

Implications of Spectroscopic Measurements of an Ultrathin Water Layer

by Peter J. Feibelman

Motivation—Many examples teach that the structure of an adsorbed layer is not understood without confirmation from several experimental approaches. Thus, our inference that water forms a partially-dissociated wetting layer on the close-packed face of ruthenium [Science **295**, 99(2002)], based on successful comparison of ab initio calculations to low energy electron diffraction (LEED) structure analysis, has recently been subjected to spectroscopic tests. The vast importance of water behavior within microns of surfaces, in technology (membranes, sensors, micromachines) and nature (biotransport, geophysical transport, raindrop formation), and the knowledge that the first water layer on a solid is a “template” determining the behavior of adjacent water over microns, has made it urgent to confirm or disprove that wetting and H₂O dissociation go hand-in-hand.

Accomplishment—Vibrational and X-ray photoelectron spectroscopies have been applied (by experimentalists in Germany, Sweden, England and the U.S.) to the water-on-ruthenium system, and we have performed first-principles calculations of the expected spectra, for both dissociated and undissociated cases, to guide the interpretation of the results, leading to a vigorous debate in the literature.

New spectroscopic data first emerged from non-linear optics (“Sum Frequency Generation”) coupled with thermally programmed desorption. Supporting dissociation, absence of a high-frequency stretching vibration mode implied that all the hydrogens of the wetting layer were involved in H-bonding. For a layer of intact water molecules (Fig. 1), this would not be the

case. But the new data also appeared to show a spectral peak at a frequency characteristic of water. We clarified the meaning of this result, producing new and marshalling old evidence that the stretch vibrations of an H-bonded system reveal the O-O distance distribution, not whether its molecules are intact or dissociated. We also estimated the breadth of the O-O distance distribution for the expected level of proton disorder, showing that it agrees both with the width of the observed vibration peak and also a new electron diffraction analysis.

New, low-fluence, high-resolution X-ray photo-electron spectra (Fig. 2) reveal an O (1s) feature with two peaks split by 1.6 eV. We have accounted for this splitting with ab initio calculations - it results from the presence of OH and H₂O in the wetting layer, which is, accordingly, part dissociated. The peak heights imply that H atoms split off from only about 40% of deposited water molecules. Our latest calculations also account for this result. There is considerable controversy over whether this O-H bond-breaking is kinetically possible in the absence of sufficient ionizing radiation. There is no question, however, that the new XPS study confirms that the ab initio calculations do explain the early LEED experiment, and that dissociation is favored thermodynamically.

Significance—Confirming an atomic-scale understanding of water on ruthenium, the only wetting system whose structure has been measured, is the key to establishing it as “the hydrogen atom” of wetting phenomena. That the H₂O molecules are partially dissociated, in this case, has potentially profound implications for nanofluidics and electrochemistry.

Sponsors for various phases of this work include: DOE Office of Basic Energy Sciences

Contact: Peter J. Feibelman; Surface & Interface Sciences, Dept. 1114
Phone: (505) 844-6706, Fax: (505) 844-1197, E-mail: pjfeibe@sandia.gov

non H-bonding hydrogen

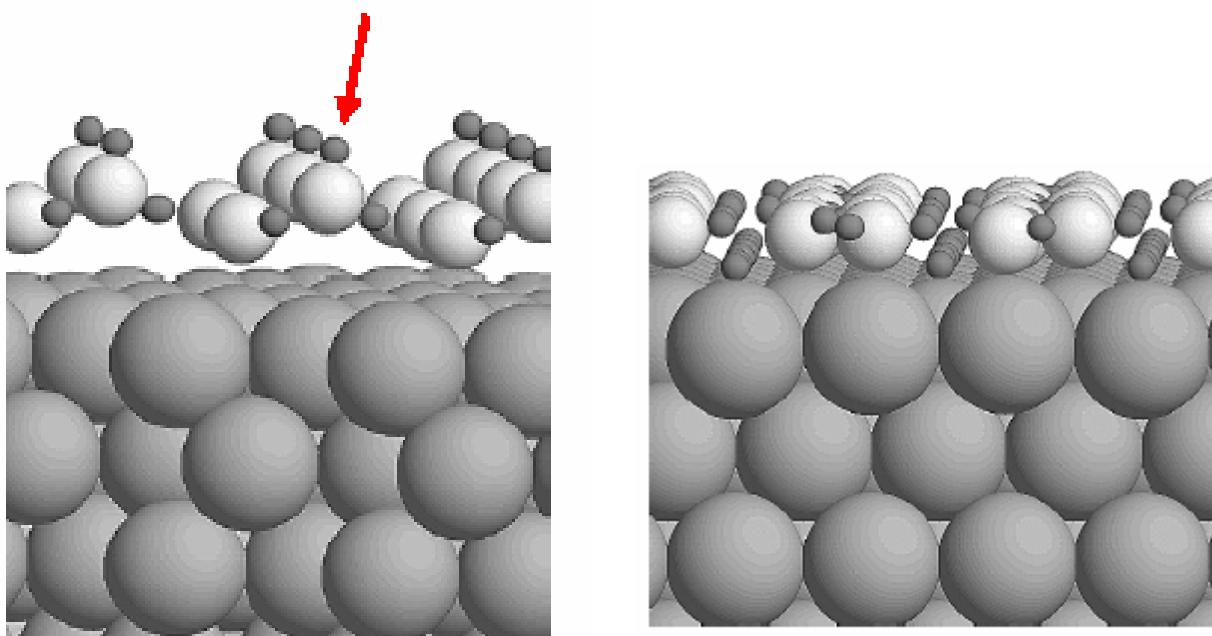


Figure 1. Left: Side view of an ice-like arrangement of a single layer of intact water molecules, adsorbed on the hexagonal surface of a ruthenium crystal. Large, medium and small spheres represent Ru, O and H or D atoms. Note the presence of non H-bonding H atoms. They should give rise to a particularly high frequency O-H stretching mode. That it is not seen is evidence that the structure depicted does not occur in nature. Right: Side view of a fully H-bonded arrangement of half H_2O molecules and half OH fragments. Note that the non H-bonding H atoms broken off water molecules to make the OH fragments are bonded directly to Ru atoms.

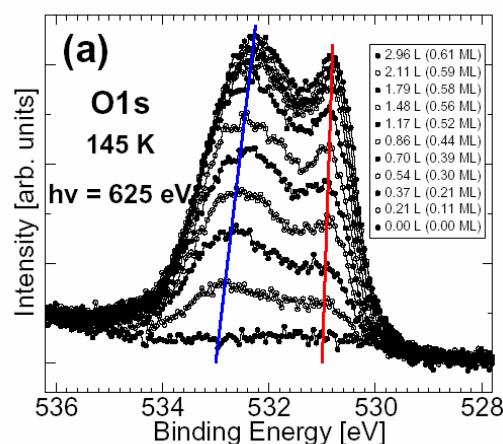


Figure 2. O (1s) X-ray photoemission spectrum up to 1ML water on ruthenium. The lower(higher) energy peak is from OH(H_2O). The smaller area under the OH peak implies that about 40% of the water molecules present are dissociated. [*Physical Review Letters* **93**, 196102 (2004)]