

## Monomer Structures of Water Adsorbed on $p(2 \times 2)$ -Ni(111)-O Surface at 25 and 140 K Studied by Surface X-Ray Diffraction

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The structures of a monomeric water molecule adsorbed on  $p(2 \times 2)$ -Ni(111)-O surface were determined by difference Fourier calculations. At temperatures of 25 K, water molecules chemisorb predominantly at  $2 \times 2$  oxygen atom sites, forming an OH---O<sub>ad</sub> ( $2 \times 2$ ) hydrogen bond. A  $2 \times 2$  oxygen atom (O<sub>ad</sub>) is surrounded by one to three monomeric water molecules, which take statistically disordered positions with threefold symmetry. At temperatures of 140 K, monomeric water molecules occupy a top site of Ni atoms via an oxygen lone pair and are stabilized as a singleton molecule on the surface.

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The structure of monomer or small water clusters and the nature of hydrogen bonding of water molecules on metal surfaces has been of fundamental importance and is also a mysterious issue in the field of surface science. Details regarding exact molecular structures on a well-defined metal surface remain controversial despite extensive surface scientific approaches [1–5]. Recently, surface x-ray diffraction using a third-generation synchrotron x-ray beam has made strict structure determination possible [6–8]. Positional parameters of not only heavy atoms such as metals and halogens but also light atoms such as carbon and oxygen on a top surface layer are straightforwardly determined with finer precision than that obtained by STM or LEED [9–11]. There exists a controversy in terms of bond distances and its interpretation for water-metal interaction for many systems. It is worth mentioning that reliable atomic positions of both oxygen atoms (water molecule and  $2 \times 2$  additive oxygen) and substrate Ni atoms are revealed simultaneously in surface x-ray study.

It is well known that water molecules adsorbed on a metal surface under UHV conditions or on an electrode surface in aqueous solution exhibit only weak interactions with surface metal atoms [12,13]. They form intermolecular hydrogen-bonding self-assembly structures, making the structure determination of a water molecule on a metal surface extremely difficult [14,15]. Because a typical OH---O hydrogen-bonding distance, 0.275 nm, matches the nearest-neighbor distances of fcc  $M(111)$  ( $M = \text{Pt, Rh, Au}$ ) and Ru(001) but differs from those of fcc  $M(111)$  ( $M = \text{Cu, Ni}$ ), the former and the latter surfaces would show commensurate and incommensurate structures, respectively [3,12,13,16–19]. It is quite rare for an ordered superlattice structure of water on the latter surface to be observed by x-ray diffraction. In contrast, water is likely to form a periodic ordered structure on oxygen-preposed  $p(2 \times 2)$ - $M(111)$ -O ( $M = \text{Pt, Ni}$ ) and  $p(2 \times 2)$ -Ru(001)-O surfaces because surface additive oxygen

atoms play an important role as anchoring atoms or have a templation effect on the surface [20–23].

The structure of the  $p(2 \times 2)$ -Ni(111)-O surface has been reported by Pfnur *et al.*, and the adsorbate-induced relaxation of the  $p(2 \times 2)$ -Ni(111)-O surface has been investigated by LEED and photoelectron diffraction [24,25]. The influence of the surface additive oxygen atoms on water adsorption and the stability of an isolated water molecule on Ni(111) was investigated in the present study. We report herein for the first time results regarding the precise oxygen atom positions of adsorbed water molecules as well as buckled Ni substrate atoms by the use of surface x-ray diffraction.

Experiments were carried out in an ultrahigh vacuum chamber built at BL13XU at SPring-8. The maximum beam flux was  $6 \times 10^{13}$  photon/s [26]. The wavelength of the x-ray beam was 0.0611 nm (20.3 keV). The adsorption of water molecules was carried out on  $p(2 \times 2)$ -Ni(111)-O surface at temperatures of 25 and 140 K. The coverage of water is  $\theta_{\text{H}_2\text{O}} = 0.67$ . The LEED pattern  $p(2 \times 2)$  remained unchanged after the introduction of H<sub>2</sub>O on the  $p(2 \times 2)$ -Ni(111)-O surface. The diffraction data were collected using a  $z$ -axis mode. The angle of incidence was fixed to 0.7 degree. After finishing intensity data collection of the  $p(2 \times 2)$ -Ni(111)-O + H<sub>2</sub>O sample surface, the LEED intensities still showed a clear  $2 \times 2$  pattern in both the 25 and 140 K phase. The intensities were reproducible over prolonged time periods during intensity data collection. We collected a total of 67 and 319 noninteger reflections at 25 and 140 K, respectively, from the new  $2 \times 2$  structures. The Texan software was used for the structure refinements. The artificial lattice parameter for the  $c(c^*)$  axis (index  $L$ ) was assumed.

At both high and low temperatures, a threefold rotation and mirror symmetry were observed in the reflection set. Therefore, at the initial stage of water adsorption, the surface symmetry appears to be  $p3m$ . However, a slight symmetry reduction appeared gradually in due course of time. The symmetry reduction was ascribed to a small

buckling of nickel atoms on the surface [27]. Because the LEED pattern showed a clear  $2 \times 2$  pattern at both high (140 K) and low (25 K) temperatures until the end of the intensity collection, we assumed the symmetry of the surfaces to be  $p3$  in the calculation. This means x-ray beams could induce a small buckling of nickel layers but never affect top-layer structure including water molecules. Since we adopted only reflection data which maintain strict  $p3(m)$  symmetry, there is no possibility of beam damage for the structure analysis. Prior to searching for water molecules, the positional parameters of Ni and  $2 \times 2$  additive oxygen atoms were refined to find a buckling structure of the substrate  $p(2 \times 2)$ -Ni(111)-O surface. The  $R$  factors at this stage converged to 26.7 (140 K) and 18.2 (25 K), which were insufficient. Because the contribution of Ni atoms (three layers of Ni surface) in the observed fractional order reflection intensities is not necessarily larger than that of the oxygen adatoms, a lack of contribution from ordered water molecules on the surfaces would

cause an inconsistency in the calculated structure factors compared with the observed structure factors (experimental intensities). The residual electron densities originating from a missing water molecule that is adsorbed on the surface can be calculated by difference Fourier synthesis. Fourier coefficients, experimental structure factor  $|Fo(hkl)|$  minus calculated structure factor  $|Fc(hkl)|$ , were used in the difference Fourier calculations.

Difference Fourier ( $Fo - Fc$ ) synthesis at the high temperature phase (140 K) was subsequently carried out using structure factors  $[Fc(hkl)]$  calculated from the refined parameters of Ni and  $2 \times 2$  oxygen atoms and structure factors  $[|Fo(hkl)|]$  observed experimentally. Because  $|Fo(hkl)|$  includes information regarding scattering power of not only Ni and  $2 \times 2$  oxygen atoms but also of adsorbed water molecules assumed to have the  $p3$  symmetry, one can straightforwardly allocate the positions of water molecules from the difference Fourier map. A large peak appeared at a top site of a Ni atom at threefold axis, as shown in Fig. 1(a). We separately calculated Patterson synthesis. The Patterson synthesis also showed exactly the similar peak on top of the Ni atom. We identified this peak as corresponding to an adsorbed water molecule and refined all the positional parameters and temperature factors. The final  $R$  factor was reduced to 0.079, which is reasonably small.

Figure 1(b) provides the surface structure at 140 K. Significant buckling shifts in the first and second layers of the  $p(2 \times 2)$ -Ni(111)-O surface were found to be 0.0039(7) and 0.0033(10) nm, respectively. The averaged Ni-Ni layer distances between first and second and second and third are 0.1932(9) and 0.2017(10) nm, respectively, which are slightly shortened compared with the bulk-phase value (0.2034 nm). The degree of lateral shift ( $d$  value in the arrow), 0.0032(3) nm, is in good agreement with that of the previous LEED result for  $p(2 \times 2)$ -Ni(111)-O [24].

Table I lists the typical bond lengths. The  $O_{ad}(2 \times 2)$ --OH<sub>2</sub> (water) distance 0.303(4) nm is much larger than the usual OH--O hydrogen-bonding distance of 0.275 nm. There exist no significant hydrogen-bonding interactions on this surface, and the water molecule is considered to be a singleton monomer molecule. Both the oxygen atom of the water molecule and the additive  $2 \times 2$  oxygen atom form a honeycomb structure, where no appreciable hydrogen-bonding network is seen. On the

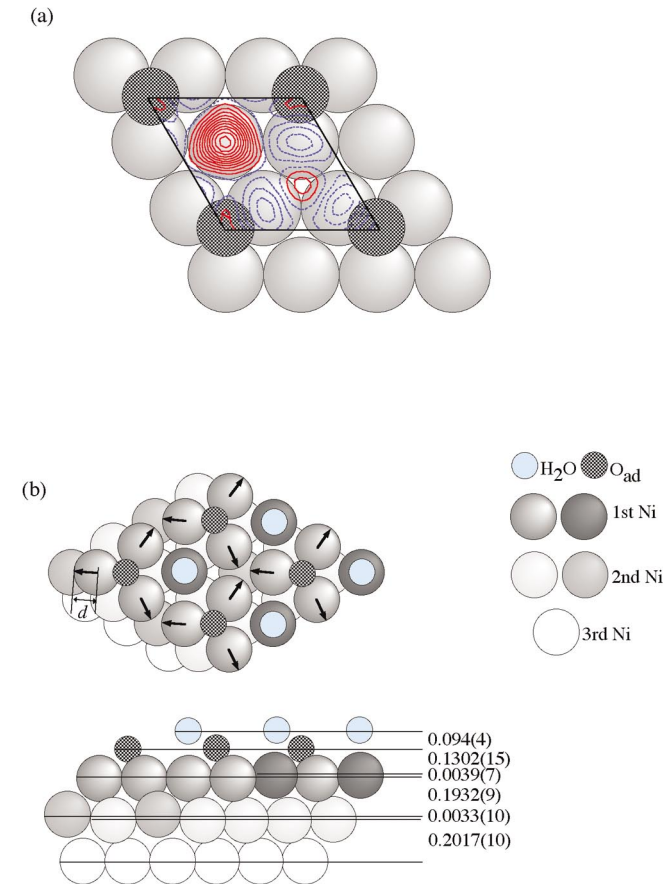


FIG. 1 (color). (a) In-plane contour map plot of difference electron densities calculated by difference Fourier syntheses at the height of 0.20 nm above  $p(2 \times 2)$ -Ni(111)-O surface at 140 K. Continuous lines and dashed lines indicate positive and negative electron densities, drawn at every  $0.05 e \text{ \AA}^{-3}$ , respectively. (b) The surface structure based on the optimum parameters for water adsorbed  $p(2 \times 2)$ -Ni(111)-O after annealing to 140 K.

TABLE I. Structural parameters of water adsorbed on  $p(2 \times 2)$ -Ni(111)-O at the high (140 K) and low (25 K) temperature phases.

| 140 K<br>Parameter        | (nm)       | 25 K<br>Parameter          | (nm)     |
|---------------------------|------------|----------------------------|----------|
| Ni- $O_{ad}$              | 0.1991(15) | Ni- $O_{ad}$               | 0.202(8) |
| Ni-OH <sub>2</sub>        | 0.2241(22) | Ni-OH <sub>2</sub>         | 0.272(8) |
| $O_{ad}$ -OH <sub>2</sub> | 0.303(4)   | $O_{ad}$ -OH <sub>2</sub>  | 0.26(2)  |
| $d$                       | 0.0032(3)  | $O'_{ad}$ -OH <sub>2</sub> | 0.28(2)  |

other hand, the Ni-O<sub>ad</sub>(2 × 2) distance of 0.1991(15) nm is slightly longer than that of the previous LEED result of 0.183 nm [24].

The distance between Ni and an adsorbed water molecule, 0.224(2) nm, is much longer than that of Ni-O values in the reported normal [Ni(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup> aquo-complexes, 0.202–0.208 nm [28,29]. The O-metal distances of D<sub>2</sub>O adsorbed on Ru(001) surface are determined to be 0.208(2) and 0.223(2) nm by LEED [3]. The present Ni-O distance [0.224(2) nm] agrees well with the longer value [0.223(2) nm] for the Ru-O distances. On the other hand, a recent x-ray absorption study shows the distance (Pt-O, 0.23–0.24 nm) which seems longer than the present value [4]. According to recent density-functional theory calculations, Feibelman has proposed the half dissociated OD + D<sub>2</sub>O monolayer on Ru(001) in which each oxygen atom lies 0.209 and 0.216 nm above the Ru atoms [30]. King *et al.* have reported that O-metal bond lengths of H<sub>2</sub>O monomer above Pt(111), Ru(001), Rh(111), and Pd(111) are 0.236, 0.229, 0.231, and 0.228 nm, respectively [31]. These theoretical and experimental results suggest that both the atomic radius of each metal atom and the bonding interaction (adsorption energy on the metal of a monomer or a bilayer water) would participate in the O-metal distance. Our result, 0.224(2) nm, is in favor of the LEED result from Menzel *et al.* [the longer counterpart of 0.223(2) nm] and the calculation results from King *et al.* The recent x-ray absorption study result (0.23–0.24 nm) is also consistent with our present result [0.224(2) nm], taking into consideration that atomic radius of Pt is longer by 0.014 nm than that of Ni.

The most pronounced feature in the buckling deviation due to water adsorption is that the three substrate Ni atoms directly in contact with the 2 × 2 additive oxygen atom deviate downward, whereas the remaining Ni atoms in contact with water molecules show an upward buckling shift (reversed deviation) in the first Ni layer.

Difference Fourier (*F<sub>o</sub> - F<sub>c</sub>*) synthesis at the low temperature phase (25 K) showed characteristic residual electron density around a threefold axis. Figure 2(a) shows the result of electron density distributions for the *F<sub>o</sub> - F<sub>c</sub>* synthesis (just before performing least-square refinements of the positional parameters). It is quite clear that the peaks correspond to water oxygen adsorbed on a 2 × 2 additive oxygen atom, and the water molecules are considered to be statistically disordered around the threefold axis. After refinements of all the parameters, including a newly observed oxygen atom of a water molecule, the oxygen position converged approximately at the center of two adjacent 2 × 2 additive oxygen atoms. The site at which the water molecule adsorbs is denoted by X. The positions are close to bridging sites rather than the threefold sites. Because the distance between the peaks related to the threefold rotation axis is 0.22(1) nm, the oxygen atoms might not occupy the three positions simultaneously, taking into consideration that the OH---O bonding distance distributes in the range of 0.255–0.285 nm. The 0.22 nm

value, however, is close to those hydrogen-bonding distances, and one cannot exclude the possibility that the disordered water oxygens occupy two or three positions simultaneously, depending upon the water coverage. Because the adsorbed water molecule is located 0.272(8) nm from the substrate Ni surface atom, the water molecule is not adsorbed on the surface but is chemisorbed (hydrogen-bonding) on a 2 × 2 oxygen atom. The Ni-O<sub>ad</sub> distance of 0.202(8) nm is slightly longer than the previous LEED result of 0.183 nm. The H<sub>2</sub>O---O<sub>ad</sub>(2 × 2) distance, 0.26(2) nm, is a typical value for OH---O hydrogen bonding. The oxygen atom of the water molecule does not reach two adjacent 2 × 2 additive oxygens with the same distance, but shifts the position to either side of the 2 × 2-O<sub>ad</sub>. Therefore, there are two short contacts, O<sub>ad</sub>-OH<sub>2</sub> [0.26(2) nm] and O'<sub>ad</sub>-OH<sub>2</sub> [0.28(2) nm]. There is no appreciable lateral shift in fcc Ni atoms in contrast with the high temperature phase. The pronounced feature in the buckling deviation due to water adsorption is also not seen in the low temperature phase as shown in Fig. 2(b).

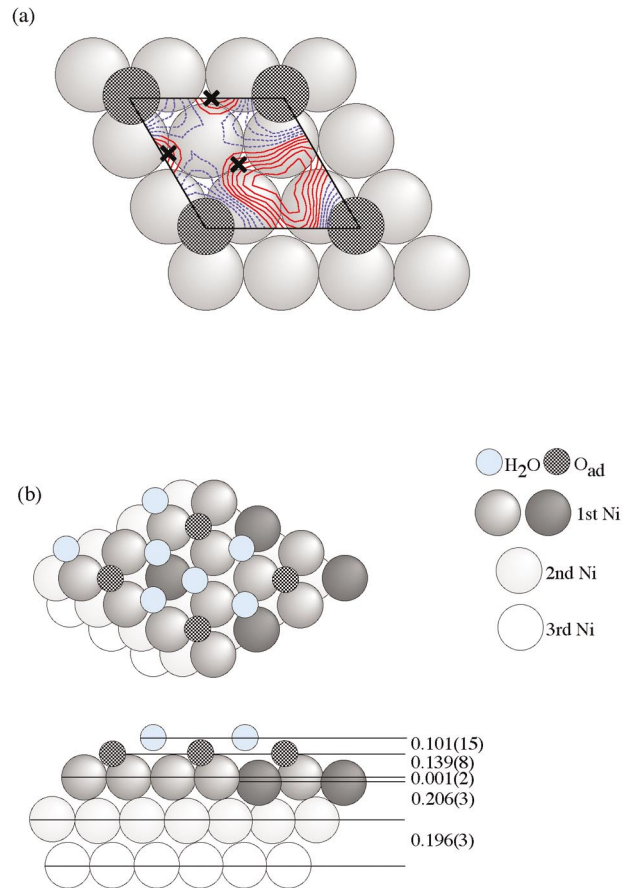


FIG. 2 (color). (a) In-plane contour map plot of difference electron densities calculated by difference Fourier syntheses at the height of 0.20 nm above *p*(2 × 2)-Ni(111)-O surface at 25 K. Continuous lines and dashed lines indicate positive and negative electron densities, drawn at every 0.01  $e \text{ \AA}^{-3}$ , respectively. (b) The surface structure based on the optimum parameters for water adsorbed *p*(2 × 2)-Ni(111)-O at 25 K.

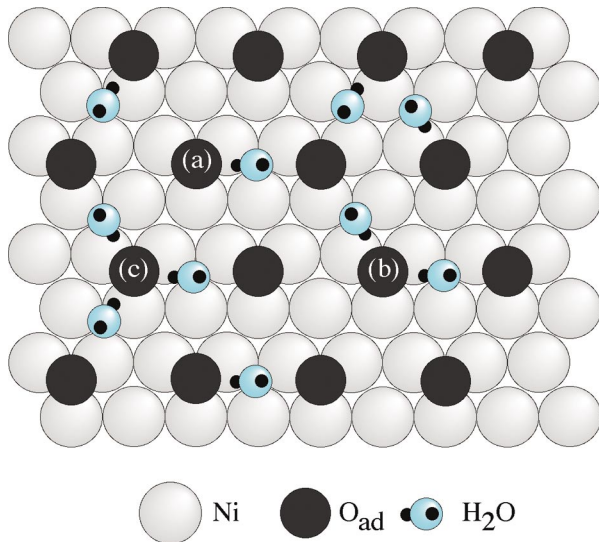


FIG. 3 (color). Schematic model of the disordered structure at 25 K.

The disordered structure of the low temperature phase is schematically shown in Fig. 3. Water molecules are likely to be captured by  $2 \times 2$  additive oxygen atoms on the surface. Because the oxygen atom is located upward away from the surface, the local potential around  $2 \times 2$  additive oxygen site is lower than that of the top site on the Ni atom. Apparently, the  $\text{H}_2\text{O} \cdots \text{O}_{\text{ad}}$  interaction is strong enough to overcome ordering introduced by  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$  hydrogen bonds. At a high coverage condition ( $\theta_{\text{H}_2\text{O}} = 0.67$ ) in the present study, the water molecule is pulled away from the Ni lattice sites by  $2 \times 2$  additive oxygen, and the surface layer becomes disordered. This could be the reason why no residual electron density was observed on a top site of a Ni atom.

It is instructive to mention that the sites of adsorbed water at the  $2 \times 2$  oxygen are statistically disordered. Each  $2 \times 2$  oxygen atom can accommodate one [(a) site in the figure] or two [(b) site] or three water molecules [(c) site], as shown in Fig. 3. The  $p(2 \times 2)$  oxygen, for which the surface symmetry is  $p3$ , influences the  $\text{H}_2\text{O}$  adsorption processes; at higher coverages, oxygen atoms are fully “saturated” by the surrounding  $\text{H}_2\text{O}$  molecules. Because the water molecules occupy either an (a), (b), or (c) site in a statistically disordered way, the surface structure crystallographically shows  $p3$  symmetry. The similar adsorption structure of water on an oxygen-predosed surface was found at low temperature on  $p(2 \times 2)$ -Pt(111)-O surface [19]. Recent infrared reflection absorption spectroscopy of water adsorption on  $p(2 \times 2)$ -Ni(111)-O surface at 25 K has shown the appearance of two different  $\nu$  OD stretching absorption bands at around  $2700 \text{ cm}^{-1}$  (free OD stretching) and  $2550 \text{ cm}^{-1}$  (bonded OD stretching), irrespective of  $\text{D}_2\text{O}$  coverages [32]. The infrared spectroscopic results indicate that double donation of a water molecule onto two adjacent  $2 \times 2$  oxygens is improbable. The infrared spectra also showed that the  $\text{H}_2\text{O} \cdots \text{O}_{\text{ad}}$  ( $2 \times 2$ ) hydrogen bonding

is destroyed by heating the sample higher than 100 K. Upon annealing the surface to a temperature higher than 100 K, desorption as well as migration of the  $\text{H}_2\text{O}$  molecule onto the top site on Ni proceeds without dissociation of water. The present x-ray result at high and low temperature phases agrees well with the IR spectra [32]. As a conclusion, we showed monomeric water molecules adsorbed on  $p(2 \times 2)$ -Ni(111)-O surface at both 140 K and 25 K. At the high temperature phase, a singleton water molecule is stabilized on a top nickel site with the Ni-O distance of  $0.224(2) \text{ nm}$ , while at the low temperature phase, monomeric water molecules are directly hydrogen bonded to a  $2 \times 2$  oxygen atom ( $\text{O}_{\text{ad}}$ ) with the  $\text{O}_{\text{ad}} \cdots \text{O}$  distances of  $0.26(2)$  or  $0.28(2) \text{ nm}$ .

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