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Electronic structure of hydrogen-bonded H_2O

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We have studied the electronic structure of H_2O adsorbed on different metal surfaces between 7 and 200 K using photoelectron spectroscopy. From the valence-orbital spectra we are able to distinguish three different phases of adsorbed H_2O: (a) single-adsorbed H_2O molecules at temperatures close to the desorption point, (b) partially hydrogen-bonded H_2O clusters for coverages of a monolayer or less, and (c) fully hydrogen-bonded ice at low temperatures and several monolayers of coverage. For phase (a), we find valence molecular orbitals which are almost rigidly shifted upwards relative to the gas phase by a final-state relaxation shift of 1.3 eV. All orbitals are broadened by 1.0—1.5 eV relative to the gas phase. For phase (b), we identify two inequivalent types of H_2O molecules whose orbital energies differ by 1.5—2 eV. This splitting is identical to the electrostatic shift of molecular-orbital energies as calculated for the hydrogen-bonded H_2O dimer by Umeyama and Morokuma. In this model the set of molecular orbitals with higher binding energy is assigned to the hydrogen-acceptor molecule and the set with lower binding energy to the hydrogen-donor molecule. At monolayer coverage we find about twice as many donors as acceptors.

I. INTRODUCTION

The hydrogen bond plays an essential role in biochemistry and electrochemistry. The structural aspects of the hydrogen bond have been studied extensively but little is known experimentally about the electronic states which are involved in the bond (see reviews in Ref. 1). The main information about electronic states comes from optical experiments where subtle changes have been observed when hydrogen bonds are formed. These spectra are difficult to interpret since both initial and final states determine the strength of an optical transition. Initial states can be separated from final states using photoelectron spectroscopy with a tunable light source. Therefore, we have used this technique to study water and ice as representatives for a simple hydrogen-bonded system. Since photoelectron spectroscopy probes only a few atomic layers, we have condensed H_2O onto different metal substrates under high-vacuum conditions. Our findings include the observation of a strong electrostatic splitting (1.5—2 eV) between hydrogen-donor and hydrogen-acceptor orbitals. In agreement with theoretical predictions, this splitting is much larger than the actual hydrogen-bond energy.

There exist several studies of the adsorption of water on metal surfaces in ultrahigh vacuum. These studies could not clarify the mechanism of bonding and the geometric arrangement though various clues have been obtained using different experimental methods. Thermal desorption experiments[2,3] have shown that water desorbs from Pt(111) and Pt(100) surfaces at about 150 K, indicating a small heat of adsorption. This was also found for water adsorbed on polycrystalline gallium films.[4] A weak interaction is in contradiction to electrochemistry, where a strong interaction between solvent and electrode is usually assumed because of the large surface potential contribution of water on gallium.[5] Electron-Pt(100),[2] Pt(111),[6] and Ru(001) (Ref. 7) single-crystal surfaces have been interpreted as being due to cluster formation of water molecules even at low coverages. This has been concluded from the intensity of a broad loss band around 3400 cm^{-1} (420 meV). From electron-stimulated-desorption results, on the other hand, it has been concluded that at low coverage, monomeric water molecules are bonded to the surface via the oxygen atom.[8] The emission from the three highest occupied molecular orbitals of the water molecule can be observed by using ultraviolet photoemission spectroscopy (UPS). These are with increasing binding energies the oxygen lone-pair orbital b_1, and the antibonding and bonding OH orbitals a_1 and b_2. By comparing the photoelectron spectra of adsorbed water layers[9–16] to those of the gaseous molecule,[17,18] no clear picture of the adsorption geometry and bonding mechanism could be obtained. This is caused by the considerably broadened peaks and by the different energy separations of the three water bands found in different experiments. In this report we show that water adsorption on metal substrates produces different photoelectron spectra depending on substrate temperature and film thickness but independent of the substrate itself. These changes reflect the transformation from monomeric adsorbed water to clusters and to ice via hydrogen bonding.

The paper is organized as follows: In Sec. II, we describe the experimental setup. In Sec. III, we give a detailed presentation of the photoelectron spectra under various preparation conditions and at different photon energies. The experimental results are discussed in Sec. IV in terms of three different H_2O phases: (a) monomers, (b) clusters, and (c) multilayers. We concentrate on the splitting of the orbital energies in phase (b) and explain it as an effect of hydrogen bonding. As a guideline, we use a cluster calculation by Umeyama and Morokuma[19,20] for a hydrogen-bonded H_2O dimer. Our conclusions concerning the effect of hydrogen bonding on the electronic orbitals of H_2O are summarized in Sec. V.

II. EXPERIMENTAL

The experiments on copper and nickel substrates were performed in a stainless-steel UHV system. A metal block in direct contact with the coolant (liquid He, N_2) was used as substrate for evaporation of the polycrystalline films. Exciting photons from a helium-discharge lamp ($h\nu = 21.2$ eV for the He I line) hit the sample under 48° (with respect to sample normal). The photoelectrons were energy analyzed in normal emission using a cylindrical mirror double-pass analyzer. The energy is referred to the vacuum level. The photon-energy dependence was measured by taking angle-integrated data (1.8 sr) with a photoelectron-spectrometer system using synchrotron radiation (see Ref. 21). In the latter case, we used a uranium nitride (100) cleavage plane (passivated by chemisorbed oxygen) as substrate (see Ref. 22) at a temperature of 33 K. Triple-distilled water was cleaned in various freezing and warming cycles. The cleanliness was checked with a mass spectrometer. Water vapor was admitted to the chamber by a leak valve. The exposure in units of langmuirs ($1\ \mathrm{L} = 10^{-6}$ Torr s) was measured via the total chamber pressure.

III. RESULTS

In this part we report on the temperature dependence of water adsorption as reflected in the photoemission spectra taken at $h\nu = 21.2$ eV (He I) (III A) and on a comparison of monolayer and multilayer adsorption of water (III B) using various photon energies.

A. Temperature dependence

To study the temperature dependence of water adsorption between 7 and 160 K, we adsorbed H_2O on polycrystalline Cu and Ni films. In Fig. 1 (curve *A*) we show He I excited photoemission spectra of 2-L water adsorbed on a polycrystalline Cu film at 160 K. For comparison, the background of the Cu sub-

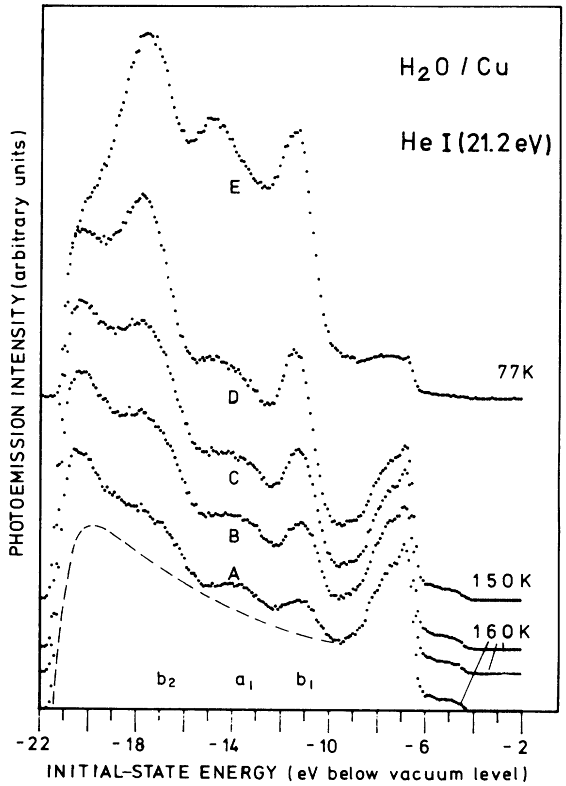

FIG. 1. Photoemission spectra of water absorbed on polycrystalline copper films at 21.2-eV photon energy. Curves *A*, *B*, and *C* were taken after adsorption at 160 K with increasing exposure: 2 L (*A*), 4 L (*B*), 6 L (*C*); curve *D* was taken after exposure of additional 3 L at 150 K. Curve *E* is from a different run and shows the spectrum of water adsorbed on a clean copper film at 77 K after 8 L exposure. The dashed line indicates the background from the Cu substrate.

strate is indicated by a dashed line. The three peaks at -10.9, -13.8, and -17 eV are identified with emission from water molecular orbitals b_1, a_1, and b_2, respectively. Curves B and C show spectra taken after additional exposure of 2 L at the same temperature, yielding a total exposure of 4 L (B) and 6 L (C), respectively. To enable multilayer growth, the temperature was lowered to 150 K and the sample was exposed to an additional 3 L of H_2O (curve D). From the attenuation of the Cu 3*d*-band emission compared to values obtained in a different experiment at fixed temperature (77 K) we can estimate that a coverage of one monolayer is reached in curve C. Spectrum E is from that different experiment at 77 K and shows the emission from multilayers of water after exposure of 8 L.

The peak maxima of the three broad water bands shift with increasing coverage. The band at highest binding energy (b_2) is very broad and shows a weak maximum at -17.0 eV at submonolayer coverages. In curve B a shoulder appears at -17.8 eV which becomes dominant at multilayer coverages. The middle band (a_1) shows the largest shifts. In curve A it peaks at -13.8 eV, it broadens and shifts to higher binding energy till the first monolayer is completed. In the multilayer spectra it peaks at -15.0 eV. The upper orbital (b_1) exhibits a shift of 0.5 eV to higher binding energy in going from a monolayer to multilayers.

In Fig. 2, spectra of about two monolayers of water adsorbed on a polycrystalline Ni film at 7 K are shown and the changes upon warming to 160 K are studied. Spectrum A is taken immediately after exposing at 7 K and shows the features of water multilayers similar to those found on Cu. After warming the sample to 110 K and cooling again to 7 K, spectrum B was measured. There are no significant shifts of the energies of the water bands, but the intensity of the middle band is strongly reduced. Further warming to 160 K changes the water-derived emission again. For comparison, the spectrum of the unexposed Ni film is shown in curve D. Both the increased Ni 3*d*-band emission and the reduced total intensity of the H_2O bands indicate sublimation of water. All peak maxima are found to be shifted to lower binding energies, the upper b_1-derived band is shifted by 0.5 eV and the b_2 band by 0.7 eV. The shift of the a_1 orbital is about 2 eV. The changes in relative intensities also indicate considerable changes in the coordination of water molecules due to annealing. In curve C the emission from the b_2 band is reduced, the intensities of the b_2 and a_1 bands are now comparable.

Differently shaped spectra of water are also obtained, when H_2O is used as a matrix for Ni clusters (curves E and F). The peak at -5.8 eV is due to the 3*d* emission of Ni clusters. The details of this experiment are described elsewhere.[23,24] Here, it is of particular interest that the spectrum of the matrix (curve E) is similar to curve C in Fig. 2, whereas additional condensation of 5 L (curve F) on top of the matrix leads to the typical emission pattern of multilayers. To show the differences in relative intensities and binding energies clearly, spectra E to F are normalized to the same intensity near the secondary threshold.

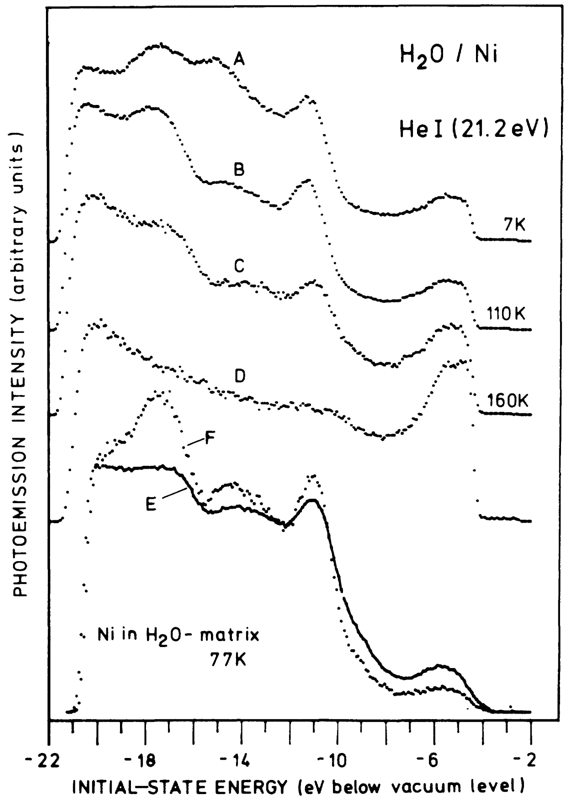

FIG. 2. Photoemission spectra of 3 L water adsorbed on a polycrystalline nickel film at $h\nu=21.2$ eV and 7 K (curve A). Spectra A–D are measured at 7 K. Spectrum B is taken after a short annealing of this film to 110 K, spectrum C after annealing to 160 K. Spectrum D represents the clean Ni surface. Curve E shows the spectrum of Ni clusters isolated in a water matrix prepared at 77 K. After additional exposure of 5 L of H_2O spectrum F was taken.

B. Photon-energy dependence

In this part we report on the photon-energy dependence of water photoemission spectra. We concentrate on the differences occurring between monolayer and multilayer adsorption. We will see that at $h\nu = 21$ eV the same characteristic features are obtained as reported in the previous part for Cu and Ni substrates, although a different substrate (uranium nitride) was used for this experiment.

The spectra shown in Fig. 3 are taken at different photon energies after an exposure of 1 L H_2O at 33 K. The substrate attenuation for the spectrum taken at $h\nu = 21$ eV is similar to that observed for a monolayer adsorbed on Cu films. The emission from the substrate influences only slightly the peak at lowest binding energy (-10.9 eV) and is smooth below -12 eV. The work function (3.7 eV as determined from the width of the $h\nu = 21$-eV spectrum) is not changed upon H_2O exposure.

The 21-eV spectrum (Fig. 3, curve *A*) resembles the spectra shown as curve *C* in Fig. 1, and curves *B* and *E* in Fig. 2; all spectra show the emission pattern of about one monolayer of H_2O on different (metal) surfaces and on small Ni particles. However, in Fig. 3, there is an additional shoulder in the band at highest binding energy for photon energies higher than 30 eV, which is best observed at 41 eV. Furthermore, the intensity of the two features at -10.9 and -12.5 eV increases with photon energy. This enables us to observe that the middle band is composed of at least two contributions. At 21-eV photon energy, however, all these fine structures are blurred.

The spectra shown in Fig. 4 are taken after additional exposure of 4 L and show multilayers of H_2O. In contrast to the monolayer spectra, there is no apparent fine structure on the three water-derived bands, but the bands at the high binding energies have a large width and especially the shape of the middle band suggests that it consists of several different states. This additional exposure caused an insignificant increase by 0.1 eV in the work function.

IV. DISCUSSION

Summarizing the results shown in Figs. 1—4, we find essentially three types of adsorbed water which are similar on the metal surfaces of Cu, Ni, and UN. In agreement with earlier UPS work,[9–16] the appearance of three bands and the absence of pronounced changes in the energy separation of the OH

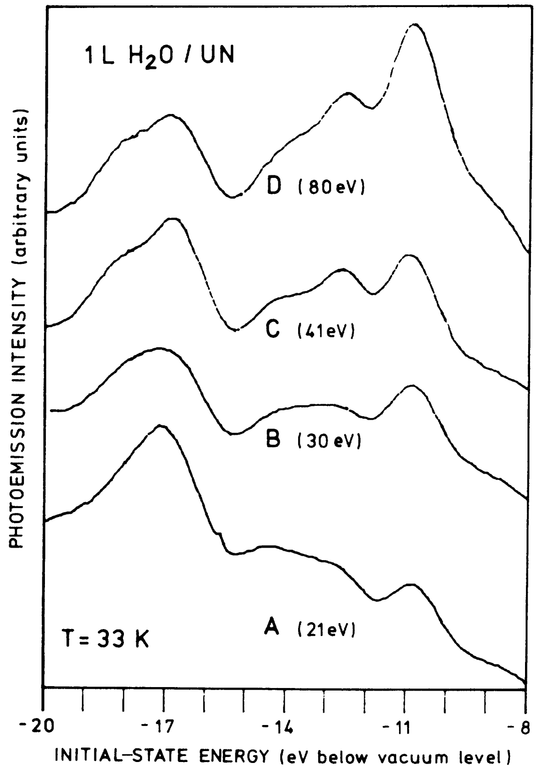

FIG. 3. Photoemission spectra of a water monolayer at various photon energies. The monolayer was obtained by exposing an oxygen-passivated uranium nitride [UN(100)] surface to 1 L of H_2O.

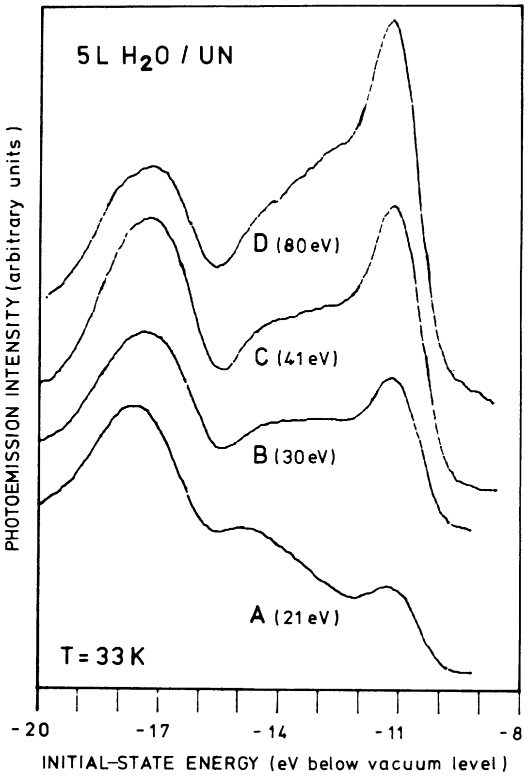

FIG. 4. Photoemission spectra of H_2O multilayers at various energies.

bonding (b_2) and the oxygen lone-pair (b_1) orbitals leads to the conclusion that H_2O does not chemically interact with the investigated metals at those temperatures. Nevertheless, the observed desorption temperature indicates a binding strength of more than 10 kcal/mole, somewhat greater than claimed for physisorption.

In the following sections we discuss the characteristic features of the three different water types as monomeric (IV A), dimeric or small clusters (IV B), and multilayers of water (IV C).

A. Monomeric adsorbed water

When H_2O is adsorbed at relatively high temperatures (160 K), i.e., near the desorption temperature, the three bands of the water spectrum (Fig. 1, curve *A*) at coverages smaller than $\frac{1}{3}$ of a monolayer show relative energy separations which are in good agreement to those of the gaseous molecule.[17,18] A similar spectrum is obtained when multilayers of water, condensed at 7 K, are warmed to about that temperature (Fig. 2, curve *C*). This leads us to conclude that at submonolayer coverages and temperatures close to the desorption temperature water molecules are adsorbed predominantly monomeric. At these temperatures we find a delicate balance of thermal energy, substrate, and intermolecular interactions to form a two-dimensional gas. At temperatures lower than 160 K, we observe spectra of water which differ from those of the monomeric adsorbed molecules, indicating clustering or multilayer growth. Even at substrate temperatures of 7 K, the surface diffusion of adsorbed molecules is not prohibited, thereby allowing clustering of neighbors. However, when Ni clusters are embedded in a H_2O matrix prepared at 77 K (Fig. 2, curve *E*), we again observe emission bands with energy separations similar to those of the free water molecule. Here, the energetic constellation is obviously changed towards monomeric adsorbed molecules. A similar behavior was observed when preadsorbed atomic oxygen hindered the formation of water clusters in the first monolayer on a Ru(001) sample.[25]

B. Hydrogen-bonded clusters of water molecules

The spectra of monolayers of water are shown in curve *C* of Fig. 1, curve *B* of Fig. 2, and Fig. 3. The photoemission spectra are very similar for the various substrate surfaces used here but are different from that of monomeric water. The peak intensities of the b_1 and b_2 bands appear to be much higher than that of the a_1 band. Furthermore, as can be clearly seen at photon energies higher than 30 eV in Fig. 3, there are distinguishable shoulders in the a_1 and b_2 bands which indicate a splitting of these orbitals. We will concentrate for this part of the discussion on the spectra taken at a photon energy of 41 eV. At this photon energy the intensities for all bands are comparable and the splitting of the water bands is best observable. A spectrum of a monolayer of water taken at $h\nu=41$ eV is shown again in Fig. 5.

It seems reasonable to ascribe the observed extra peaks to the formation of hydrogen-bonded water clusters as this splitting is too large to be explainable as an image-charge screening effect of the first layer with respect to a second layer. In recent investigations on several metal surfaces it has been found[1,6,7,25] that water clusters form at similar experimental conditions and even at lowest coverages.

To analyze the influence of hydrogen bonding, we

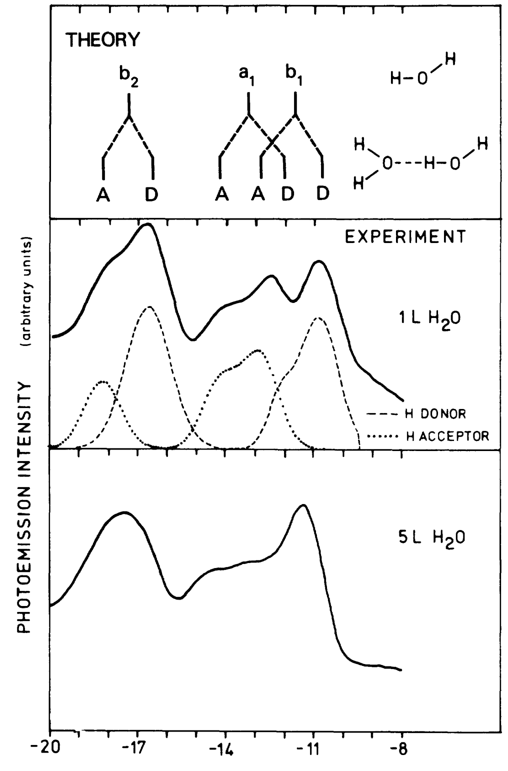

FIG. 5. Analysis of the photoemission spectrum of a monolayer (1 L exposure) of adsorbed water at 41-eV photon energy. The observed splitting of the three molecular orbitals is explained by comparison with the calculated binding energies (Ref. 20) of the proton-acceptor (*A*) and proton-donor (*D*) levels for the linear water dimer (schematic sketch). Further details are given in Table I and in the text. For comparison, the spectrum of a multilayer is shown in the lower panel where the splitting disappears since most of the molecules are equivalent (such as in ice).

have compared our photoemission spectra to molecular-orbital calculations. Self-consistent-field—molecular-orbital (SCF-MO) calculations have been published by Morokuma and co-workers.[19,20] Their energy-decomposition study shows for the linear H_2O dimer (see Fig. 5) that charge (proton) donation causes a splitting of the binding energies for the molecular orbitals of $(H_2O)_2$. The dominating effect is a simple electrostatic effect: All the orbitals of the H-acceptor molecule (left in Fig. 5) are pulled down in the electrostatic field of the positively-charged H-bridge atom, and all the orbitals of the H donor molecule (right in Fig. 5) are raised by the negatively-charged oxygen atom of the proton-acceptor molecule. In Fig. 5, we show the molecular-orbital energies as calculated[20] for the monomeric water molecule and for the H donor and H acceptor in the linear water dimer. We shifted the calculated energies uniformly by 1.88 eV towards lower energies to fit to our spectrum. This shift is necessary as the calculations do not account for final-state relaxation effects, which for most physisorbed systems are found in the 1.5—2-eV range.

Following the theoretical predictions, we have decomposed (after subtraction of the substrate emission and the secondary electron background) the photoemission spectrum of 1 L water into 6 Gaussians using a least-squares-fit routine. We then composed the spectra of the H acceptor and H donor which are shown in Fig. 5. For comparison, the theoretically calculated orbital energies (−1.88 eV) are indicated by bars. Experimental values and theoretical orbital energies are given in Table I. Our analysis further shows that the percentage of H donors (63%) is larger than the percentage of H acceptors (37%) in the monolayer. This is reasonable, as some of the oxygen lone-pair orbitals interact with the metal surface thereby allowing no hydrogen-bond formation.

In spite of the good agreement between our experiments and the theory, we do not conclude that water is adsorbed in linear dimers only. An electron-stimulated-desorption experiment shows some evidence for chains of water dimers at a coverage of $\frac{1}{2}$ monolayer on Ru(001).[8] It should be noted that the very small work-function change implies an arrangement of water molecules which cancels their dipole moment, e.g., linear H_2O dimers parallel to the surface or H_2O with alternating dipoles perpendicular to the surface or cluster formation.

C. Multilayers of water

Adsorption of water at higher exposures than 2 L and temperatures substantially lower than the desorption temperature enables the formation of multilayers. The photoemission spectra are changed again as can be seen from curves 1*E*, 2*A*, and in Fig. 4. The characteristic features of these spectra compared to the monolayer spectra are shifted towards higher binding energy. Most remarkable, however, is the disappearance of the splitting between acceptors and donors. This is consistent with the structure of ice where all H_2O molecules are equivalent in a tetrahedral geometry with two hydrogen bonds and two regular bonds per oxygen atom. The H_2O molecules act as donors as well as acceptors. Several sources of broadening could contribute to the observed width of the multilayer spectra, e.g., an incomplete tetrahedral bonding in the outermost layer which accounts for about 30% of the photoemission signal or a statistical disorder in the arrangement of hydrogen bonds and regular bonds[1] which leads to a residual electrostatic interaction.

TABLE I. Comparison of calculated molecular-orbital binding energies (eV) for the linear water dimer (SCF-MO) (Ref. 20), corrected for the final-state relaxation (1.88 eV) with the electronic binding energies (relative to the vacuum level) obtained after deconvolution of the experimental data into 6 Gaussians. Following the calculated order, the values are organized for H acceptors and H donors. For an alternative decomposition of the spectra, see Ref. 26.

	$(H_2O)_2$ Calculation (Ref. 20)	Experiment (Monolayer)		
	Energy	Energy	Width	Area
H acceptor	−18.3	−18.3	1.5	
	−14.3	−14.3	1.4	0.37
	−12.9	−12.9	1.5	
H donor	−16.6	−16.7	1.2	
	−12.1	−12.2	1.0	0.63
	−10.8	−10.9	1.6	

V. SUMMARY

Our photoemission study reveals for the first time how the electronic structure of water changes when the density of H_2O molecules adsorbed on a surface is increased until hydrogen bonds are formed. Single adsorbed water molecules are found only at submonolayer coverage and substrate temperatures around the desorption temperature in vacuum (160 K). Their molecular-orbital structure is similar to the free H_2O molecule except for a rigid shift towards lower binding energies due to final-state screening. For a monolayer of adsorbed water, H_2O

molecules are bonded to each other by hydrogen bonds. We can distinguish between hydrogen-acceptor and hydrogen-donor molecules. The molecular orbitals of the hydrogen acceptor are lowered by 1.5–2 eV with respect to the donor by the electrostatic field of the positively-charged hydrogen which forms the bridge between donor and acceptor. For multilayers of adsorbed H_2O (i.e., for ice) the splitting disappears and only a broadening of the molecular orbitals occurs. This is explained by the fact that all H_2O molecules are equivalent in ice and represent donors as well as acceptors. Our findings explain the unusual peak widths in the photoemission spectra of adsorbed water. Also, we can explain the variations in peak separations observed in earlier work as depending on the ratio of proton donors and acceptors.

A recent study of the H_2O dimer in the gas phase[27] finds two vertical ionization potentials at 12.1 and 13.2 eV which are interpreted as the b_1 orbital of the donor and as a mixture of the b_1 acceptor and a_1 donor orbitals, respectively, in agreement with our findings.

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[1] For comprehensive reviews, see D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, London, 1969); S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding* (Van Nostrand Reinhold, New York, 1971); P. Schuster, G. Zundel, and C. Sandorfy, *The Hydrogen Bond* (North-Holland, Amsterdam, 1976).

[2] H. Ibach and S. Lehwald, Surf. Sci. 91, 187 (1980).

[3] G. B. Fisher and J. L. Gland, Surf. Sci. 94, 446 (1980).

[4] D. Schmeisser, K. Jacobi, and D. M. Kolb, in Proceedings of the IVth International Conference on Solid Surfaces and IIIth European Conference on Surface Science, Cannes, 1980 [Le Vide-Les Couches Minces (Suppl.) 201, 256 (1980)].

[5] See, e.g., S. Trasatti, in *Advances in Electrochemistry and Electrochemical Engineering,* edited by H. Gerischer and C. W. Tobias (Wiley, New York, 1977), Vol. 10, p. 213.

[6] G. B. Fischer and B. A. Sexton, Phys. Rev. Lett. 44, 683 (1980); B. A. Sexton, Surf. Sci. 94, 435 (1980).

[7] P. A. Thiel, F. M. Hoffmann, and W. H. Weinberg, J. Chem. Phys. 75, 5556 (1981); *Proceedings of the 3rd International Conference on Vibrations at Surfaces, Namur, Belgium, 1980,* edited by R. Caudano, J. M. Giles, and A. A. Lucas (Plenum, New York, 1982).

[8] T. E. Madey and J. T. Yates, Chem. Phys. Lett. 51, 77 (1977).

[9] C. R. Brundle and M. W. Roberts, Surf. Sci. 38, 234 (1973).

[10] P. J. Page, D. L. Trimm, and P. M. Williams, J. Chem. Soc. Faraday Trans. 170, 1769 (1974).

[11] S. J. Atkinson, C. R. Brundle, and M. W. Roberts, Discuss. Faraday Soc. 58, 62 (1974).

[12] M. J. Campbell, L. Liesegang, J. D. Riley, R.C.G. Leckey, and J. G. Jenkin, J. Electron Spectrosc. 15, 83 (1979).

[13] I. Abbati, L. Braicovich, and B. DeMichelis, Solid State Commun. 29, 511 (1979).

[14] K. Y. Yu, J. C. McMenamin, and W. E. Spicer, Surf. Sci. 50, 149 (1975).

[15] C. R. Brundle and A. F. Carley, Faraday Discuss. Chem. Soc. 60, 51 (1975).

[16] J. N. Miller, I. Lindau, and W. Spicer, Surf. Sci. 111, 595 (1981).

[17] J. W. Rabalais, T. P. Debies, J. L. Berkosky, J. J. Huang, and F. O. Ellison, J. Chem. Phys. 61, 516 (1974).

[18] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA, Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[19] K. Morokuma, J. Chem. Phys. 55, 1236 (1971).

[20] H. Umeyama and K. Morokuma, J. Am. Chem. Soc. 99, 1316 (1977).

[21] D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods 172, 327 (1980).

[22] B. Reihl, G. Hollinger, and F. J. Himpsel, J. Magn. Magn. Mater. 29, 303 (1982).

[23] D. Schmeisser, K. Jacobi, and D. M. Kolb, J. Chem. Phys. 75, 5300 (1981).

[24] K. Jacobi, D. Schmeisser, and D. M. Kolb, Chem. Phys. Lett. 69, 113 (1980).

[25] K. Kretschmar, J. K. Sass, A. M. Bradshaw, and S. Holloway, Surf. Sci. 115, 183 (1982).

[26] Alternatively, one could argue that the spectra for the H-donor and H-acceptor molecules ought to be similar to each other. A corresponding decomposition of the monolayer spectrum into two identical spectra yields a splitting of 1.55 eV and an intensity ratio of 0.45 for ac-

ceptors relative to donors. By comparing these figures with the average splitting of 1.87 eV and the intensity ratio of 0.58 as obtained from the decomposition into 6 Gaussians (Table I) one can estimate systematic errors for our data analysis.

[27] S. Tomoda, Y. Achiba, and K. Kimura, Chem. Phys. Lett. 87, 197 (1982).