

Water Adsorption on Perfect $\text{CaF}_2(111)$ Studied with He Scattering: Experimental Evidence for Ordering of Nanoclusters

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Elastic and inelastic He-atom scattering were used to nondestructively investigate the water adsorption on UHV cleaved $\text{CaF}_2(111)$ surfaces. Below 145 K a $p(4 \times 4)$ adsorbate structure was observed. The corrugation function deduced from the diffraction intensities directly shows the formation of a two-dimensional periodic structure from water nanoclusters. Using the observed lateral extension and employing the Bernal-Fowler-Pauling rules, we arrive at six H_2O molecules per cluster. This surprising result is confirmed by the observation of a very low energetic Einstein mode at ~ 6 meV.

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The interaction of water with solid surfaces is of general importance in the field of basic and applied research (see [1] and references therein). Recently, adsorbed water was shown to enhance significantly the observability of atomic periodicity with the atomic force microscope on highly ionic samples [2,3]. However, water adsorption on such polar substrates is not well understood [1,4], although the influence of adsorbed water, e.g., in degradation of optical coatings [5], has been known for more than 20 years. The main reason for this lack of knowledge is the instability of polar surfaces against ionizing radiation, which is commonly used for surface preparation and analysis. The variety of contradictory experimental results concerning water adsorption on the $\text{CaF}_2(111)$ surface is discussed in the recent x-ray photoemission spectroscopy paper of Wu *et al.* [4] where adsorption via defects could not be excluded. In the present work high purity synthetic CaF_2 crystals (UV quality, Zeiss Jena) were prepared by cleavage in UHV (base pressure below 2×10^{-10} mbar) and investigated with the nondestructive methods of He diffraction [6] and inelastic scattering [7,8]. Therefore, defects due to preparation and analysis are definitely excluded, which enables the characterization of adsorption phenomena on perfect $\text{CaF}_2(111)$ surfaces for the first time.

In our experiment [9] a supersonic He beam with an energy of 25 meV (energy resolution 4%) and a scattering angle of 90° is used. The He diffraction peaks for the bare cleavage plane [Fig. 1(a)] correspond to the translational symmetry of an ideal, unreconstructed $\text{CaF}_2(111)$ surface with lattice vector length 3.85 Å. In the adsorption studies the total pressure was measured with an ion gauge, and the partial pressures were controlled via mass spectra. The distilled water was stored in a quartz glass reservoir. Freeze-pump-thaw cycles to remove dissolved gases were repeated until the partial pressures of CO and CO_2 did not increase if the leak valve was opened. During H_2O exposure, the intensity of the specular peak, which is very sensitive

to changes of surface order and symmetry [10,11], was recorded. With the sample at room temperature (RT) exposed to 10^{-6} mbar H_2O for several hours, no intensity changes could be seen; this proves that H_2O molecules do not adsorb at RT on perfect $\text{CaF}_2(111)$ surfaces. In further experiments we exposed a freshly cleaved surface at lower temperatures to H_2O . Below 145 K and a water pressure of 10^{-8} mbar, the specular intensity initially decreased [Fig. 2(a)], but started to increase after ~ 10 s. At the following maximum of the specular intensity, the angular distributions in

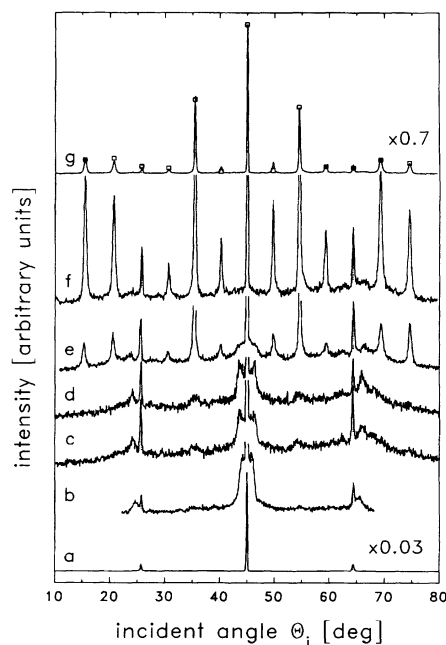


FIG. 1. Angular distributions along $[\bar{1}10]$ with primary energy $E_p = 25$ meV measured at 130 K for the bare $\text{CaF}_2(111)$ surface (a) and for various H_2O exposures from 0.04 Langmuir (b) to 0.08 Langmuir (g). Angular variation is achieved by rotating the sample. As a visual guide, the first-order diffraction peaks of the substrate are marked with dotted lines. The squares indicate best-fit peak intensities (see text).

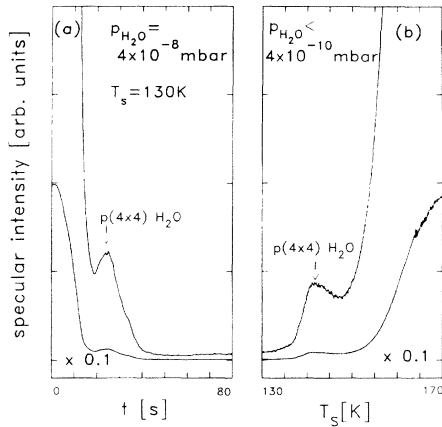


FIG. 2. (a) Development of the specular intensity upon H_2O exposure. (b) Temperature dependence of the specular intensity after large H_2O exposures. The He beam is incident parallel to the $[\bar{1}10]$ direction. The minimum in (a) approximately corresponds to Fig. 1(b).

both the $[\bar{1}10]$ and $[\bar{2}11]$ directions showed three new diffraction peaks between the diffraction maxima of the substrate [see Fig. 1(g) for the $[\bar{1}10]$ direction]. This proves that the adsorbate has arranged into a $p(4 \times 4)$ structure. The exposure dependent development of the diffraction intensities (Fig. 1) shows that the adsorption proceeds via the formation of islands: the side maxima of the specular peak at low coverages [Figs. 1(b)–1(d)] develop into broad shoulders at intermediate coverages

[Figs. 1(e)–1(f)] in analogy to low energy electron diffraction observations for islandlike growth [12]. The large diffraction intensities observed for the high-order beams in the optimally developed $p(4 \times 4)$ [Fig. 1(g)] directly reflect the strong enhancement of the surface corrugation amplitude due to the adsorbate. Water exposure after formation of the $p(4 \times 4)$ destroys the order completely as revealed by the vanishing of the specular [Fig. 2(a)] and all diffraction peaks. Upon heating above 150 K the original $\text{CaF}_2(111)$ diffraction pattern reappears as indicated by the temperature behavior of the specular in Fig. 2(b). We have repeated this adsorption-heating cycle more than 10 times without significant changes of the diffraction pattern characteristic for the clean substrate.

Our experimental findings are not consistent with a solid (ice) structure as expected for icelike structures on (111) metal surfaces [1]. Empirically, formation of an ice structure on $\text{CaF}_2(111)$ should be hampered as the intralayer nearest-neighbor distance of 3.85 Å dictated by the substrate is smaller than the nearest-neighbor distance of more than 4.31 Å of the water molecules in ice. From the distribution of the diffraction intensities we derived the surface corrugation function, from which we could deduce important information about the adsorbate structure within the $p(4 \times 4)$ unit cell [13]. The measured intensity distributions of the H_2O $p(4 \times 4)$ phase could be reproduced remarkably well within the hard corrugated wall model [13] with the simple two-parameter Fourier ansatz for the surface corrugation function:

$$z(x, y) = (z_{10}/2) \{ \cos(2\pi x/a) + \cos(2\pi y/a) + \cos[2\pi(x+y)/a] \} \\ + (z_{11}/2) \{ \cos[2\pi(x+y)/a] + \cos[2\pi(x-2y)/a] + \cos[2\pi(2x-y)/a] \}.$$

The best fit coefficients were found to be $z_{10} = 1.31 \text{ \AA}$ and $z_{11} = 0.82 \text{ \AA}$ [$a = 15.42 \text{ \AA}$ and x and y along the unit cell vectors \mathbf{a}_1 and \mathbf{a}_2 , $\angle(\mathbf{a}_1, \mathbf{a}_2) = 120^\circ$]. The calculated peak intensities are indicated as squares in Fig. 1(g). A grey scale representation of the corrugation is presented in the upper part of Fig. 3. The pronounced maxima showing up as the bright patches in the corrugation have to be attributed to the adsorbate particles. Taking into account the heights and the lateral extensions of these patches, we arrive at the striking conclusion that the water molecules form two-dimensional (2D) nanoclusters. With respect to the atomic structure of the substrate, a number of three or six molecules per cluster appears possible. Only hexagonal H_2O arrangements are compatible with the symmetry and the width of the bright patches of the corrugation. Indeed, clusters of six H_2O molecules are the smallest aggregates which obey the Bernal-Fowler-Pauling (BFP) rules adapted for molecular water adsorption [Ref. 1, Sec. 2]. The interpolation of theoretical

results for small free water clusters [14] gives an O-O distance about 2.8 Å in free hexamers, which matches the lateral extension of the observed patches very well. The number six H_2O molecules per cluster is also in accord with the predictions of the molecular dynamics (MD) studies of the water adsorption on the perfect $\text{CaF}_2(111)$ surface by Wassermann, Reif, and Matthias [15]. For direct comparison with the corrugation, a model of the surface with water hexamers is shown in the lower part of Fig. 3 on the same scale as the upper part. In this model the oxygen and hydrogen atoms are arranged in a way that the BFP rules are obeyed and the (4×4) periodicity is taken into account. The increase of the maximum corrugation amplitude from $\sim 1.4 \text{ \AA}$ for the clean surface to 4.3 Å for the H_2O $p(4 \times 4)$ structure is in favorable agreement with the increase estimated from the ionic radii of the CaF_2 substrate constituents and the van der Waals radius of the water molecules of 1.45 Å, whereby the bonding distance of the H_2O molecules to the topmost Ca

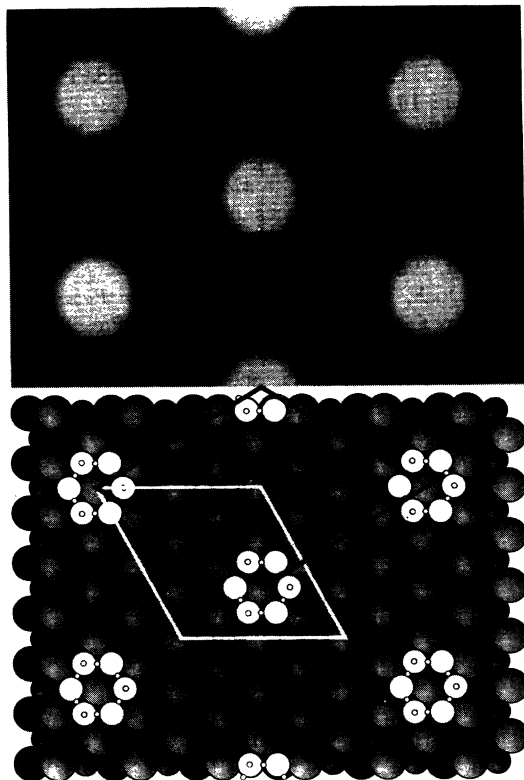


FIG. 3. Upper part: Grey scale representation of the corrugation of the $p(4 \times 4)$ H_2O adsorbate structure on $\text{CaF}_2(111)$ as determined from experimental diffraction intensities. Lower part: Model of the ordered H_2O adsorbate structure with the water hexameres positioned around the top fluorines as predicted in [15]. The dark lines indicate the observed $p(4 \times 4)$ unit cell, the light lines the $2\sqrt{3} \times 2\sqrt{3}$ unit cell predicted in [15].

ions of 4.62 \AA as calculated by Wassermann [16] is taken into account.

The MD simulations [15] show that at coverages around 0.5 monolayer (ML) a $2\sqrt{3} \times 2\sqrt{3}$ structure from hexameres should form (1 ML is defined with respect to the 2D lattice points). The $p(4 \times 4)$ structure observed corresponds to a coverage of 0.375 ML reasonably near to the predicted value. At lower coverages dimers and trimers were predicted which are little influenced by the substrate attraction and, therefore, are mobile at the surface [15]. The observed minimum of the specular intensity for exposures below the ordered $p(4 \times 4)$ [Fig. 2(a)] is in accordance with the disorder produced by such mobile aggregates. For coverages above the ordered structure the theoretical simulations [15] again yield a disordered adsorbate structure. The observed specular intensity [Fig. 2(a)] agrees also with this prediction.

The clustering of the water molecules is further confirmed by our inelastic He-scattering measurements. Time of flight (TOF) spectra were taken at a total flight path of 1.14 m including a sample-detector distance of

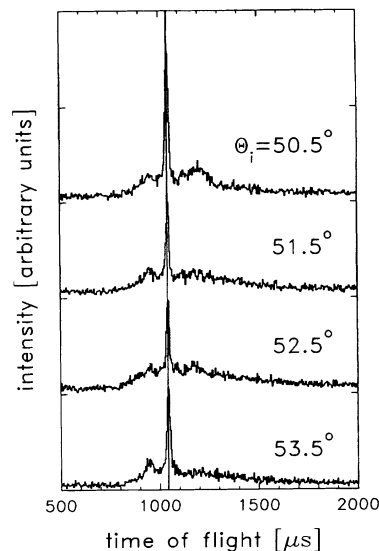


FIG. 4. TOF spectra along $[110]$ for $E_p = 25 \text{ meV}$ and for various angles of incidence θ_i , i.e., for various surface wave vectors. The elastic energy corresponds to a flight time of $1020 \mu\text{s}$. The dispersionless energy gain caused by water adsorbed in the $p(4 \times 4)$ phase is marked.

0.79 m . He atoms scattered from the $p(4 \times 4)$ structure yield, in addition to TOF features of the bare surface [9], a dispersionless mode at about $950 \mu\text{s}$ as shown in Fig. 4. The phonon energy of this low energy Einstein mode is $\sim 6 \text{ meV}$. In contrast to high resolution electron energy loss spectroscopy (HREELS) and IR spectroscopic investigations of adsorbates on metals, which are most sensitive to the vibration-induced dipole moments perpendicular to the surface, He-atom inelastic scattering is caused by the vibrational modulation of the surface corrugation. Due to the large unit cell dimensions of the ordered adsorbate structure and the large corrugation amplitude, the individual diffraction peaks of the $p(4 \times 4)$ structure are of low intensity. Consequently, inelastic intensities are also very poor, and only perpendicularly polarized vibrations that strongly change the corrugation should be measurable. Therefore, we can attribute the vibrational mode of the $p(4 \times 4)$ structure at $\sim 6 \text{ meV}$ to the vibration of the water hexameres against the substrate. According to Wassermann, Reif, and Matthias [15], this vibrational energy should be $\sim 4 \text{ meV}$ for hexameres positioned around the topmost anions (as shown in the lower part of Fig. 3) in reasonable agreement with our experimental result. It should be noted that this energy is much lower than the values determined with HREELS for the vibration of chemisorbed water against metallic substrates (e.g., $\sim 25 \text{ meV}$ on Ag [17] and $\sim 50 \text{ meV}$ on Ni [18]). As no dispersion of the surface mode could be resolved in our experiments, we may conclude that the lateral interactions of the water aggregates on CaF_2

as well as their bonding to the substrate are very weak. Thus, we may regard the present case as belonging to the category of physisorption systems.

In conclusion, molecular water adsorption on perfect $\text{CaF}_2(111)$ surfaces takes place only at temperatures below 145 K. An ordered $p(4 \times 4)$ H_2O structure is observed, whose corrugation, in connection with the Bernal-Fowler-Pauling rules, leads to the conclusion that the water molecules form hexameres, which arrange into the $p(4 \times 4)$ pattern. The bonding to the substrate is much weaker than for water chemisorption on metallic surfaces, as proved by the measured frequency of the water vibration against the substrate. These results are the first experimental proof of the formation of water nanoclusters and their lateral interactions to arrange in a 2D regular structure with large periodicity. Due to the weak bonding to the surface resulting in a very narrow coverage and temperature range in which the $p(4 \times 4)$ orders, the clusters represent a quasiliquid water phase which, regarding the vital role of the hydrogen bond, should also be of interest in biochemistry [19]. Essential features of the recent theoretical predictions by Wassermann, Reif, and Matthias [15] are confirmed. The discrepancies between the predicted $2\sqrt{3} \times 2\sqrt{3}$ and observed 4×4 periodicity of the hexameres and between the predicted and the observed temperature dependence leave, however, room for improvement in the theoretical work (see [20]). We note in closing that we observe completely different adsorption behavior on CaF_2 surfaces into which we deliberately induce defects [21]. Thus, the results of Zink, Reif, and Matthias [22], claiming to have observed water adsorption at RT, are most probably explained by residual defects on their mechanically polished surfaces.

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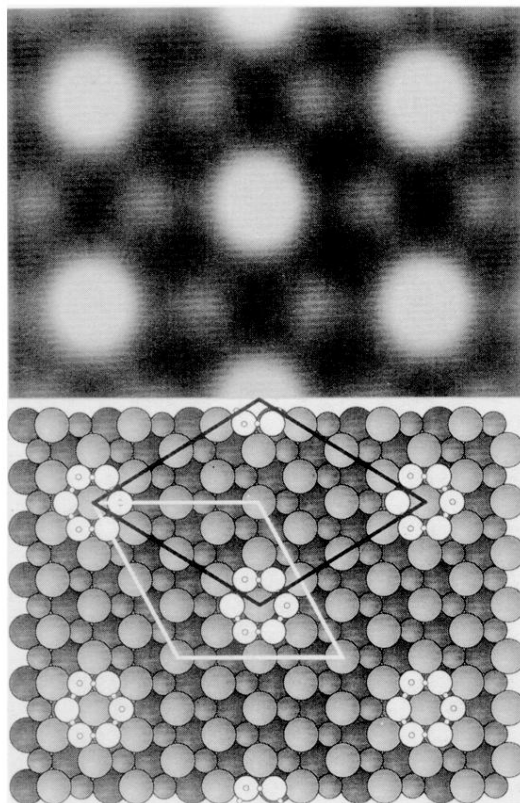


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