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Interaction of formic acid with solid water

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The interaction of formic acid (HCOOH) with solid water, deposited on tungsten at 80 K, was investigated. We have prepared and annealed formic acid (FA)/water interfaces (FA layers on thin films of solid water and H₂O adlayers on thin FA films). Metastable impact electron spectroscopy and ultraviolet photoemission spectroscopy (He I and II) were utilized to study the electron emission from the 10a' to 6a' molecular orbitals (MOs) of FA, and the 1b₁, 3a₁, and 1b₂ MOs of H₂O. These spectra were compared with results of density-functional theory calculations on FA-H₂O complexes reported in Ref. 14 [A. Allouche, *J. Chem. Phys.* **122**, 234703(2005), (preceding paper)]. Temperature programmed desorption was applied for information on the desorption kinetics. Initially, FA is adsorbed on top of the water film. The FA spectra are distorted with respect to those from FA monomers; it is concluded that a strong interaction exists between the adsorbates. Even though partial solvation of FA species takes place during annealing, FA remains in the top layer up to the desorption of the water film. When H₂O molecules are offered to FA films at 80 K, no water network is formed during the initial stage of water exposure; H₂O molecules interact individually via H bonds with the formic acid network. Experiment and theory agree that no water-induced deprotonation of the formic acid molecules takes place. © 2005 American Institute of Physics. [DOI: 10.1063/1.1929732]

I. INTRODUCTION

The capability of ice surfaces to promote dissociation of acids is still a controversial issue.¹ Even for the well-studied system HCl/water ice the situation appears to be under debate: On the one hand, it was concluded that HCl inserted into the top bilayer of the water ice lattice, thereby substituting a water molecule, rapidly undergoes deprotonation.² On the other hand, it was concluded that steric hindrance effects and electrostatic repulsion prevent configurations in which the Cl⁻ becomes surrounded by four water molecules and, as a consequence, is forced into the rather rigid ice lattice.³ This has to be contrasted with the results of constrained molecular-dynamics (MD) simulations where the free-energy profiles calculated for 235 K show no barrier against HCl penetration into the ice crystal.⁴

For formic and acetic acid interacting with ice surfaces, free-energy profiles obtained from classical MD calculations demonstrate that carbonic acids are strongly trapped at the ice surface at 250 K.⁵ The results indicate that the adsorption sites are located inside the surface layer, i.e., a partial solvation takes place during the acid adsorption at that temperature. It was suggested that the formation of hydrogen bonds at the ice surface could be responsible for the initiation of further processes, as the acid molecule's ionization, leading

to formate formation via an HCOO⁻-H₃O⁺ contact ion pair in the case of formic acid (FA). On the basis of time-of-flight secondary-ion-mass spectrometry (TOF-SIMS) measurements it was concluded that FA species, top deposited on water ice at 15 K, start to become hydrated above 110 K, and it is concluded that at 140 K the top layer of the surface consists of pure water.⁶ Density-functional theory (DFT) calculations were performed in order to determine the energetically most favorable FA/water configurations responsible for the solvation of FA.⁷ It is found that FA tends to form H bonds with two H₂O molecules, themselves interlinked by H bonds, and stabilized by H bonds to adjacent water molecules. On the other hand, combined electron energy-loss spectroscopy (EELS) and TPD results obtained during the coadsorption of FA and H₂O on Pt surfaces in the range of 100–200 K suggest that FA-H₂O complexes (1:2 to 3 stoichiometry) are formed; a model was favored in which small water aggregates become attached to FA chains.⁸

The surface-sensitive analytical techniques at our disposal, MIES (metastable impact electron spectroscopy),^{9,10} UPS (He I and II), and TPD spectroscopy (temperature programmed desorption), are well suited to answer some of the open questions concerning the FA-water interaction (see our previous work on multilayered water for details^{11–13}). MIES, an ultimately surface-sensitive technique, will identify the surface-adsorbed species and their electronic structure; in addition, it can pursue the progress of an eventual solvation process, leading to the disappearance of the FA species from

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the surface, as a function of the surface temperature. In combination with UPS, providing depth information, the distribution in depth of the solutes can be studied. The employed spectroscopies can also detect an eventual deprotonation reaction occurring as a consequence of the FA-water interaction. Moreover, the comparison with the corresponding spectra from free FA species gives information on the distortion of the FA species by the surrounding medium, on their lateral interaction, and on their H bonding with the solvent molecules.

In the present work, water films, grown on a tungsten substrate at 80 K, were exposed to FA; the change of the electronic structure with the temperature of the FA-exposed film was monitored under the *in situ* control of MIES and UPS. Additional information on the processes at FA-water interfaces was obtained by studying the interaction of water molecules with FA films produced at 80 K. The spectra are compared with the density of states (DOS) obtained from DFT calculations on FA-water complexes¹⁴ (preceding paper, in the following denoted by I).

TPD gives details on the thermally induced desorption kinetics, in particular, on the species desorbing from the bulk, without having a sufficiently long dwell time at the surface in order to become accessible to the electron spectroscopic techniques.

II. EXPERIMENTAL DETAILS

A. Electron spectroscopy

Experimental details on the apparatus employed for the electron spectroscopic studies can be found elsewhere.^{15–19} Briefly, the UHV apparatus is equipped with a cold-cathode gas discharge source for the production of metastable $\text{He}^*(^3S/^1S)$ ($E^*=19.8/20.6$ eV) atoms with thermal kinetic energy and He I photons ($E^*=21.2$ eV) as a source for ultra-violet photoelectron spectroscopy (UPS). The intensity ratio $^3S/^1S$ is found to be 7:1. Since the metastables approach the surface with a near-thermal kinetic energy (60–100 meV), this technique is nondestructive and highly surface sensitive (see Refs. 9 and 10 for more detailed introductions into MIES and its various applications in molecular and surface spectroscopies). The spectral contributions from metastables and photons are separated by time of flight. MIES and UPS spectra were acquired with incident photon/metastable beams 45° with respect to the surface normal; electrons emitted in the direction normal to the surface are analyzed. Collection of a MIES/UPS spectrum requires approximately 100 s. In order to minimize charge-up phenomena, we worked with low beam current densities, and thus an energy resolution of 600 meV was employed for MIES/UPS. The spectra showed no basic changes at 250 meV resolution. A second photon source is at our disposal providing He I and He II (40.8 eV) photons. The variation of the onset of the spectra at low kinetic energies with exposure gives the exposure dependence of the surface work function.

The sample can be cooled with LN_2 to 80 K. The temperature, measured with a thermocouple in direct contact with the front of the tungsten single crystal, is estimated to be accurate within ± 10 K. The surface was exposed to water

by backfilling the chamber. The water was cleaned by several freeze-pump-thaw cycles. The amount of surface-adsorbed water is estimated on the basis of our previous results concerned with the water-titania interaction:¹⁹ essentially, we make use of the fact that (a) water adsorption leads to an initial work-function decrease up to half the coverage of the surface, and (b) the MIES signal from water saturates for full coverage of the surface. From this we conclude that at 2 L exposure the surface is covered by one bilayer (BL) of water. At 5 L emission from the tungsten substrate has essentially disappeared in the UPS(He II) spectra.

Annealing of the prepared films is done stepwise; during the collection of the MIES or UPS spectra the substrate temperature is kept constant.

B. Temperature programmed desorption (TPD)

The TPD experiments (controlled via Pfeiffer QUADSTAR software) are carried out using a differentially pumped quadrupole mass spectrometer (QMS, Pfeiffer, type QMS 422), available at the UHV apparatus employed for the MIES/UPS studies. The TPD housing is connected via a small opening ($d=3$ mm) to the main chamber and is pumped separately via a turbomolecular pump (60 l/s; N_2). In order to obtain TPD spectra exclusively from the relevant surface area, the opening of the TPD housing is positioned ca. 2 mm in front of the sample. The sample, whose temperature was measured using a W/Re thermocouple type C, could be heated by radiation from a tungsten filament positioned behind the crystal. The TPD spectra are collected at a linear heating rate of 1 K/s, and routinely five different masses are measured simultaneously. Under these circumstances the onset of desorption in the MIES/UPS spectra (data collection time is 60 s, typically) is seen about 15 K below the desorption peak maximum temperature.

III. RESULTS AND INTERPRETATION

This section starts with the discussion of the spectral features seen during the interaction of FA and water. The similarity of the MIES and UPS spectra indicates that the spectral features seen in MIES are due to Auger deexcitation (AD) of He^* ; thus, the position of the spectral feature gives the binding energy of the electron emitted from the considered species.^{9,10} All results are presented as a function of the binding energy E_B of the emitted electrons. Electrons emitted from the Fermi level appear at zero energy in the MIES and UPS spectra. Quantitative methods are available to either synthesize the MIES spectra^{20,21} (see Ref. 22 for an example) or to deconvolute them.⁹ In the present work we confine ourselves for simplicity to a qualitative analysis of the spectra: we suppose that the intensity of the spectral features from the AD process reflects directly the density of states initially populated. Within this framework we can compare the MIES results directly with the DOS from electronic structure calculations. In the present work, we compare with the hybrid (B3LYP) DFT results of paper I. In order to arrive at a DOS suited for comparison with MIES, the quantum molecular energy levels were dressed with Lorentzian functions of 0.5 eV half-width. On the other hand, the compari-

son of the DOS with UPS results is less direct, the spectra depending on both the DOS of the initial and final states involved in the photoionization process. The focus is on the structure of the spectra, rather than on the variation of the intensity of the spectral features with annealing temperature. A full analysis of the spectra, together with the corresponding IR spectra, will be presented in a forthcoming publication.²³

A. Signature of formic acid (FA) and water species in MIES and UPS

Water exposure between 80 and 130 K produces the three features, $1b_1$, $3a_1$, and $1b_2$, seen both with MIES and UPS (see Figs. 1 and 2, top).^{11,19} It should be noticed that the UPS data for solid water films are rather similar to those for liquid water.²⁴ The broad $3a_1$ feature is characteristic for condensed water, either in the liquid or solid phase, and signals the presence of a water network, formed by hydrogen bonds.^{25,26}

UPS(He I) and Penning ionization spectra from isolated FA monomers can be found in Refs. 27–29. Our spectra are characteristically different in several points: The gas phase spectra show well-resolved emission from $10a'$ and $2a''$. These two peaks are separated by 1.2 eV, and should be resolved by our setup. The same holds for the features $9a'$ and $10a''$ which are also not resolved in the present results. Moreover, the distance between the centers of the structures attributable to $9a'/10a''$ and $8a'/7a'$ is smaller in the present results than in the gas phase spectra. The deviations seen in the present spectra with respect to the available gas phase spectra are independent on the type of substrate on which the condensation takes place, i.e., the same spectra are seen for the adsorption on tungsten and on water. The He I spectra reported for FA dimers in the gas phase^{27,28} show a structure similar to, although not identical with, the present MIES and UPS spectra for condensed FA. This suggests that the lateral interaction between FA species is important.

The DOS presented in paper I for FA monomers, dimers, and trimers [Figs. 1(a) and 3 of I] can be compared with the MIES spectra, assuming that the spectra reflect the DOS of the occupied cluster states (which is a reasonable assumption for MIES). The calculations both for the dimers and trimers reproduce the finding of four structures in the MIES spectra rather well, whereby structures (2) and (3) are not as well resolved as in the experiment; (4) is only seen in the UPS(He II) spectra.

Summarizing, the present spectra must be attributed to FA species displaying strong lateral interactions among each other, although we are not able to identify the particular oligomers: Structure (1) is composed of contributions from the ionization of states that originate from the $10a'$ and $2a''$ (f12 and f11) MOs. Structure (2), located at about 3.2 eV larger binding energy, is dominated by contributions from states originating from MOs $9a'$ and $1a''$ (f10 and f9). Peak (3), at a binding energy about 2 eV larger than (2), originates from states formed from the $8a'$ and $7a'$ (f8 and f7) MOs. The notation used in I is shown in parentheses. He II detects, in addition, the emission from $6a'$ -based states (f6) at about 16 eV binding energy [peak (4)].

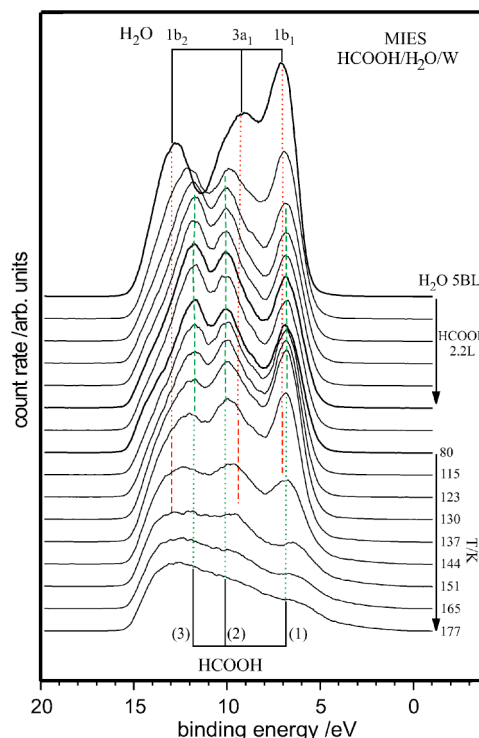


FIG. 1. Upper set: MIES spectra obtained during the deposition of a FA adlayer (about 1 ML) onto a H_2O film (5 BL thick) held at 80 K. Lower set of spectra: MIES spectra registered during the annealing of the prepared FA/water system to 180 K.

B. Adsorption of formic acid (FA) molecules on water films prepared at 80 K

Figure 1 (upper set of spectra) displays the MIES spectra recorded during the exposure of a water film (5 BL thick) to FA. According to MIES, a closed FA layer is present at 2-L exposure on a water film prepared at 80 K; this is concluded from the fact that, from this exposure, the $1b_2$ H_2O feature, which is well separated from any FA spectral features, has practically disappeared. We find that the take-up rate is as for tungsten, and therefore conclude that no penetration of FA takes place upon adsorption at 80 K. Figure 2 (upper set of spectra) presents the corresponding results for He II; here, a typical FA spectrum develops only for FA exposures beyond 15 L.

Theory agrees that FA species, interacting with H_2O ice, form two H bonds via its C=O and OH ends with two molecules of the water film.^{5,7} As pointed out above, the strong distortion of the FA-induced spectra, with respect to those obtained from isolated molecules, must be explained by the formation of FA aggregates. The resulting complex, oriented perpendicular to the surface of the water film, becomes stabilized by additional H bonds of the two H_2O molecules with adjacent water molecules. These findings find general support from TOF-SIMS for FA/ice where the enhancement of the H_3O^+ yield in the low-exposure regime is best understood as due to proton transfer from the ice film to the adsorbed FA molecules.⁶ The strong interaction of the FA adsorbates with molecules of the underlying water film via two H bonds manifests itself in the TPD results (see below) which demonstrate that some FA desorbs simultaneously with water around 155 K.

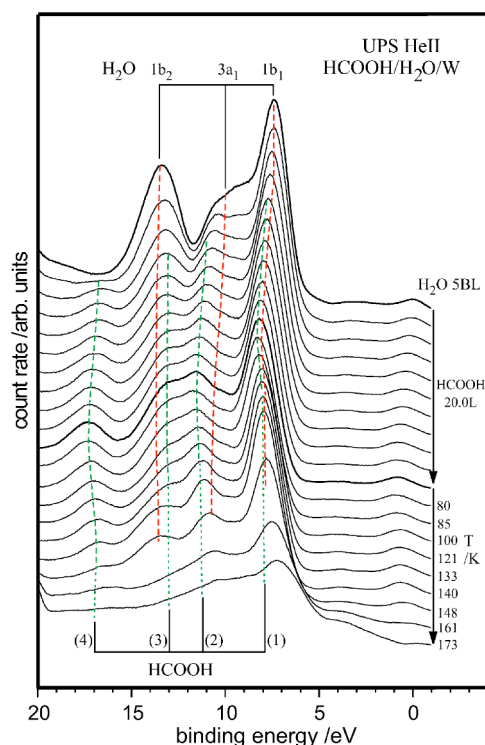


FIG. 2. Upper set of spectra: He II spectra obtained during the deposition of a FA adlayer (about 5 ML) onto a H₂O film (5 BL thick) held at 80 K. Lower set of spectra: He II spectra registered during the annealing of the prepared FA/water system to 175 K.

In order to substantiate these remarks, the MIES and He II results are compared with the results of the DFT calculations reported in I for the adsorption scenario given above: Fig. 7(b) of I presents the results for a FA layer growing perpendicular to a water cluster, starting with the adsorption of one and two FA molecules. We suppose that the spectra represent essentially the DOS of the occupied cluster states, and compare the DOSs with the He II results obtained for exposures at which, according to MIES, a closed FA layer has not yet formed (Fig. 3, He II results). Inspection of Fig. 7(b) of I indicates that FA-induced emission can only be noticed between 7 and 11 eV, superimposed on a comparatively strong water emission; due to the finite depth resolution of He II, all other FA features are hidden by the strong water features $1b_1$ and $1b_2$. Therefore, a detailed comparison with He II spectra will not be made. More information can be obtained from the comparison of the theory with the MIES results. In Fig. 3 the MIES results are compared with the FA part of the full DOS, extracted by subtracting the water contribution. This models the situation that MIES, for geometrical reasons, sees predominantly FA species. The agreement is satisfying with the DOS of FA structures oriented perpendicular to the water film. As pointed out in paper I, the FA network developing during the layer growth is similar to that of the FA trimer F341 of Ref. 30; indeed, its DOS (see Fig. 3(c) of I) is rather similar to the MIES spectrum shown in Fig. 3. We have also included FA dimers, adsorbed with their molecular plane parallel to the surface, into the comparison shown in Fig. 3. Shown is the FA-related part of the DOS of the cluster 2FA+10H₂O (Fig. 6 of I). The overall

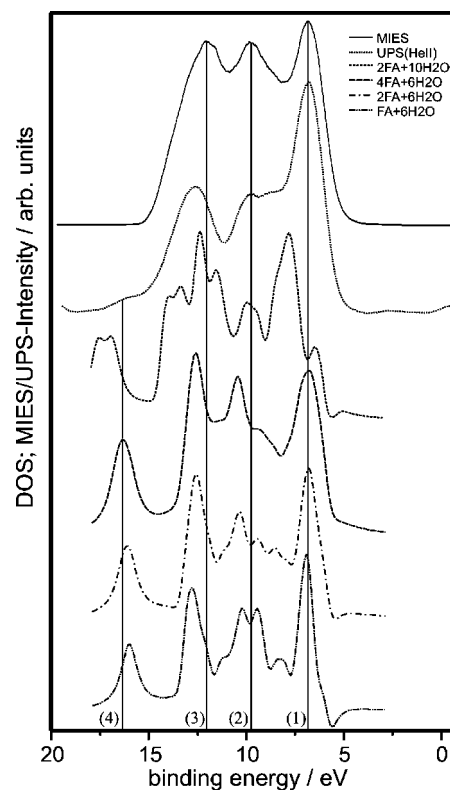


FIG. 3. FA-related part of the DOS of FA-H₂O clusters (see Ref. 14), consisting of 1, 2, and 4 FA and 6 (10) H₂O molecules (for the notation, see I). Comparison with MIES spectra for 1.5 L exposure. The corresponding UPS (He II) spectrum is included for comparison.

agreement is less convincing than for the FA network developing perpendicular to the surface of the water cluster.

The lower set of spectra in Figs. 1 and 2 presents the MIES and He II spectra, respectively, recorded during the annealing of the mixed FA/water films. The MIES and He II spectra are to some extent complementary: upon heating, water features become again visible above 115 K in He II, namely, a shoulder around 13 eV due to $1b_2$ and an increase of peak (2) caused by a $3a_1$ contribution. Above 138 K water features dominate the He II spectra up to 145 K where water desorption becomes noticeable. On the contrary, the MIES spectra remain dominated by FA features in the entire temperature range studied, although a small admixture of water features [see Fig. 1(b): increase of the intensity of (1) and a shoulder of (3), attributable to $1b_2$] can be noticed between 125 and 145 K. A more careful analysis on the basis of difference He II spectra suggests that the FA:water stoichiometry, averaged over the uppermost two layers, is about 1:3 at 140 K; from MIES, on the other hand, we estimate that in the top layer it is rather 3:1. At any rate, partial solvation of the FA species (remaining, however, top adsorbed) is noticeable above 120 K. Weak FA-like features are still seen, in particular with MIES, when all water has desorbed. The respective electron spectra, both as far as the shape and positions of the spectral features are concerned, are, within the accuracy of our measurements, identical with those for FA. Thus, we attribute the species responsible for the emission seen up to about 190 K to FA (not to formate) species in direct contact with the tungsten substrate.

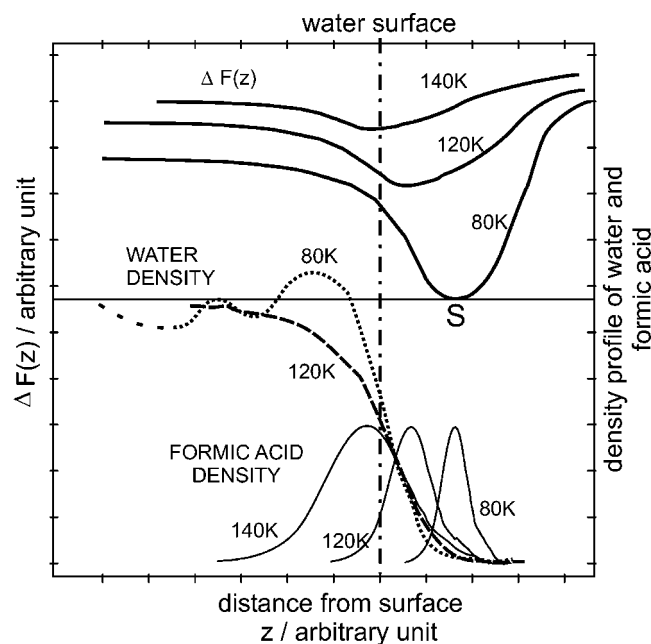


FIG. 4. Qualitative free-energy profiles for the interaction of FA with ice for various temperatures between 80 and 140 K. Also shown is the water density near the film surface.

We can visualize the annealing results on the basis of the change of the free energy $\Delta F(z)$ vs z , the distance of the FA species from the H_2O surface.^{4,5} As indicated in Fig. 4, an initial decrease of $\Delta F(z)$ with decreasing z accounts for the increasing interaction of FA with ice, in particular, for H-bond formation. A minimum of $\Delta F(z)$, denoted by S , located at the edge of the water surface at 250 K, accounts for FA adsorption at the water surface. At 80 K the minimum of $\Delta F(z)$ occurs in front of the surface accounting for the fact that at 80 K the FA signal is strong, but that of water in the MIES and UPS spectra very weak, characteristic for FA adsorption above the water film. At the low temperatures under study, FA species moving to distances inside S experience a strong rise of $\Delta F(z)$, caused by the strong entropy decrease (similar to that of the potential energy) experienced by FA during the eventual penetration into the water network which is rather rigid at those temperatures.^{4,5} Thus, the hindering of the FA's degrees of freedom by the adjacent water molecules prevents the solvation of FA into the ice film. As stated above, the entropy contribution to the free energy becomes increasingly less important with increasing temperature due to the decrease in rigidity of the water network. This leads to a gradual reduction of the barrier for penetration into the film in $\Delta F(z)$ (see Fig. 7), accompanied by a shift of S towards the surface of the water film.⁴ This shift into the region with the nonvanishing density of water molecules leads to the embedding of FA species into the edge of the water film, i.e., they become partially solvated with increasing temperature. On the other hand, H_2O species become integrated into the top layer (consisting of FA species only up to 120 K). Indeed, the observed appearance of the H_2O signal with increasing temperature, in particular in He II, is a consequence. However, according to MIES, FA remains located in the toplayer, i.e., any deeper penetration below the first bilayer

before the onset of desorption cannot be derived from the present results. Possibly, the formation of FA oligomers during the adsorption process, featuring strong lateral bonds, does not allow for the complete hydration of the FA structure.

Our findings can be compared with the results of a recent TOF-SIMS study on the solvation of FA on water ice.⁶ It is concluded that the evolution of the D_3O^+ yield, seen above 110 K, is an indication for the beginning hydration of the surface, and it is claimed that above 140 K complete hydration of the FA molecules leads to a top layer of pure water. The strong FA signal, as seen with MIES, seems to exclude the complete hydration of the FA species in the top layer, at least under the chosen experimental conditions. As was already pointed out in Ref. 6, we find no indication in the entire temperature range that FA deposition on water may lead to deprotonation, also not as a consequence of the FA solvation.

More information on the desorption process comes from the TPD spectra for FA on the water film. Numerous TPD studies were carried out on FA adsorbed on metals. The sublimation temperature is found between 145 and 190 K, while that for the desorption of the chemisorbed layer is between 160 and 210 K.³¹ Indeed, in auxiliary measurements (not shown³²) we have established that the sublimation peak from the FA multilayer occurs at 158 K while that for the desorption of the layer chemisorbed on tungsten takes place at 183 K. In addition, the sublimation for multilayered water on tungsten is seen around 163 K; an extra peak for monolayer (ML) desorption is not observed. Figure 5(a) presents TPD spectra for a FA layer (one ML) on a water film (five BLs) for the range from 80 to 200 K. H_2O (mass: 18) and FA (mass: 29) are recorded simultaneously. Desorption of both H_2O and FA sets in at 140 K. But while water has essentially desorbed at 170 K (desorption peak maximum at 162 K), relatively little FA has desorbed up to this temperature. Most of the FA desorbs above 170 K, in the range where FA chemisorbed on tungsten desorbs (see above). Because MIES indicates that FA remains the top layer in the entire studied temperature range, it follows from TPD that the H_2O desorption must take place through the FA adlayer. If in the initial phase of FA adsorption the chainlike structure of the FA crystal would form, most of the FA species would be expected to desorb as for the FA multilayer, and the TPD spectra should closely resemble those for multilayered FA on tungsten which is not the case.³²

The high temperature for FA desorption from water confirms the finding in paper I that the FA molecules in the adlayer experience both strong lateral interactions among themselves and, at the same time, are strongly interacting with the H_2O molecules of the underlying water film: the binding energy of a FA monomer on the water cluster is 73.7 kJ mol^{-1} while that for the removal of a H_2O molecule from the same cluster is only 37.2 kJ mol^{-1} . The binding energy of a FA monomer to $2\text{FA} + 6\text{H}_2\text{O}$ is $102.9 \text{ kJ mol}^{-1}$; that for desorbing the FA dimer from the same cluster is $102.8 \text{ kJ mol}^{-1}$. This is underlined by the different shapes of the TPD spectra observed on masses 29 (HCO) and 46 (HCOOH), i.e., by the extra emission seen on mass 29, but

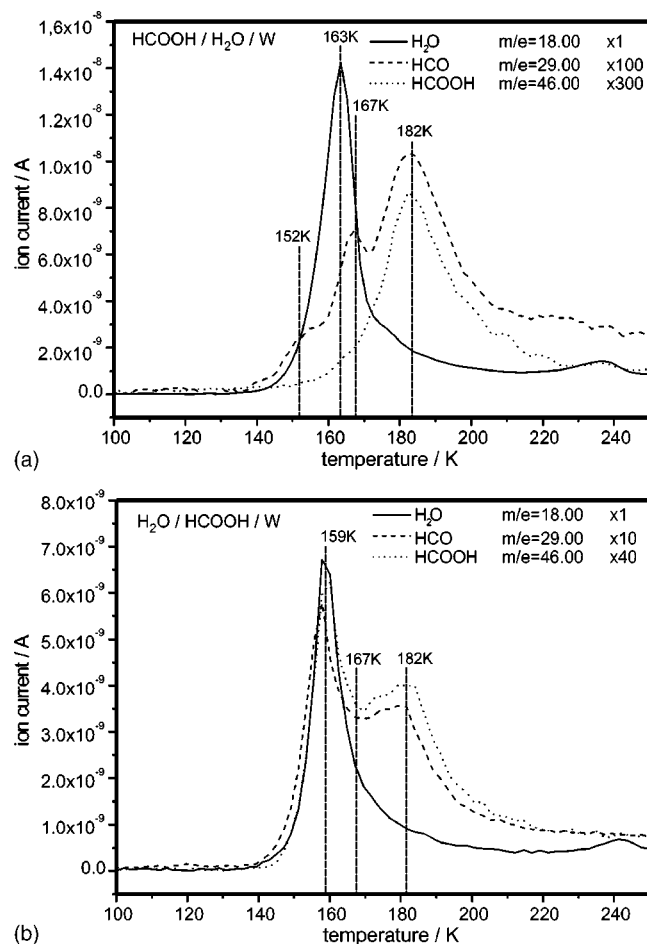


FIG. 5. Thermal desorption (TPD) traces for (a) FA (1 ML) on a water film (5 BL thick) and (b) H₂O on a FA film between 80 to 200 K. Mass 18: water; mass 29 and 46: HCO and HCOOH, respectively.

not on mass 46, in the region where water desorption takes place. This extra emission is also not seen during desorption from multilayered FA.³² We attribute it to the desorption of FA-water complexes which, under electron bombardment, will probably have a fragmentation pattern that is different from that of the FA monomers that desorb preferentially at higher temperatures.

C. Adsorption of H₂O molecules on formic acid (FA) films prepared at 80 K

Figure 6 (upper set of spectra) presents the MIES spectra collected during the deposition of H₂O molecules onto a FA film held at 80 K. The top spectrum is for the pure FA (about five MLs thick) on tungsten. The corresponding results for He II are presented in Fig. 7. FA films on tungsten display the same spectral features as seen for FA/water; in particular, peak (2) features the same shift against the corresponding peak in the gas phase spectrum. The FA spectra show no dependence on FA exposure, suggesting that on tungsten the condensation, probably in the form of islands,⁶ sets already in at the lowest exposures. According to MIES, a spectrum typical for a closed water film requires more than 8 L, an exposure four times as large as that for producing a closed FA layer on water (see Fig. 1). In He II, a spectrum typical for condensed water, featuring the diffuse 3a₁ feature, requires

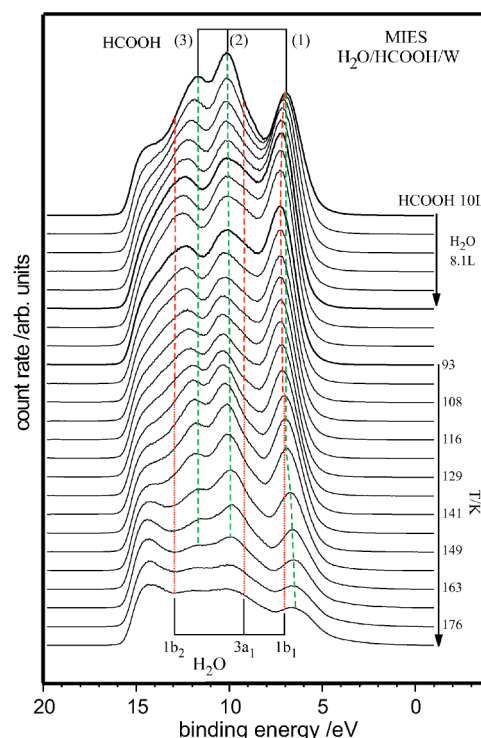


FIG. 6. Upper set of spectra: MIES spectra obtained during the deposition of an H₂O adlayer (4 BL thick) onto a FA film (5 ML) held at 80 K. Lower set of spectra: MIES spectra registered during the annealing of the H₂O/FA film to 200 K.

about 15 L. On the basis of these findings we suggest that even at 80 K the water molecules possess the ability to penetrate into the FA film surface, in contrast to what happens in the reverse case, FA on a water film. MIES shows that up to 8 L no water network has formed; instead, single H₂O molecules get associated with preexisting FA structures.

FA condenses in the form of chains formed by FA species connected via H bonds.^{8,31} For liquid aqueous FA solutions the following solvation model has been suggested: H₂O molecules become attached to FA chains via H bonding, leading to a H₂O:FA stoichiometry of 2 to 3:1.⁸ Evidence exists that a similar structure develops during annealing a film of FA and water coadsorbed at 100 K on Pt(111).⁸

In order to substantiate these remarks, we compare our MIES spectra with DFT calculations of I, carried out on the basis of this adsorption scenario: we assume that complexes formed from FA trimers and one H₂O molecule can serve as models for the structures that develop during the interaction of water with FA film. The optimized structures of such complexes are shown in Fig. 8 of I. In Fig. 8 the cluster DOS (not shown in I) of selected complexes (T1, T14, T16) is compared with the MIES results for small water exposures at which, according to MIES, a closed H₂O layer has not yet formed on the FA film. Indeed, good qualitative agreement exists, in particular, with the DOS for the cyclic structure T1.

The lower part of Figs. 7 and 8 shows the MIES and UPS(He II) results, respectively, obtained when annealing the film prepared in the upper part of the respective figures. At 145 K the 3a₁ feature has become sharp again, suggesting that no water network is existing anymore. Up to 150 K a considerable portion of both H₂O and FA has desorbed, in

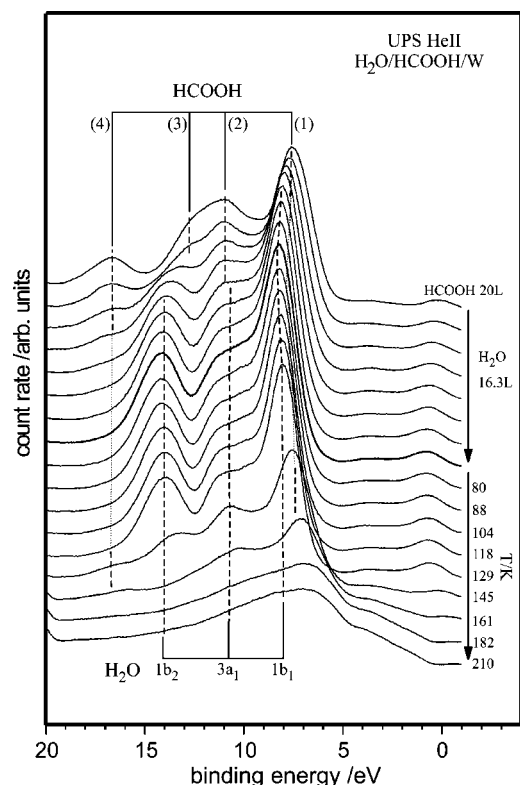


FIG. 7. Upper set of spectra: He II spectra obtained during the deposition of a H_2O adlayer (4 BL thick) onto a FA film (5 ML) held at 80 K. Lower set of spectra: He II spectra registered during the annealing of the water/FA film to 200 K.

particular, in the range of 140–150 K. MIES indicates that at higher temperatures only those FA species that are chemisorbed to the tungsten substrate remain. There is no indication, neither in He II nor in MIES, that part of the species remaining at the surface after all water has desorbed, i.e., between 150 and 180 K, would have suffered deprotonation as a consequence of their previous interaction with water.

More details on the desorption process can be derived from the TPD spectra of Fig. 5(b). In contrast to the reverse order of adsorption, a large desorption peak is seen in the TPD spectra on the FA masses ($m=29,46$ for CHO, HCOOCH , respectively) at the same temperature as for H_2O desorption ($T=158$ K), suggesting a correlation in the desorption process of both species. In contrast to water, FA shows a structure, peaked at 182 K, from the desorption of FA species chemisorbed to tungsten. In fact, the TPD spectra from water adsorbed on FA films resemble those from multilayered FA on tungsten.

Table V of I shows that H_2O can be attached to or incorporated into existing FA structures with a gain of energy comparable to that provided by a FA-FA interaction. This is due to the rather similar strength of the FA-FA and H_2O -FA hydrogen bonds (30 and 37 kJ mol^{-1}), respectively. Thus, a mixed structure can be expected to display TPD spectra similar to those for multilayered FA.

IV. SUMMARY

We have shown that MIES, in combination with UPS(He II), and supplemented by TPD, can be employed suc-

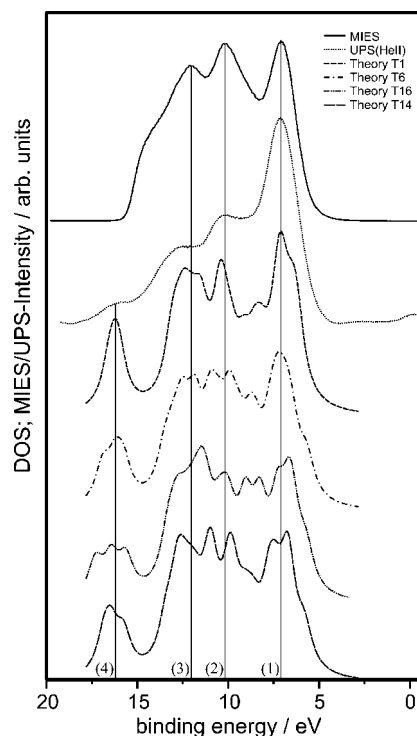


FIG. 8. DOS of H_2O -FA clusters, consisting of one H_2O and selected trimers (for the notation, see paper I). Comparison with the MIES and UPS spectra obtained at a water exposure of 2 L.

cessfully to investigate the processes between FA molecules and solid water. We have prepared FA-water interfaces at 80 K (FA layers on thin films of solid water and water adlayers on thin FA films) which were then annealed between 80 and 200 K. In order to interpret the spectra and to get information on the electronic structure of the FA-water system, they were compared with the DOS of DFT calculations on FA- H_2O complexes, reported in Ref. 14.

FA molecules are top adsorbed at 80 K. According to theory, H-bonded FA oligomers, oriented perpendicular to the water surface, are formed in the initial stage of FA exposure; they are themselves strongly H bonded to the H_2O molecules of the surface. Up to 120 K, the top layer consists of FA species only. Above 120 K, changes can be noticed in the MIES and He II spectra. They indicate that reorganization of the top layer takes place. Our interpretation is that, with increasing temperature, the adsorption sites of the FA species become located inside the edge of the water top layer. This “partial solvation” does not, however, lead to deprotonation. FA remains located in the top layer of the surface up to the desorption of the water film. During the sublimation of the H_2O (peak maximum at 159 K in TPD), FA species reach the tungsten substrate (peak maximum at 182 K in TPD).

For the reverse order of adsorption, H_2O molecules on FA films, the comparison of the DFT (Ref. 14) and MIES and He II results suggests that the interaction of H_2O with FA films does not in the initial phase of exposure, lead to the formation of an H-bonded water network at 80 K. Rather, the H_2O molecules become attached individually to the preexisting FA network by H bonding or become integrated into it.

From TPD we conclude that the hydrogen bond strength between FA and H₂O is rather similar to that between FA species.

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