

THE INTERACTION OF Na ATOMS WITH THE MOLECULAR SURFACES H₂O AND CH₃OH: THE ROLE OF DELOCALIZED Na3s ELECTRONS

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Received 02.07.2003

The interaction of Na atoms with H₂O and CH₃OH films is 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 water dissociation takes place whereby OH and CH₃O – species are formed, 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 OH and CH₃O – species, located at the film surface, occurs at larger exposures. In the same exposure range also emission from Na3s – ionization can be detected. The corresponding spectral structure occurs at an energetic position different from that found on metals or semiconductors. For the (Na – water) system the results are compared with First – Principles calculations on (Na)₂(H₂O)₁₀ clusters concerned with the electron and proton exchange within the cluster. Experiment and theory agree in the energetic positions of the main spectral features from water and sodium ionization. The calculations suggest that the 3sNa emission observed experimentally is due to the ejection of solvated 3s electrons which are trapped between the Na – core and water molecules of the surrounding water shell. The simultaneous emergence of dissociation products, OH and CH₃O, and solvated 3s electrons suggests that the delocalization and, consequently, the solvation plays an important role in the Na – water (methanol) reaction. Keywords: metastable impact electron spectroscopy (MIES), water, methanol, ice, solvation, alkali.

INTRODUCTION

The chemistry on molecular films, water in particular, is a challenging field for surface science because of the complexity of the three – dimensional system under study: in the mobile molecular environment the balance between solvation, chemical reactions, stabilization of the solute and the reaction products are important factors. Although the reaction of Na atoms with water, yielding NaOH and H₂, is a well – known exothermic reaction, 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 3sNa electron which plays an active role in this process. In order to overcome this problem we have started to study the interaction of Na with films of amorphous solid water (SW) by combining the Metastable Impact Electron Spectroscopy (MIES) and Ultra-violet photoemission spectroscopy (UPS) [1, 2, 3, 4]. As compared to UPS, MIES possesses a rather large sensitivity for the detection of the 3sNa electron, and its pronounced surface sensitivity allows, in combination with UPS, to distinguish between species adsorbed atop and underneath the surface under study. So far, the main findings are that Na – induced water dissociation is

certainly efficient above 110K, and that the 3sNa electron is involved in the dissociation reaction. As compared to Na adsorption on solid surfaces, metals and semiconductors in particular, a peculiar shift of the Na3s – structure is seen in the MIES spectra [3, 4], namely for adsorption on water the 3s – ionization energy is smaller by 1eV. A qualitative explanation for the lowering of the 3s – ionization energy has been attempted [4] using Born's model in which Na is thought to be surrounded, at least partially, by water molecules; this situation is modeled by embedding the Na in a cage formed by the surrounding dielectric medium.

Theory has studied the Na – water interaction by applying First – Principles and/or Molecular Dynamics methods to Na – water clusters [5, 6, 7, 8]. This work shows that the 3s – electron becomes delocalized from its respective core and is trapped between Na and the protons of the shell of hydrating water molecules pointing towards the Na. The electron distribution is unique in the sense that the electron becomes trapped by the surrounding (O – H) – bonds, and has no positive charge near the center of the charge distribution. It was demonstrated that the solvated 3s – electron plays an important role for the dissociation of the water [8]. In this last paper,

First – Principles calculations were carried out on clusters consisting of one or two Na atoms and their water environment with the goal to shed light into the mechanisms for exchange of electrons and protons between the constituents of the cluster. In particular, the 3s molecular orbital energy becomes 0,9 eV smaller after hydration.

The new detailed MIES data reported in the present paper were collected with the purpose to make a detailed comparison with the predictions of Ref.[8]. This required the extraction of density functional theory (DFT) density of states (DOS) information from Ref.[8]; this information, before and after the transfer of the delocalized electron to the protons of the surrounding water has taken place, is compared with the MIES spectra. In addition, we present MIES data for the interaction of Na with methanol in order to check the predictions of theory concerning the mechanism for the Na – CH₃OH reaction.

EXPERIMENTAL REMARKS

The experiments, described in detail elsewhere [9, 10], were carried out under ultra high vacuum (UHV) conditions (base pressure $< 2 \times 10^{-10}$ Torr). AES and XPS are used to characterize the chemical composition of the tungsten substrate employed for the deposition of the molecular films. With 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 [11, 12]. 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 [13]. 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 0,5ML [11, 12]. This underlines the power of MIES for investigating the chemistry between Na and water, which is 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 3sNa electron.

The primary result of the experiments are electron energy spectra versus the kinetic energy of the emitted electrons. By choosing a suitable bias voltage between the target and the 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 19.8eV (which is the potential energy of the metastable He atoms employed for MIES). With this particular choice of the 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, i.e. those with the 19,8 eV kinetic energy, appear at binding energy $E_B = 0$ eV with respect to the Fermi level.

Na atoms were dosed employing carefully out-gassed 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 [14]. The exposure is given in units of monolayer equivalents (MLE); at 1MLE 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 water by backfilling the chamber at a substrate temperature between 110 and 130K. This ensures the formation of a closed, non – porous and amorphous SW film [15]. The formation of an ordered film would require a certain degree of mobility of the water molecules; below 140K this mobility does not exist anymore. The relative amount of surface – adsorbed water can be estimated on the basis of earlier work with thermal desorption spectroscopy (TPD) and MIES [1, 10]. Prior to Na exposure the surface prepared as described above was cooled to the desired temperature.

COMPUTATIONAL DETAILS

The method of computation was fully exposed in [8]. A Density Functional Theory (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 to neutral sodium hydrolysis.

The first model included only one sodium atom in a cluster consisting of seven water molecules. The calculated barrier of activation was equal to 31,6 kJ·mol⁻¹ after correction of the zero point energy. The two others clusters involved two atoms embedded into clusters of seven and ten water

molecules, respectively. The associated barriers of activation were 37,2 and 33,2 kJ·mol⁻¹, respectively, i.e. the barriers decrease with the number of hydrating molecules.

The calculation of the free activation energies shows that at low temperature the two Na mechanism is more easy. However, all the investigated models involve the 3sNa electron solvation, and are strongly dependent of the electrostatic fields generated by the water cluster.

It was established previously that the interaction of He* with clean and Na covered water films is via the Auger deexcitation process. This implies that the MIES spectra image the surface density of states (SDOS) directly [11, 12]. The SDOS, needed for the comparison with the MIES spectra, have been obtained by dressing the DFT molecular energy level distributions with Lorentzian functions of arbitrary height and an half width of 0,25 eV.

RESULTS

The following spectral features are expected when Na and water interact with surfaces [1, 2, 3, 4]: the 2pNa-orbital, due to its high ionization energy, is not accessible by the chosen techniques. If the Na adsorbate is not fully ionized, a spectral feature is expected from the presence of 3s – charge density at the Na core. It causes a prominent feature, Na(3s), close to E_F which is clearly seen on metals and semiconductors for coverages larger than about 0,5ML [11, 12].

Molecularly adsorbed water produces three peaks, both in MIES and UPS, identified as emission from the three uppermost occupied water orbitals 1b₁, 3a₁, and 1b₂ [16, 17] (binding energies 7,8; 10,0 and 13,2 eV, respectively). In contrast, the adsorption of water onto partially alkalated titania leads to water dissociation provided the precoverage is larger than about 0,5 monolayers [10]. The ionization of the OH 1π and the 3σ orbitals yields peaks at $E_B = 7,0$ and 11,2 eV, respectively [16, 17]. On metal substrates the Na – H₂O interaction can lead to complete dissociation of H₂O. In this case atomic oxygen species, stabilized by Na⁺ ions, will be seen. As a particular example, the ionization of O²⁻ species will give rise to a single peak around $E_B = 3,6$ eV [18].

Fig. 1 (upper set of spectra) presents the MIES results obtained during Na deposition on a water film (3 bilayers of water) held at 90K. For pure water we see indeed the structures 1b₁, 3a₁, and 1b₂ from the ionization of the three highest occupied water MO's (top spectrum). Under Na exposure the spectra remain unchanged initially except for a change of the peak positions simultaneously with the observed

Na – induced WF decrease (1 eV), and a smearing – out of the water features 1b₁, 3a₁, and 1b₂.

Above 0,5MLE a shoulder emerges at the position where emission from 1π of OH is expected [16, 17]. Accordingly, we have denoted the shoulder by 1π. The contribution expected from the ionization of 3σ of OH at a binding energy larger by 3,7 eV [16, 17] is obscured by the emission from 3a₁. In the same exposure range emission, labeled Na (3s), appears. It resembles closely to the Na – induced emission seen with metals and semiconductors for coverages larger than about 0,5 ML. In these cases, the emission is due to the presence of s – charge density at the alkali core, i.e. the Na adsorbate is not fully ionized anymore. We assume that Na (3s) has the same origin. However, the emission is peaked at $E_B = 2,3$ eV which is about 1 eV larger than on solid surfaces. This binding energy is with respect to E_F . As determined from the onset of the MIES spectra at low kinetic energies, the work function (WF) is 2eV, and thus E_B is located 2eV below the vacuum level. Thus, under the present conditions the 3s – ionization energy is $(E_B + WF)eV = 4,3$ eV. Although no Na signature is seen in the early stage of exposure, Na species must become adsorbed/incorporated into the water film as suggested by the decrease of WF and the concomitant shift of the water spectra. Since no 3s – emission is seen, we conclude that no 3s electrons are present at the film surface.

Compared to 130 K [3, 4], Na(3s) appears already at lower exposures, and, thus, Na penetration into the water film is less likely. In addition, other than at 130 K, H₂O and OH features appear simultaneously over the entire studied range of exposures, indicating that the (Na – water) reaction is blocked before the entire film surface is converted into NaOH complexes. The present results are rather similar to the 10 K results [3] where little reaction was seen, and the Na species stayed at the surface.

The surface prepared by Na exposure was heated stepwise between 90 and 650 K. The results (lower set of spectra in fig. 1) support the interpretation given to the feature 1π: the molecular water desorbs at 155 K while OH – species can be detected on the surface up to 390 K as suggested by the presence of the two peaks 1π and the 3σ at a distance of 3,7 eV at positions that agree well with [16, 17]. The 1π shoulder develops smoothly into the peak labeled 1π, suggesting that 1π, seen before the water desorption, is indicative for OH – species from the reaction of Na with water molecules.

When annealing further, the OH – features disappear at 390 K. Apart from the tungsten substrate emission, seen between about 5 and 13 eV, a promi-

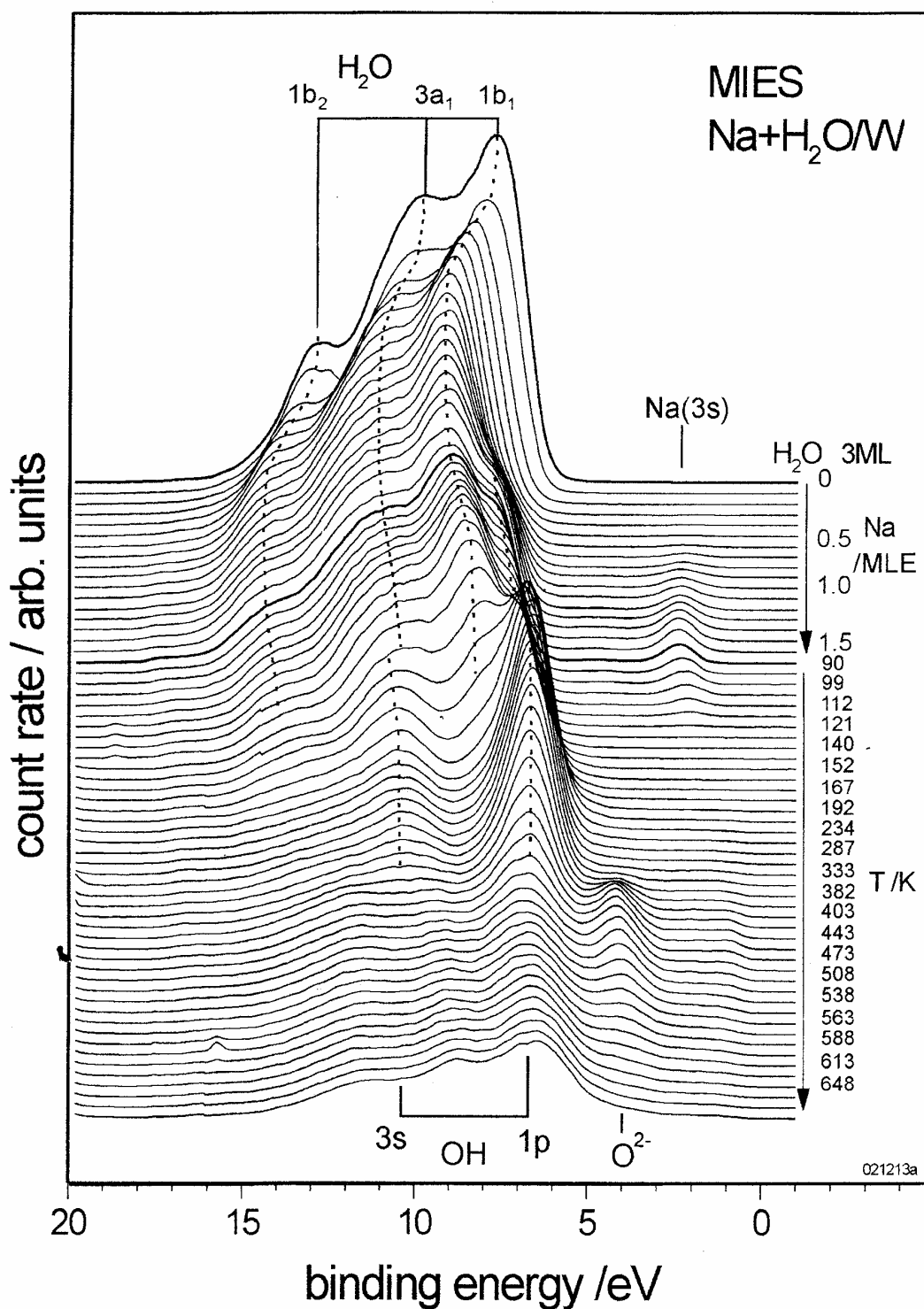


Fig. 1. MIES spectra for the adsorption of Na on solid water (3 layers) prepared on tungsten (90K) (upper set of spectra), and the spectral changes resulting from annealing the Na/H₂O system over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

ment peak appears at 4 eV; it persists up to 600 K. This finding is consistent with OH – decomposition whereby atomic oxygen remains at the surface. The energetic position is characteristic for O²⁻ species, stabilized by Na ions.

Na disappears from the surface when heating from 90 to 110 K, presumably because the mobility of the water molecules increases which leads to the solvation of Na in the film.

Fig. 2 presents MIES results for CH₃OH, obtained in the same manner as described above (fig.1) for water. The tungsten substrate is held at 90 K during the film preparation. The top spectrum is for the methanol film (4 layers thick) prior to Na exposure.

The upper set of spectra is obtained during the Na exposure of the film. According to Refs.[2, 19, 20], M₁ to M₅ have n_{O1}, n_{OII}, σ_{CO}, π_{CO}, and σ_{OH} character, respectively. As a consequence of the exposure to Na M₁ to M₅ shift to larger E_b's, simultaneously

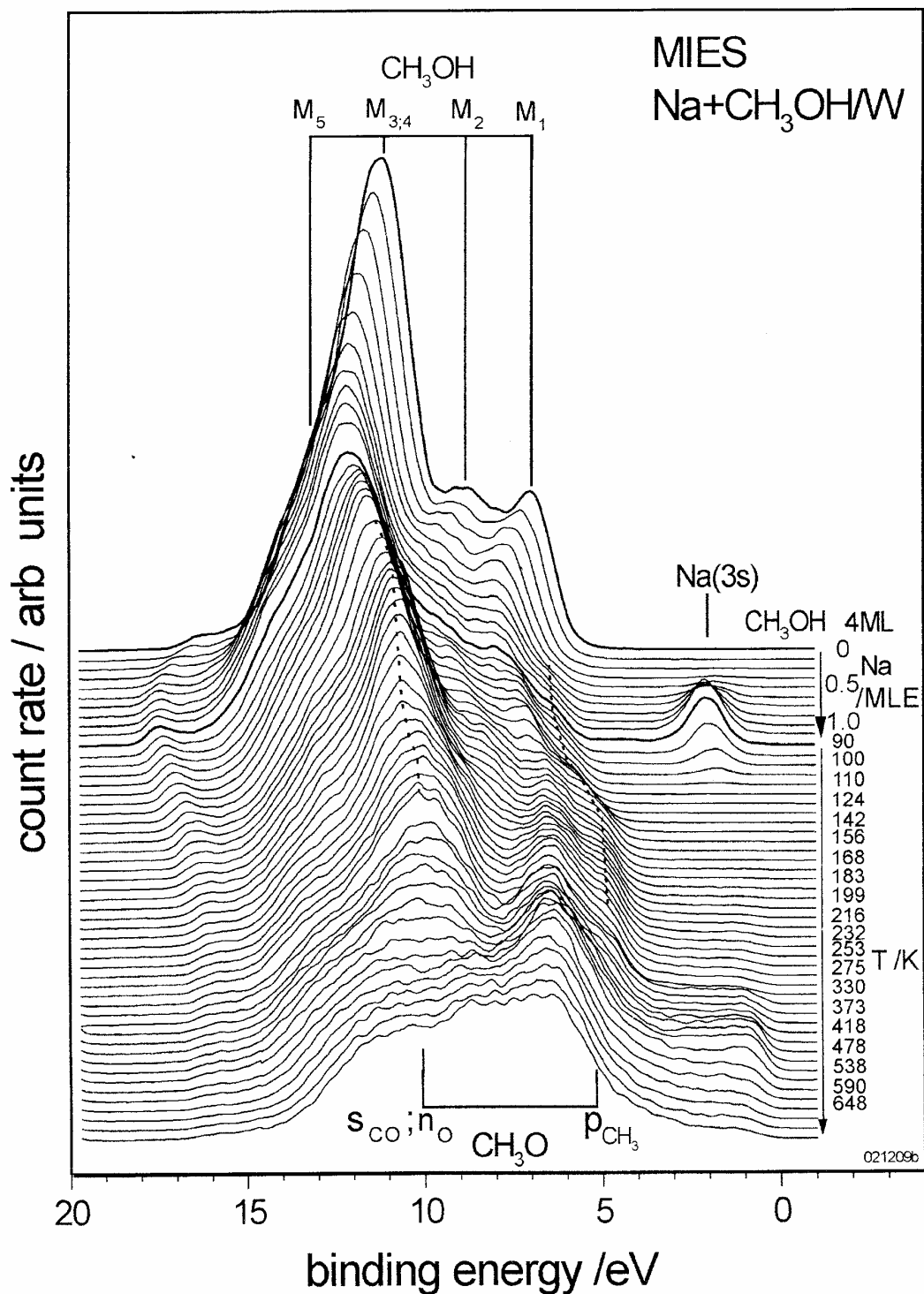


Fig. 2. MIES spectra for the Na – exposed film of solid CH₃OH (4 layers prepared on tungsten (90K) (upper set of spectra), and the spectral changes resulting from annealing the Na/CH₃OH system over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

with the observed decrease of WF by 1,3 eV. In addition, the structure, labeled π_{CH_3} , develops. In studies which concentrate on the electronic structure of CH_3OH – ice, we established that π_{CH_3} together with $(\sigma_{\text{CO}}; n_{\text{O}})$, overlapping with $M_{3,4}$, must be attributed to methoxy, CH_3O , species from the dehydrogenation of CH_3OH by Na [21]: the structures π_{CH_3} and $(\sigma_{\text{CO}}; n_{\text{O}})$, separated by about 5 eV, result from the ionization of the antibonding π – MO's, located at the CH_3 – group and the oxygen core (π_{CH_3} and n_{O}), and from the σ – MO along the (C – O) – direction. Support for this identification comes from the study of the oxygenation of CH_3OH on a oxygen precovered Cu (111) surface [22]. The structure Na (3s) at $E_B = 2$ eV develops as a consequence of the Na – exposure, and can clearly be noticed above 0,4 MLE; the WF of the Na – exposed film saturates after a WF decrease of 1 eV.

The lower set of spectra in fig. 2 was obtained when heating from 90 to 650 K. M_1 to M_5 from CH_3OH disappear when annealing to 165 K while the structures attributed to CH_3O , in particular π_{CH_3} , persist up to 460K. We attribute the emission seen between 5 and 13 eV at higher temperatures to the tungsten substrate. During annealing Na (3s) behaves similar as for water, shifts to smaller E_B 's and disappears at 110 K. In auxiliary experiments on films prepared at 120K we have established that there is no Na desorption at these temperatures; instead Na penetrates into the CH_3OH film.

DISCUSSION

A qualitative explanation of the observed lowering of the 3s Na ionization energy in aqueous environment has been attempted [4] using Born's model, applied previously to explain photoelectron spectra from liquid water [23]: the Na atom is thought to be surrounded, at least partially, by water molecules. In Born's model this situation is modeled by embedding the Na in a cage formed by the surrounding dielectric medium. This leads to a decrease of the 3s – ionization energy by $\delta W = 1/8\pi\epsilon_0 r_0 (1 - 1/\epsilon)$, where r_0 is the cage radius (about 0,2 nm for water [23]) and ϵ the dielectric constant of water. Using $\epsilon = 1,5$ [23], one obtains an 1eV reduction of the 3s – ionization energy for the embedded Na atom, in reasonable agreement with experiment [4]. Of course, this naive model gives no hint how to explain the observed Na – induced water dissociation.

The sodium interaction with water ice will now be discussed on the basis of the theory results for sodium hydroxyl formation in water clusters [8]. The key point was to consider the consequences of the hydrolysis of a single Na atom as well as of Na_2 di-

mers interacting with water clusters. The role of 3s Na electrons solvated by three surrounding water molecules was studied. As a consequence, the 3s – electrons are located very far from their original nuclei. The fundamental role of the electric field generated by the metal atoms inside the water cluster was also pointed out. A major effect of the Na trapping is the strong perturbation of the molecular energy levels distribution, narrowing the DOS bands. The following considerations go beyond ref. [8] in as much as a DOS, suitable for comparison with the MIES spectra, has been generated from the energy levels of the sodium – water clusters considered in ref.[8].

As pointed out in section 3, significant Na(3s) and 1π emission (attributed to the reaction product OH) is not seen below 0,5 MLE. This could be indication that this minimum Na concentration is required for the water dissociation to occur. Indeed, the First – Principles calculations carried out on clusters consisting of one and two Na atoms and their water environment [5, 6, 7, 8] suggest that the presence of Na dimers (or even trimers [6]) facilitates the water dissociation.

We show now that the MIES spectra and the DFT results for the DOS for two sodium atoms trapped in a $(\text{H}_2\text{O})_{10}$ cluster before and after Na_2 hydrolysis are consistent (Fig. 3). As suggested by the results of section 4, we suppose in the following that unreacted, but solvated Na – species (prior to the reaction) and OH – species from the Na – induced hydrolysis are both present at the surface. The DFT – DOS before Na – ionization shows 4 peaks in the 0 to 20 eV window labeled A, B, C and D as in ref.[8]. Peak A corresponds to the solvated electron (denoted by Na (3s) in the MIES spectra). Peaks B and C correspond mainly to the π and σ water lone pairs of electrons involved in OH bonds (denoted $1b_1$ and $3a_1$ in MIES). Peak D (labeled $1b_2$ in MIES) is the antisymmetric OH contribution. B is well reflected in the experimental spectrum. C is also seen in the MIES spectrum, but overlaps with the contribution of the “ionized” system, consisting of Na^+ , the solvated electron and the water cluster, since as mentioned before, the MIES DOS is a superposition of “ionized” and “non – ionized” (before the transfer of the solvated electron to nearby protons takes place) species. D is also present in the experimental DOS, but merely as a shoulder.

After hydrolysis, the solvated electron signal disappears from the DFT – DOS. Two shoulders appear in the DFT – DOS corresponding to the shift of the two water LP's combined to the two hydroxyl groups issued from Na_2 ionization; a larger cluster

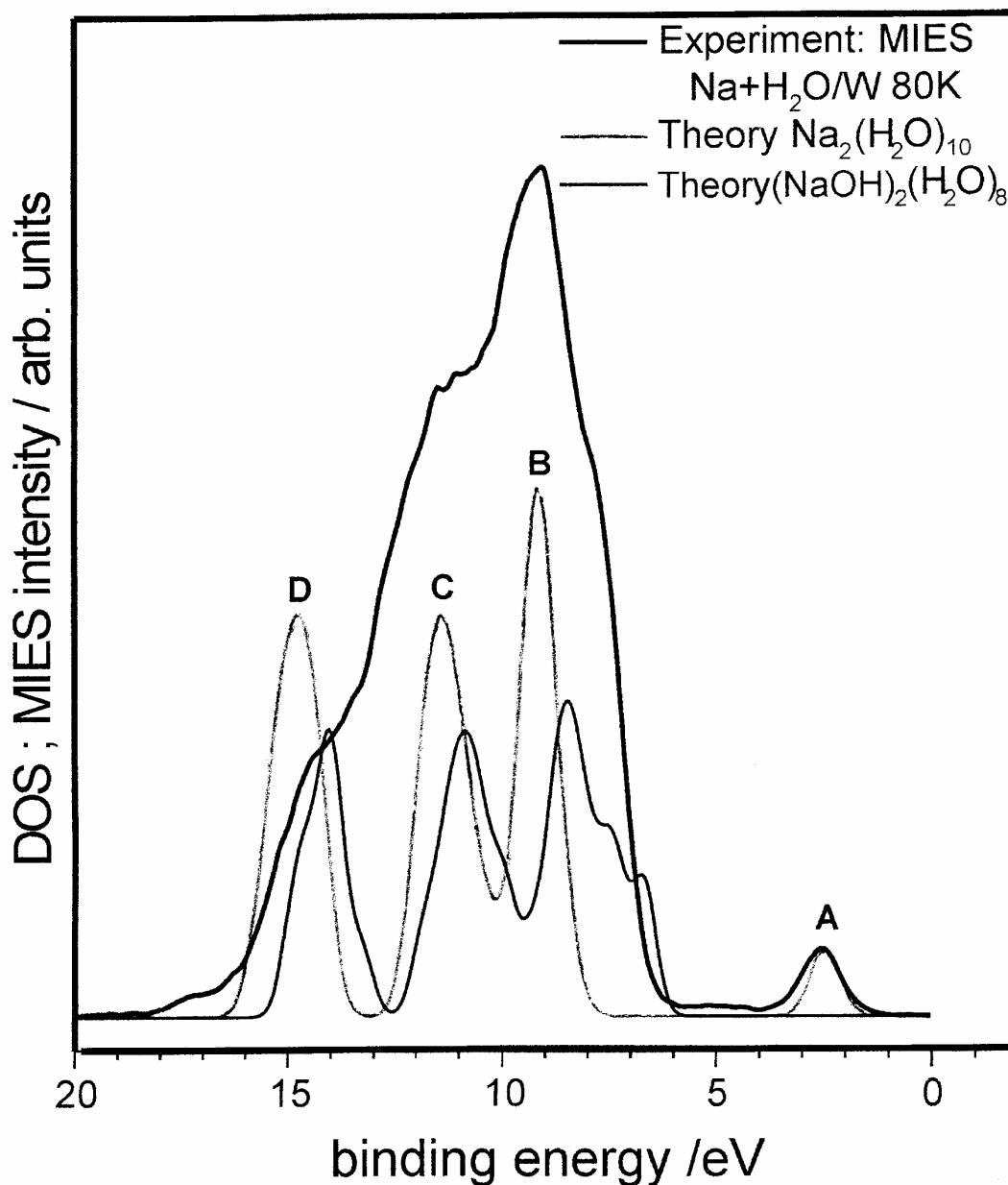


Fig. 3. DOS of the Na₂(H₂O)₁₀ – cluster defined in the text and comparison with the results of fig.1 (heavy spectrum).

would have produced a broad band analogous to the shoulder in the MIES pattern in the same energy region. The former peaks B, C and D are shifted towards the Fermi level, and the overall combination is well reflected in the experimental curve. The σ hydroxyl OH, located around 25 eV, is not displayed in this figure.

From the present experiment it is not possible to determine unambiguously whether the active Na species are single atoms, dimers (as assumed in the present work) or, as proposed in ref. [6], as trimers. Nevertheless, the comparison between theory and

experiment appears to be meaningful enough to support the reaction pathway involving Na dimers: in the first step, after film adsorption, Na is trapped inside the cluster. This perturbs strongly the original water DOS in mixing more intimately the lone pair and antisymmetric water OH wave functions. Therefore, the proton tunneling from one water molecule to a neighbouring one is greatly facilitated. The acceptor molecule releases one of its own protons to another neighbour. This process continues from site to site until the end of the H – bonded chain is reached. This happens at the protons pointing to-

ward the solvated electrons. Such a proton is therefore able to capture one of these electrons producing, in the first step, an H radical atom, and then a H_2 molecule.

When heating beyond 115K Na species disappear from the surface, becoming solvated in the water film. Therefore, a comparison of MIES results and theory is limited to temperatures below 115 K.

A few comments are in order concerning the mechanism for the interaction of Na with methanol. The experiment demonstrates that, as for water, delocalization of the 3s – electron takes place, and plays an important role in producing H radical atoms by dehydrogenation of methanol as documented by the formation of CH_3O species. In analogy to water, we expect that the 3s – electron is trapped between the Na – core and protons of the OH – group of CH_3OH molecules surrounding the Na^+ core. A possible reaction path that resembles that of the single Na case discussed in Ref. [8] for the reaction of Na with water, is as follows: the delocalized electron is transferred to one of the protons of the methanol molecules surrounding the Na species. The particular proton that captured the solvated electron is released from its molecule, and leaves CH_3O^- species behind. The Na^+ core and the CH_3O^- species form $(Na^+ CH_3O^-)$ – complexes. This is in agreement with MIES which simultaneously detects 3sNa, CH_3OH (prior to the reaction), and CH_3O^- species (after the reaction) at the surface.

CONCLUSIONS

The present study, employing the Metastable Impact Electron Spectroscopy (MIES), gives insight into the chemistry between Na and water (methanol) ice films held at 80 K. It concentrates on the role of the Na3s electron for the reaction between Na and the molecular films. For water the interaction leads to OH – formation which, at 80 K, appears to be confined to the film surface mainly. This is in contrast with previous results at 130 K film temperature where the reaction involves the entire film. For methanol the reaction products are identified as CH_3O^- species. As for water, at 80 K the reaction is mainly confined to the film surface. For water the MIES spectra are in good agreement with the density of the states in $Na_2(H_2O)_{10}$ clusters as obtained from First – Principles DFT calculations. In particular, theory and experiment agree well in the energetic position of the 3s electron. Theory predicts that the 3s electron is delocalized from its Na^+ core, and is trapped between the core and surrounding solvent molecules. It is therefore suggested that in both cases, water and methanol, the 3sNa electrons are solvated in the

respective molecular surroundings. Calculations and experiment both underline that the delocalized electron triggers the Na – water reaction leading to the formation of NaOH.

On the basis of the available theory results for the Na – water system and the comparison of the experimental results for Na – water and – methanol we propose a scenario for the Na – methanol reaction. As for water, it is initiated by delocalized 3sNa electrons which become transferred to one of the protons of surrounding CH_3OH molecules leading to its dehydrogenation.

ACKNOWLEDGEMENTS

The Marseille – Clausthal cooperation was supported by the COST 19 action of the EU.

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**ВЗАЄМОДІЯ АТОМІВ Na
З МОЛЕКУЛЯРНИМИ ПОВЕРХНЯМИ H₂O
І CH₃OH: РОЛЬ ДЕЛОКАЛІЗОВАНИХ
Na3s ЕЛЕКТРОНІВ**

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Взаємодія атомів Na із плівками H₂O та CH₃OH вивчалася методом електронної спектроскопії метастабільних зіткнень (ЕСМЗ) в умовах надвисокого вакууму. Плівки були вирощені при температурі 90 (+/-10) К на вольфрамових підкладках і піддавалися впливу Na. Індукована Na дисоціація води відбувалася при формуванні груп OH і CH₃O та іонізації атомів Na. За малих експозицій Na, найбільш віддалений розчинний шар залишається, в значній мірі, неушкодженим, що випливає з відсутності сигналів ЕСМЗ, зумовлених продуктами реакції. Однак, за великих часів експозиції спостерігається випромінювання від груп OH та CH₃O, які локалізовані на поверхні плівки. У цьому ж діапазоні експозиції може бути визначена емісія, яка пов'язана з наявністю Na3s іонізації. Відповідний спектральний склад характерний для енергетичних спектрів відмінних від знайдених для металів і напівпровідників. Для системи (Na–вода) результати порівнюються з розрахунками для кластерів (Na)₂(H₂O)₁₀, з урахуванням електронної і протонної взаємодії усередині кластера. Експеримент і теорія збігаються за основними спектральними характеристиками енергетичних спектрів від води та іонізованого натрію. Розрахунки підтверджують, що 3sNa емісія, яка спостерігається експериментально пов'язана із випусканням розчинених 3s електронів, що локалізовані між ядром Na та молекулами води навколишньої водяної оболонки. Одночасне виділення продуктів дисоціації, OH і CH₃O, та розчинених 3s електронів підтверджує, що делокалізація і, відповідно, розчинення відіграють важливу роль у реакціях Na–вода (метанол).

**ВЗАИМОДЕЙСТВИЕ АТОМОВ Na
С МОЛЕКУЛЯРНЫМИ ПОВЕРХНОСТЯМИ
H₂O И CH₃OH: РОЛЬ ДЕЛОКАЛИЗОВАННЫХ
Na3s ЭЛЕКТРОНОВ**

**А. Бородин, О. Хоффт, У. Канерт,
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Взаимодействие атомов Na с пленками H₂O и CH₃OH изучалось методом электронной спектроскопии метастабильных соударений (ЭСМС) в условиях сверхвысокого вакуума. Пленки были выращены при температуре 90 (+/-10) К на вольфрамовых подложках и подвергались воздействию Na. Индуцированная Na диссоциация воды происходила при формировании групп OH и CH₃O и ионизации атомов Na. При малых экспозициях Na наиболее удаленный растворенный слой остается в значительной степени неповрежденным, что следует из отсутствия сигналов ЭСМС, обусловленных продуктами реакции. Однако, при больших временах экспозиции наблюдается излучение от групп OH и CH₃O локализованных на поверхности пленки. В этом же диапазоне экспозиции может быть определена эмиссия, связанная с наличием Na3s ионизации. Соответствующий спектральный состав характерен для энергетических спектров отличных от найденных для металлов и полупроводников. Для системы (Na–вода) результаты сравниваются с расчетами для кластеров (Na)₂(H₂O)₁₀, с учетом электронных и протонных взаимодействий внутри кластера. Эксперимент и теория совпадают по основным спектральным характеристикам энергетических спектров от воды и ионизированного натрия. Расчеты подтверждают, что 3sNa эмиссия, наблюдаемая экспериментально, связана с испусканием растворенных 3s электронов, локализованных между ядром Na и молекулами воды окружающей водной оболочки. Одновременное выделение продуктов диссоциации, OH и CH₃O, и растворенных 3s электронов подтверждает, что делокализация и, соответственно, растворение играют важную роль в реакциях Na–вода (метанол).