

# Application of the metastable impact electron spectroscopy (MIES), in combination with UPS and TPD, to the study of processes at ice surfaces

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## Abstract

We report studies of the interaction (80–200 K) of atoms and molecules with ice films, deposited on tungsten, by combining photoelectron spectroscopy, UPS with HeI and II, metastable impact electron spectroscopy (MIES), and temperature programmed desorption (TPD). The focus is on the following issues:

- (1) Interaction of Na Atoms with films of solid NH<sub>3</sub> and CH<sub>3</sub>OH: the delocalization of the 3sNa electrons and their role in the deprotonation of ice molecules (seen for CH<sub>3</sub>OH, but not for NH<sub>3</sub>) is studied. DOS (density of states) information from density functional theory (DFT) is compared with the MIES spectra. It is concluded that the 3s electron, delocalized from its Na core and trapped between the core and surrounding molecules, triggers the CH<sub>3</sub>OH deprotonation; for NH<sub>3</sub>, Na dimers appear to play an important role in the delocalization process.
- (2) Interaction of salt (NaCl) and acid (HCOOH) molecules with H<sub>2</sub>O ice: neither NaCl nor HCOOH penetrate into the ice film during adsorption below 90 K. However, ionic dissociation of NaCl occurs as a consequence of the NaCl–ice interaction. At 105 K the solvation of ionic species becomes significant. The desorption of H<sub>2</sub>O from the mixed film takes place between 145 and 170 K; those species bound to Na<sup>+</sup> and Cl<sup>−</sup> are removed last. No dissociation of HCOOH is observed as a consequence of the interaction with ice. Partial solvation of formic acid species takes place above about 120 K whereby these species become embedded into the rim of the water film. However, no deeper penetration of formic acid molecules into the water film can be detected before H<sub>2</sub>O desorption becomes significant. The TPD spectra of HCOOH display structure, around 160 K, close to or coinciding with the sublimation temperature of water, and around 180 K, caused by species chemisorbed on the tungsten

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substrate supporting the ice film. The interaction of both NaCl and HCOOH with ice is discussed on the basis of qualitative free energy profiles.

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## 1. Introduction

The study of molecular surfaces, with water ice as an important example, and processes taking place thereupon, is of considerable interest for our atmosphere [1–5]: the processes taking place at the surface and in the near-surface region of icy particles can catalyze processes that are suspected to be responsible for the ozone “hole” formation over the polar regions. Under atmospheric conditions (180–250 K, relevant partial pressures) it has proved difficult to separate and study each of the elementary reaction steps which might be involved in surface-induced transformations (adsorption, solvation, reaction and desorption processes).

At low temperatures, water tends to condense in the form of crystalline films. However, the mobility required for their formation does not exist anymore below 140 K. At these temperatures the condensation takes place as amorphous solid water. It can, to a certain extent, be considered as a substitute for liquid water, having however a much lower vapor pressure. This makes amorphous solid water (and the study of reactions with it) accessible to the application of sophisticated surface analytical techniques. Hence, such studies supplement those on liquid water which is barely accessible for this approach [6].

Several surface-sensitive methods have been applied to the study of molecular surfaces: in reactive ion scattering (RIS), low-energy (10–30 eV, typically)  $\text{Cs}^+$  ions impinge onto the surface. Their impact induces desorption of molecules or their fragments from the surface, and, in the same event,

the  $\text{Cs}^+$  picks-up desorbed molecules in a reactive scattering event. Mass analysis of the  $\text{Cs}^+$ –molecular cluster allows the identification of the desorbed molecules. Low-energy SIMS (20–100 eV, typ.) can be performed simultaneously with RIS, using the same  $\text{Cs}^+$  beam, giving, in particular, information on ions preexisting on the surface [7,8]. When applying SIMS with light ions ( $\text{He}^+$ ) in the low-keV region care has to be taken to disentangle the ionic signals coming from the surface and the near-surface bulk [9,10]. RIS/SIMS, appears to be well-suited to the study of the first step in the interaction of an adsorbate with a molecular surface, ices in particular, where typically the formation of the H-bonds between the adsorbate and the molecules of the ice substrate takes place. Not only can the chemical composition of the near-surface region be studied, but also the nature of the bonding of the adsorbates. It has been demonstrated that the hydration of molecules, as  $\text{NH}_3$  and formic acid, together with the thermally activated proton exchange, can be explored successfully by applying temperature-programmed RIS/SIMS [9,10].

Despite its large potential, surface-sensitive vibrational spectroscopy, employing HREELS for this purpose, has not been applied to molecular surfaces to a great extent. The application of HREELS, in combination with TPD, to the study of the codeposition of water and formic acid on Pt(111) between 100 and 200 K may serve as an example: it was demonstrated that water has the capability to participate in H-bonding in the formic acid network [11]. In general, HREELS is capable to identify the active groups involved in

the adsorbate interaction with the molecular surface, to give information on the orientation of the adsorbate molecule at the surface, to identify the groups active for adsorbate bonding, and to establish deprotonation reactions as those taking place during the ionic dissociation of acid and salt molecules. Thus, as RIS, HREELS appears to be ideally suited to furnish information on the initial steps of process sequences, prior to an eventual incorporation of molecular species into the bulk of the molecular surface.

This contribution reports studies of the interaction of atoms and molecules with ice surfaces (water, methanol, ammonia) by combining photoelectron spectroscopy, UPS with HeI/II, and metastable impact electron spectroscopy (MIES). With MIES, in combination with UPS, information is obtained on the species that terminate surfaces, without provoking their removal by particle impact. Charge exchange processes, of the Auger-type, are initiated by the interaction of metastable He-atoms with the surface under study; they take place well in front of the surface, and, consequently, the resulting electron emission is sensitive to the DOS of the outermost layer of the surface, including the contribution of the adsorbed species. Moreover, in contrast to UPS, the probability for electron ejection depends only on the density of states (DOS) of the initial states at the surface, prior to the Auger process [12]. Thus, the MIES spectra produce a rather direct image of the surface DOS. Since the metastables approach the surface with near-thermal kinetic energy (60–100 meV), this technique is non-destructive and ultimately surface sensitive (see [13,14] for more detailed introductions into MIES and its various applications in molecular and surface spectroscopy). MIES gives information on the electronic structure of the species that terminate the surface, as well as on its modification by the chemical environment of these species, by lateral interactions between the adsorbed species as well as by their H-bonding to species of the underlying molecular surface, for example. Being exclusively surface sensitive, MIES gives direct information on solvation processes when studying the disappearance of the MIES signals that characterize the species becom-

ing solvated. By performing temperature-programmed MIES, or by combining MIES with TPD, information can also be obtained on the bonding of surface species.

## 2. Experimental remarks

Experimental details can be found elsewhere [15–19]. Briefly, the apparatus is equipped with a cold-cathode gas discharge source for the production of metastable  $\text{He}^*(^3\text{S}^1\text{S})$  ( $E^* = 19.8/20.6$  eV; intensity ratio 7:1) atoms with thermal kinetic energy and HeI photons ( $E^* = 21.2$  eV) for ultraviolet photoelectron spectroscopy (UPS). The spectral contributions from metastables and photons are separated by means of a time-of-flight technique. Electrons emitted in the direction normal to the surface are analyzed. A second photon source is at our disposal providing HeI and HeII (40.8 eV) photons.

The onset of the spectra at low kinetic (high binding) energies occurs at the work function of the sample; the variation of the onset of the spectra with exposure gives directly the exposure dependence of the surface work function.

The TPD experiments are carried out using a differentially pumped quadrupole mass spectrometer. The TPD housing is connected via a small opening to the main chamber and is pumped separately via a turbomolecular pump. 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 60 s, typically) is seen about 15 K below the desorption peak maximum temperature, typically.

The sample can be cooled with  $\text{LN}_2$  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  $\pm 10$  K. The surface was exposed to water by backfilling the chamber. The thickness of the ice films and the amount of species adsorbed there upon is estimated by combining TPD with MIES/UPS.

### 3. Results and discussion

#### 3.1. Interaction of Na atoms with ice films: the role of solvated Na3s electrons

Previously, we studied the interaction of Na with films of amorphous solid H<sub>2</sub>O and CH<sub>3</sub>OH by combining metastable impact electron spectroscopy (MIES) and UPS [5,20–22], focusing on the role played by the 3sNa electron for the deprotonation process. The comparison with DFT cluster calculations suggests that the 3sNa electron becomes delocalized from its Na<sup>+</sup> core and is trapped between the Na<sup>+</sup> and surrounding “solvent” molecules; it plays a key role in their deprotonation, leading to the formation of hydroxyl (OH) and methoxy (CH<sub>3</sub>O) species [23,24]. Methoxy species are of interest considering their role in the methanol conversion into dimethyl ether (DME) or formaldehyde which represent important routes to non-pollutant fuel production [25–27].

As an example, Fig. 1 shows the comparison of the MIES and DOS results prior (a) and after (b) the Na-induced deprotonation of CH<sub>3</sub>OH [22,24]. Prior to the Na-induced reaction both DOS and MIES display the CH<sub>3</sub>OH features M<sub>1</sub> to M<sub>5</sub>, and peak Na(3s), caused by the presence of delocalized 3sNa electrons at the film surface. After the reaction additional structure develops, caused by the ionization of the 2e, 5a<sub>1</sub>, 1e MOs of CH<sub>3</sub>O species. On the other hand, Na(3s) has disappeared because 3sNa became involved in the deprotonation reaction. Thus, calculations and experiment both underline that the delocalized 3s electron triggers the formation of CH<sub>3</sub>O.

Fig. 2 presents MIES results for the interaction of Na with a NH<sub>3</sub> film held at 90 K [28]. The top spectrum is for the NH<sub>3</sub> film (2 layers thick) prior to Na exposure. The upper set of spectra is obtained during the Na exposure. The lower set of spectra displays the spectral changes observed during film annealing in the indicated temperature range. According to [29] and to own DFT results the two broad features observed at  $E_B = 6.5$ ; 11.3 eV in the MIES spectra of the ammonia film are due to the ionization of the 3a'(n<sub>N</sub>) and le'(π(NH<sub>3</sub>)) ammonia MOs, respectively. The features shift as a consequence of the Na-induced de-

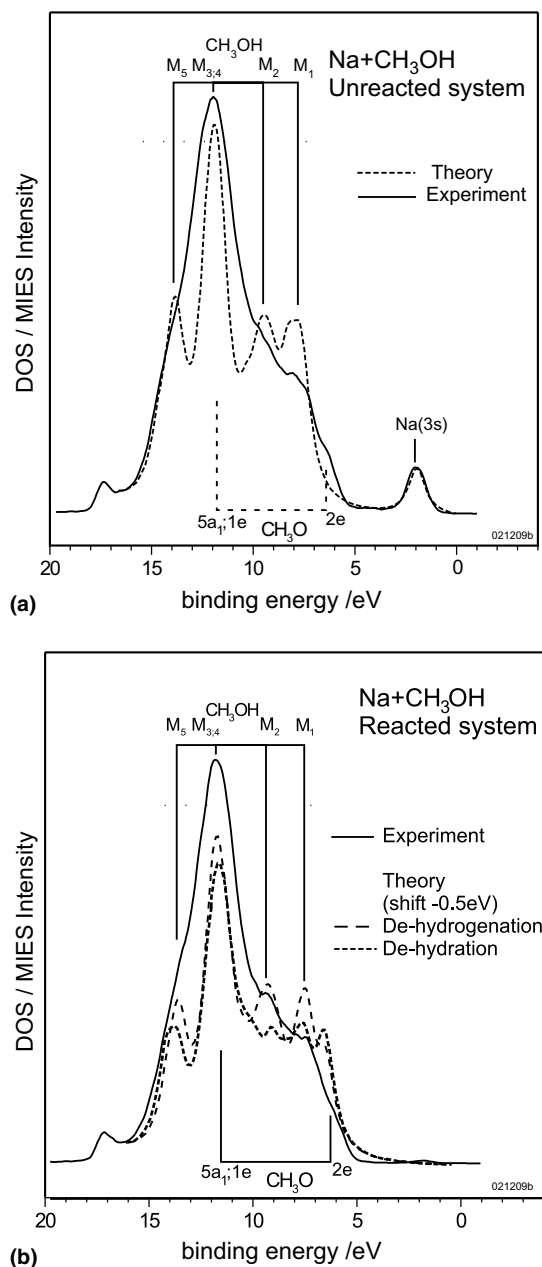


Fig. 1. DOS of Na<sub>2</sub>(CH<sub>3</sub>OH)<sub>10</sub>-clusters (a) before and (b) after their reaction, and comparison with MIES results (heavy spectrum).

crease of the surface work function. With increasing Na exposure three Na-induced structures (1)–(3) appear, located at 1.3, 2.3 and 4.5 eV with respect to the Fermi level ( $E_B = 0$  eV).

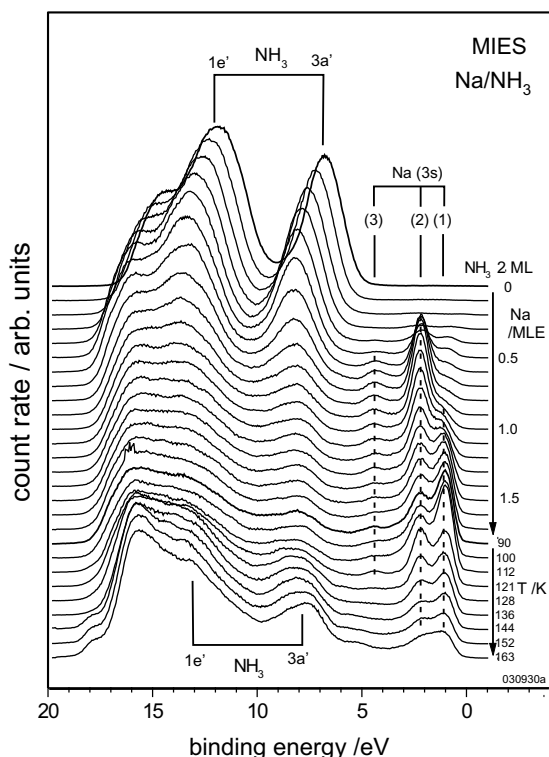


Fig. 2. MIES spectra for the adsorption of Na on solid ammonia (three layers) prepared on tungsten (80 K) (upper set of spectra), and the spectral changes resulting from annealing the Na/NH<sub>3</sub> system over the indicated temperature range (lower set of spectra) (see text for the acronyms employed in the figure).

By comparison with the corresponding feature for Na adsorption on metals and semiconductors, we attribute (1) to 3sNa ionization from neutral Na atoms, probably aggregated in patches with metallic-like properties. As for the interaction of Na with water and methanol ice [21–24] and supported by DFT cluster calculations [28], we attribute (2) (at 2.3 eV) to delocalized 3sNa electrons. When heating from 90 K to 163 K, 3a'NH<sub>3</sub>, (2) and (3), but not (1), pass through maxima around 120 K, and finally decay with temperature. According to MIES, NH<sub>3</sub> has practically sublimated from bare tungsten at 130 K; due to its interaction with Na, sublimation is delayed by at least 30 K.

Comparison of MIES with DFT cluster calculations [28] shows general agreement in the positions

of the observed main features, namely those from the ionization of the NH<sub>3</sub> MOs and the peak (2), attributed to 3sNa delocalization (2.3 eV). Peak (1), attributed to emission from 3s electrons localized at the Na core, is not reproduced by the chosen model; neither do the calculations reproduce structure (3) centered around 4.5 eV. The good agreement noticed otherwise between theory and experiment suggests that (3) may not be a feature of the DOS of the system (see below). The inspection of the results without and with Na confirms that, as under liquid conditions, no Na-induced reaction takes place.

In order to arrive at a convincing explanation for the origin of (3), we anticipate that partially ammoniated Na<sub>2</sub> species are produced during the Na exposure onto the solid ammonia film. This may happen quite naturally by attaching an additional Na atom to an existing Na(NH<sub>3</sub>)<sub>n</sub> cluster. We assume that simultaneous excitation and ionization of the ammoniated Na<sub>2</sub> takes place in MIES during its ionization in the Auger de-excitation process, and is responsible for the satellite peak. Hereby, a transition takes place to excited states of the ammoniated Na<sub>2</sub><sup>+</sup> system during the ionization process. This process sequence was studied for ammoniated Na<sub>2</sub><sup>-</sup> anions by combining first-principles calculations with photoelectron spectroscopy [30]; here, spectral contributions are seen which correspond to transitions from the ground state of ammoniated Na<sub>2</sub><sup>-</sup> to excited states of ammoniated neutral Na<sub>2</sub> – i.e. to electron detachment accompanied by excitation of the cluster.

### 3.2. Interaction with ice: NaCl and formic acid

The understanding of the interaction of salts and acids with ice surfaces is of interest in various fields, ranging from biological systems to catalysis and environmental sciences.

Hydrated NaCl particles from the ocean and also from some volcanos may become part of the atmosphere or deposited on the ocean shore. In both situations they play an important role as providers for chloride species and/or catalysts for pollution reactions as f.i. those involving (N–O)-compounds [31,32]. The MIES and UPS results obtained for a NaCl-exposed film of water ice,

held at 82 K (abbreviated by NaCl/H<sub>2</sub>O) can be summarized as follows [33]: a closed NaCl layer can be produced on ice at 82 K. When heating beyond 110 K, the spectral features of water reappear, constituting the dominant structures in the spectra between 120 and 140 K; clearly, water species penetrate deep enough into the NaCl top layer to become accessible to MIES. Around 145 K water desorption becomes significant as signaled by the renewed rise of Cl(3p), concurrent with the decrease of the water features; around 170 K, according to MIES, all water has desorbed, and Cl(3p) is seen only. The sharp Cl(3p) peak, found by us in aqueous environment, can be considered as evidence for ionic dissociation during NaCl adsorption [33]. This is in full accord with the findings of RIS where dissociative adsorption of NaCl on ice, followed by the formation of Na<sup>+</sup>–water clusters, was found at 100 K [7]. Support for cluster formation comes also from the study of the ions emitted during ESD when NaCl and water were coadsorbed on a condensed Ar substrate (35 K) [9].

Fig. 3(a) displays a qualitative free energy profile  $\Delta F(z)$  for NaCl interacting with ice, suited to explain our results (for a systematic discussion of  $\Delta F(z)$  profiles see [34]. Furthermore, we consult the free energy profile for the interface between Na<sup>+</sup> (Cl<sup>−</sup>) and water [35] and those for the related system HCl/ice [36]. We propose that  $\Delta F(z)$  possesses two minima, one for adsorption at a “surface” site, denoted by  $S_1$ , and another, denoted by  $S_2$ , for adsorption at a “solvent-separated” site. At 80 K only  $S_1$ , located in front of the surface, is occupied; the barrier for the transition  $S_1 \rightarrow S_2$  cannot be surmounted. As discussed for HCl/ice [36], the details of  $\Delta F(z)$  will depend on temperature considering of the decrease of the entropic contribution with rising temperature (due to the increase in the mobility of the water molecules). As a consequence of the increase in disorder of the water film, the barrier between  $S_1$  and  $S_2$  becomes reduced or even disappears, and the transition  $S_1 \rightarrow S_2$  can take place – i.e. the Cl<sup>−</sup> (Na<sup>+</sup>) ions become embedded into the water film, completing their solvation shell.

The capability of ice surfaces to promote acid dissociation is still a controversial issue. Free en-

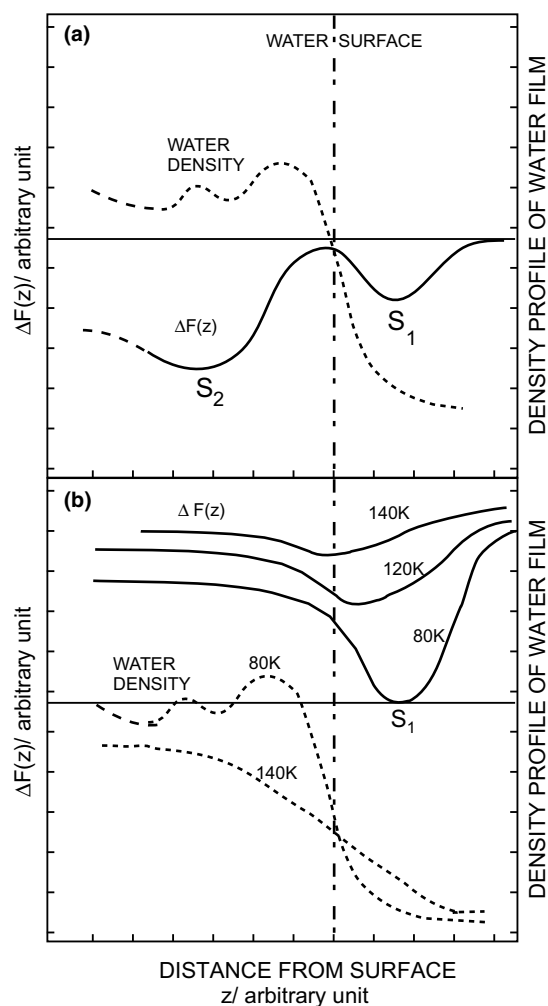


Fig. 3. Free energy profiles (qualitatively) for the interaction of (a) NaCl, and (b) HCOOH with ice as a function of the distance of the molecules,  $z$ , from the ice surface. The density profile of the water film is also indicated.

ergy profiles, obtained from classical MD calculations, demonstrate that formic acid (FA) species are strongly trapped at the ice surface at 250 K [37]. The results indicate that partial solvation takes place during the acid adsorption at that temperature – i.e. the adsorption sites are located within the surface layer. 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.



We have collected MIES, HeII and TPD spectra during the exposure of an ice film to FA at 80 K [38], followed by the annealing of the FA–water films. We find that FA adsorption at 80 K produces MIES and HeII spectra that are characteristically different from those in the gas phase [39] as far as the energetic distance between the observed spectral features is concerned. As DFT cluster calculations show, this can be attributed to the formation of lateral bonds between FA molecules [40]. There is no indication of dissociation as a consequence of FA interaction with ice, even not during the annealing procedure. Fig. 4 presents the analysis of the electron spectra and TPD results [38]; displayed are, as a function of the annealing temperature, the TPD spectra of H<sub>2</sub>O

(mass: 18) and FA (mass: 29 and 46) and the contributions of FA and water to the MIES (a) and HeII (b) spectra in arbitrary, but comparable units. The main conclusions are as follows: according to MIES, a closed FA layer is present at 2 L; this is concluded from the fact that, from this exposure on, the H<sub>2</sub>O features, in particular 1b<sub>2</sub> which is separated from any FA spectral features, have become rather weak. We find a take-up rate comparable to that for tungsten, and, therefore, conclude that no penetration of FA takes place into the water film at 80 K. During annealing, as judged from the MIES spectra, the toplayer remains mainly composed by FA species, although a rise of the water features can be noticed between 120 and 140 K. The maximum of the H<sub>2</sub>O desorption occurs at 163 K. The TPD spectrum of FA displays a pronounced peak at 183 K, also found for FA on tungsten and caused by the desorption of chemisorbed species; it saturates at an intensity which corresponds to a completed chemisorbed FA layer. All FA species, not in contact with W, contribute to the emission between 140 and about 170 K, noticed, in particular, on mass 29. MIES and HeII results indicate that above 150 K H<sub>2</sub>O and FA have both desorbed to a large extent. Weak FA features can however be seen up to about 170 K. Note that the decay of the intensity in MIES/HeII and the corresponding structures in TPD are shifted by about 20 K, typically. This is due to the longer data collection time required for MIES and HeII. Details of the results, as in particular the temperature dependence of the TPD fragmentation pattern, will be discussed in a forthcoming publication. The comparison of the MIES spectra with DFT cluster calculations suggests that small, top-adsorbed FA oligomers interact with the ice film [40]. We propose that the structure, seen in the TPD spectra between 140 and about 170 K, is caused by the desorption of FA–H<sub>2</sub>O aggregates (152 K) while the peak at 167 K, also seen for FA/W, is due to the desorption of FA species that are not involved in the interaction with H<sub>2</sub>O.

The qualitative  $\Delta F(z)$  profiles presented in Fig. 3(b) can account for the results summarized in Fig. 4; they are inspired by the results for FA interacting with an ice film of proton-ordered geometry

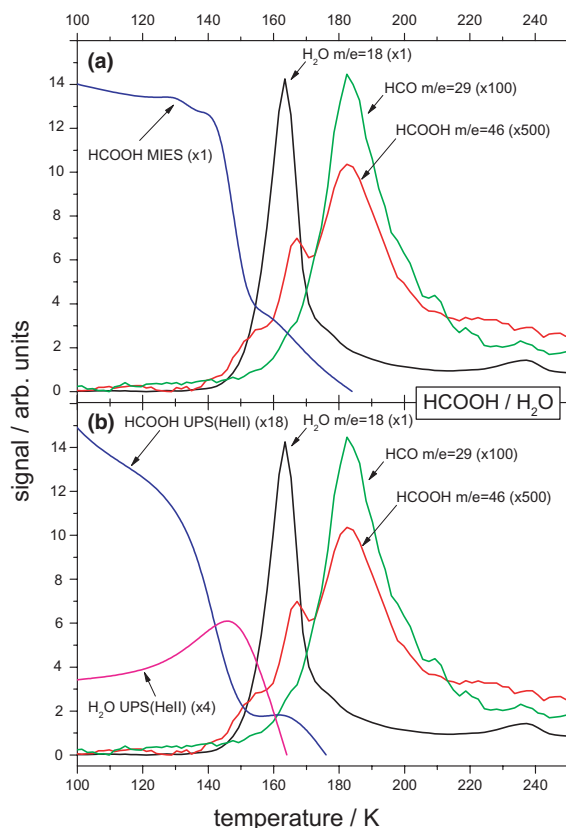


Fig. 4. Thermal desorption (TPD) traces for FA (1 ML) deposited on an ice film (5 BL) at 80 K. Also shown are the contributions of FA and H<sub>2</sub>O to the MIES spectra (a) and HeII spectra (b).

at 250 K [37]. We propose that above 120 K the well  $S_1$  becomes increasingly shallow, i.e. the height of the barriers for penetration into the bulk and for desorption into the vacuum both decrease. The reason is that both the potential energy and entropy contributions to  $\Delta F(z)$  depend on the water density via the coordination number experienced by the FA species. The lower part of Fig. 3(b) indicates how the density profiles of water and FA may change with temperature. Above 140 K the two barriers have become low enough to allow, on the one hand, for FA desorption into the vacuum, and, on the other hand, for FA penetration into the film. When reaching the tungsten substrate, FA species form a comparatively strong bond with the substrate that accounts for the TPD peak at 183 K. We do not think that FA species spend long time in the water film; rather, all species, not chemisorbed at the substrate, will desorb into the vacuum on a nanosecond time scale [34]. Beyond about 140 K a discussion in terms of  $\Delta F(z)$  profiles cannot be made because, according to both TPD and MIES/He, both FA and  $H_2O$  desorb.

#### 4. Summary

The present study, combining metastable impact electron spectroscopy (MIES), UPS, and TPD, gives insight into the interaction of atoms and molecules with ice ( $H_2O$ ;  $CH_3OH$ ;  $NH_3$ ) films at temperatures between 80 and 200 K. For Na emphasis was on the role played by the Na3s electron for the reaction between Na and the ice film. First-principles DFT calculations, in good qualitative agreement with the MIES data, predict that the 3s electron is delocalized from its  $Na^+$  core and trapped between the core and surrounding solvent molecules. Calculations and experiment both underline that the delocalized 3s electron triggers the Na– $CH_3OH$  dissociation producing methoxy ( $CH_3O$ ) species. No Na-induced reaction occurs for  $NH_3$ ; here, the role of Na dimers in the delocalization process could be studied.

Two examples are presented for the interaction of molecules with water ice: for NaCl/ $H_2O$  the solvation of the  $Na^+$  and  $Cl^-$  species resulting from

the dissociative adsorption at 80 K was studied. It is found that the solvation is complete around 120 K. No formic acid ( $HCOOH$ ) dissociation is observed as a consequence of its interaction with ice. Partial solvation takes place above 120 K because  $HCOOH$  becomes embedded into the rim of the ice film; no deeper penetration of the species into the water film can be detected. The TPD spectra of  $HCOOH$  can be separated into two regions, up to about 165 K, coinciding with the region where the sublimation of water takes place, and between about 170 and 200 K, where  $HCOOH$  species chemisorbed on the tungsten substrate desorb. For both NaCl and formic acid the interaction with ice is discussed on the basis of qualitative free energy profiles.

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