The molecular structure of the wetting layer of ice on Pt(111) is resolved using scanning tunneling microscopy. Two structures observed previously by diffraction techniques are imaged for coverages at or close to completion of the wetting layer. At 140 K only a $3\sqrt{3} \times 3\sqrt{3}R25.3^\circ$ superstructure can be established while at 130 K also a $\sqrt{39} \times \sqrt{39}R16.1^\circ$ superstructure with slightly higher molecular density is formed. In the temperature range under concern the superstructures reversibly transform into each other by slight changes in coverage through adsorption or desorption. The superstructures exhibit a complex pattern of molecules in different geometries.

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domains of the hexagonal superstructure. The angle \( \alpha = (52 \pm 2) ^\circ \) between rotational domains and the periodicity of \((17.1 \pm 0.9) \text{ Å} \) \((a, \bar{a}=16.9) \text{ Å} \) indicate that we observe the \( \sqrt{37} \times \sqrt{37} R 25.3^\circ \) superstructure in real space [equivalent matrix notation \( M_{\sqrt{37},P(111)} = (7 4, -4 3) \) with respect to the substrate, see also Fig. 4]. In Fig. 1(b), the molecular structure of the \( \sqrt{37} \) is resolved. The triangular depressions have an apparent depth between 0.6 and 1.0 Å with a mean value of \((0.7 \pm 0.1) \text{ Å} \), the error mainly given by the varying sharpness of the tip. They are separated by ridges containing dark spots. The dark spots are part of a hexagonal lattice with primitive translations \( \mathbf{a}_1, \mathbf{a}_2 \). The dense-packed rows of this lattice enclose an angle \( \beta = 5^\circ \) with the ones of Pt(111). With respect to \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) the superstructure has a matrix

![FIG. 1.](image1)

FIG. 1. (Color online) (a) STM topograph of the H\(_2\)O wetting layer on Pt(111) formed by adsorption at 140 K \((\sqrt{37} \times \sqrt{37} R 25.3^\circ) \). The superstructure is characterized by a lattice of depressions spaced by 17 Å. Shading in false colors (dark, light) indicates two rotational domains (domain boundaries marked by black and light lines). The lines in the respective shadings are parallel to rows of depressions in the appropriate domain (also indicated by parallel thin lines). The angle bisector (white line) is parallel to the step edges of Pt vacancy islands, i.e., parallel to the direction of lines, and inset as in depressions and additional protrusions. Color coding, construction of the superstructure we derive from the partly preserved upon cooling. The wetting layer can only be re-formed from the second HOC superstructure: \( \sqrt{39} \times \sqrt{39} R 16.1^\circ \) \((a, \bar{a}=17.3) \text{ Å} \) or \( M_{\sqrt{39},P(111)} = (7 5, -5 2) \). Figure 1(d) shows that also the \( \sqrt{39} \) builds from an ordered arrangement of triangular shaped depressions but with additional small bright protrusions imaged on the ridges with an apparent height above the water layer of \((0.9 \pm 0.1) \text{ Å} \) (i.e., 70% of the water layer height under comparable tunneling conditions) and an average diameter of \((5.5 \pm 0.6) \text{ Å} \). For the superstructure we derive \( M_{\sqrt{39},H,O} = (4 3, -3 1) \) with \( \beta = 2^\circ \). We could also prepare islands of the \( \sqrt{37} \) at 130 K by adsorbing only 0.55 molecules per site.

The proposed arrangement of the H\(_2\)O lattice (forming the ridges) with respect to the substrate is backed by the evaluation of the spot intensities found in previous diffraction studies.\(^{5,11,12}\) The spots with the highest intensities coincide with the reciprocal-lattice points calculated from the partly populated black dot lattice in our model. Note that this is not the case for the structure proposed originally\(^{11}\) (for more details see Ref. 19).

FIG. 2. (Color online) Phase transition from (a) \( T = 138 \text{ K} \), \( \sqrt{39} \times \sqrt{39} R 16.1^\circ \) symmetry to (b) \( T = 140 \text{ K} \), \( \sqrt{37} \times \sqrt{37} R 25.3^\circ \) symmetry within 8 min. The white dots vanish, enabling the water layer to reorganize as indicated by the change of the orientation of the superstructure. Image width 820 Å, \( U = 0.5 \text{ V} \), and \( I = 160 \text{ pA} \).

\( M_{\sqrt{37},H,O} = (4 2, -2 2) \). We interpret the dark spots as centers of hexagonal ice rings. The structural model proposed in Ref. 11 does not comply with these observations.

For lower \( T \) at 130 K, a second superstructure forms with prominent protrusions [Fig. 1(b)]. The Fourier transform shows two rotational domains with \( \alpha = (32 \pm 2) ^\circ \). The measured periodicity is \((18.0 \pm 0.5) \text{ Å} \). We identify this structure with the second HOC superstructure: \( \sqrt{39} \times \sqrt{39} R 16.1^\circ \) \((a, \bar{a}=17.3) \text{ Å} \) or \( M_{\sqrt{39},P(111)} = (7 5, -5 2) \).
The wetting layer can be modified by prolonged scanning with $|U| \geq 4$ V as shown in Fig. 3(a). As the structure of this modified layer gives important clues on the structure of the intact layer, we will describe the effect of the protracted scanning in more detail. First a $\sqrt{3}$ structure results, as typical for H$_2$O/Pt(111) after electron irradiation, usually explained by electron-induced partial dissociation of H$_2$O.\textsuperscript{5,14} STM-induced dissociation is also known from related systems.\textsuperscript{23} Continued scanning leads to the complete removal of the water layer from the surface. At the edge of water-free areas [Fig. 3(b)] a transition from the Pt surface (left) via the dissociated $\sqrt{3}$ (middle) to the $\sqrt{37}$ (right) can be observed. Three associated height levels can be determined in the respective line profile. For $U=0.5$ V, the dissociated phase has a height of (0.7 ± 0.1) Å, whereas the $\sqrt{37}$ has a height of (1.4 ± 0.1) Å. In literature, the established model for the equilibrium structure of a 1:1 mixed ($\sqrt{3} \times \sqrt{3}$)R30° OH + H$_2$O structure is composed out of OH and H$_2$O in the same height above the substrate and with their molecular planes oriented parallel to the surface, i.e., a flat-lying geometry.\textsuperscript{22} As we find the $\sqrt{3}$ motif and a comparably low apparent height after dissociation we interpret the structure observed in Fig. 3(a) as this flat-lying phase. A distinct $\sqrt{3}$ pattern was also observed after adsorption of H$_2$O under impure conditions. Here, the structure is imaged with the same apparent height as the surrounding wetting layer, in contrast to the structure described above. Note that the bottom of the triangular depressions in the intact water layer has approximately the same height as the $\sqrt{3}$ structure.

In the following we analyze the nature of the depressions as the common structural element of both the $\sqrt{3}$ and the $\sqrt{37}$. Several examples of an inhomogeneous appearance of an H$_2$O wetting layer have been reported. In Refs. 7 and 13 the structure was interpreted as a moiré pattern, i.e., an interference pattern arising when two similar grids are superimposed. However, this effect can be ruled out here as it cannot explain the different appearance of neighboring depressions, the rather large depth, or the sharp edges of these pits. Another possible explanation for the depressions are molecular vacancy clusters, similar to the lace structure reported for submonolayer coverages of H$_2$O on Pd(111).\textsuperscript{10} which indeed bears a striking resemblance to the structures observed here. Geometrically, in such a flat hexagonal structure an imbalance between hydrogen bond donors and acceptors arises which leads to the appearance of holes in the water film.

It is reported that about 5% of the saturation coverage of CO adsorbs to the $\sqrt{39}$ and only a two-layer-thick ice film has a zero sticking probability for CO.\textsuperscript{14} Does this observation corroborate the hole model? We tested this by dosing CO on a closed water layer. However, the appearance of the triangular depressions did not change even upon exposure in excess of 1 MLE CO. Instead, widely spaced islands of the CO $\sqrt{3} \times \sqrt{3}$ or $c(4 \times 2)$ structure\textsuperscript{23} appeared inside the water layer [visible in Fig. 3(c) right from the center] indicating that CO is able to partly break up the H$_2$O layer here. Also for Xe no change in the appearance of the triangular depressions was observed.

During the CO experiments occasionally an inverted contrast STM imaging mode was encountered. We tentatively attribute this imaging mode to a CO molecule adsorbed to the PtIr tip. In inverted contrast mode the triangular depressions are imaged as protrusions with their triangular envelope rotated by 30°. The other parts of the wetting layer and CO islands are imaged 0.8 Å lower than the protrusions. Prolonged scanning in the inverted contrast mode causes the triangular protrusions in the wetting layer to grow to a connected pattern of the $\sqrt{3}$ [Fig. 3(d)], which displays the same height as the original protrusions. Apparently, the triangular protrusions are nuclei of the $\sqrt{3}$.

Based on the experimental results we suggest the following elements for the $\sqrt{37}$ and $\sqrt{39}$ as shown in Fig. 4. (i) The ridges of the superstructures consist of a hexagonal network of ice molecules derived from the lattice generated by the primitive translations $a_1$ and $a_2$ in Fig. 1. Each lattice point visible as a dark spot in Figs. 1(b) and 1(d) is surrounded by an ice ring. Consistent with previous results the ridges of the intact wetting layer are assumed to consist of a structure according to the H-down model.\textsuperscript{4–7} Previous work rules out that a significant number of dangling hydrogen bonds points into the vacuum, which makes the first water layer hydrophobic, exemplified by three-dimensional ice growth on top. Consequently, we propose that the molecules in the ridges are arranged similar to the H-down model. However, as the position of the hydrogen atoms cannot be determined using STM we made no attempt to propose an orientation of individual water molecules shown in Fig. 4. Furthermore, we
FIG. 4. (Color online) Sketches of the molecular structure (dismissing hydrogen atoms). Left: $\sqrt{3}7 \times \sqrt{3}7R25.3^\circ$ supercell. The ridge phase (circles) is an ice sheet in the H-down geometry whereas the depressions are segments of a $\sqrt{3}$ structure. The unit-cell vectors of the Pt $(e_1, e_2)$, the H$_2$O lattice $(a_1, a_2)$, and the superstructure $(s_1, s_2)$ are indicated. Right: model of the $\sqrt{3}7 \times \sqrt{3}9R16.1^\circ$ supercell. Symbols as in (a), in regions where the second-layer admolecules are found are marked by light circles.

made no attempt to relax the molecular positions. In the resulting $\sqrt{3}7$ ($\sqrt{3}9$), the hydrogen bond length of the molecules in the ridges is extended only by 0.7% ($1.8\%$) compared to the one in bulk ice even if one neglects possible relaxations through the presence of the depressions. (ii) The triangular depressions are filled with water molecules forming the basic building block of the $\sqrt{3}$ or something very similar (gray hexagons in Fig. 4). As the triangular depressions are not empty, have under regular imaging conditions the same height as the $\sqrt{3}$ and act as their nuclei they are most probably filled with flat-lying molecules and/or flat-lying fragments in an $\sqrt{3}$ geometry. It has to be noted that a small flat-lying segment does not have to contain dissociated H$_2$O in order to avoid the occurrence of frustrated hydrogen bonds. If a complete hexagon of a nondissociated $\sqrt{3}$ phase is placed inside the depression one arrives at the structures recently proposed in Ref. 16. (iii) In addition, to the $\sqrt{3}9$ in each unit-cell water in the second layer is adsorbed, thereby saturating dangling bonds, and thus lowering the energy.24 This provides a simple explanation for the bright protrusions observed in Fig. 1(d). We assume that the protrusions are formed by a single water molecule, as we infrequently observe protrusions consisting of two or three dots which are most probably composed out of two or three water molecules.

In order to obtain a coverage estimate, we assume the same molecular density in the triangular depressions as in the ridge phase, leading to 0.65 (0.70) molecules/site for $\sqrt{3}7$ ($\sqrt{3}9$), in fair agreement with uptake measurements25 for the $\sqrt{3}9$. The ease of the phase transformation can be rationalized by the similarity of the two structures, the almost identical length of the OH bonds and the similar orientation of the dense-packed molecular rows. Note that the $\sqrt{3}7$ is most probably identical to phase II in Ref. 13 whereas phase I from this reference could not be reproduced.

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19 See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.82.161412 for further experimental results regarding the phase transformation and a detailed comparison of our model with the scattering data of Refs. 5, 11, and 12.