The interaction of water and hydrogen with nickel surfaces

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Chapter 3

The interaction of water with Ni(111) and H/Ni(111)

We have used temperature-programmed desorption in combination with specular and off-specular high resolution electron energy loss spectroscopy to study the interaction of H_2O *and* D_2O *with bare and hydrogen-covered Ni(111) surface. Our results for the bare metal surface agree with previous reports and we are able to relate two prominent features in vibrational spectra to nuclear motions at the surface. Pre-covering Ni(111) with hydrogen alters both adsorption and desorption of water significantly. The strong H-Ni bond does not allow for isotopic exchange with co-adsorbed* D_2O*. Strong resemblance of desorption traces and vibrational spectra of submonolayer coverages on H-covered Ni(111) and multilayers on bare Ni(111) suggests that adsorption of hydrogen makes this nickel surface hydrophobic.*

3.1 Introduction

The interaction of water with metal surfaces has attracted much attention in recent years [1]. This is not surprising considering the importance of water in many reactions such as corrosion, heterogeneous catalysis and electrochemistry. Despite the rather simple structure of water molecules, the understanding of the adsorbed water structure on many metal surfaces, as well as the bulk water structure, still remains limited [1,2].

Experimental studies of the interaction water with metal surfaces generally focus on close packed metal surfaces, e.g. Pd(111) [3,4], Pt(111) [5-11], Ru(0001) [12-14], and Ni(111) [15-17]. Recently, STM studies on Pd(111)[3] and helium-scattering investigations on Pt(111)[5] have shown that below 40 K, water initially adsorbs as isolated molecules (monomers). With increasing coverage and temperature, they form dimers, trimers, tetramers and so on. For the saturated monolayer, low-energy electron diffraction (LEED) studies show various structures on close-packed surfaces. On Pd(111) and Ru(0001), the $(\sqrt{3}\times\sqrt{3})R30^{o}$ structure has been observed [3,12], whereas on Pt(111) a $(\sqrt{39}\times\sqrt{39})R16^{o}$ structure develops [7-10]. Recently, Hodgson *et al.* observed a “labile” $(2\sqrt{7}\times2\sqrt{7})R19^{o}$ structure on Ni(111) that changed into the previously reported $(\sqrt{3}\times\sqrt{3})R30^{o}$ structure [15] due to impact of the electron beam. Formation of the incommensurate structure was related to the small lattice constant of Ni(111) in comparison to Pd(111), Pt(111) and Ru(0001).

Vibrational spectroscopy of water layers also yields information on water adsorption. Jacobi *et al.* recently performed a high-resolution electron energy loss (HREELS) study of water on Pt(111) and observed, with unprecedented resolution, the OH stretching vibration near 425 meV, H-O-H bending vibration near 200 meV, various librations between 50 and 100 meV, and frustrated translations below 50 meV [18]. High resolution studies employing IR spectroscopy can provide additional insight. For example, results of a recent study of water adsorption implied the presence of a ring hexamer structure over a wide coverage range on Ni(111) [17].

Desorption of water from, among others, Pt(111) and Ni(111) has been characterized in terms of (sub)monolayer desorption and multilayer desorption [11,15]**.** A temperature-programmed desorption (TPD) feature near 170 K saturates whereas a feature near 160 K does not saturate with increased exposure to water. In addition, the 160 K feature shows zero-order desorption characteristics and is therefore believed to be due to the multilayer desorption. The feature at 170 K is attributed to (sub)monolayer desorption.

Besides studies of pure water adsorption, several studies have probed co-adsorption with other molecules and atoms. Considerable attention has focused on co-adsorption with oxygen on platinum, nickel and their alloys, since reactions at the cathode in low-temperature fuel cells are rate limiting [19,20]. A fuel cell is an electrochemical conversion device. It produces electricity by a chemical reaction. Every fuel cell has two electrodes, one positive and one negative, called, respectively, the anode and cathode. The reactions that produce electricity take place at the electrodes. On the other hand, co-adsorption with hydrogen has received much less attention and is currently poorly understood. Of the few co-adsorption studies with hydrogen, some claim formation of H_3O^+ (or hydrated forms of the hydronium ion) under UHV conditions on platinum surfaces [21]. A quick survey of the literature, however, indicates many inconsistencies. For example, for Pt(111) co-adsorption of hydrogen and water has been described to results in “strong changes” in TPD spectra[18] and was found to have “little if any effect”[21].

In the present study, we use TPD and HREELS to investigate the interaction of (sub)monolayer and multilayers of water with the bare and hydrogen-covered nickel surface. This co-adsorbed system is of particular interest due to the simultaneous presence of hydrogen and water in alkaline fuel cells that use nickel as its catalyst and electrode material. After presenting our data, we discuss our results and compare them to similar results found previously in UHV studies employing comparable nickel and platinum surfaces. Our analysis allows us to assign several features observed in HREEL spectra and suggests how hydrogen changes the chemical nature of Ni(111) with respect to water adsorption.

3.2 Experiment

Experiments are carried using an UHV system, which consists of two chambers. The upper level and the lower level are separated by a gate valve. The top chamber contains a quadrupole mass spectrometer (QMS) used for TPD measurements and residual gas analysis, an ion sputter gun, an atomic hydrogen source, a stainless steel gas doser, and a home-built capillary array doser [22]. The lower chamber contains an upgraded ELS22 high resolution electron energy loss spectrometer and an Auger Electron spectrometer. The base pressure of the system is less than 1×10^{-10} mbar.

The Ni(111) single crystal, cut and polished to <0.1° of a low Miller-index plane (Surface Preparation Laboratories, Zaandam, the Netherlands), can be heated to 1200 K by electron bombardment and cooled to 85 K. The sample temperature is measured by a chromel-alumel thermocouple spot-welded to the edge of the crystal. The crystal is cleaned by Ar^+ sputtering, annealing at 1100 K, followed by oxidation in 10^{-7} mbar of O_2 and reduction in 10^{-6} mbar of H_2. Auger electron spectroscopy verifies surface cleanliness. H_2O (18.2 MΩ resistance) and D_2O (99.96% isotopic purity, Aldrich Chemical company) are cleaned by repeated freeze-pump-thaw cycles. Both are dosed through the capillary array doser. During dosing, the sample is placed 15 mm in front of the doser. Water coverages are estimated from integrated TPD traces. We have also determined the obtained hydrogen coverage as a function of dose using integrated TPD traces. All TPD measurements were performed with a heating rate of 1.0 K/s. The HREEL spectra were recorded at 5 to 9 meV resolution (FWHM) with typical 1×10^4 cps for the scattered elastic peak.

3.3 Results

3.3.1 H_2O and D_2O on bare Ni(111)

Figure 3.1 displays a set of TPD spectra of H_2O and D_2O on bare Ni(111) at various initial coverages. The sample temperature was kept at 85 K while dosing water through the capillary array doser. As observed previously [15,16,23,24], there are two distinct desorption features. At low coverage, spectra show a single feature at ~170 K. With increasing coverage, this feature reaches saturation, and a second feature appears at ~155 K. This low temperature feature does not saturate with increasing exposure and shows zero-order desorption kinetics at high coverages. For clarity, we only show lower coverages here. We have deconvoluted the TPD traces using two Gaussian profiles and observe that the feature at low temperature appears slightly before saturation of the feature at high temperature. For the water coverage, we define 1 ML as the integration of the deconvoluted, saturated high temperature feature. For example, the total desorption of 1

ML D_2O in figure 3.1 consists of 0.15 and 0.85 ML of the two individual features. We note that the similarity of H_2O and D_2O in the TPD spectra indicates no isotope effects in desorption. However, in agreement with previous study on Pt(111) [25], isotopic scrambling in TPD traces after dosing mixed layers of H_2O and D_2O are also observed in our study.

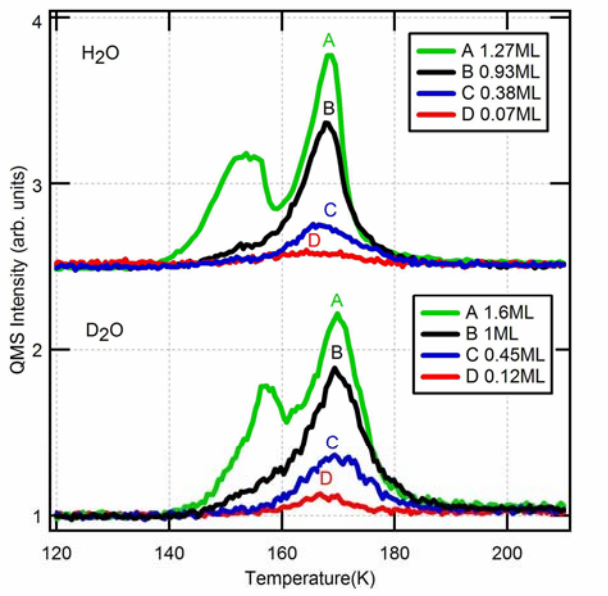

Figure 3.1 TPD of various exposures of H_2O and D_2O on Ni(111) at 85 K.

HREEL spectra of various coverages of H_2O and D_2O, adsorbed at 85 K, are shown in Figure 3.2. These spectra are taken in the specular direction with an incident angle of 60º and an impact energy of 5 eV. The indicated water coverage was determined by integration of the TPD spectrum after obtaining the vibrational spectrum. In the sub-monolayer regime, we observe five main regions. For D_2O, they are centered at 315, 145, 80, 45 and 28 meV. The weak 315 and 145 meV features increase in intensity with coverage and are most clearly distinguished in the multilayer spectrum. The frequency of the strong feature appearing at 80 meV appears coverage-independent. The 45 meV broad feature shifts to higher frequencies with increasing coverage, which is much more pronounced for H_2O. The latter also increases in intensity and broadens. It dominates the region centered at 75 meV in the multilayer spectrum. Finally, a weak feature at 28 meV is only clearly observed in the shoulder of the specular peak for multilayers (see also the top trace in figure 3.5). The H_2O spectra show similar features with the same dependencies around 420 (see inset), 200, 105, 50, and 30 meV. The feature around 50 meV shifts to higher frequencies with increasing coverage as does the 45 meV feature for D_2O. We believe that variations in intensity and resolution in the comparison of H_2O and D_2O spectra are primarily due to variations in experimental conditions and signal averaging. We also observe a feature at 175 meV in HREEL spectra after combined dosing of H_2O and D_2O. This feature has been observed in similar experiments on Pt(111) and was assigned to the HOD bending vibration [25]. This observation indicates that isotopic scrambling observed in TPD experiments has already occurred at 85 K. Finally, we have taken HREEL spectra of D_2O layers that were formed at 85 K and subsequently annealed at 140 K. These spectra show no differences to the ones presented in figure 3.2.

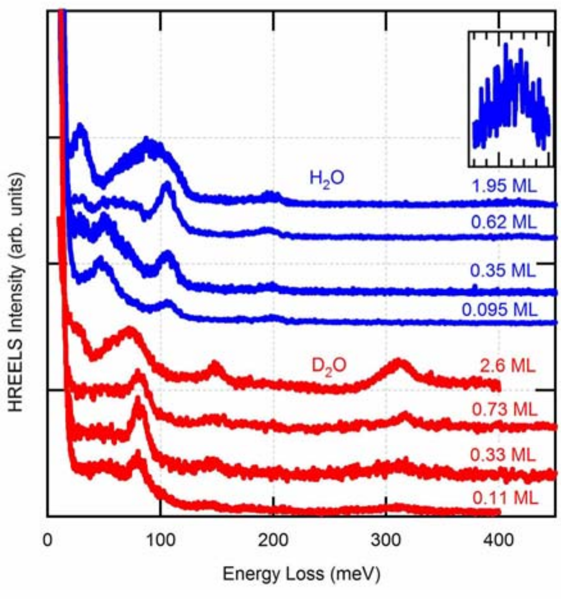

Figure 3.2 HREEL spectra of H_2O and D_2O on Ni(111) at 85 K for various coverages. The inset shows the spectrum for 1.95 ML H_2O in the 380 to 440 meV region.

Figure 3.3 compares HREEL spectra of H_2O and D_2O taken at the specular angle and 10° off-specular. Comparison of spectra taken at specular and off-specular angles can be used to differentiate between dipole and impact scattering mechanisms in vibrational excitation [26]. For H_2O, we only show spectra for a multilayer, whereas for D_2O we show spectra ranging from 0.11 to 2.6 ML. Noteworthy are the strongly angle-dependent intensities for the 30 meV feature in the multilayer spectra (28 meV for D_2O) and the 80 meV feature in the sub-monolayer regime of D_2O.

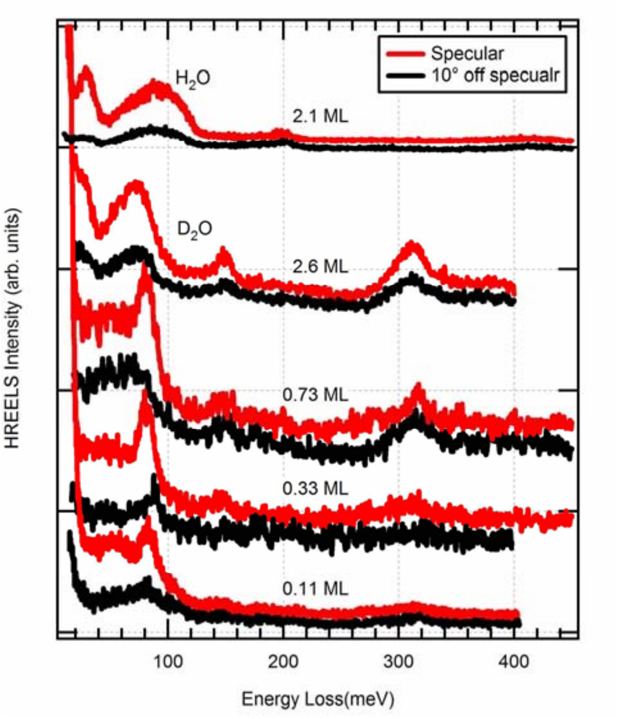

Figure 3.3 Comparison of HREEL spectra taken at the specular and off-specular angle for H_2O and D_2O on Ni(111).

3.3.2 D_2O on hydrogen-covered Ni(111)

In order to examine the influence of co-adsorbed hydrogen on the binding of water on Ni(111), we have performed similar experiments to those mentioned above for the H-precovered surface. Hydrogen is known to dissociatively adsorb on Ni(111) with a low barrier to reaction, although large exposures are necessary to (nearly) complete saturation

[27,28]. Comparison of our integrated TPD traces for a large range of H_2 doses up to 2×10^{-2} mbar*s indicates that a dose of 2×10^{-3} mbar*s H_2 at 85 K nearly saturates the surface. Figure 3.4 shows TPD spectra taken after an H_2 exposure of 2×10^{-3} mbar*s at 85 K with consecutive exposure to D_2O. For comparison, Figure 3.4 also shows the D_2O TPD spectra from the bare Ni(111) surface. At a D_2O coverage of 1.8 ML, desorption from a hydrogen covered surface shows a single peak that traces the zero-order desorption onset exactly. No separation of this peak is observed. Also, at the low D_2O coverage of 0.18 ML, we only observe desorption near 155 K. The inset shows the difference between 0.11 ML of D_2O for the bare and hydrogen-covered surface in detail. The D_2O desorption peak has shifted 10 K downward by prior adsorption of hydrogen. Associative desorption of H_2 occurs in two peaks at 320 K and 360 K and is not affected by the D_2O overlayer. By also monitoring m/z 3 (3, M – HD) and 19 (19, M – HOD) in these experiments, we find no evidence of isotopic mixing between H_{ads} and the D_2O.

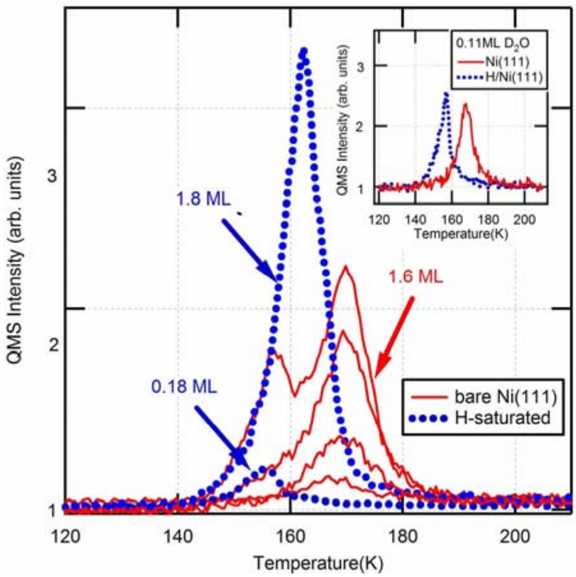

Figure 3.4 TPD of various amounts of D_2O from H-saturated and bare Ni(111). The inset shows the same comparison for 0.11 ML D_2O. For coverages, see also figure 3.1.

Figure 4.5 compares HREEL spectra of D_2O on the H-covered and bare surface. The middle and bottom spectra are taken after dosing 0.11 ML of D_2O, whereas the top spectrum was taken after dosing a multilayer of D_2O on the bare surface. The spectra for the sub-monolayer coverages show various differences. The strong 80 meV feature is either obscured or has disappeared upon pre-adsorption of hydrogen. Also, the 45 meV feature is replaced by a feature centered around 70 meV, which resembles the broad feature observed in this regime for multilayers. Finally, the 28 meV feature, observed clearly for multilayers on the bare surface, is already distinguishable for 0.11 ML on the hydrogen-covered surface. In HREEL spectra we again find no evidence of isotopic exchange between the saturated H-layer and D_2O.

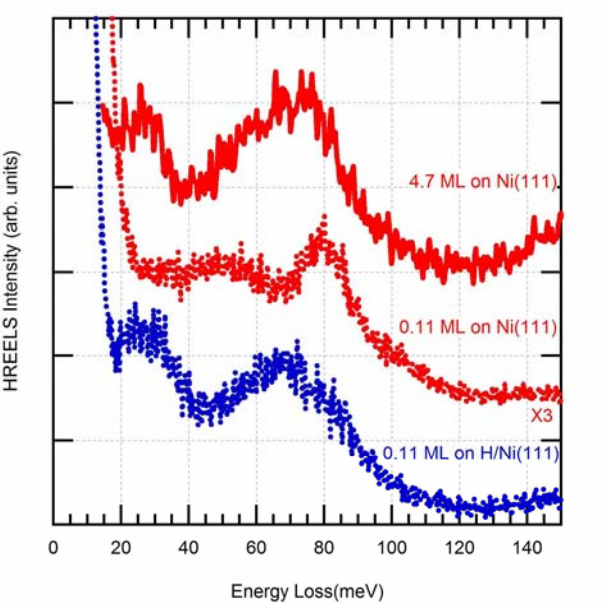

Figure 3.5 HREEL spectra of 0.11 ML D_2O on hydrogen-saturated Ni(111) compared to 4.7 ML and 0.11 ML D_2O on bare Ni(111).

3.4 Discussion

First, we turn our attention to the TPD spectra in figure 3.1. Our spectra are in excellent agreement with recently published spectra by Gallagher *et al.* who deposited water layers from exposure to a molecular beam at 135 K [15]. They are also in good agreement with other previous studies [16,23,24]. It is generally agreed that the peak at ~170 K is due to (sub)monolayer adsorption of water, whereas the peak developing near 155 K is due to consecutive multilayer growth. Our TPD spectra show no evidence of the presence of steps or other defects on our surface, which would result in desorption of H_2O at higher temperatures. Since dissociation of H_2O at such defects also leads to H_2 associative desorption at higher temperatures [24], we have traced m/z 2 (2, M – H_2) in these TPD experiments and find no evidence for H_2O dissociation. Although our results do not provide information whether water layers grown at 85 K are amorphous or crystalline, we can conclude that our experimental procedures form layers of non-dissociated H_2O molecules. Combined with the absence of the 127 meV vibrational signature of adsorbed hydroxyl groups in HREEL spectra [18], the TPD experiments that indicate formation of HOD in mixed H_2O/D_2O layers allow us to conclude that at 85 K isotopic scrambling takes place without dissociation of water at the surface.

In the literature, several reports discuss adsorption of water in terms of a bilayer structure [1,2]. For example, Jo *et al.* interpreted a double maximum in the high temperature TPD features of water desorbing from Pt(111) [29] as a result of such a bilayer structure. More recent results for Pt(111) both confirm [18] and dispute the experimental results and interpretation [6]. Our TPD spectra for Ni(111) show only a single feature in the high temperature region, as was found by Gallagher *et al.* [15]. Therefore, these results yield no basis for a more detailed interpretation of the structure of adsorbed water.

Next, we attribute the features of our HREELS results shown in figure 3.2 by comparison to results from IR and HREELS studies of water adsorbed on Ni(111) [17], Pt(111) [18,25], and Ni(100) [30]. From the five main regions in the sub-monolayer D_2O spectra, the features centered at 315 and 145 meV have consistently been attributed to the O-D stretch and D-O-D bend. In HREEL spectra of H_2O these vibrational modes appear at 420 and 200 meV, in agreement with the expected isotopic frequency ratio between 1.3 and 1.4. The similarity in frequency of the stretching and bending modes of water on Pt(111) and Ni(111) and of water in the gas phase [1,17,18,25], indicate that these modes are not strongly affected by the metal substrate. Although the bending and stretching modes increase in intensity with coverage, the intensities observed here are too weak to use a change between specular and off-specular intensity (figure 3.3) for commenting on possible molecular orientation with respect to the surface normal. We note that it is commonly assumed that water bonds through the oxygen atom to the metal surface. We also note that we do not observe a clear feature that could be attributed to the free OH or OD stretch, which has been reported for a bilayer structure [1,2]. This feature would be expected around 460 meV for OH and 340 meV for OD [17,18].

Two of the three remaining features in the spectra for D_2O submonolayer coverages fall within the frequency range generally attributed to librations, namely the peaks around 80 and 45 meV. For the latter, the intensity increases and the frequency shifts with increasing dose, resembling librations observed on Pt(111) [18,25] and Ni(100) [30]. The apparent decrease in off-specular intensity suggests that this feature at 45 meV is, at least in part, due to dipole scattering.

For the dominant libration at 80 meV, both the intensity at low coverage and its strongly decreased off-specular intensity suggest a dipole scattering mechanism. The same feature appears in the H_2O spectra at 105 meV, yielding an isotopic frequency ratio of 1.31. Our spectra at much higher coverages suggest that this mode is obscured by formation of multilayers. Although an unspecified libration appears with similar frequency in deconvoluted spectra of H_2O and D_2O on Ni(100) [30], it is much less pronounced. For Pt(111), two narrow features at comparable frequencies are observed, but only for bilayers and also not nearly as dominant [18]. A DFT study of gas phase $(H_2O)_n$ clusters finds vibrational frequencies of similar energy for $n \geq 3$ [31]. However, this study does not specify the accompanying nuclear motions. Since an assignment can not be based on this previous work, we consider the possible librations: wag, rock and twist. We note that when water is bound through the oxygen atom, only the rocking and the wagging librations become dipole active when the site symmetry is reduced from C_{2v} to C_S. We also note that frequencies of these librations are not expected to vary much between monomers and weakly bound structures, such as clusters [3,5,6] and hexamer rings [17]. Finally, we find that, in comparison to IR spectra of nickel aquocomplexes, e.g. $Ni(H_2O)_6SiF_6$, the frequency of the rock agrees well with our observed feature at 80 meV [32], whereas the wag and twist have lower frequencies. We therefore suggest that the broad librations at lower frequencies consists of nuclear motions resembling the twist and wag, whereas the higher libration resembles the rock for (sub-)monolayer coverages. Additionally, we note that Gallagher *et al.* showed that the delicate balance between interaction of water molecules with the surface and the lateral hydrogen-bonded network is easily disrupted by multilayer formation [15]. The 80 meV peak seems characteristic of (patches of) this (2√7x2√7)R19° structure as it remains clearly distinguishable after annealing at 140 K, but is not observed when forming multilayers.

We are left with one discernable feature at 28 meV for D_2O (30 meV for H_2O). The rather small isotopic frequency ratio of ~1.05 is characteristic for a vibration which involves the whole water molecule. Indeed, features in this regime are generally attributed to frustrated translations and a mode at the same frequency has been observed on Pt(111) [18,25]. Strong weakening in the off-specular intensity for both H_2O and D_2O suggests that this translation mode is dipole active. Although it was first assigned by Sexton [25] to a motion parallel to the metal surface, Jacobi *et al.* recently proposed it to be the frustrated translation normal to the surface [18]. Our data support the latter assignment. In addition, since this mode is only clearly observable for both Pt(111) and Ni(111) in the multilayer regime, we believe it corresponds to the frustrated translation normal to the surface of hydrogen-bonded water molecules in multilayers, i.e. the $D_2O\cdots DOD$ stretch. The $D_2O\cdots M$ stretch in the submonolayer regime has been connected by Jacobi *et al.* [18] to an energy loss feature around 15 meV, which is unobservable in our spectra.

Figure 3.4 and 3.5 provide clear evidence that pre-covering the surface with hydrogen affects the interaction of water with Ni(111). Hydrogen atoms are known to adsorb to the Ni(111) surface on three-fold hollow sites forming a (1x1) overlayer [27]. Contrary, water on the bare nickel surface has been shown to form a labile, incommensurate (2√7x2√7)R19° layer that has water molecules residing above various sites [15]. We consider whether our results from figure 3.4 and 3.5 indicate how water molecules bind to the H-covered surface and whether the first layer of water wets this surface. In this respect we recall that previous experiments using co-adsorption of H and H_2O on Pt(111) indicate shifts in TPD features that may be compared to those shown in figure 3.4. Jacobi *et al.* mention that very small amounts of hydrogen affect TPD features of H_2O such that the two desorption peaks merge [18]. Contrary, Wagner and Moylan note that they observe little if any effect [21] for the same system. Instead, they observe changes in HREEL spectra that are ascribed to formation of H_3O^+. This (hydrated) hydronium ion was also proposed to be formed in co-adsorption studies on Pt(100) [33] and Pt(110) [34].

Our data in figure 3.4 clearly indicate weakened bonding of water with the surface when pre-covering it with hydrogen. For 0.11 ML of D_2O, the desorption temperature shifts downward by 10 K upon pre-adsorption of a full monolayer of H, corresponding to the temperature regime for desorption from multilayers. Additionally, our HREELS data for the same small quantity of water clearly features the peak around 28 meV, which we assigned, in agreement with a HREELS study at higher resolution [18], to the frustrated translation of hydrogen-bound D_2O normal to a D_2O layer. This suggests that a small amount of water already forms multilayered islands on hydrogen-covered Ni(111). This behavior resembles the hydrophobic character observed for the first layer of water on Pt(111) [11,35]. This suggestion of a hydrophobic character of hydrogen-saturated Ni(111) is strengthened by the absence of the pronounced feature around 80 meV, which we suggest to be characteristic of the labile (sub)monolayer structure observed in a low-intensity LEED study [15].

Contrary to the presented interpretation, we observe that the leading edge of the 0.18 ML trace does not follow the same zero-order desorption for 1.8 ML D_2O on the hydrogen-saturated surface or the 1.6 ML desorption from the bare surface. This causes some doubt regarding the proposed multilayered island formation. Therefore, we also consider another bonding geometry that does not imply multilayered island formation. One could imagine that individual D_2O molecules preferentially bind to H_{ads}. The observed frequency at 28 meV could then be due to a similar frustrated translation normal to the surface, whereas the 80 meV feature characteristic of (patches of the) incommensurate $(2\sqrt{7}\text{x}2\sqrt{7})\text{R}19°$ layer has disappeared since the lateral ordering of water molecules is now dominated by interaction with the H-lattice. For this bonding geometry, desorption from submonolayer coverages would resemble multilayer desorption since it also requires breaking of the $D_2O\cdots H$ hydrogen-bond. However, we would expect at least some frequency shift for the 28 meV feature since it is unlikely that the dipole-dipole interaction between water molecules strongly resembles the interaction between a water molecule and a hydrogen atom adsorbed onto Ni(111). In addition, we note that, if these hydrogen bonds were comparable, this bonding geometry would also require overlap of the onset in the TPD traces for 0.18 and 1.8 ML. We therefore conclude that, although we can not exclude the latter bonding geometry, the multilayered island formation due to a hydrophobic character of hydrogen-covered Ni(111) is more plausible. We note that adsorption-desorption techniques using rare gases, chloroform, and bromoform, which have been shown to be sensitive to the local topography of the surface (see e.g. Ref. 11, 15 and 36) may provide more conclusive evidence of the proposed hydrophobicity.

Finally, we consider whether we have reason to believe that hydronium-ions are formed on the Ni(111) surface, as has been suggested for co-adsorption of hydrogen with water on platinum surfaces [21,33,34]. For Pt(111), the existence of this ion was based on the appearance of an additional peak around 143 meV in HREEL spectra after flashing hydrogen and water, co-adsorbed at 95 K, to 150 K. We do not observe such a peak nor any other significant changes in our HREEL spectra upon flashing to 140 K. In addition, we find no isotope exchange between H_{ads} and D_2O, which would be expected if a transiently formed H_3O-moiety decomposed prior to water desorption. The Ni-H bond has considerable strength and an activation barrier may be preventing such species to form. Therefore, we conclude that our data show no evidence of formation of a hydronium ion or hydronium-like species. In this regard, we stress that the hydrogen-bonding between D_2O and H_{ads} considered in the previous paragraph is very different from a chemical bond between these species. The HREEL feature at 28 meV is only indicative of an O···H hydrogen-bond and not of an O-H intramolecular chemical bond.

3.5 Conclusions

Based on TPD and HREEL spectra we conclude that hydrogen, atomically bound to Ni(111), affects the interaction between this metal surface and water significantly. Whereas a hydrogen-bonded network of water multilayers shows isotopic scrambling without water dissociation at 85 K on the surface, the H-Ni bond is too strong to allow isotope exchange with co-adsorbed water. We expect that the same H-Ni bond strength prevents formation of H_3O^+ or similar species. In contrast, our data actually suggest that saturating the Ni(111) surface with hydrogen makes the surface hydrophobic, and that multilayered islands of water molecules form at submonolayer coverages.

3.6 Rererences

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Chapter three