

Sodium Interacting with Amorphous Water Films at 10 and 100 K

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In the present study, we compare the adsorption of Na on amorphous D₂O ice films, held at 10 and 100 K. OH, D₂O, and Na are easily distinguished by their characteristic signatures in metastable impact electron spectroscopy (MIES). It is found that at 10 K substrate temperature the donation of 3sNa charge to the ice film, which is regarded as a precursor for water deprotonation, is significantly reduced relative to 100 K. This observation is discussed on the basis of recent theoretical work, suggesting that a rearrangement of the water molecules at the outermost water surface is the prerequisite for hydration/solvation of the 3sNa electron in the water ice bulk. The MIES spectra, showing spectral features from both OH and D₂O, can be interpreted as reflecting the composition of the Na–water complexes in the near surface region. The relative intensity of the OH and D₂O features is the same for 10 and 100 K. This finding suggests that two different sites for Na adsorption exist, one on the perfect water network and the other at OH dangling bond sites whereby, at 10 K, only the latter one leads to deprotonation of D₂O. Finally, charge exchange phenomena observed when applying electron spectroscopies to ice films are discussed.

Introduction

Because of its general importance for heterogeneous catalysis, environmental research, and astrophysics, the chemistry of water ice films has attracted considerable attention recently.^{1–6} For making the rich chemistry of bulk water accessible to standard surface science techniques, water is commonly prepared as an ultrathin film on a supporting substrate at temperatures below 140 K. To gain insight in the chemistry of thin water films, these experiments have been concentrated on thin amorphous water ice layers, the molecular structure of which is, in contrast to crystalline ice, likely more similar to liquid water. Nonporous amorphous water films can be prepared by condensing water on a substrate, incommensurate with crystalline ice, held at a temperature between 110 and 140 K.⁷ On the so-prepared substrate, additional species can be deposited, to study their aqueous chemistry.

In the present work, we deposited Na onto amorphous D₂O films supported on Pt(111). It is established (see refs 8–10) that water molecules can, depending on the substrate temperature, react spontaneously with coadsorbed sodium, forming hydroxide species, similar as in the liquid phase. In a first step, alkali metal atoms donate their outer s-electron to adjacent water molecules.^{8–10} The so-formed complex, consisting of an ensemble of water molecules accommodating the s-electron of an associated alkaline ion, is thought to act as a precursor for a

chemical reaction. In the final step, proton diffusion results in the formation of Na⁺ and OH species. It has been shown¹¹ that it is possible to inhibit an immediate reaction between D₂O and coadsorbed Na on a water ice layer held at a temperature of 100 K. Increasing the substrate temperature while monitoring the surface electronic structure, then, makes single steps in the Na–water reaction accessible. Previously, in comparable experiments, electron spectra have been recorded at various temperatures, down to about 80 K.^{12–15}

While Na hydration/solvation is well-established at $T > 130$ K, it is not yet clear to which extent Na can donate charge or even penetrate into the water film at lower temperatures. It has been shown that the water environment can alter the reactivity by stabilizing reaction intermediates,¹⁶ and therefore the question about the ability of amorphous water layers to hydrate electrons from alkaline atoms and alkaline ions even at $T < 100$ K should be addressed. In the present study, we will compare the electronic structure of Na adsorbed onto amorphous D₂O films, held at a temperature of 10 and 100 K, respectively. Furthermore, to facilitate discrimination between the chemistry which occurs in the water environment and at the surface of the water film, the adsorption onto films with varying thicknesses as a function of the substrate temperature will be discussed. As electron spectroscopic techniques, X-ray photoelectron spectroscopy (XPS) and metastable impact electron spectroscopy (MIES) have been employed. For the investigation of alkali metal adsorption, the specific merits of MIES are twofold:¹⁷ (i) its ability to reveal changes in the surface density of states introduced by the adsorbed species and (ii) its high sensitivity, as compared to UPS, for the detection of the charge density of the alkali s-electron. XPS, in contrast, provides information about the substrate composition in the surface near region.

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Experimental Section

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure 2×10^{-10} mbar) equipped with facilities for surface characterization, X-ray photoelectron spectroscopy XPS, ultraviolet photoelectron spectroscopy UPS (HeI, HeII), and metastable impact electron spectroscopy MIES employing metastable He atoms (He^{*}). The apparatus was located at NIMS Advanced Materials Laboratory, Tsukuba, Japan. More details on MIES and its various applications can be found elsewhere.¹⁸

Electron spectra were acquired with incident metastable beam 45° with respect to the surface normal in a constant pass energy mode using a hemispherical analyzer. The analyzer, operated at 20 eV pass energy, has an energy resolution of approximately 300 meV. The Fermi energy E_F in the MIES spectra is defined as the Fermi edge of the Pt(111) substrate determined from UPS but shifted on the kinetic energy scale by the difference between the photon energy and the asymptotic excitation energy of He^{*}. In the spectra, all binding energies are referenced to E_F . Since the metallic Pt substrate and the analyzer are in electrical contact, the Fermi energy appears, independent of the substrate work function, at a constant position in the spectra. Then, an additional biasing of the sample (40 V, negative on the sample) permits the work-function change of the surface to be measured directly from the high-binding-energy cutoff of the spectra.

The Pt(111) substrate was mounted on a sample holder which can be cooled to 10 K by means of a closed-cycle He refrigerator. The substrate was cleaned by repeated He⁺ sputtering and annealing to about 1200 K. Water films have been prepared by backfilling the vacuum system with high-purity D₂O from Fisher Scientific (partial pressure 1×10^{-7} mbar) at a substrate temperature of 110 K. As already introduced, this procedure ensures the formation of nonporous, amorphous water ice films.⁷ After preparation of a water ice film, the substrate has been cooled to the desired temperature, that is, 100 and 10 K, respectively, followed by a constant sodium exposure. In the present setup, a water exposure of 3.25 Langmuirs would form one geometric water bilayer on the metal substrate held at a temperature of 100 K. Na was deposited onto the surface using a SAES Getters source.

Results

Figure 1 compares two sequences of MIES spectra taken during Na exposure to a water film (thickness approximately seven D₂O bilayers) held at a temperature of 10 K (a) and 100 K (b), respectively. Because of the insulating character of the D₂O covered Pt surface, the MIES spectrum is dominated by contributions from Auger deexcitation of He^{*}, whose energy balance is similar to that of UPS.¹⁸ The Na exposure increases linearly toward the bottom spectrum. Both sequences are made with the same deposition rates as confirmed by XPS (see discussion of Figure 3).

With increasing Na exposure, three major changes in the electron spectra are noteworthy: (i) a lowering of the overall intensity of the water bands and (ii) at 5.9 eV, just above the highest occupied water molecular orbital (HOMO) 1b₁ and (iii) at the metal substrate Fermi edge (E_F) the appearance of new features assigned as 1 π and Na(3s), respectively. The prominent Na(3s) band, being the only spectroscopic feature directly associated to Na adsorption, originates from the ionization of the 3sNa state.¹¹ Apart from the prominent Na(3s) band, a broader structure, assigned as $\hbar\omega_{SP}$, develops in the Na(3s) region, which previously has been attributed to a collective oscillation of electrons (plasmon) in the alkali s-like surface band.¹⁹ The attenuation of the water bands between the high-

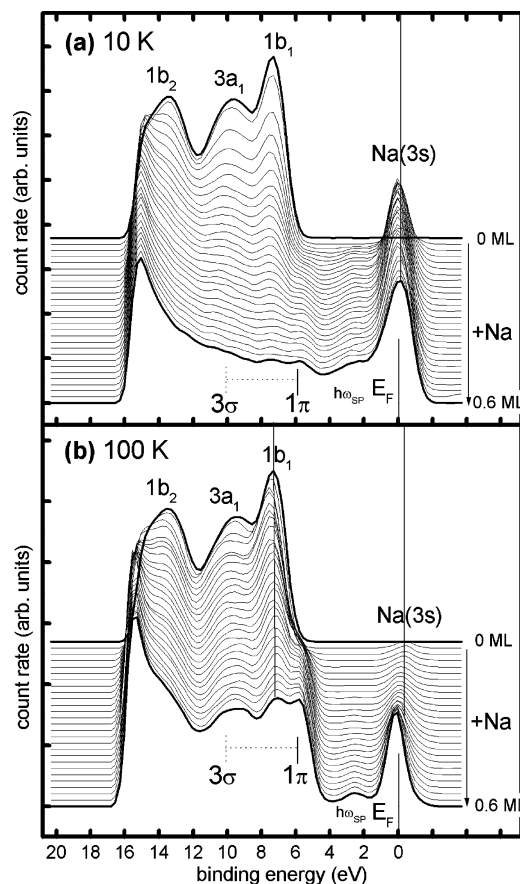


Figure 1. Sequence of MIES spectra taken from Pt(111) supported water films (seven bilayers thickness) held at a temperature of (a) 10 K and (b) 100 K, as a function of the Na coverage. The top spectra correspond to the clean water surface. Emission from the D₂O valence band states is assigned as 1b₁, 3a₁, and 1b₂.³⁴ The Na coverage increases linearly toward the bottom. The bottom spectra correspond to water films covered by approximately 60% of a closed packed Na monolayer. Straight lines mark the positions (peak maxima) of the D₂O HOMO, as taken from the clean water film, and the Na(3s) band at lowest Na coverage.

binding-energy cutoff of the spectra and 5 eV, seen when increasing the Na coverage, is due to a subsequent buildup of a sodium adlayer covering the water surface and, bearing in mind that we have a limited flux of He^{*} impinging the surface, is due to a subsequent increase of the probability for He^{*}-quenching by Na(3s) charge density. We assign the feature denoted by 1 π to the formation of a hydroxide-like species at the outermost water surface, since a corresponding feature which unambiguously can be attributed to a Na- and K-bound OH evolves from the 1 π molecular orbital at elevated substrate temperatures.^{12,13} 1 π is, thus, indicative for the Na-induced deprotonation of D₂O. With this in mind, the expected position of the hydroxyl 3 σ emission at ~4.1 eV higher binding energy^{20,21} is indicated in the figure. The intensity ratio 1 π to 3 σ as seen by MIES is typically 3:1. Therefore, the 3 σ emission is masked by the still strong 3a₁ emission from D₂O. The prominent structure seen at 16 eV is believed to be dominated by secondary electrons and electrons backscattered from the underlying substrate. Because details of the peak shape are not well understood at present, we will not base any conclusion on it in the following.

Major differences are seen in the coverage dependence of the Na-induced feature Na(3s) (Figure 2): clearly, the Na(3s) band develops much faster in a than in b. Furthermore, its final intensity, relative to the water 1b₁ band, is higher in a. On the

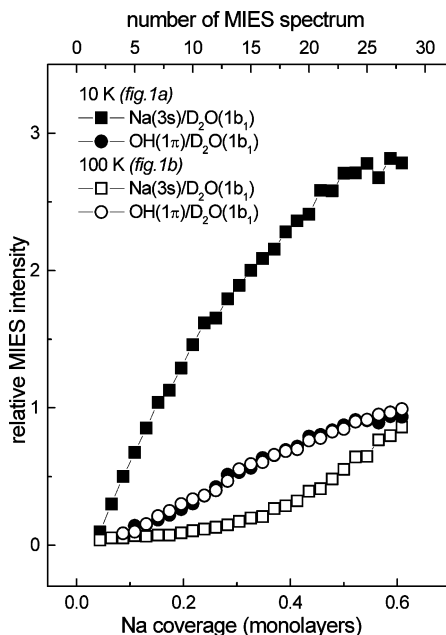


Figure 2. MIES intensities (relative to $D_2O(1b_1)$) of the $Na(3s)$ and $OH(1\pi)$ bands versus Na coverage, as extracted from Figure 1.

other hand, the evolution of the 1π feature relative to $1b_1$ is very similar for both temperatures. In this context, it is important to recall that toward higher Na coverages more obvious attenuation of the water bands in Figure 1a is due to an enhanced accessibility of the $3sNa$ charge density for the He^* deexcitation: in a, the relatively steep increase of the $Na(3s)$ intensity directly correlates with the fast attenuation of the water bands at the onset of Na dosage.

The differences observed at 10 and 100 K suggest that for a given Na dosage the relative amount of $Na(3s)$ charge density accessible for an impinging He^* is at 10 K significantly higher than at 100 K.²² This observation can be attributed to a reduced Na diffusivity into the water bulk at 10 K. Then, the Na concentration at the surface increases faster versus Na exposure in a, resulting in an increasing probability for neutral adsorption.

Figure 3 compares the XPS $O(1s)$ and $Na(1s)$ narrow scans taken from the surfaces represented by the bottom spectra in Figure 1. From tabulated XPS $O(1s)$ and $Na(1s)$ atomic sensitivity factors,²³ we calculate a Na to O ratio of about 0.3 in the surface near region. With an XPS information depth of about 10 nm, a Na coverage of 50–70% of a closed packed Na-layer, that is, 0.5–0.7 monolayers (ML), is estimated for the bottom spectra of Figure 1. We do believe that Na adsorbs on the water film, at least at 10 K substrate temperature. Therefore, the electrons emitted from the sodium will suffer little scattering. Electron intensity from the underlying water film might be attenuated somewhat stronger. Within this respect, the given Na coverage must be understood as an upper limit with, however, the lower limit within the error bars given.

At 10 K, a clearly broadened $Na(1s)$ emission is observed which can be attributed to neutral Na species. However, no significant difference is seen in the $Na(1s)$ intensity relative to that of $O(1s)$. In this context, we have investigated the ability of sodium to penetrate the water bulk at varying temperatures.

In Figure 4, the relative XPS intensities of the $Na1s$ and $O1s$ core level states, as obtained from an adsorbate system prepared as in Figure 1, are plotted as a function of the substrate temperature. For traces a, b, and c, the water layers have been prepared in the same fashion as in Figure 1, that is, by exposing the supporting Pt substrate held at a temperature of 110 K to 6,

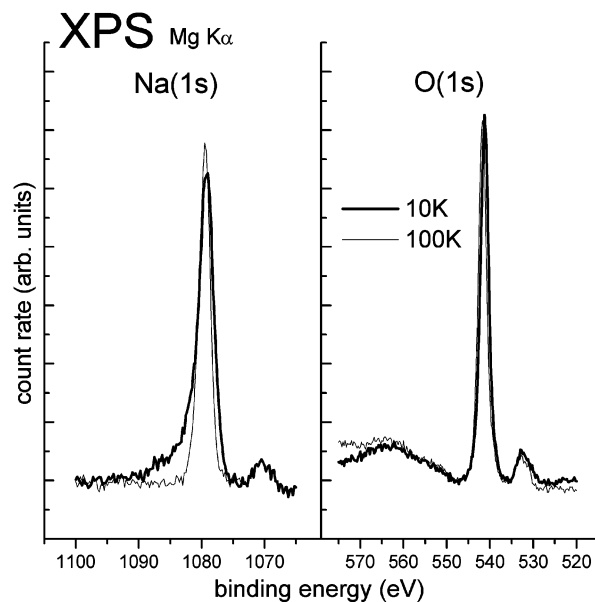


Figure 3. XPS $Na(1s)$ and $O(1s)$ narrow scans taken from the surfaces represented by the two bottom spectra in Figure 1, that is, water films covered by approximately 0.6 monolayers of Na. The shape of the $Na(1s)$ line obtained at 100 K resembles that of $NaCl$;²³ the $Na(1s)$ line obtained at 10 K is clearly broadened indicative for a final state (shake-up) effect due to neutral Na.

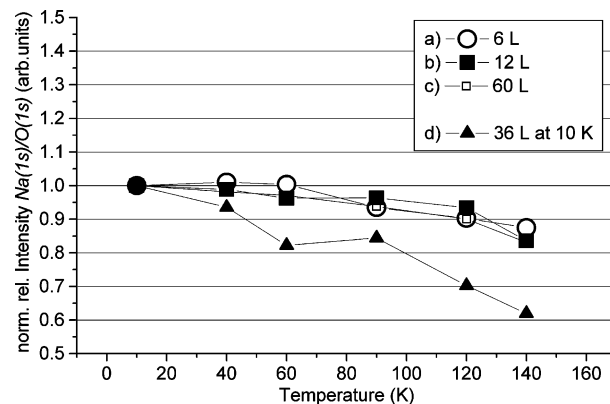


Figure 4. Relative XPS intensities of the sodium $1s$ and oxygen $1s$ core level states ($Na(1s)/O(1s)$) for Na covered water films (varying thickness, but the same amount of Na) as a function of the substrate temperature.

12, and 60 Langmuirs of water, resulting in water films with an approximate thickness of 2, 4, and 18 water bilayers, respectively. Then, the so-prepared water films were cooled to 10 K and were finally exposed to 0.5 monolayers of Na. The trace, however, denoted by d represents a water film (36 Langmuirs exposure) adsorbed on the supporting substrate held at a temperature of 10 K and, thus, is expected to be highly porous.⁷ Since the $O(1s)$ XPS intensity depends on the water layer thickness, the relative intensities ($Na(1s)/O(1s)$) have been normalized to facilitate their direct comparison. From the so-obtained data, for all three traces (a–c), an attenuation of the $Na(1s)$ intensity relative to the $O(1s)$ by about 7% (12%) is noticeable upon annealing the sample to 100 K (140 K). Unfortunately, because of advanced water desorption above 140 K substrate temperature, it is not possible to discuss data obtained at temperatures higher than 140 K. In the observed temperature regime, however, it can be concluded that the water layer thickness has no influence on the Na concentration near the surface: From the qualitatively similar evolution of the three traces (a–c), irrespective of the amount of water adsorbed, we

deduce that no intermixing of Na with the underlying water occurs and that Na remains in the near surface region. In case of a significant intermixing of hydrated Na with the underlying water bulk, an enhanced attenuation of the sodium intensity would be expected for thicker water layers but is not observed.

To prove that this experiment is indeed sensitive to an intermixing of the adsorbed Na with the underlying water film, Na was adsorbed on porous water ice, see trace d. With this experiment, we did not intend to study the diffusivity of Na into the porous water films, but it was expected that the porous structure of the water film might enhance the Na–water intermixing and could, in turn, prove the sensitivity of the applied technique to such a phenomenon. An enhanced intermixing was found as manifested by a 37% attenuation of the Na(1s)/O(1s) intensity at elevated temperatures (140 K). From this experiment, it cannot be decided whether the adsorbed Na diffuses along the porous water microchannels before those channels are collapsing upon annealing the water film or whether Na accidentally hits the channels during Na exposure. From previous studies it is, however, known that the porosity of amorphous water ice films is lost when annealing the film up to 140 K.²⁴ Each way, the involved diffusion of water molecules must enhance the intermixing with the adsorbed Na.

Discussion

The following possibilities exist for impinging Na: after being shortly captured in an adsorption intermediate, (1) detachment from the surface, capture at the surface (2) with or (3) without being ionized, and after an ionization, (4) hydration and diffusion into the water bulk. From XPS, it is deduced that for 10 and 100 K substrate temperature the sodium sticking coefficient, that is, the probability of an impinging Na atom to be captured by the water surface, is similar (Figure 3), suggesting a sticking coefficient close to unity and, thus, excluding channel 1. On the other hand, XPS measurements obtained from Na covered water films as a function of the film temperature and thickness (Figure 4) are showing no significant Na–water intermixing in a temperature regime between 10 and 140 K, excluding channel 4. The observed slight attenuation of the XPS sodium signal upon annealing the water ice film to 100 K most likely originates from a reorganization of the initial Na–water conformation established at 10 K substrate temperature. Subsequent annealing to 140 K then provides, according to previous temperature-dependent measurements,¹² sufficient mobility of the water molecules for establishing a first hydration shell around the Na adsorbate. This hydration shell is responsible for an attenuation of the Na/water signal by 12% in Figure 4.

In a previous study, we have presented electron spectroscopic data taken during Na exposure to amorphous water ice films condensed on Pt(111). The temperature of the water film was held at 10 K.²⁵ A marked contrast has been found in the Na coverage dependent development of the water and Na induced spectroscopic features for a 2 and 10 water bilayer thick water film: not only did the Na(3s) band appear much weaker in case of a thinner water ice film but also a shift of all water bands, concomitant to a 2.2 eV lowering of the substrate work function, has been observed. It was concluded that for thin water films a direct transfer of the 3sNa charge to the metallic substrate is still possible via resonant tunneling, whereas the charge density of the supporting metal substrate and the alkaline atom is sufficiently shielded in case of a thick water film. In the latter case, which corresponds to the present study, Na donates its 3s-electron directly to the water ice film where the electron resides as a hydrated species in the vicinity of the Na⁺ ion.^{9,26}

The influence of the substrate temperature on this process is investigated in the present study, which compares Na adsorption on seven water bilayers held at 10 and 100 K, respectively.

In the initial stages of Na adsorption, we find a marked difference in the Na coverage dependent evolution of the Na-(3s) band; however, OH(1 π) develops similarly for 10 and 100 K (Figure 2). Apparently, at 10 K the Na resides mostly as a neutral at the water surface, while at 100 K the Na(3s) electron is delocalized from its Na⁺ core.^{9,15} This is supported by XPS results (Figure 3): the broadened XPS Na(1s) line at 10 K suggests metallic-like Na,^{19,27–29} while at 100 K the Na(1s) line resembles that obtained from NaCl.²³ Since all water films have been prepared in the same fashion, differences in the water ice structure do not account for an enhanced delocalization of the Na(3s) electron at 100 K. It is likely that the mobility of the water molecules plays a key role in this scenario. Without a minimum D₂O mobility, Na is not able to significantly donate charge to the underlying water, because electron hydration is associated with a polarization of the water environment. Recent theoretical work suggests this process to be spontaneous in case of Na interacting with water clusters.⁹ On the other hand, it has been shown that this hydrolysis corresponds to a loss of entropy of the Na(H₂O)₇ system which implies that the cluster undergoes a significant structural change. It is furthermore found that, toward larger water clusters, the Na species is preferably located at the cluster surface.^{9,30} Within the framework of this model, at 10 K substrate temperature, the mobility of the water molecules is reduced to an extent that affects the Na(3s) charge delocalization. On the other hand, it is commonly accepted that the donation of 3sNa charge is the prerequisite for the reaction between water molecules and the adsorbed Na.^{8,9}

Remarkably, Figure 2 shows that the intensity ratio 1b₁/OH-(1 π) is the same for 10 and 100 K, depending only on the Na exposure. Since for a deprotonation reaction proton diffusion is required, which should strongly depend on the substrate temperature, we tend to believe that the appearance of the OH-(1 π) structure upon Na adsorption is an intrinsic feature of the prepared water surfaces: Dangling OH groups on the water film surface likely provide a local environment which favors the formation of Na⁺OH⁻ after association of a Na atom. Consequently, we consider two Na adsorption sites on the water film surface, one in the vicinity of dangling OH groups and one on the perfect water H-bridging bond network. Only in the latter configuration does the substrate temperature influence the charge transfer from the Na to the substrate, that is, only on the perfect water network does Na survive as a neutral at 10 K and, thus, can contribute to the Na(3s) band. In turn, this interpretation implies that the coordination of Na to dangling OH groups results, independent of the water film temperature, that is, 10 and 100 K, in an ionization of the adsorbed Na. In this scenario, the evolution of the 1 π feature results from adsorption in the vicinity of dangling OH groups. Since the final 1 π intensity is comparable to the 1b₁, see the bottom spectra of Figure 1, a relative high density of dangling OH groups must exist at the water film surface prepared by our procedure.

Charge-Up Phenomena during Electron Spectroscopy on Ice. When monitoring the water ice valence band structure with MIES or UPS, electrons are continuously ejected from water orbitals. The vacancies, created in this way, must recombine with electrons from the metallic substrate within a sufficiently short time to avoid a charging-up of the water films surface. Since such a charging-up has been rarely observed, we believe that vacancies created in the water orbitals do recombine with electrons from the metal substrate via intermolecular hopping.

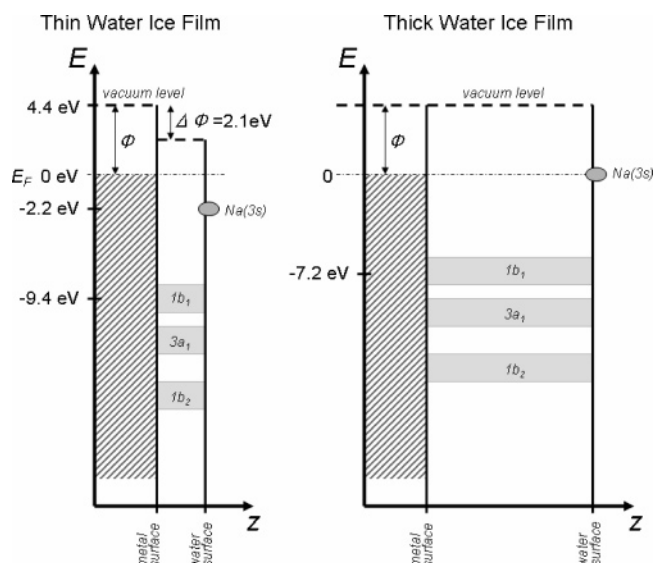


Figure 5. Energy diagram of a water-covered Pt(111) substrate as extracted from ref 25 and Figure 1. Left side: Pt(111) substrate covered by a thin water ice film (approximately two water bilayers). Φ is the work function of the water-covered Pt(111) surface, and $\Delta\Phi$ is its change upon Na coverage. Right side: Pt(111) substrate covered by a thick water ice film (approximately 10 water bilayers). The surface density of states (SDOS) of the water valence bands, as seen by MIES, is indicated by horizontal bars.

The water bands $1b_1$, $3a_1$, and $1b_2$ are located energetically resonant to occupied metal states (Figure 5). On the other hand, the sodium $3s$ level is not located resonantly to one of the water bands and in case of a thick water film the density of states (DOS) of the metal substrate surface is out of reach. Indeed, while monitoring the electronic structure of highly porous amorphous water ice films, condensed at 10 K substrate temperature, a severe charging-up has been observed as soon as sodium dosage was started. However, for nonporous water films, as prepared in the present study, such an effect is not seen. Therefore, the question about an effective recombination mechanism of $3sNa$ vacancies on water films arises. Figure 5 presents an energy diagram of a water ice covered Pt(111) surface, which has been exposed to Na; the scenario is shown for a thin and a thick water ice film, as extracted from ref 25 and Figure 1. As for thin (thickness < three water bilayers) water films, sodium can directly interact with the DOS of the supporting Pt(111) substrate surface; upon sodium dosage, all features observed are comparable to the adsorption of alkali metal atoms on a clean metal surface:^{22,31–33} a lowering of the substrate work function and occupied alkaline state density located just below the Fermi energy of the metal substrate. On the other hand, for a thick water ice film, the adsorbed Na is well-shielded from the metal surface DOS, and a donation of $Na(3s)$ charge to the metal surface is not possible. We propose that vacancies created in $Na(3s)$ related surface states may recombine by a ballistic electron tunneling through the water film. Sufficient electron density is provided at the Fermi level of the Pt substrate. On the other hand, the proposed mechanism may not be effective for porous films which, as a consequence, will show serious charge-up effects.

Summary

We have compared the adsorption of Na on amorphous D_2O ice films held at 10 and 100 K. It is found that at 10 K the $Na3s$ charge donation to the ice film, connected with $3sNa$ solvation, is significantly reduced relative to 100 K. However,

at both temperatures, Na resides above or is embedded into the film surface. This observation fits to recent theoretical work, suggesting that a rearrangement of the water molecules at the water surface is a prerequisite for $3sNa$ solvation. We propose that the association of Na to dangling OH groups, which are inevitably present at water ice surfaces, results in OH^- formation, both at $T = 10$ and 100 K. On the other hand, Na adsorption on the perfect water network does not result in a water deprotonation reaction but at 100 K relative to 10 K to an enhanced $3sNa$ solvation.

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