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Adsorption geometry of OH adsorbed at *F* centers on a NaCl(100) surface

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The orientation of molecular H_2O in a bilayer on defect-free NaCl(100) and of chemisorbed OH adsorbed at *F* centers on the (100) surface of NaCl was investigated using angle-resolved O *K* edge near-edge x-ray-absorption fine-structure spectroscopy (NEXAFS). High-quality single crystalline thin films of NaCl(100) of about four monolayers thickness were grown on Ge(100). These films were bombarded with 250 eV electrons so that *F* and *F'* centers of a maximum density of about 10% of a monolayer were created. Whereas on the defect-free surface only molecular water is adsorbed, dissociation occurs at the *F* centers and OH^- is bound. NEXAFS of molecular water shows almost no angular dependence even in the monolayer. This finding is consistent with formation of a hydrogen bonded bilayer of water suggested earlier. The OH species formed at the *F* centers is found to be inclined with respect to the surface normal by $39° \pm 4°$. An adsorption model is proposed.

I. INTRODUCTION

The adsorption of one of the most common molecules, namely, water, has been investigated on a variety of metal and semiconductor surfaces. Much less work, however, has been invested in the adsorption of this molecule on insulating materials like alkali halides,[1] for the obvious reason that H_2O is considered to be less reactive or even nonreactive on these surfaces. This expectation turns out to be correct for the interaction of H_2O with crystalline NaCl surfaces, which has been investigated systematically in recent years under UHV conditions using cleaved bulk crystals[2–4] or thin epitaxially grown films.[5–8] The use of epitaxially grown thin films on Ge(100) opens the possibility to apply electron spectroscopies to these systems without disturbing charging effects, and to easily control electron- and radiation-induced damage. Only molecular water is adsorbed on ideal, defect-free alkali halide surfaces in the temperature range up to 400 K, in contrast to the chemically more reactive metal or semiconductor surfaces, on which water tends to dissociate.[1] The water adsorption on NaCl(100), in particular, leads to formation of physisorbed long range ordered structures of $c(4\times2)$ symmetry at temperatures around 140 K and water partial pressures of 10^{-6} Pa, as demonstrated by several recent investigations.[2,3,7] Molecular dynamics calculations support the model of a hexagonal bilayer with six molecules per unit mesh, but slightly modified bond angles in the water molecules compared to gas phase water.[4]

Surfaces of ionic crystals, however, can never be expected to be free of defects. These defects are in many cases chemically much more reactive than the ideal surface of these crystals, and are hence of interest. Some of the best known defects in alkali halide crystals and on their surfaces are color centers (*F* centers) produced by missing negative ions. These missing halide ions can be replaced by other ions, e.g., by OH^-, which stems from the dissociation of a water molecule. Dissociative adsorption of water has indeed been observed at color centers of *F* and *F'* type.[6,8] To our knowledge, no information is available yet about the bonding geometry of these OH molecules.

Lateral interactions between these defects seem to be small, so that they do not form ordered structures. Therefore, methods based on long range order properties, such as conventional low-energy electron diffraction (LEED) *I-V* analysis, cannot be used, so that one has to resort to other methods sensitive to the local bonding geometry. In addition, the small scattering cross section of hydrogen for electrons prohibits the use of any nonresonant electron scattering method, especially at the low concentrations experimentally achievable. With a saturation coverage far below one monolayer (see below), the hydrogen-related contribution to the total scattering intensity is most likely too small for a quantitative analysis with the former methods. Measurements of the angular dependence of the near-edge x-ray-absorption fine structure (NEXAFS) are therefore particularly attractive in this case, because NEXAFS is not only chemically selective but also one of the very few methods which is highly sensitive to the configuration of hydrogen bonds. Although atomic positions are not directly measurable, the orientation of molecular orbitals on surfaces, i.e., the direction of bonds, can be determined very well (see, e.g., Ref. 9).

Nevertheless, the present case turned out to be a challenge, since the adsorbate orientation for a 10% coverage had to be determined, based on a small peak on an intense and strongly structured background originating from the substrate (see below). The reason for this relatively small coverage is that the creation of surface color centers by bombardment with 250 eV electrons saturates at a concentration of about 10% of a monolayer.[8] This concentration of defects does not destroy long range order of the NaCl(100) surface, as found with LEED. In addition, no indication has been found for agglomeration of sodium metal or for formation of clusters of color centers (e.g., *M* centers).

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II. EXPERIMENT

The experiments have been carried out at the Berlin electron storage ring BESSY at the SX 700-1 monochromator. For electron detection a 150° spherical analyzer (VG CLAM 2) was used. A double-chamber UHV system was directly connected to the beamline and equipped with a four-grid LEED optics and with two quadrupole mass spectrometers, one in each chamber. The preparation chamber also contained a sputter gun, a NaCl evaporator, and a H_2O gas inlet system. The manipulators of both chambers were coolable down to 120 K by liquid N_2. For a more detailed description, see Ref. 10.

The Ge sample was mounted by tantalum foils on two tungsten rods, which were attached to a transferable sample holder. The sample holder also carried a thermocouple connected close to the sample surface and a filament located behind the sample. The complete sample holder was transferable from one chamber to the other by combined use of the manipulator in the preparation chamber and a wobble stick.

The (100)-oriented Ge sample was polished by diamond paste down to 0.25 μm grain size in several steps and cleaned by sputtering and annealing cycles (sputtering at 400 K, annealing at 1100 K) until optical LEED revealed a brilliant (2×1) surface reconstruction at 180 K, and no impurities were detectable by electron spectroscopy for chemical analysis (ESCA). The crystal quality further improved in the course of our investigation by continued cleaning treatment so that this reconstruction became visible even at room temperature.

Thin NaCl films of typically four monolayers thickness were prepared by vacuum evaporation of NaCl onto the Ge substrate at a sample temperature of 175 K and by subsequent annealing to 480 K. Relative amounts were determined with a quartz microbalance, which in turn was calibrated using the characteristic changes of intensities of Ge and Na core levels when the first bilayer of NaCl was completed.[11] Layers prepared in this way yielded a sharp and bright (1×1) LEED pattern with spot widths comparable to those of the bare Ge surface. This finding shows that the NaCl films are pseudomorphic with the Ge substrate, but without the (2×1) reconstruction of the clean Ge surface.

Molecular water monolayers on these films were prepared by isobaric adsorption at 5×10^{-7} Pa and 140 K, recording the emergence of broad, but intense, $c(4\times 2)$ superstructure spots in LEED. After complete formation of the structure, the temperature and the water partial pressure were lowered simultaneously, which allowed us to maintain the monolayer even under UHV conditions without additional water background pressure.

Color centers in the NaCl(100) layer were prepared by directing a defocused 250 eV electron beam at the surface, which was set to a temperature of 150 K. An exposure of typically 3×10^{14} cm^{-2} (exposed area $\simeq 4$ mm^2) was sufficient to yield the saturation concentration of surface F centers.[8] According to the calibration carried out in Ref. 8 a saturation concentration of about 10% of a monolayer can be reached under these conditions. The surface was then immediately exposed to 18 L of H_2O. Water adsorbs dissociatively at the F centers and saturates them.[8] The remaining coadsorbed molecular water was desorbed by raising the substrate temperature to 220 K.

X-ray photoemission spectroscopy (XPS) and NEXAFS measurements at the O 1s absorption edge were carried out on samples prepared as just described. The KVV Auger yield at a kinetic energy of 513 eV was taken as a measure of the absorption cross section. In order to maximize the sensitivity the CLAM was operated at its maximum pass energy of 480 eV, yielding an energy window of about 10 eV width. The corresponding low resolution is tolerable because the width of the NEXAFS signal is determined only by the monochromaticity of the synchrotron light, whereas the broadening of accompanying photoemission peaks is even advantageous for the data analysis. The use of a 20 μm exit slit at an energy of 500 eV in the SX 700-1 monochromator results in a photon energy resolution of about 1 eV.[12] The energy calibration was carried out by using substrate photoemission peaks and the characteristic absorption of the synchrotron radiation by impurities on the monochromator.

III. RESULTS AND DISCUSSION

We start with a comparison of O 1s XPS peak positions of molecular water adsorbed on an undistorted NaCl surface, and of OH on the same surface after electron bombardment, as described above. After subtraction of a small shift (-0.3 eV) observed for all photoemission peaks, i.e., also for those of NaCl, presumably due to an altered charging effect on the damaged surface, we found a reduction of the O 1s binding energy on the damaged surface by 1.9 eV. The value of this chemical shift, compatible with that found earlier,[8] is an indication of the ionic character of this chemisorbed species. It can be easily explained as being due to increased screening of the nucleus by the additional charge on the oxygen atom.

An overview of the raw data obtained close to the oxygen K edge with a fixed detection energy of 513 eV is shown in Fig. 1. As is obvious from this figure, the interpretation and data evaluation of the oxygen K edge NEXAFS data are complicated by the occurrence of a variety of additional photoemission peaks. Because of the small thickness of the NaCl film the spectra contain contributions from Ge 3d, Na 2p and 2s, and Cl 3s, in addition to the signals from OH and H_2O, respectively, and a broad plasmon loss originating from the Ge substrate around 556 eV. Photoemission peaks were separated from the NEXAFS resonance by variation of detection energy. The corresponding assignment is shown in Fig. 1. The spectrum with adsorbed OH shows a sharp feature at 534.5 eV photon energy in addition to the photoemission peaks. This peak can be attributed to the excitation from 1σ to the $4\sigma^*$ resonance of chemisorbed OH. No other adsorbate-induced peaks were found. According to our energy calibration, the $4\sigma^*$ resonance is still located slightly below the vacuum level, in agreement with the small width measured. The topmost spectrum reveals the NEXAFS resonance of a molecular water monolayer around 539 eV. This spectrum has little in common with the first adsorbed layer (‘‘monolayer’’) of water on transition metal surfaces,[13,14] but resembles qualitatively that of condensed multilayers of water. The close resemblance of our bilayer spectrum to that of condensed water layers reflects the reduced interaction of the

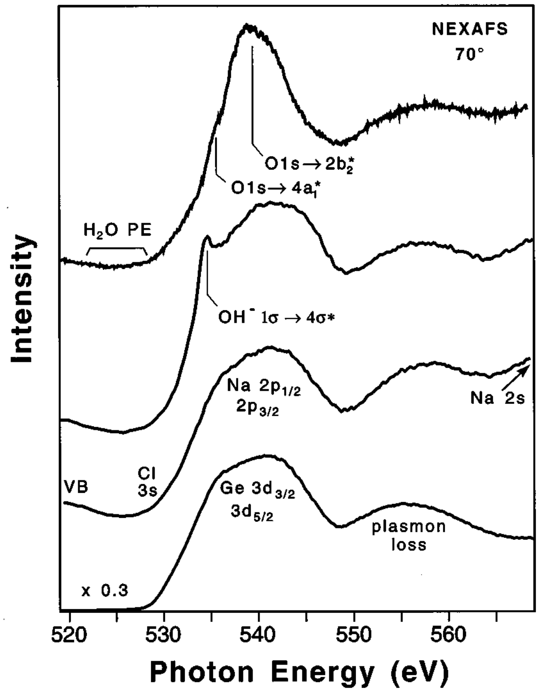

FIG. 1. O *K* edge NEXAFS at an angle of incidence of 70°. From bottom to top: clean Ge(100), clean NaCl(100)/Ge(100), OH^-/NaCl(100)-*F*, and H_2O/NaCl(100). Broad structures are photoemission peaks of Ge and NaCl as indicated. The OH^- $1\sigma\rightarrow 4\sigma^*$ resonance is located at 534.5 eV. The H_2O NEXAFS signal consists of peaks at 535.5 and 538.8 eV and a broad shoulder. For identification, see text. The NaCl film thickness is about 4 ML, the OH^- coverage roughly 10% of a monolayer.

water molecules with the insulating surface of NaCl compared to the more polarizable metal surfaces, and is not surprising, therefore. Two peaks can clearly be identified in the topmost spectrum of Fig. 1 at 535.5 and 538.8 eV. A comparison with the NEXAFS spectrum of water in the gas phase[15] shows that the two excitations with the lowest energy are transitions from O 1*s* to $4a_1/3s$ and to $2b_2/3p$, both with σ character. The latter peak is dominating in the gas phase spectrum. If we identify the shoulder at 535.5 eV and the main peak at 538.8 eV with these transitions, we see that the peaks are shifted and the separation of these peaks is somewhat larger than in the gas phase. The shift is a well known effect of the condensed phase[16,14] due to the overlap of the resonance states. Additional modifications of the peak positions might be due to the fact that the bilayer in our case (see below) considerably deviates from the structure in bulk ice. We therefore use the assignment just mentioned as our working hypothesis. According to the gas phase spectra, a series of peaks with mixed symmetry character follows at higher excitation energies. In our bilayer spectrum only a broad shoulder appears which can be associated with these excitations. Since we cannot separate these contributions, we made no attempt to quantitatively analyze these features, and used only the main peak for the analysis of the orientation of the water molecule.

For the determination of the local orientation of the adsorbate molecules, spectra at various angles of incidence have been measured. In order to extract the pure NEXAFS signal it is necessary to subtract the spectra of the clean substrate from the raw data and normalize the difference spectra to equal heights at the nonresonant part of the absorption edge. On a substrate with threefold or higher symmetry no dependence on azimuthal angle should be expected.[9] For the probability of excitation of a σ state into a σ resonance, as in our case, the following dependence on the angle of incidence of the radiation, θ, on the tilt angle α of the molecular orbital with respect to the surface normal, and on the degree of polarization P (here $P=85\%$) is expected:[9]

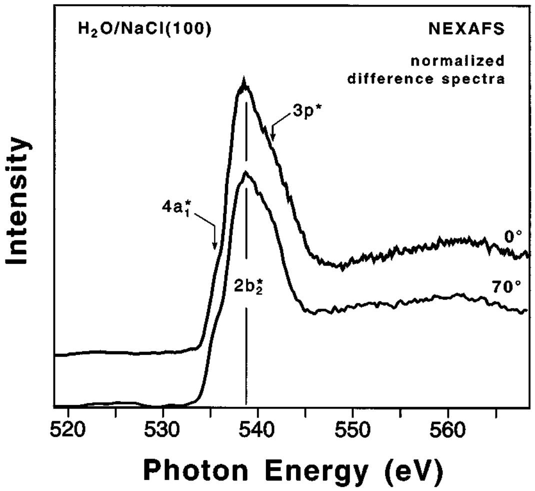

FIG. 2. O *K* edge NEXAFS of a H_2O bilayer at angles of incidence 0° and 70°. Properly attenuated substrate photoemission peaks were subtracted, and spectra were normalized to the nonresonant absorption edge.

$$I_\sigma \simeq \frac{P}{3}[1-(3\cos^2\alpha-1)(\tfrac{3}{2}\cos^2\theta-1)]+\frac{1-P}{2}\sin^2\alpha. \tag{1}$$

Curve fitting of the resonance intensities as a function of θ to Eq. (1) yields the tilt angle α. It is also possible to carry out a simpler evaluation using only the ratio of intensities at 0° and at 70°, the so-called I_0/I_{70} method,[9] for which any constant of proportionality cancels out.

For the pure $c(4\times2)$ ordered H_2O layers the standard I_0/I_{70} method was used after subtraction of the properly attenuated spectrum of the clean surface. The normalized difference spectra are shown in Fig. 2 for angles of incidence 0° and 70°. Within error bars only a very small angular dependence of the σ-like resonance of the water molecule was found, which results in an average tilt angle of $57°\pm6°$. This value is clearly compatible with the model of an icelike bilayer structure as proposed earlier by Fölsch *et al.*[7] and corroborated by the molecular dynamics calculations.[4] Because of the two domains of the $c(4\times2)$ structure formed on NaCl(100), no azimuthal dependence should be expected again so that the determined angle represents a weighted average of the polar tilt angles of the H_2O molecules of different orientations with respect to the surface normal. Assuming an angle of 52° for the upper water molecule, i.e., one water O-H bond perpendicular to the surface with a bond angle and an orientation similar to

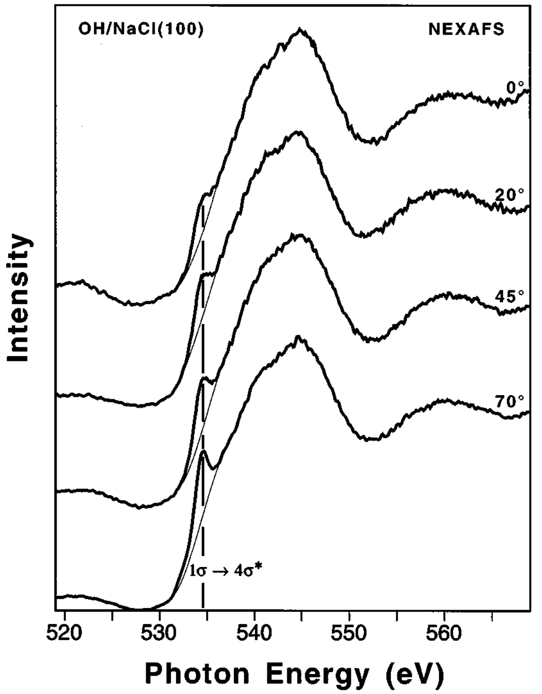

FIG. 3. O 1*s* NEXAFS spectra of a NaCl(100) surface covered with OH^- at various angles of incidence. OH^--coverage is roughly 10%, analyzer set to 513 eV.

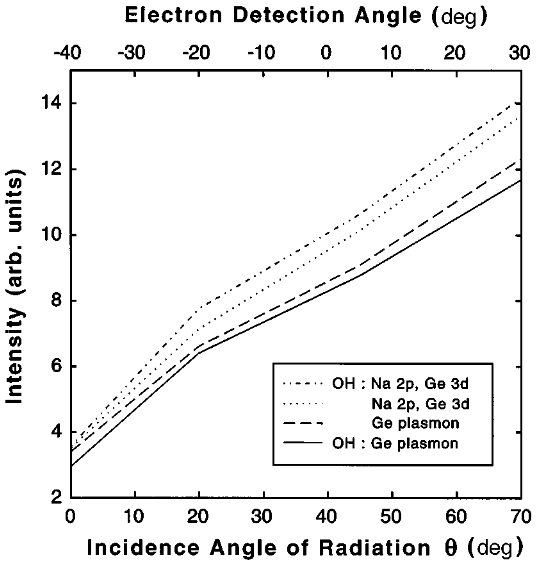

FIG. 4. Angular dependence of several substrate photoemission peaks of clean and OH^--covered NaCl(100), showing the main influence of the incidence angle. The upper abscissa designates the angles of electron detection relative to the surface normal.

hexagonal ice,[17] a theoretical average tilt angle of 60° to 70°, as found in the molecular dynamics calculations,[4] would clearly be compatible with our average angle within error bars. These values, however, can only serve as rough guidelines in order to demonstrate compatibility of the experimental results with a model of a water bilayer, because the formation of a $c(4\times2)$ structure on this surface indicates considerable deviations from the hexagonal ice structure. An ideal ice structure would have to be expanded by 17% in one direction and by 1.5% in the other in order to fit the adsorbate unit cell. This makes deviations from the angles in ice most likely, but leaves us with a wide variety of possible angular combinations.[1,18] As an extreme, a bilayer compressed almost into one layer was recently found by structural analysis for D_2O on Ru(001),[19] resulting in angles of inclination of 46° and 88°, respectively. An influence by electron-induced formation of *F* centers on the formation of a strained ice layer cannot be excluded in our case.[20]

While the NEXAFS data for water can only be shown to be compatible with the model of bilayer formation, the corresponding data for OH yield a much clearer result. A sequence of spectra for chemisorbed OH is shown in Fig. 3 for angles of incidence from 0° to 70°. A pronounced angular dependence of the resonance intensity is found with a nonzero intensity at normal incidence. This finding clearly excludes an OH orientation normal to the surface for a pure σ-like final state.

For a quantitative determination of the angle of molecular inclination standard procedures (subtraction of a spectrum of the clean substrate, normalization to the height of the nonresonant part of the absorption edge) were not applicable because of the high reactivity of the NaCl surface containing *F* centers and the small OH-induced signal measurable in our case. The reason is that uptake of residual gas on the freshly prepared surface within normal measuring times would make the quality of a ''clean'' spectrum rather questionable. Therefore attempts with two alternative procedures of normalization were carried out.

One consisted of using the angular-dependent data of the molecular water bilayer on the defect-free NaCl surface. We assumed that the angular dependences of the oxygen *K* absorption edge far away from the NEXAFS region are identical for OH and H_2O, and that the angular dependence of the subsequent Auger decay for OH and H_2O is averaged out due to the large detection window used. In the H_2O case, data of the clean, defect-free surface could be recorded.

The second method uses a normalization to equal intensities of substrate peaks. It can be justified by the fact that there was no detectable change in their angular dependence due to adsorbed OH, and by the common change of detection yield as a function of angle of incidence for both the clean and the electron-bombarded surfaces. This is illustrated in Fig. 4 for both Ge and Na photoemission peaks. The angular dependences are shown both for the clean, defect-free surface and for the OH^--covered surface. It can be clearly seen that there is a major dependence on the angle of incidence of radiation (lower abscissa), but not on the detection direction (upper abscissa), which passes through zero while the intensity is still rising monotonically.

Both kinds of normalization were used for data evaluation. We determined the orientation of the adsorbed molecules on the surface by fitting the intensities obtained in both ways to the form of Eq. (1). Alternatively we carried out the simpler I_0/I_{70} method. The degree of polarization was assumed to be constant over the measuring time and set to values between 0.8 and 0.9. The value of *P* influences the final result of the tilt angle by less than 0.5°. Due to their small width the NEXAFS resonances could be easily separated from the rest of the spectrum by spline interpolation, indicated as thin lines in Fig. 3.

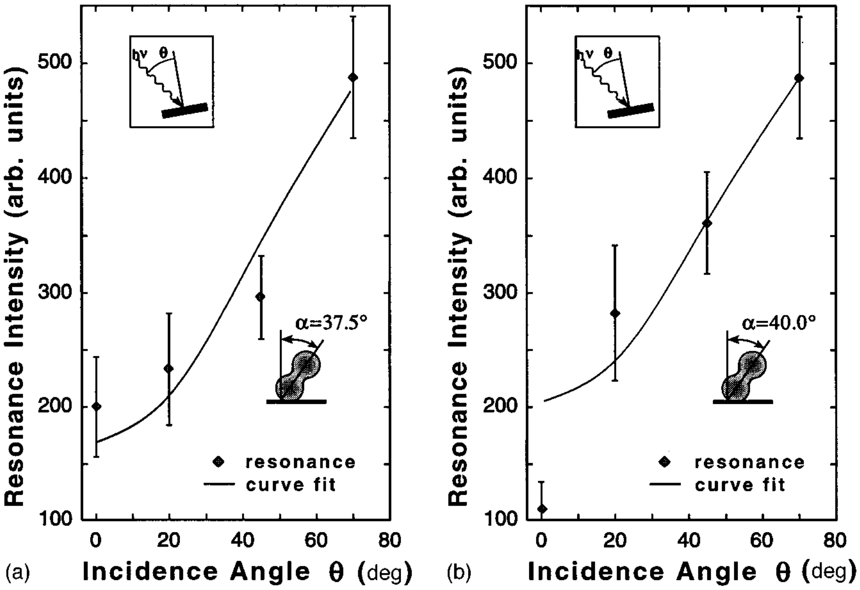

FIG. 5. Results of a two-parameter fit of measured resonance intensities to Eq. (1). Fit parameters are absolute intensity and tilt angle α. The polarization was assumed to be $P=0.85$. (a) Normalization by substrate intensity; (b) normalization by the height of the oxygen *K* absorption edge of a molecular water bilayer on defect-free NaCl(100). The corresponding best fits are indicated.

The fits are shown in Fig. 5 for the two different kinds of normalization. The results for the tilt angle α of the $4\sigma^*$ orbital, which is parallel to the molecular axis, are summarized together with those obtained by the I_0/I_{70} method in Table I. Except for the small value obtained from the I_0/I_{70} evaluation with H_2O *K* edge normalization, which arises from just one data point obtained for normal incidence, the values for both normalizations agree surprisingly well. This indicates that the coupled angular dependence of the photoemission peaks of Ge and NaCl and the detection efficiency are very similar to those of the NEXAFS Auger yield under the measuring conditions used, although each process itself is expected to have a rather different angular distribution. As an average of entries 1, 2, and 4 of Table I one obtains a tilt angle of 39°. From the uncertainties in the determination of the exact height of the absorption edge and in the subtraction of the resonance peak we estimate the error to be ±10% or 4°.

At first sight it is not easy to understand that a chemisorbed OH molecule is tilted with respect to the surface normal. The adsorption site has clearly fourfold symmetry. Therefore, assuming that OH is predominantly ionically bound, as indicated by the chemical shift in XPS and the charge neutrality of the surface, normal orientation of this molecule may be expected. In this picture, however, only the monopole contributions to the adsorption potential are taken into account. As obvious already from the nonspherical charge distribution of the unfilled *F* center (Fig. 6), this is not correct. For the electron captured in the anion vacancy there is a higher probability to be found close to a cation than in the center of the vacancy. Assuming a similar spatial distribution for the outermost electron of the adsorbed OH^- ion as for the electron in the unfilled *F* center, this is a clear indication that higher multipoles must be taken into account. Because of its strong dipole moment the OH molecule will react strongly to these multipole fields so that significant dipole-dipole or dipole-quadrupole interactions between the OH^- and the substrate ions have to be expected to lowest order, and an off-normal adsorption geometry will result. Direct identification of the nature of this bond is difficult as it is most likely below the resolution of photoemission spectroscopy. Any expected energy shift is at best on the order of magnitude of the strength of a hydrogen bridge bond, i.e., 0.1 eV. We hope that future calculations, using well known ionic potentials and an estimate for the OH dipole, will reveal more details.

Figure 7 shows our proposed model of chemisorbed OH^- located deep in the vacancy. The OH^- molecule is

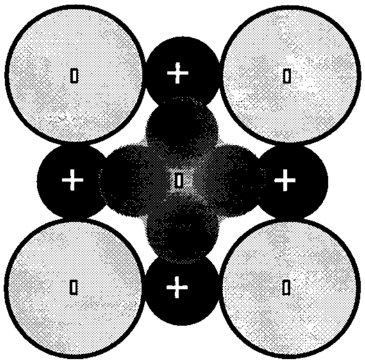

FIG. 6. Charge density distribution of an *F* center.

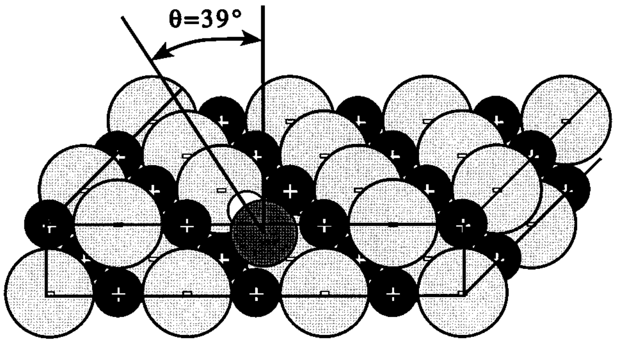

FIG. 7. Proposed model of the local geometry of chemisorbed OH^- in an anion vacancy on NaCl(100).

TABLE I. Tilt angle α of the OH $4\sigma^*$ molecular orbital with respect to the surface normal for various normalization procedures and evaluations. The quoted angles have error bars of $\pm 5°$.

Normalization by	I_0/I_{70}	Fit
Substrate photoemission	40.8°	37.5°
H_2O K edge height	32.5°	40.0°

slightly displaced from the center of the vacancy and tilted by 39°. As can also be seen from this figure, a direct interaction between the hydrogen atom and the opposite chlorine ion in the [11] direction appears to be possible so that a hydrogen bridge bond can be formed between OH and Cl. This would naturally explain the position of the H atom and the tilt angle.

Finally, the possibility of a covalent contribution to the OH-surface bond cannot be ruled out. Indeed, the OH-surface bond cannot be expected to be fully ionic, as a bond between the highest occupied OH 1π orbital and the NaCl Δ_5 or Δ_1 valence band appears possible for energetic reasons. This type of bond formation could also be responsible for the observed tilt of the OH molecule. In any case, relative changes of photoemission peaks are expected to be very small due to the weak covalent interaction. Moreover, the energetic difference between OH^- 3σ and 1π measured by Fölsch and Henzler[6] nearly equals those of solid sodium hydroxide[21] and of chemisorbed OH on various substrates with different binding geometries of OH.[1]

Concluding, the properties of water adsorption on sodium chloride (100) surfaces depend strongly on the presence of defects on the substrate. On defect-free NaCl(100) molecular water bilayers of $c(4\times 2)$ symmetry are formed. The model of an icelike hexagonally distorted bilayer structure[7] is supported by our angular-dependent NEXAFS study. The existence of a shoulder below the H_2O $4a_1^*$ resonance could be attributed to empty states induced by the important hydrogen bridge bonds in the bilayer structure, but further elucidation of this question appears to be necessary.

OH formed after dissociation of water at F centers of an electron-bombarded NaCl(100) surface was found to be inclined with respect to the surface normal by $39° \pm 4°$. Principally three different mechanisms can be envisioned to cause the inclination of the OH molecule. A combination of these effects is, of course, possible and even likely. First, the charge distribution of the F center filled with an OH^- ion is expected to be nonspherical. Secondly, a direct interaction via a H bridge bond between the OH and the neighboring chlorine ions is possible. And thirdly, covalent contributions to the bond between OH and the surface can cause the inclined configuration.

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