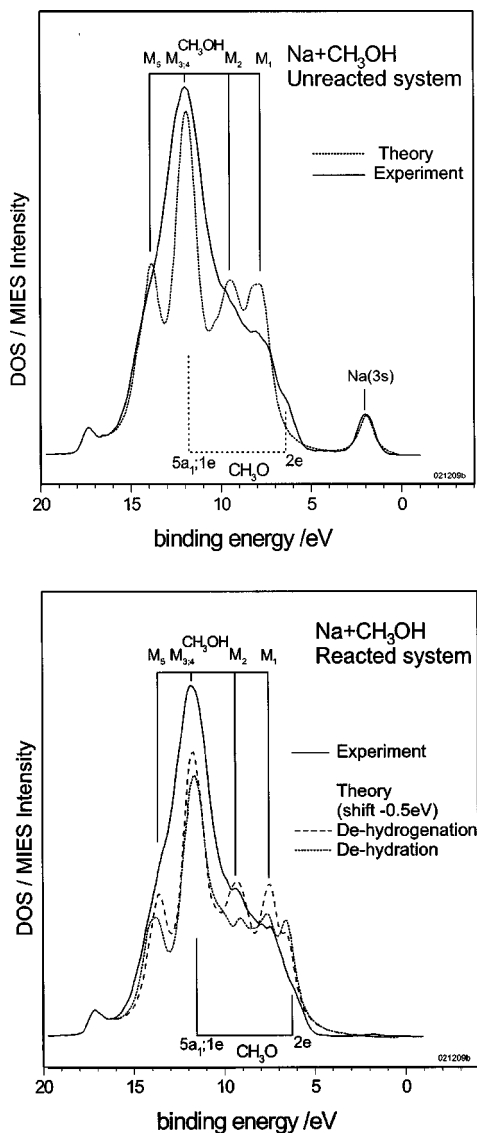
FIG. 4. DOS of the Na–methanol cluster defined in the text and comparison with the MIES results: DFT-DOS for Na–$CH_3OH$ (unreacted system) and MIES results at 90 K before heating (Fig. 2: see text) (a), DFT-DOS for Na–$CH_3OH$ (reacted system) for the dehydrogenation and dehydration channels (b).

$CH_3O$; this situation cannot be modeled by the present calculations which take into account only well-separated Na atoms or $Na_2$ dimers. Included in Fig. 4(b) are the DOS of the reacted systems, after dehydrogenation and dehydration have taken place. The predictions of theory for the reacted system can also be tested by comparison with the results of Fig. 2, lower set of curves, at temperatures above 110 K where Na($3s$) has disappeared completely; hereby, we suppose that all solvated electrons contribute to $CH_3O$ formation. The result of this comparison is very similar to Fig. 4(b) and, therefore, is not displayed here.

For the dehydrogenation reaction the DOS is composed from contributions of $CH_3O$ and the surrounding shell of methanol molecules. In particular, $CH_3O$ accounts for the additional peak in the DOS seen around 6.5 eV and contributes to the large peak at 11.4 eV. For the dehydration channel, in addition, the products $CH_3$ and $H_2O$ give contribu-

tions to the DOS; they overlap with those from the $CH_3OH$ network. For both reaction channels good qualitative agreement is obtained with the MIES spectra, in particular as far as the location of the feature $2e$ is concerned. However, the comparison of MIES and DOS alone does not allow us to distinguish in a unique way between the two reaction channels. We can state that, at present, there is no indication for the presence of $H_2O$ (or $OH^-$ after its reaction with Na) which would establish the presence of the dehydration channel. In the future, TPD will be available to get additional information on the reaction products, $CH_3$ species in particular.

Theory suggests the following explanation for the different temperature dependence of Na($3s$) seen at different film temperatures: at 90 K, Na stays initially at the surface without reacting with methanol, but becomes solvated which causes the peak at 2.3 eV. When heating beyond 110 K, the solvated $3s$ electron starts to react with surrounding methanol species, and, for this reason, Na($3s$) disappears. On the other hand, at 120 K film temperature all methanol species in the surface layer react readily, provided enough Na is available. Na($3s$) appears only after the entire surface layer has been converted into $CH_3O$. As a consequence of this conversion, Na species cannot be solvated anymore; surplus Na stays at the surface, forming metallic regions, and desorbs above 260 K. On the other hand, Na species bound to $CH_3O$ remain at the surface. Even after at 450 K the $CH_3O$ features have disappeared, Na species remain at the tungsten probably in a configuration resembling to the surface of Na–W–bronze (see above).

Finally, we discuss the findings of Ref. 8 using the results of the present calculations: a thick film of methanol was adsorbed at 100 K onto Na-predosed Cu(111) and flashed to 270 K (Fig. 5 of Ref. 8). The UPS spectra obtained after recooling were characteristic for $CH_3O$. It is evident that, as a consequence of the annealing, only the reaction products $(Na^+ - CH_3O)$–complexes remain on the substrate; unreacted methanol has desorbed around 160 K. Considering the chosen preparation conditions—namely, Na species which very likely become embedded into their methanol environment during the annealing to 270 K—it appears likely that the mechanism proposed by us does also apply: formation of solvated $3s$ Na electrons, trapped between the $Na^+$ core and surrounding methanol molecules, takes place and constitutes the first step in the Na/$CH_3OH$ reaction.

In another set of experiments a close-packed Na film was produced at 100 K (Fig. 8 of Ref. 8). Methanol exposure at 100 K produced a two-dimensional layer on top of the Na film. UPS spectra were measured at 100 K, again after annealing to 270 K. Only emission from $CH_3O$ groups was observed. As a consequence of the heating, the surface becomes transformed into $(Na-CH_3O)$–complexes. Hereby, the $3s$ Na electron becomes solvated, and the reaction scheme proposed in Ref. 17, leading to $CH_3O$ formation, can be applied.

## V. CONCLUSIONS

The present study, combining the metastable impact electron spectroscopy with DFT cluster calculations, gives

insight into the chemistry between Na and films of methanol ice at temperatures between 90 and 120 K. It concentrates on the role played by the Na $3s$ electron for the reaction between Na and $CH_3OH$ molecules. The MIES spectra at 90 K—i.e., before the Na-induced reaction becomes efficient—are in good agreement with the density of the states of Na–$CH_3OH$ clusters as obtained from the density functional theory. In particular, theory and experiment agree well in the ionization energy of the $3s$ electron in the $CH_3OH$ environment. Theory predicts that the $3s$ electron is delocalized from its $Na^+$ core and is trapped between the core and surrounding solvent molecules; this reduces the ionization energy by 1 eV as compared to isolated Na species. It is suggested that the $3s$ Na electrons become solvated by the surrounding molecules. Methoxy ($CH_3O$) species are identified as products of the Na-induced reaction which takes place with large probability already at 120 K. Calculations and experiment both underline that the delocalized $3s$ electron triggers the formation of $CH_3O$. Two channels with similar activation energies, both leading to $CH_3O$ formation— namely, dehydrogenation and dehydration of $CH_3OH$—were considered theoretically. At present, the qualitative agreement of the MIES spectra with the predictions of both channels does not allow us to distinguish conclusively between them.

## ACKNOWLEDGMENT

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