Reorientation of Chemisorbed Water on Ni(110) by Hydrogen Bonding to Second Layer

B. W. Callen, K. Griffiths, and P. R. Norton

Interface Science Western and Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Water chemisorbs molecularly on Ni(110) at 180 K producing a $c(2\times2)$ overlayer, at 0.5 ML (ML = monolayer = 1.15×10^{15} molecules cm^{-2}). This water is undetectable by ir methods which indicates the absence of clustering (and, hence, no intermolecular H bonding) in the first 0.5 ML. Population of a second "icelike" layer, which is nearly saturated after an additional 0.5 ML, makes the first 0.5 ML ir active and produces strong H-bonding interactions. The plane of the chemisorbed water, which is originally parallel to the surface, is reoriented towards the surface normal on filling of the second layer.

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The interaction of water with solid surfaces has become of increasing interest in recent years.[1] This is due both to practical considerations related to electrochemistry and corrosion and to the rich chemistry and physics that arise from the complex interactions between adsorbed water molecules and the substrate and/or each other. The presence of hydrogen bonding (H bonding), which can be of comparable magnitude to the molecule-surface bond strength, leads to a range of phenomena such as clustering at low coverages, low-order desorption kinetics, and control of the double-layer properties in electrochemical systems, etc.[1]

In this Letter, we show that it is possible to produce ordered chemisorbed overlayers of water on Ni(110) in which clustering is not present, and to detect the molecular reorientation in the first layer of chemisorbed water caused by the adsorption of a specific coverage of water into the "second" layer. This second layer still shows residual interactions with the Ni(110) surface and is distinguishable from bulk ice. We show that the H-O-H plane of the water molecules in the first chemisorbed layer must lie close to parallel to the plane of the surface. After adsorption into the second layer to form a bilayer, the H-O-H plane must lie much closer to the surface normal.

The apparatus have been described in detail elsewhere.[2-4] Briefly, the measurements were carried out in a standard ultrahigh vacuum chamber (base pressure $\sim1\times10^{-10}$ torr) to which water can be admitted through a differentially pumped, shuttered capillary array and by admission to the background. The chamber is equipped with an automated multimass quadrupole mass spectrometer and Kelvin probe to measure changes in work function $\Delta\phi$ (sensitivity ~1 mV, $t_c \sim 0.1$ s), and is interfaced to a Fourier-transform ir spectrometer for Fourier-transform ir-reflection-absorption spectroscopy (FTIR-RAS).[4] The ir radiation is incident at about 82° from the surface normal and a mercury cadmium telluride (MCT) detector is used. The lowest detectable absorbance has proven to be $\sim(2-3)\times10^{-5}$ absorbance units (a.u.) for a single reflection. A signal-to-noise ratio

of $>100{:}1$ can be obtained on adsorbed CO on Ni(110) in 90 s. The crystal was cleaned by a combination of Ar$^+$-ion sputtering and annealing. The cleanliness was judged by Auger electron spectroscopy, by nuclear reaction analysis (NRA) in another chamber[2] (to determine bulk plus surface purity levels), and finally by the work-function change ($\Delta\phi$) produced by hydrogen (or deuterium) saturation at ~130 K (>500 mV).[2] The surface exhibited all the expected H-induced phase transformations as observed by low-energy electron diffraction.[2]

We have previously shown[5] that it is possible to saturate the chemisorbed layer of water on Ni(110) by adsorption at 180 K. This lies above the desorption temperature of the second (icelike) layer but below the desorption temperature for the chemisorbed layer. This saturation occurs at 0.49 ∓ 0.05 ML (monolayer) and at the maximum intensity of the half-order beams of the $c(2\times2)$ LEED pattern. Video-LEED measurements[6] of the coverage dependence of the intensity of the half-order beams indicate the presence of repulsive nearest-neighbor (nn) and attractive next-nearest-neighbor interactions. These data clearly indicate that the saturation $c(2\times2)$, 0.5 ML, chemisorbed layer must consist of an ordered array of adsorbed water molecules spaced apart by 0.431 nm. The typical H-bonding distance (O-H-O) for water ice is 0.276 nm (Ref. 7) and clearly the molecules are spaced too far apart for H-bonding interactions. The estimated value of the nn attraction is only a few kJ mol^{-1} (few kT), too small to be ascribed to intermolecular H bonding. No H bonding would therefore be expected, and indeed the thermal-desorption (TD) spectra did not show significant evidence of strong attractive lateral interactions. The work function associated with the completion of the chemisorbed layer is -780 mV. If the adsorption is carried out at $T<150$ K, the chemisorbed and ice layers no longer populate in a strictly sequential manner, with icelike desorption peaks appearing at total coverages above about 0.35 ML.

If the chemisorbed layer (absorption $T=180$ K) is cooled below ~150 K and reexposed to water, to a *total* coverage of 1.0 ML, an additional peak appears in the

TD spectra, close to, but at the upper end of the T range associated with desorption of ice. Desorption of this state is accompanied by an increase in $\Delta\phi$ of $\sim$400 mV, the same magnitude as the *decrease* observed during its population. At higher coverages, $\Delta\phi$ does not change any further. The absolute coverages associated with any work-function change for the two-stage adsorption process (180 and < 150 K) were determined from the NRA calibration and from the relative areas of TD spectra.

The saturation of $\Delta\phi$ and the fact that the TD spectra of the second 0.5 ML occur at slightly ($\sim$10 K) higher T than the bulk ice led us to propose that these molecules still retain a weak interaction with the Ni(110) surface, but must be H bonded to other water molecules. This picture coupled with the NRA and LEED results led to the following predictions: No intermolecular H bonding should be present in the $c(2\times2)$ chemisorbed layer and H bonding should be detectable at coverages above 0.5 ML. A corollary of this argument is that H bonding should be visible whenever an icelike peak is detected in the TD spectra; this situation arises for $\theta > 0.35$ ML for adsorption at $T < 150$ K.

ir methods were used to test the predictions because the ir-absorption coefficient of the O-H stretch is enhanced by H bonding, factors of between 10 and 30 times being reported.[8,9] FTIR-RA spectra were therefore obtained of adsorbed D_2O as a function of known *absolute* coverages (θ).[5,6] Examples of such spectra of the O-D stretch region versus θ are illustrated in Fig. 1, for $\theta = 0.49$ (180 K exposure, no ice), 0.7, 0.8, 1.8, and 3.4 ML. The surfaces with $\theta > 0.5$ ML were produced by exposing the chemisorbed layer [180 K, $c(2\times2)$, 0.5 ML] to additional water at 130 K. The spectrometer resolution was set at 16 cm^{-1}.

No intensity was detectable in the O-D stretch region for the 0.49-ML coverage; in fact, no intensity was detectable for any coverage in the range $0 < \theta < 0.5$ ML for adsorption at 180 K. The absorbance of the O-D
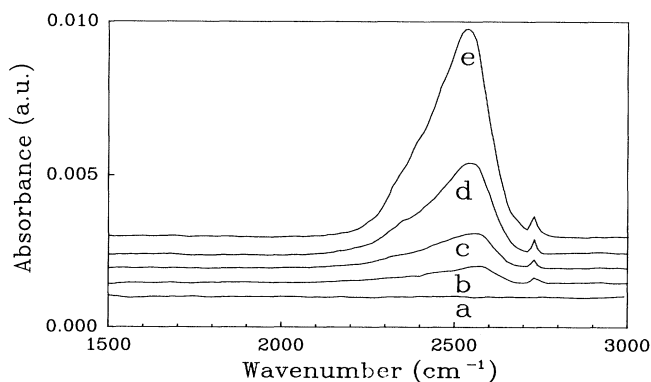
stretch is less than 3×10^{-5} a.u. on our scale. For $\theta > 0.5$ ML, intensity appears in the O-D stretch region. This is shown in the spectrum for 0.7 ML. The broad band characteristic of H-bonded water molecules is visible at 2524 cm^{-1}. A sharp (10 cm^{-1} FWHM in higher-resolution experiments) band also appears at 2731 cm^{-1}. This originates from the dangling (non-H-bonded) OD groups at the ice surface.[10] As the coverage of the water is increased to 1.0 ML, both features increase in intensity monotonically. For $\theta > 1$ ML, the H-bonded band continues to increase in intensity, but the 2731-cm^{-1} feature saturates at coverages a little above 2 ML. The surface still exhibits a $c(2\times2)$ LEED pattern. We believe that the structure of the water overlayer at 1 ML can be well described in terms of Benndorf and Madey's bilayer model.[11] The number of dangling OD bonds in this model is $\sim$0.5 ML ($\sim$5.8 $\times10^{14}$ cm^{-2}).

Figure 2 illustrates the coverage dependence of the integrated intensity of the O-D stretch bands as a function of coverage for $0 < \theta < 4.5$ ML. The intensity increases rapidly between 0.5 and $\sim$1.0 ML, whereafter the slope decreases, the variation with coverage becoming linear above 2 ML. The linear region extends to about 15 ML (not illustrated) and extrapolates to zero at zero coverage.

By 1.0 ML therefore, almost *all* adsorbed water molecules exhibit the same ir absorption on average as in the thicker layers. If completion of this effect occurs when the second *layer* (remembering that each water *layer* is composed of 0.5 ML with respect to the Ni substrate) is full, then a simple statistical model, in which water molecules "hit and stick" without subsequent migration, predicts the second *layer* should be completed around 2 ML total coverage (4 *layers*) (some parts of the surface will exhibit higher local thicknesses if each of the first two *layers* contains 0.5 ML of water). The molecules which were originally undetectable must now be contributing to
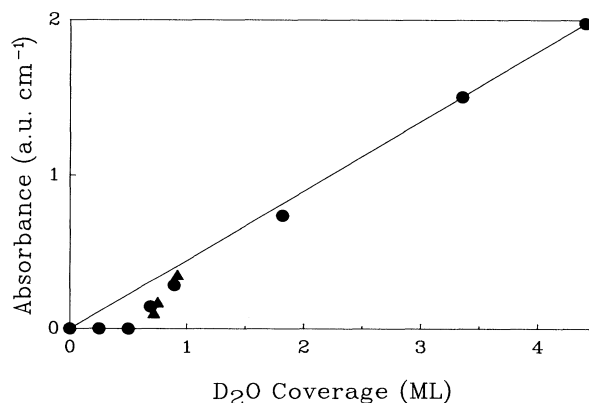

FIG. 1. ir-absorption spectra of D_2O layers on Ni(110): Curve a, 0.49 ML; b, 0.7 ML; c, 0.8 ML; d, 1.8 ML; e, 3.4 ML.

FIG. 2. Variation of integrated ir intensity of O-D stretch region vs absolute D_2O coverage.

the intensity; population of the second (icelike) *layer* has "switched on" the absorption by molecules in the first, chemisorbed *layer*. The broad band clearly indicates the presence of H bonding above 0.5 ML, in agreement with prediction. The O-D stretch band appears at the same coverage as the occurrence of a detectable "ice" peak in TD spectra. [For adsorption at < 150 K, a H-bonded band is detected as soon as a TD peak is detected in the ice desorption region (θ ~ 0.35 ML).]

The question remains as to whether the increase in intensity contributed by the chemisorbed layer (the first half monolayer) can be solely attributed to the enhancement due to H bonding. We have directly measured an enhancement factor of about 30 on this system by converting dangling OD groups to hydrogen-bonded ones and monitoring the change in absorption.[10] Since it is the coupling between the O-D vibrations in the ice lattice that leads to the broad band, we assume that the non-H-bonded O-D stretch band would be narrow. Using the observed width of the 2731-cm^{-1} band, we should expect a band close to 2731 cm^{-1} with a peak height of about 0.001 a.u. for the half monolayer. This is 20 to 30 times above the detection limit; i.e., the ir-absorption intensity of the chemisorbed layer must be over 20 times less than that predicted if H bonding were solely responsible for the enhancement.

The assumption of a narrow bandwidth and detectability of adsorbed OD groups is supported by our recent observation[4] of the O-D stretch of isolated chemisorbed hydroxyls on Ni(110) with widths of ~ 10 cm^{-1}.

If the bilayer [1.0 ML, $c(2\times2)$] consists of hexagonal ice,[11] then there should be about 0.5 ML of these "dangling" OD groups oriented normal to the surface. If the OD groups in the original $c(2\times2)$ chemisorbed layer exhibited the same absorption coefficient, then a peak of comparable or even larger intensity would have been expected (two OD groups per molecule). That no intensity is observed below 0.5 ML indicates a total enhancement factor of at least 500 times when the second *layer* (0.5 ML) is populated. We therefore postulate that the remaining enhancement factor of more than 17 (=500/30) arises from the dipole surface selection rule; only vibrations with a significant dipole component normal to the surface are ir active. The intensity is believed to decrease proportionally with cosα, where α is the angle between the active vibration and the surface normal.[12] In the present case cosα must be < 0.06 for the chemisorbed 0.5 ML, or α > 86°; i.e., the D-O-D plane must lie close to parallel to the Ni(110) surface. Recent ESDIAD (electron stimulated desorption ion angular distribution) measurements made by us under identical conditions[4] did not detect any emission from the $c(2\times2)$ surface (or at any coverage below 0.5 ML at 180 K). This confirms that the O-H bonds in the $c(2\times2)$ array must be highly inclined to the surface normal (we estimate that the angle must be $\gtrsim 50°$, assuming no bending of

the trajectories by the image force or compensating compression of the pattern by the applied field resulting from the sample bias of 50 V). The "turn-on" of the intensity between 0.5 and 1.0 ML and the fact that the slope of the absorbance-coverage relationship is roughly twice that observed for increasing ice coverage above 1.0 ML indicate three effects: (a) The orientation of the original chemisorbed molecules is altered so that the D-O-D plane lies much closer to the surface normal; (b) each second-layer molecule reorients one or more chemisorbed molecules; and (c) each second-layer molecule is H bonded to at least one chemisorbed molecule. The final layer probably has the hexagonal ice structure even at 1.0 ML. The energy for reorientation is clearly available from H bonding.

The ESDIAD results, which indicate a highly inclined orientation, seem to reduce the possibility that the "invisibility" of the $c(2\times2)$ water is due to local-field effects decreasing the effective dipole moment of the O-H(D) groups. Also, we have been able to produce a surface with a low (< 0.1 ML) coverage of hydroxyls which are clearly visible by ESDIAD and exhibit the expected absorbances in the infrared.[4] The observation of H-bonded molecules at lower coverages at lower adsorption temperatures correlates exactly with the detection of icelike desorption. In a hit-and-stick model (appropriate at low temperature, $T < 150$ K in this system), significant population of the second icelike layer would indeed be expected from coverages above ~ 0.3 ML, and there is no need to postulate more complex explanations. The excellent agreement between the measured coverage and that expected for a $c(2\times2)$ layer indicates a single adsorption site and adsorbed species, most likely a highly inclined non-H-bonded water molecule. The near in-plane orientation of the water molecules probably arises from bonding of the water molecules in a pseudo three-fold site in the troughs via the water $(1b_1)^2$ and $(3a_1)^2$ molecular orbitals. This would mean that the water molecules are bonded to Ni atoms in the first *and* second layers of Ni simultaneously.

The lack of clustering in the chemisorbed half monolayer is surprising, but must indicate that the preference for a particular site overcomes the tendency for H bonding; i.e., there is a net energy cost for moving water molecules out of the site preferred *in the absence* of H bonding. The temperature and coverage at which the present experiments indicate the presence of water monomers contrast with the low coverage and temperature for their observation on Cu(100).[12] We postulate that the corrugated nature of the fcc (110) surfaces might play a role.

In summary, we have demonstrated that the D_2O molecules in the chemisorbed $c(2\times2)$ half monolayer on Ni(110) are ir inactive and do not cluster. The enhancement of the ir absorbance upon H bonding of these molecules to a second half monolayer indicates that they must originally be bonded with the D-O-D plane highly in-

clined to the surface normal and reorient to form an ice-like hexagonal bilayer which is complete at a total coverage of 1.0 ML.

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