

THE ADSORPTION OF WATER ON Ru(001) : CHEMISORPTION AND HYDROGEN
BONDING ★

P.A. Thiel **, F.M. Hoffmann and W.H. Weinberg †

Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

ABSTRACT

The adsorption of H₂O on Ru(001) at temperatures of 95 K and 165 K has been investigated using electron energy loss spectroscopy, low-energy electron diffraction, and ultraviolet photoelectron spectroscopy. The vibrational data, together with the structural information available, supports a model in which aggregates of water molecules form via population of a first (chemisorbed) layer and subsequent hydrogen bonded layers. At the higher temperature of adsorption, 165 K, major differences in the vibrational spectra are apparent. Possible reasons for these differences are discussed.

We have investigated the adsorption of water on the (001) surface of ruthenium using a combination of techniques : electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED) and ultra-violet photoemission spectroscopy (UPS). In addition, we have utilized data previously reported by Madey and Yates¹ concerning electron-stimulated desorption-ion angular distribution (ESDIAD) patterns of H₂O adsorbed on Ru(001) at 90 K. This has provided a uniquely detailed description of the properties of this adsorption system, in which strong intermolecular interactions (i.e., hydrogen bonds) are reflected in the vibrational and geometric properties of the adsorbate. Previous investigations of the

★ Supported by the National Science Foundation under Grant n° CHE77-16314.

** IBM Predoctoral Fellow and American Vacuum Society Predoctoral Scholar.

† Camille and Henry Dreyfus Foundation Teacher-Scholar.

vibrational properties of water have dealt mainly with dissociative adsorption^{2,3}. A study of molecular H₂O adsorbed on Pt(100)⁴ concluded that small clusters of H₂O form at submonolayer coverages at 150 K, on the basis of coverage-dependent features in the vibrational spectra. We conclude also that aggregates of H₂O molecules form at low coverage, and we propose a model for their structure based upon the more complete set of information available for this system.

The isolated water molecule is characterized by C_{2v} symmetry. There are three fundamental internal vibrations: the symmetric O-H stretch, the asymmetric O-H stretch and the deformation, or scissoring (ν_s) mode. Adsorption on a metal surface fixes the molecule such that the gas-phase translational and rotational modes are "frustrated" and may also be observed in vibrational spectra. In the infrared spectra of isolated water molecules, crystalline ice, and aquo-metal complexes, the region of the vibrational spectrum between 3200 and 3750 cm⁻¹ is associated with the symmetric and asymmetric O-H stretches, and the region between 1570 and 1650 cm⁻¹ corresponds to ν_s ⁵⁻⁶. Absorption in the region 300 to 900 cm⁻¹ has been assigned to frustrated rotations, known as "librations" and frustrated translations⁵⁻⁸. In our experiments, electron energy loss spectra show that the vibrational modes of water adsorbed on Ru(001) occur in similar energy ranges. Figure 1 shows loss spectra taken following exposure of the Ru surface to various amounts of H₂O at 95 K. Note that the clean surface spectrum is featureless, indicating the absence of contamination. At very low exposures of H₂O, such as 0.03 L, the data indicate that the spectra are particularly sensitive to the "chemisorbed" H₂O molecules, i.e., those directly in contact with the metal surface. Experiments to be discussed later support the assignment of the low-energy feature at 370 cm⁻¹ as due to two overlapping modes: a metal-oxygen stretch at 370 to 400 cm⁻¹ and a librational mode. A Ru-OH₂ vibration at 370 to 400 cm⁻¹ is consistent with bonding through the oxygen atom to a single metal atom, by analogy with the infrared spectra of aquometal complexes. In such complexes, this vibration is observed between 310 and 440 cm⁻¹⁷⁻⁸. Molecular adsorption is indicated by observation of the deformation mode at 1510 cm⁻¹. This feature is clearly visible in Fig. 2, where the spectral region above 1000 cm⁻¹ is shown on an expanded vertical scale.

At slightly higher coverages of H₂O, there is distinct evidence for strong attractive interactions between the water molecules which lead to aggregation at even submonolayer coverages. One indication of this is the position of the broad and weak O-H stretch at 3320 to 3380 cm⁻¹, which is characteristic of intermolecular hydrogen bonding (cfr. Fig. 2). Non-hydrogen bonded OH groups would be expected to occur at 3750 to 3630 cm⁻¹, from gas-phase and matrix isolation data^{5,6,9}.

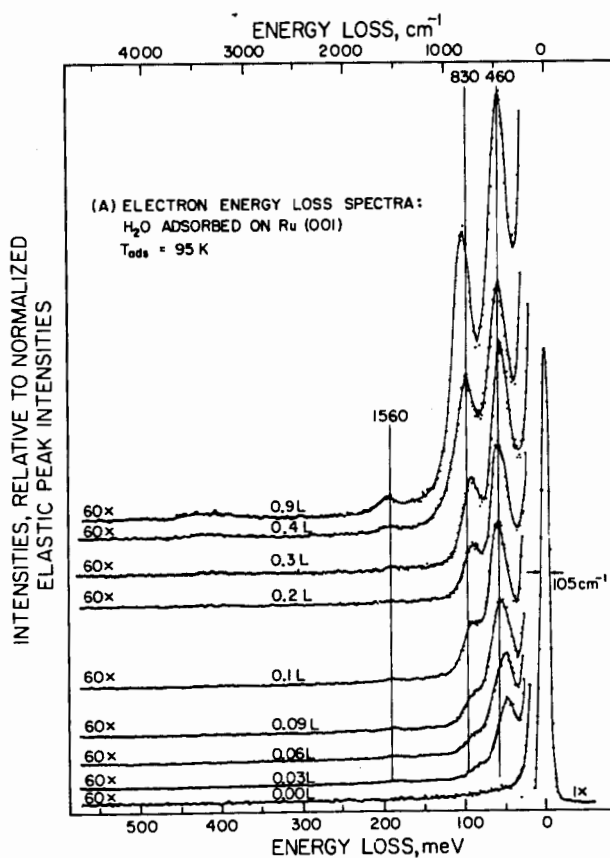


Fig. 1 - Electron energy loss spectra of H₂O adsorbed on Ru(001) at 95 K. The experimental apparatus is described in 17. The incident beam energy is 4 eV, and it is 57° from the surface normal.

The second indication that clusters of water molecules are forming at submonolayer coverage comes from an examination of the intense vibrational features between 370 and 900 cm⁻¹. They are assigned as frustrated rotational and translational modes on the basis of the following arguments :

1. The frequencies of these modes occur in a range appropriate to their assignment as such⁵⁻⁸; and
2. The shifts in frequency observed for D₂O relative to H₂O are consistent with the assignment of these modes as frustrated rotations based upon the ratios of the moments of inertia of the isolated H₂O and D₂O molecules, 1.41 to 1.34. The average experimental values of the frequency shifts are 1.40 and 1.37

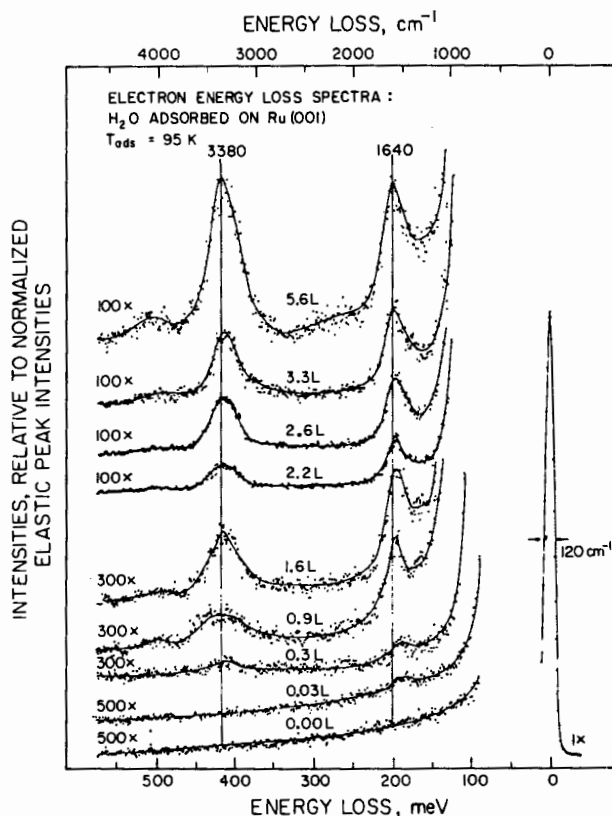


Fig. 2 - Electron energy loss spectra for various exposures of H_2O on Ru(001) at 95 K, showing the spectral range between 1000 and 4800 cm^{-1} on an expanded vertical scale, relative to Fig. 1.

for the modes which occur below 1000 cm^{-1} in Fig. 1, except at exposures less than 0.08 L. In the latter case deuteration causes the frequency of the single low energy feature to shift by an anomalous factor of 1.22. This observation supports the earlier argument that the low energy mode at very low exposures is caused by two overlapping modes, one of which (the Ru-OH₂ stretch) shifts negligibly upon deuteration.

An examination of the scattering mechanism which governs these low-frequency modes is further enlightening. For a molecule adsorbed in a site such that local C_{2v} symmetry is preserved, none of the librational modes are dipole allowed. However, they are the

most intense features observed in the specular scattering experiments of Figure 1. One possible explanation, which we have investigated, is that the scattering mechanism for these modes is non-dipolar. In Fig. 3 are shown angle-resolved EEL spectra, taken by moving the energy analyzer from the specular direction along the polar angle, θ_s . It is assumed that non-dipolar scattering is distinguished in these experiments by a relatively isotropic distribution of scattered electrons away from the specular direction¹⁰. These data show that all of the modes, except the O-H stretch and ν_s , decrease in intensity rapidly away from the specular direction, as does also the elastic peak. This has been illustrated in Fig. 4 by plotting the intensity of the inelastically scattered electrons as a function of scattering angle. This indicates that the librational modes are dipole-enhanced. It is interesting to note that the lowest frequency loss feature changes from 440 to 520 cm^{-1} as $\Delta\theta_s$ changes from zero; again, this is consistent with the previous assignment of two overlapping features at this energy, which may decrease at different relative rates with respect to $\Delta\theta_s$ and give rise thereby to the apparent change in frequency. The scattering mechanism is discussed in detail elsewhere¹¹.

Another possible explanation for the observation of the librational modes is that the C_{2v} symmetry of the gas phase molecule is reduced to C_s or C_1 as a result of adsorption. Under the latter two symmetry groups, one or more of the librational modes, respectively, could become dipole-active. A model in which clusters of H_2O molecules form, wherein the molecules occupy a distribution of orientations relative to the surface and are coupled via hydrogen bonds, provides an adequate and consistent explanation of the observed dipole enhancement of the librational modes.

The third piece of evidence which supports the formation of clusters comes from a combination of LEED and ESDIAD¹ data, as shown in Fig. 5. At exposures greater than 0.5 L, we observe a faint and diffuse ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern, arising from an ordered array of oxygen atoms with respect to the ruthenium substrate, as shown in Frame (C) of Fig. 5. (Scattering from the hydrogen atoms is assumed to be insignificant in forming this pattern). This pattern has been observed also following adsorption of H_2O at 95 K on the (111) surfaces of Rh^{12} , Ag^{13} and Pt^{13} . Further, at sub-monolayer coverages of water, an hexagonal pattern of H^+ emission has been observed to result from electron bombardment¹. Under the assumptions that :

1. the pattern of H^+ emission reflects the initial orientation of the molecular O-H bond; and
2. the C_2 axis of the gas phase molecule is perpendicular to the metal surface in the chemisorbed state, the hydrogen atoms must be positioned with respect to the oxygen atoms of the ($\sqrt{3} \times \sqrt{3}$) R30° lattice as shown in Fig. 5(C).

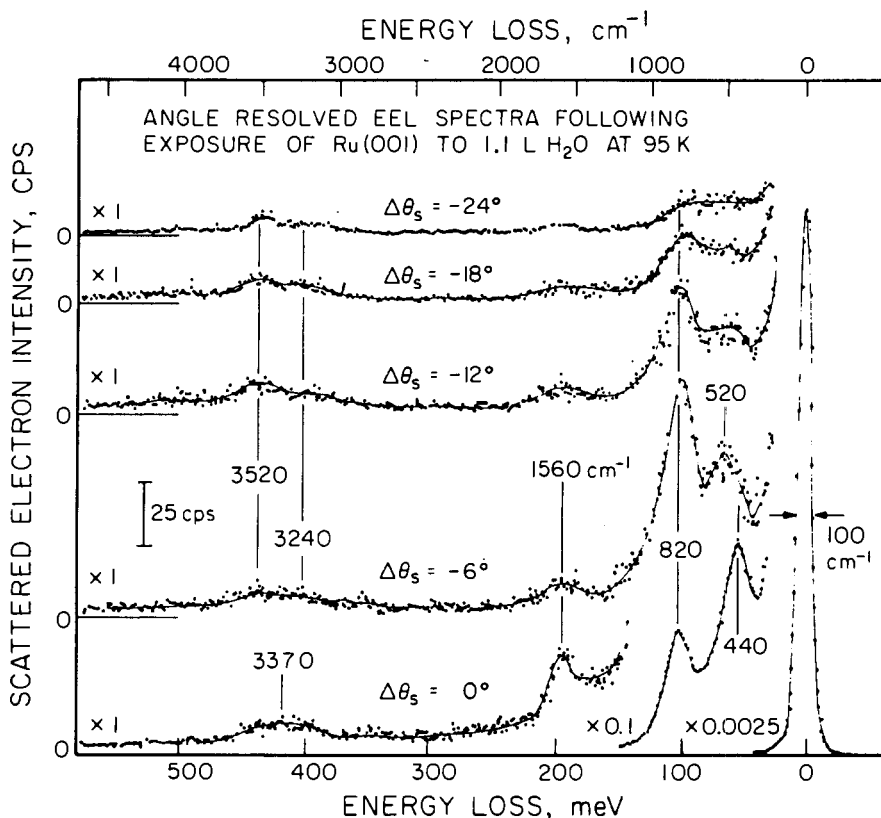


Fig. 3 - Angle-resolved EEL spectra of the Ru(001) surface following exposure to 1.1 L H₂O at 95 K. $\Delta\theta_s$ is the deviation of the analyzer position (polar angle) from the specular direction.

An intuitively appealing explanation of the physical forces which create this combination of orientations is available if a second-layer H₂O molecule is positioned within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell, hydrogen-bonded to at least two of the first-layer H₂O molecules. Such a structure is suggested from an examination of the crystal structures of ices Ic and Ih^{5,6,13}. Two possible structures of this type are shown in Fig. 6. Thus, the combination of LEED and ESDIAD data further support the hypothesis that aggregates of hydrogen-bonded H₂O molecules form at submonolayer coverages.

Heating a surface covered with H₂O causes irreversible thermally-induced changes which do not simply reflect a change in coverage, because the vibrational spectra do not merely revert to lower-coverage forms. This phenomenon was investigated therefore by adsorbing H₂O at a slightly higher temperature of adsorption,

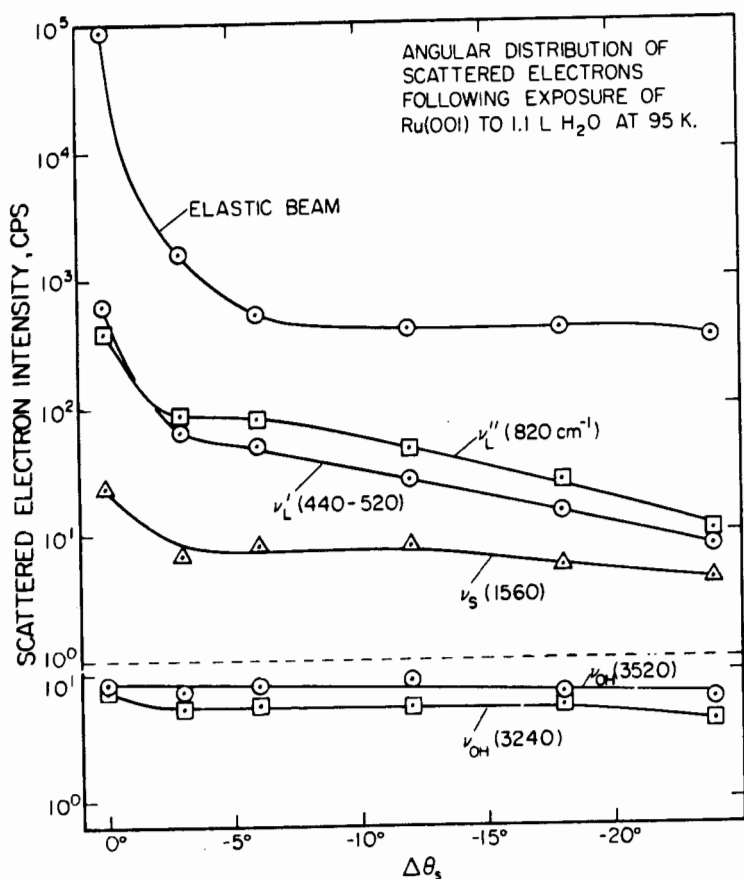


Fig. 4 - Intensities of the loss features of Fig. 3 as functions of polar scattering angle, θ_s . In the specular direction, $\Delta\theta_s \equiv 0^\circ$.

165 K. Thermal desorption spectra indicate that at this temperature and these pressures of H₂O ($\leq 1 \times 10^{-7}$ torr), multilayers of ice do not form on the surface; saturation is achieved with a 3 L exposure of H₂O. The vibrational spectra obtained under these conditions differ markedly from those obtained at an adsorption temperature of 95 K, particularly for exposures of H₂O greater than 1 L. The loss due to the O-H stretching mode remains at a value typical of intermolecular hydrogen bonding, 3240 cm⁻¹, and the scissoring mode is somewhat lowered in frequency; the most noticeable differences, however, are in the region below 1000 cm⁻¹ (cf. Fig. 7). At saturation at 165 K, three modes are now resolved. Isotopic substitution reveals that the two modes at 940 and 710 cm⁻¹ are librational modes with an average isotopic frequency ratio of

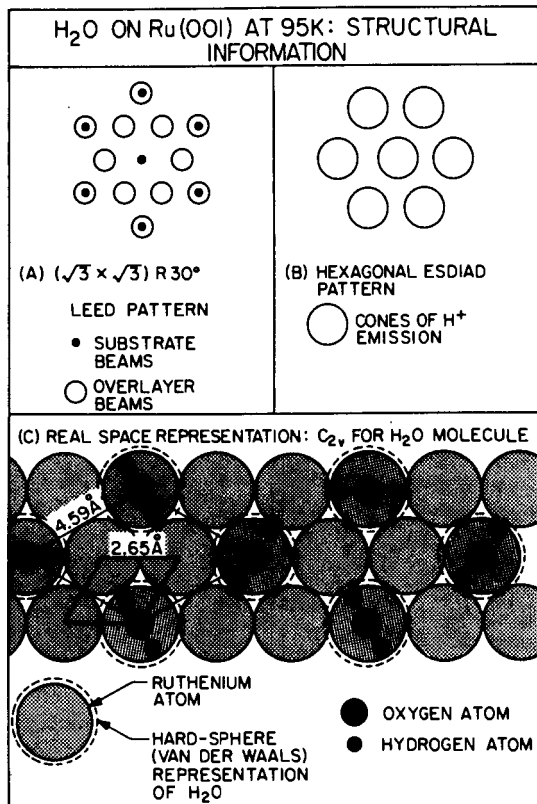


Fig. 5 - Structural information for H₂O on Ru(001) at 90 to 95 K.

1.37, whereas the mode at 370 to 400 cm⁻¹ is the frustrated translation of the molecule against the metal surface, with an experimental isotopic frequency ratio of 1.04. This again supports the assignments in this region discussed previously.

An investigation of the scattering mechanism for a surface prepared in this manner confirms that in this case, also, the librational modes are dipole-enhanced whereas the O-H stretching mode is not. Figure 8 illustrates the intensities of these modes as functions of scattering angle, which are discussed in detail elsewhere¹¹. One possible explanation for the differences in the vibrational spectra taken at the two temperatures of adsorption is that at 165 K, the adsorbed H₂O is chemically different, perhaps dissociated. In fact there is evidence that a small fraction of water dissociates as the surface is heated beyond 200 K^{1,11}. However, the results of photoemission experiments, shown in Fig. 9,

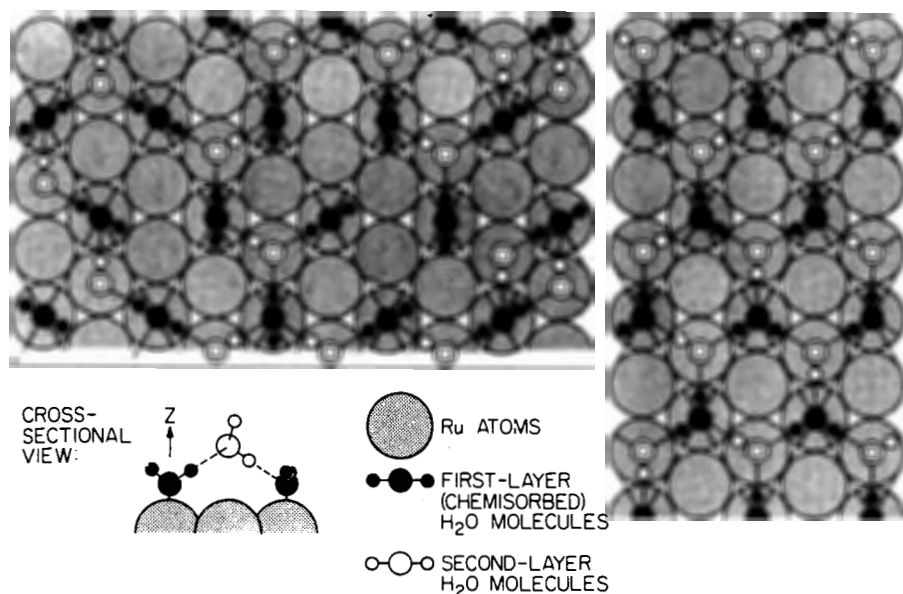


Fig. 6 - Adsorption of a second-layer H₂O molecule, hydrogen-bonded to the chemisorbed H₂O, provides a model which is consistent with both the LEED and ESDIAD data of Fig. 5. Possible structures are shown here.

do not support the hypothesis that significant dissociation occurs at 165 K. In these experiments, photoelectron intensities were analyzed at two different exit angles for comparison. In the HeI photoemission spectra of gaseous H₂O¹⁴ and also of ice^{15,16}, three features are observed which are ascribed to the antibonding O-H orbital (1b₂), the bonding O-H orbital (3a₁), and the nonbonding oxygen orbital (1b₁). Possible overlap of the latter feature with emission from the ruthenium substrate at 5 to 6.5 eV in these spectra makes identification of the 1b₁ orbital ambiguous for exposures of 2 L or less. At higher exposures (cf. Fig. 9(D)), the UP spectrum resembles that of ice. The similarity of spectra B and C, taken following exposure to 2 L of H₂O at 95 K and following saturation with H₂O at 165 K, respectively, indicates that major differences in the chemical composition of the adsorbate layers prepared under these two sets of conditions are not present.

A more probable hypothesis is that, following adsorption at 165 K, the vibrational spectra reflect a surface with a higher proportion of first-layer (chemisorbed) H₂O molecules, and that the structure of this adsorbed layer is different at saturation than at lower temperature.

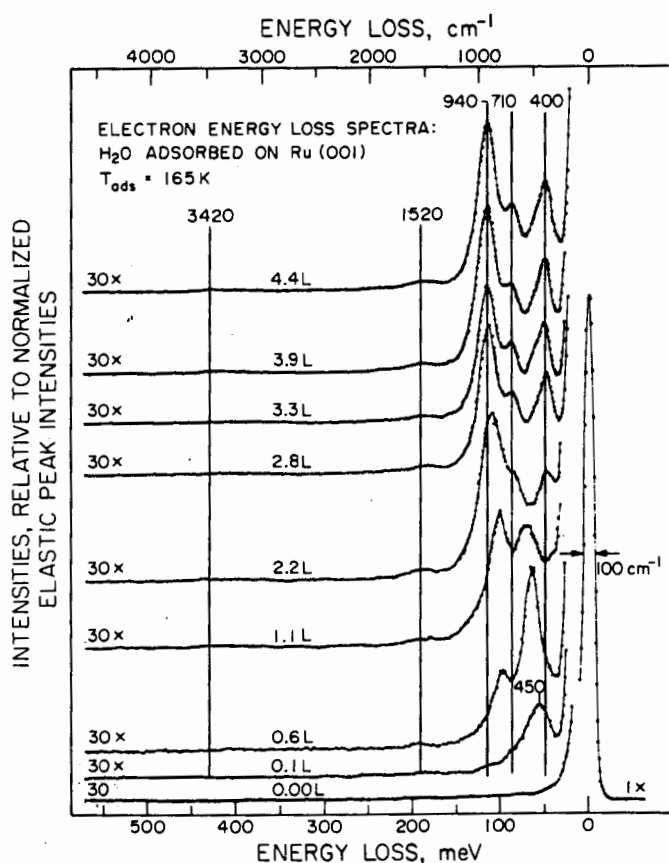


Fig. 7 - Vibrational spectra of H₂O adsorbed on Ru(001) at 160 to 170 K.

The results of this investigation can be summarized as follow :

1. The direct interaction of water with the metal surface is characterized by molecular adsorption through the oxygen atom.
2. At 95 K, clusters of H₂O molecules form even at submonolayer coverages via hydrogen bond interactions. The evidence which supports this conclusion is :
 - a. The O-H stretching frequency at 3320 to 3380 cm⁻¹;
 - b. Analysis of the scattering mechanism and selection rules for the librational modes; and
 - c. Analysis of the LEED and ESDIAD data, which provides a physical model for the structures of the clusters.
3. Following adsorption at 165 K, the vibrational spectra reflect a greater proportion of chemisorbed (first-layer) water molecules

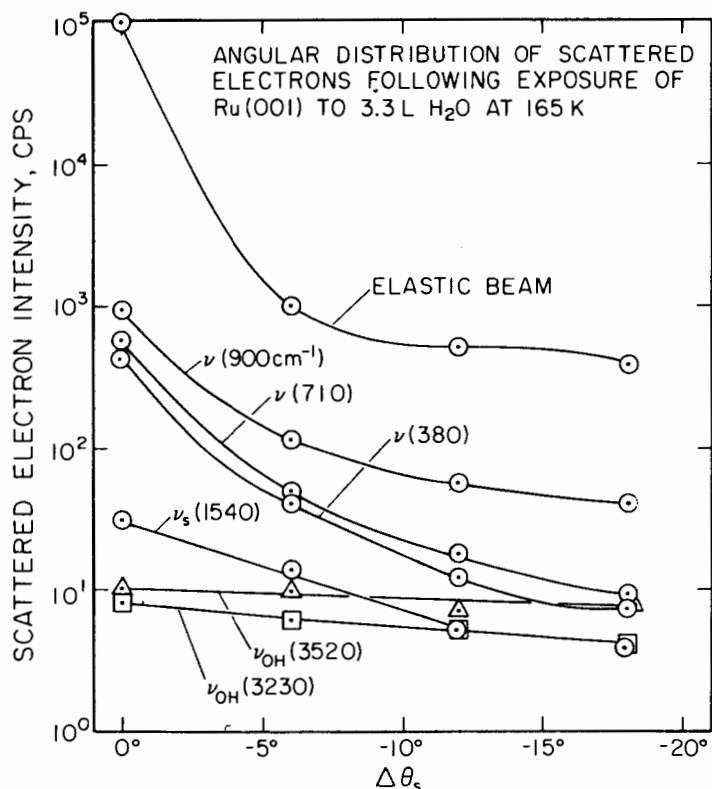


Fig. 8 - Intensities of electron energy loss features as functions of polar scattering angle, θ_s , following exposure of the Ru(001) surface to 3.3 L H₂O at 160 to 170 K. In the specular direction, $\Delta\theta_s \equiv 0^\circ$.

and possible structural changes in the overlayer, relative to adsorption at 95 K.

REFERENCES

1. T.E. Madey, J.T. Yates, Jr., Chem. Phys. Letters 51 (1977) 77.
2. S. Andersson, J.W. Davenport, Solid State Commun. 28 (1978) 677.
3. G.B. Fisher, B.A. Sexton, Phys. Rev. Letters 44 (1980) 683.
4. H. Ibach, S. Lehwald, Surface Sci. 91 (1980) 187.
5. F. Franks, Ed., Water : A Comprehensive Treatise, Plenum Press, New York (1972).
6. P. Schuster, G. Zundel, C. Sandorfy, Eds., The Hydrogen Bond, North-Holland Publishing Co., Amsterdam (1976).
7. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York (1978) 226.

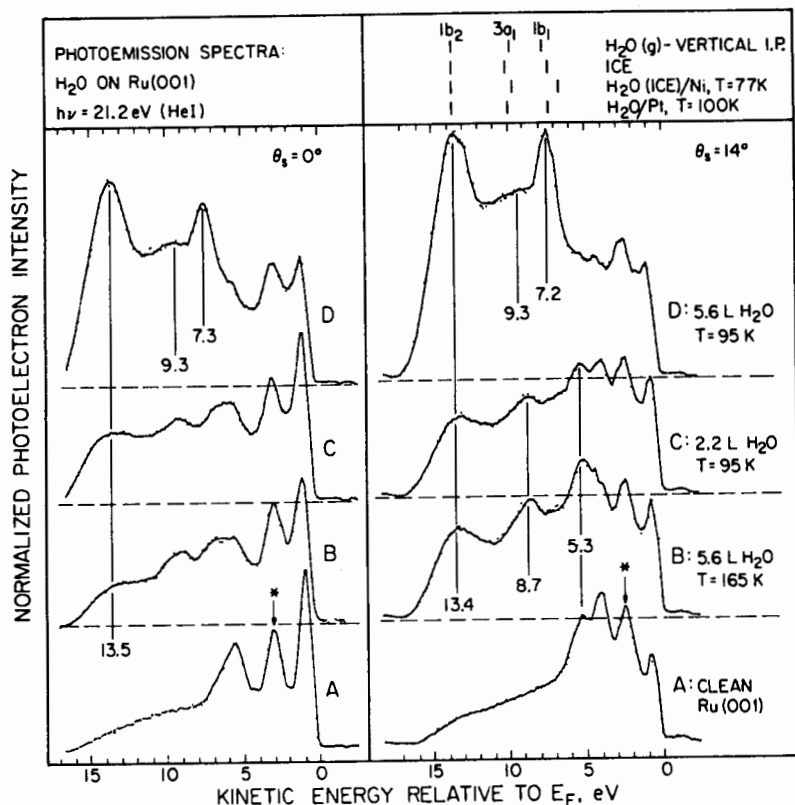


Fig. 9 - Photoemission spectra taken following exposure of the Ru(001) surface to H_2O . The angle of incidence of the HeI radiation is 80° from the surface normal. Experimental details are discussed in 17. The three molecular orbitals shown in the upper right panel are referenced to the $1b_2$ orbital in energy. From top to bottom, the energy values are taken from 14, 15, 16, and 3. The spectra have been normalized to the substrate feature of the clean surface indicated by (*).

8. J.R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York (1971) 65-76.
9. M. Van Thiel, E.D. Becker, G.C. Pimentel, J. Chem. Phys. 27 (1957) 486.
10. S.Y. Tong, C.H. Li, D.L. Mills, Phys. Rev. Letters 44 (1980) 407.
11. P.A. Thiel, F.M. Hoffmann, W.H. Weinberg, in preparation.
12. J.J. Zinck, W.H. Weinberg, J. Vacuum Sci. Technol. 17 (1980) 188.
13. L.E. Firment, G.A. Somorjai, Surface Sci. 84 (1979) 275; J. Chem. Phys. 63 (1975) 1037.
14. D.W. Turner, C. Baker, A.D. Baker, C.R. Brundle, Molecular

Photoelectron Spectroscopy, Wiley-Interscience, London (1970) 77.

15. I. Abbati, L. Braicovich, B. De Michelis, Solid State Commun. 29 (1979) 511.
16. P.J. Page, D.L. Trimm, P.M. Williams, J. Chem. Soc. Far. Trans. I 70 (1975) 1769.
17. G.E. Thomas, W.H. Weinberg, Rev. Sci. Instrum. 50 (1979) 497.