

Water on Si(111)(7×7): An *in situ* study with electron-energy-loss and photoemission spectroscopies

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The adsorption of H₂O on a Si(111) surface has been studied *in situ* by electron-energy-loss and photoemission spectroscopies. Two different phases of water are prepared on this surface as determined by photoemission, which have been previously interpreted as molecular and dissociatively adsorbed water. Unlike photoemission spectra, which reveal strong differences between these two states, the electron-energy-loss spectra are very similar. We analyze the differences and find that the existence of molecular water is reasonable and discuss why molecular water may not be detectable in the electron-energy-loss data.

INTRODUCTION

The properties of the water molecule have been investigated extensively.¹ Its behavior upon adsorption on metal surfaces has been of particular interest in recent years.² Investigations of water adsorption on semiconductor surfaces, especially that on silicon surfaces, are still in progress. At present, photoemission^{3,4} and electron-energy-loss spectroscopy⁵⁻⁷ (EELS) experiments have come to opposite conclusions about whether the H₂O molecule stays intact or dissociates into H and OH on a Si surface. In the photoemission spectra three H₂O-induced valence orbitals are observed and have been assigned to chemisorbed molecular H₂O. It has been concluded that the molecule is adsorbed with the oxygen end down, which results in the observed bonding shift of the oxygen lone-pair molecular orbital.⁴ On the other hand, in all EELS studies on the H₂O-Si system, the observed losses are assigned to Si-H, Si-OH, and Si-O-H vibrations, and it is concluded that water is dissociated on silicon surfaces.⁵⁻⁷

Ultraviolet photoemission spectroscopy (UPS) data taken with a cylindrical Si crystal showed that the molecular species exists only on the (100)-oriented surfaces when the sample was dosed at room temperature (RT), whereas dissociation occurs on other Si orientations. However, the molecular species was observed on all orientations after warming a condensed-water layer to about 250 K. The details and mechanism of this experimental observation are discussed elsewhere.⁸ Using these experimental findings, we can prepare two phases of adsorbed H₂O on a single-orientation Si surface. Here, we have chosen an (111)-terminated surface, as its preparation at low temperatures is well established.⁹ We report on the first EELS and UPS data obtained *in situ* for these two differently prepared water states. We find that while UPS spectra show remarkable differences, the EELS data are very similar. The data clearly show the existence of two different adsorption states of water on this Si surface. Besides the dissociation products OH and H, we conclude

that molecular chemisorbed water cannot be excluded on the basis of EELS measurements alone. We discuss several reasons why the molecular state may be difficult to observe in electron-energy-loss spectra.

EXPERIMENTAL

The experiments have been performed in a ultrahigh-vacuum system ($p = 6 \times 10^{-11}$ Torr) described in detail elsewhere. Briefly, the system was equipped with a cylindrical mirror analyzer to analyze uv photoemission spectra excited with a He resonance lamp. The sample could be moved into a pair of hemispheres used as monochromator and analyzer to record EELS spectra. The surface cleanliness was checked by Auger electron spectroscopy and low-energy electron diffractions (LEED). The later revealed a sharp 7×7 pattern.

RESULTS

In the following we first describe the spectra obtained by exposing the sample to H₂O at RT and later those obtained after warming a condensed layer of ice. The UPS spectrum in Fig. 1, curve C, shows water adsorption on a Si(111)(7×7) surface with the sample at RT. Exposure to 60 L (1 L = 10⁻⁶ Torr sec) (curve C) causes the appearance of a broad band centered around 7 eV binding energy which tails up to 11 eV, above the Si valence band. The corresponding EELS spectrum [Fig. 2(c)] shows a prominent peak at 96 meV, as well as two weaker losses at 260 and 460 meV. Upon warming, the OH loss at 460 meV disappears; above 700 K the Si-H loss at 260 meV first splits and then disappears around 800 K.

When a condensed layer of water is warmed to 300 K the UPS spectra clearly show a different species than for RT exposure, as in spectra B and C, of Fig. 1, respectively. Curve A is that of a condensed water layer, in good agreement with previous work.^{4,8} Curve B is obtained upon warming to 300 K. The spectrum now shows two

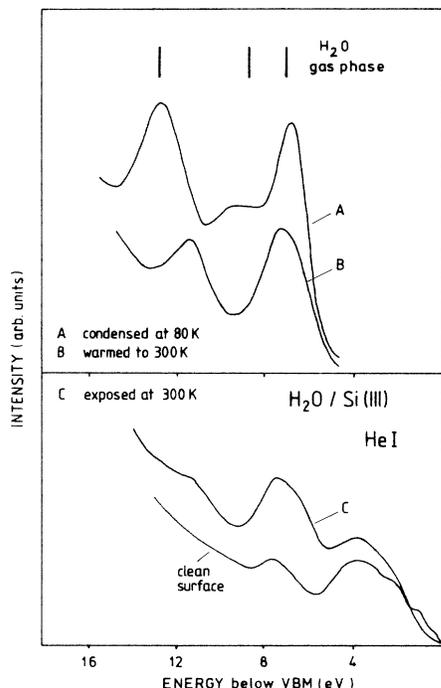


FIG. 1. Photoemission spectra of water on Si(111)(7 \times 7) adsorbed at 80 K (curve A) and annealed to 300 K (curve B) and exposed at 300 K (curve C). Spectrum of clean surface is also given. The energy is given in reference to the valence-band maximum (VBM).

bands centered at 7 and 11.7 eV, and is quite similar to the characteristic spectra of what has been attributed to molecularly chemisorbed water on Si(100).^{4,8} There is only a slight difference in the spectra, as the first band on Si(100) shows a shoulder at 7.7 eV which is not resolved

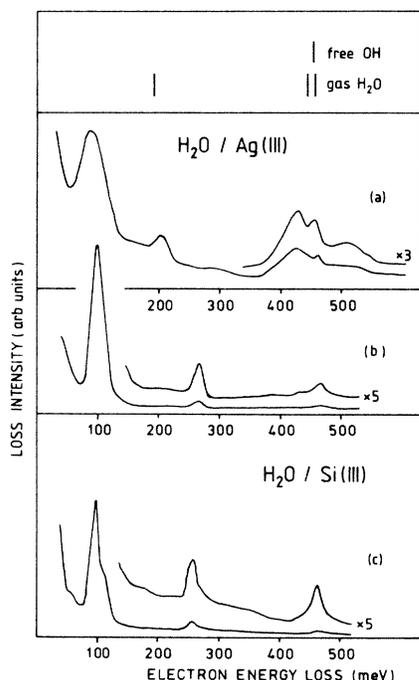


FIG. 2. Electron-energy-loss spectra for water adsorption on Ag(111) at 20 K (a); on Si(111)(7 \times 7) adsorbed at 80 K and annealed to 300 K (b); and on Si(111)(7 \times 7) exposed at 300 K (c).

on Si(111). However, this finding is in agreement with the results of Ref. 8.

Before considering the EELS spectra for condensed H₂O on Si we first consider EELS spectra for a condensed water layer on Ag(111). As shown in Fig. 2(a) we see losses due to the excitation of hindered translations around 95 meV, the scissor mode at 210 meV, and the OH stretching modes around 435 meV. The latter are broadened by the hydrogen-bonding water network.¹ On Si(111), the spectra for condensed water layers are very similar, but upon warming to 300 K [Fig. 2(b)] the spectrum is different and has been interpreted as produced by dissociated water, with the Si-H vibration at 262 meV and the Si-OH vibration at 95 meV, which is a very strong feature. With this explanation the OH stretching modes appear as a single loss at 460 meV.^{1,5}

DISCUSSION

As the interpretation of the UPS data has been published previously,¹⁰ we only summarize the most important facts. Starting in Fig. 1, curve C, we find that water is adsorbed in a mixture of chemisorbed oxygen, OH radicals, and, possibly, chemisorbed hydrogen. After low-temperature adsorption followed by annealing to RT (curve B) very few OH species are observed; there is only molecular chemisorbed water best characterized by the second band at 11.8 eV.

When we now compare the EELS data shown in Figs. 2(b) and 2(c), we see that unlike the UPS spectra, the EELS data show no difference, independent of whether water is adsorbed at RT or is first condensed at 100 K and subsequently annealed to RT. In more detail, the EELS data for the two different preparation conditions agree well in the loss energies and relative loss intensities, and in the peak shapes. For example, in both data sets there is a shoulder at 110 meV near the loss peak centered at 95 meV.

We will now contrast our EELS and UPS results, and first will go back to the interpretation of the UPS spectra. By assuming that only dissociated OH groups exist, we must consider different states of OH which could give rise to the differences in the UPS spectra. Generally, differences may occur if an adsorbate is chemisorbed on different bonding sites or with different orientations on the

TABLE I. The electronic configuration of the OH neutral molecular ground state, the possible final states for two upper molecular orbitals, and the corresponding gas-phase ionization energies (in eV) (Ref. 11).

Molecular orbital	Final state	Ionization energy (eV)
$1\pi^3$	$^3\Sigma$	13.01
	$^1\Delta$	15.22
	$^1\Sigma$	16.67
$3\sigma^2$	$^3\Pi$	16.48
	$^1\Pi$	
$2\sigma^2$		
$1\sigma^2$		

surface, and/or penetrates into the bulk. The latter possibility has to be excluded by the Si $2p$ core-level analysis in Ref. 4. Different surface orientations are not expected to show such remarkable differences in the UPS spectra, as unpolarized light and an angle-integrating instrument have been used. Also, the similarities of the loss energies for the two phases imply no differences in surface orientations. We therefore consider the molecular orbitals of the OH radical, to explain further the UPS spectra. Since the OH radical is an open-shell molecule, different final states are possible when the topmost molecular orbitals are ionized. The electronic configuration, the possible final states, and the experimental ionization energies for the free radical¹¹ are summarized in Table I. If the 1π orbital becomes completely filled by charge donation from the surface, the OH is no longer neutral and the final-state splitting is lifted. OH⁻ spectra have been reported for the ionic hydroxides NaOH and CsOH,¹² and in both cases only two peaks are found, separated by about 4 eV. Even for this highly unlikely ionic form of OH⁻ on Si, the observed peak splitting of 5 eV is too large to be accounted for by such a OH⁻ species. However, for covalent bonding of OH to Si we do not expect a complete charge donation to form an OH⁻ species, and the final-state splitting should still be observable, as it is for O₂/Ag(111).¹³ We then expect an emission pattern consisting of three peaks with a separation similar to that in the gas phase. Within that picture the molecular orbitals for OH adsorbed on Si should give rise to emission around 6, 8, and 10 eV. The spectra of Fujiwara³ might well be interpreted to be from adsorbed OH groups, consistent with the later model calculations of Ciraci.¹⁴ Thus, in addition to arguments already published^{4,8} favoring the interpretation of the UPS spectrum as showing molecular H₂O, the consideration of local bonding changes as well as that of charge transfer fail to resolve these spectra and reconcile both UPS and EELS results. We next consider the EELS interpretation in more detail.

In considering EELS we find one cannot exclude the possibility of the presence of molecular water together with some H + OH groups. In order to understand better our EELS results we first discuss the adsorption of water on a Ag(111) surface as a model for a nonreacting, i.e., physisorption, system, as well as EELS data found in the literature for adsorption of water on a variety of metals.² We will show that there exist similarities in the spectra for the different substrates, which have been reported but have never been considered in detail. In general agreement with a variety of papers, the EELS spectra of water adsorbed around 90 K on bare metal surfaces show three groups of losses. First, there is a broad band centered around 100 meV which is due to excitation of frustrated translations and rotations. The second group is due to the bending or deformation mode. It is found at 198 meV for the gaseous molecule and increases in energy to 204 meV due to hydrogen bonding in ice. For silver we observe this loss at 205 meV. At 281 meV a broad band of loss features is related to the combination and/or overtone of ($3\nu_1, \nu_2 + \nu_1$). The third group represents the OH stretching vibration. For the free water molecule it is split into a symmetric stretch (453 meV) and an asymmetric stretch

(465 meV). These two bands are not resolved in the liquid or condensed (ice) phases. Hydrogen bonding shifts the center of these bands from 459 to 453 meV (300 K) and to 406 meV (100 K), as studied in dilute solutions, and also increases the total oscillator strength by a factor of at least 10.¹⁵ Furthermore, intra- and intermolecular vibrational coupling in ice splits this shifted band resulting in losses between 440 and 372 meV. For Ag(111) we observe in the same energy range a broad loss centered at 430 meV (20 K) and 420 meV (80 K) which can be directly assigned to the OH stretching modes of hydrogen-bonded water molecules (ice), indicating a lowering of the OH bond strength of about 10%.¹ However, at low coverages and especially at an adsorption temperature of 20 K there is a well-separated peak at 462 meV which is also observable at an adsorption temperature of 80 K and higher coverages. It is the existence of this loss which we discuss in more detail in the following. The 460-meV loss is observed in all published experimental work on the adsorption of water on surfaces that are listed in Ref. 2. One possible explanation for this loss is that it arises from monomeric, non-hydrogen-bonded water molecules on the surface. This hypothesis is based on the close correspondence to the gaseous OH stretching frequencies and its small full width at half maximum which implies absence of hydrogen-bonded OH groups. As a second explanation electron-beam-induced dissociation may produce adsorbed OH groups. Dissociation would result in adsorbed OH radicals; their free gaseous analogue has its stretching frequency at 460 meV. According to this explanation, the losses observed for all EELS studies at 460 meV may be due to some beam-induced dissociation.

Since we fail to see marked changes in our UPS spectra after EELS examination such dissociation is likely incomplete. However, our UPS actually probes a significantly larger area than our EELS beam and thereby may not detect these changes. Thus, the observed loss at 460 meV is not well suited to decide between associative and dissociative adsorption of water on silicon surfaces. This is particularly true if the other vibrations of the beam-induced dissociation products Si-H and Si-OH have relatively large dipole-active vibrational modes while the dynamic dipoles of adsorbed monomeric water are small.

Considering the other fundamental vibrations of water, the scissor mode around 205 meV should be observable for a chemisorbed water molecule. Actually, a loss in that energy range has been reported in Ref. 5 for water adsorbed at RT on a Si(100) surface, but has been assigned as a double loss with its origin being the strong Si-OH vibration around 100 meV. However, this assignment is questionable, as the double loss is not observed on Si(111)(7×7) surfaces, although this Si-OH loss appears with a similar strength. The ability to observe this scissor mode with EELS may depend upon scattering conditions so as to allow resonance scattering or impart excitation, which we have not explored.

In summary, by comparing EELS and UPS results for H₂O on Si(111), we see striking differences which can be most easily rationalized as follows: Neither the OH stretching mode nor the scissor mode in EELS are unambiguous in deciding whether molecular water exists on sil-

icon surfaces. From the combined results presented here it appears that two different phases of adsorbed water occur but are not detected in EELS. There may be some dissociated OH and H groups (less than 20%), that give rise to a strong loss intensity by a dipolar scattering mechanism in EELS. Considering reasons why the molecular species is not observed, it may be either dissociated by the incident electron beam or may have a very low vibrational cross section. In this respect we have to consider the results of Ref. 15, where by matrix-isolation techniques it has been shown that the intensity of non-hydrogen-bonded water is lowered by a factor of at least 10. A low vibrational cross section also is expected if the molecular is oriented such that the oxygen end is bonded to a single atom of a Si-Si dimer, whereas the hydrogen ends are attached to dangling bonds within the neighboring row of dimers. This strongly inclined absorption geometry may explain several of the experimental observations, especially the fact that the LEED pattern after water adsorption

still shows a 2×1 superstructure [on Si(100)]. Such a geometry is also in agreement with the analysis of the chemical shift of the Si $2p$ core levels. In addition, it has been suggested that water adsorbs with the oxygen end down on a single Si atom, i.e., not in a bridged position.⁴ Thus, the resulting component of the dipole moment perpendicular to the surface would be very low so as to cause only a small work-function change. Indeed, the work-function changes only are less than -0.3 eV.^{3-4,8} Finally, such a strongly inclined geometry will also suppress dipolar scattering from H₂O in contrast to the Si-H and Si-OH vibrations of dissociated water which have a considerable higher dipole moment perpendicular to the surface.

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