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Displacement of Cyclohexane by Water on a Ruthenium Surface

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Water can displace cyclohexane from chemisorption sites on a Ru(001) surface. In so doing, thermal desorption spectroscopy indicates that the water forms three-dimensional, hydrogen-bonded clusters which are two layers deep, much as it would on the clean surface. Water forces the cyclohexane into weakly bound states. This is apparently driven by a combination of effects: first, a single water molecule is more strongly bound to the ruthenium surface than a cyclohexane molecule, and second, the packing density of water in the hydrogen-bonded bilayer is much greater than the packing density of the chemisorbed cyclohexane. Taking both effects into consideration, replacement of a chemisorbed cyclohexane layer with a water bilayer is energetically favored by 5 to 8 kcal per mole of surface metal atoms. The data also show that the preferential chemisorption of water on ruthenium is not limited by the kinetics of diffusion or displacement in these experiments, but rather reflects a true equilibrium state. © 1986 Academic Press, Inc.

1. INTRODUCTION

Catalytic hydrogenation of aromatic hydrocarbons over Group VIII metals most often proceeds to complete hydrogenation of the reactant, even though it may be desirable to obtain a product which is only partially hydrogenated. For example, hydrogenation of benzene usually yields only cyclohexane (C_6H_{12}), even though cyclohexene (C_6H_{10}) may be a desirable product. Hartog showed that C_1 to C_4 alcohols act to promote cyclohexene formation in this reaction over ruthenium catalysts (*1*), which subsequently led Don and Scholten to investigate the influence of H_2O as a simple model for the alcohols (*2*). The latter authors found that reversible adsorption of water plays a decisive role in bringing about selectivity for cyclohexene over nonsupported ruthenium powders. They postulated that water might weaken the chemisorption bond of the hydrogenation intermediate cyclohexene, allowing it to desorb before further hydrogenation to cyclohexane could occur. Their results have led us to undertake an investigation of the interaction between water and cyclic C_6 hydrocarbons in simple well-defined model systems, with the aim of clarifying the role which water plays in this hydrogenation reaction.

Previous studies of model ruthenium surfaces have shown that both cyclohexane (*3, 4*) and water (*5–8*) desorb from a Ru(001) single crystal in several distinct states between 150 and 230 K. In both cases, these states have been attributed to desorption of molecules from sites in the first (chemisorbed) layer, the second (intermediate) layer, and the physisorbed multilayer. Water shows evidence for strong intermolecular hydrogen-bonding within the first two layers (*6–10*), and does not dissociate on Ru(001) (*5–10*). In the first layer, cyclohexane adsorbs on Ru(001) and other hexagonal metal surfaces with three axial C—H bonds pointing into the surface. These bonds have a distinctive "soft" C—H stretching frequency and are (presumably) easily broken (*3, 4, 11*).

We report evidence from thermal desorption spectroscopy (TDS) that water competes very strongly with cyclohexane on a Ru(001) single crystal, physically displacing the saturated hydrocarbon from sites close to the metal surface and forcing it out of the chemisorbed state. The water is not mea-

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surably perturbed by the presence of the hydrocarbon. These results are independent of the order of the adsorption sequence, i.e., they represent a true equilibrium state rather than a kinetically limited state. Displacement of cyclohexane by water is somewhat surprising, given previous measurements which have shown that the binding energy of chemisorbed cyclohexane is comparable to or even greater than that of water on Ru(001), ca. 14 vs 12 kcal/mole, respectively (*3–7*). Because these heats of adsorption indicate that cyclohexane is *more* strongly bound than water, one might not expect that water could displace cyclohexane, as we have observed. Our measurements, in fact, indicate that cyclohexane is *less* strongly bound by at least 2 kcal/mole; furthermore, the displacement is also driven by the much higher packing density of water compared to cyclohexane.

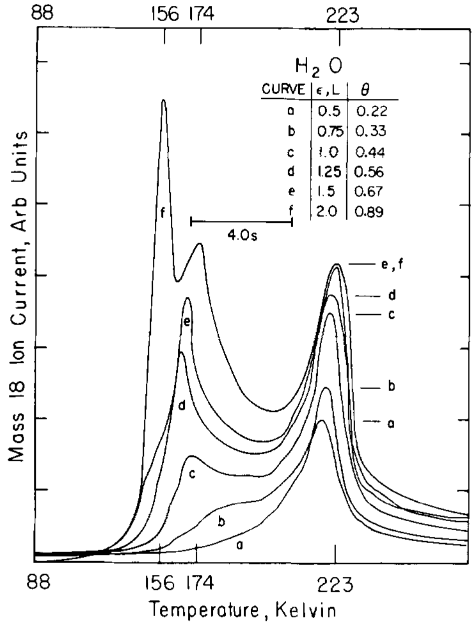
2. EXPERIMENTAL METHODS

The experiments were performed in an ultrahigh vacuum (UHV) apparatus with a typical base pressure of 1×10^{-10} Torr (1 Torr = 133.3 N m^{-2}). The Ru(001) sample, ca. 1 cm^2 in area, was grown at the Ames Laboratory Materials Preparation Center. It was oriented and polished to within 0.5 degrees of the (001) face on both sides. Sulfur and silicon were the major initial bulk contaminants. They were removed by successive heating, ion bombardment, and oxidation cycles, similar to the procedure described by Williams and Weinberg (*12*). The cleanliness of the sample was regularly checked by using a Varian single-pass cylindrical mirror analyzer to measure Auger electron spectra, and by measuring TDS of CO following oxygen exposure to remove carbon. The sample was mounted by spotwelding two 0.020-in-.diameter Ta wires to the edges. These wires were attached to a liquid-nitrogen-coolable cold finger, and could be used to resistively heat the sample (*13*). A W-5% Re vs W-26% Re thermocouple was spotwelded to the edge of the crystal.

Both water (triply distilled) and cyclohexane were purified by repeated freeze–thaw cycles under vacuum. The water was introduced to the sample by backfilling the entire UHV chamber. Cyclohexane was introduced via a directed, capillary-array doser (*14*). Water exposures are reported in units of Langmuirs, L (1 L ≡ 1×10^{-6} Torr-s), and cyclohexane exposures are reported in units of Langmuir equivalents. For both cyclohexane and water, no correction has been made for ionization gauge sensitivities in the reported exposures. The sample was cleaned with oxygen after each experiment to ensure the removal of carbon residue. The sample was held at <88 K during gas exposures. In the thermal desorption experiments, partial pressure of several species having different atomic mass units could be measured simultaneously as functions of temperature and time by using a mass spectrometer (EAI Quad 150) interfaced to a Commodore 64 computer. Temperature was controlled using an independent feedback circuit described by Herz *et al.* (*15*). With this device the heating rate was held constant at 0.09 mV s^{-1}, which corresponds to a temperature change of 5 to 9 K s^{-1} between 110 and 250 K, the region where desorption occurs in these experiments.

3. RESULTS AND DISCUSSION

In Figs. 1 and 2 we show the thermal desorption spectra of water and cyclohexane adsorbed separately on Ru(001) for increasing initial exposures. In both cases, the spectra agree well with those reported previously (*3–8*). For both adsorbates, the time-integrated peak intensity (which is proportional to coverage) varies linearly with exposure, implying a constant sticking coefficient. For water, we shall take as our reference point the coverage at which the multilayer first begins to appear, in order to define other coverages. There is ample evidence that at this point the water is two layers deep (a "bilayer"), and each layer has an absolute coverage of $\theta_{H_2O} = 0.33$ (*7–*

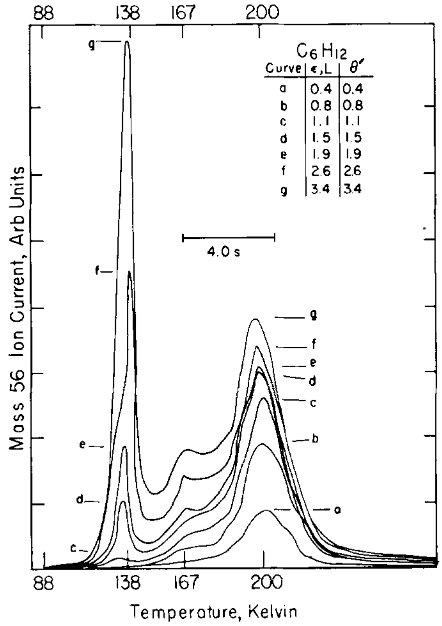


CURVE	ε,L	θ
a	0.5	0.22
b	0.75	0.33
c	1.0	0.44
d	1.25	0.56
e	1.5	0.67
f	2.0	0.89

FIG. 1. Thermal desorption spectra of water from Ru(001) following exposure at <88 K. The abscissa is linear in time.

9). [θ is the ratio of adsorbate particles to surface metal atoms.] Therefore this reference point, illustrated by curve e of Fig. 1, has an absolute coverage of $\theta_{H_2O} = 0.67$. For cyclohexane, absolute coverages are not experimentally established and so we shall introduce a relative coverage, θ'_{cycl}. We arbitrarily define $\theta'_{cycl} = 1$ as the coverage at which the cyclohexane multilayer first appears; this is approximately represented by curve c of Fig. 2. All coverages of water and cyclohexane are referenced to these two points.

As shown in Fig. 1, at low coverage ($\theta_{H_2O} < 0.22$), water mainly occupies the primary chemisorbed state with the peak temperature of 219 ± 4 K. At intermediate coverages, the second-layer chemisorbed state (169 K) is populated. Finally, at $\theta_{H_2O} > 0.67$, the zero-order multilayer state appears (ca. 155 K). We note that an alternative assignment of the two high-temperature states is that they are caused by successive desorption from large and small hydrogen-bonded clusters, respectively (*8*), rather than H_2O desorption from successive layers (*5–7*). In *either* case, the two high-temperature desorption peaks reflect desorption of H_2O molecules from hydrogen-bonded clusters which are two layers deep (*5–8*). We have modeled the high-temperature desorption peak shape, with particular attention to the peak position and full-width at half-maximum (FWHM). We assume simple first-order kinetics and treat the desorption energy and preexponential rate factor as adjustable parameters. For water, we obtain a good fit, within experimental error, for a range of desorption barriers from 12.9 to 15.3 kcal/mole; the preexponential rate factor varies correspondingly from 1×10^{13} to 3×10^{15} s^{-1}. This range of parameters reflects the range of fits obtained at two different coverages (curves a and b in Fig. 1) and also indicates that we have considered experimental peak-broadening of up to 4 K as a reasonable possibility. We note that strong attractive interactions (= a strongly coverage-dependent desorption barrier) or half-order desorption kinetics, both of which might be physically reasonable models for



Curve	ε,L	θ′
a	0.4	0.4
b	0.8	0.8
c	1.1	1.1
d	1.5	1.5
e	1.9	1.9
f	2.6	2.6
g	3.4	3.4

FIG. 2. Thermal desorption spectra of cyclohexane from Ru(001) following exposure at <88 K. The abscissa is linear in time.

the dissolution of tightly bound clusters during TDS, should both result in a stronger shift of the desorption peak to higher temperatures with increasing coverage than we observe. We take this to be supporting evidence for the assumption of simple first-order desorption kinetics.

In Fig. 2, the TD spectra of cyclohexane are shown. These data also show evidence for a chemisorbed state at 200 ± 2 K and a multilayer state at 136 K, which develop sequentially with increasing exposure. In Fig. 2, the small feature at 167 to 172 K may be due to desorption from crystal edges and defect sites, or it may be due to desorption from the second layer, as previous authors have suggested (*3*, *4*). Its relatively small size in these measurements leads us to favor the former explanation.

For the high-temperature state of cyclohexane, the peak position and FWHM can be well modelled, within experimental error, if one assumes a desorption barrier of 9.1 to 10.8 kcal/mole [somewhat lower than the 14 kcal/mole reported by Madey and Yates (*3*)] and a corresponding preexponential factor of 1×10^{10} to 1×10^{12} s^{-1}. As for the TD spectra of water, this range is mainly due to our allowance for an experimental broadening of up to 4 K. Comparison of the binding energies of H_2O and C_6H_{12} in these experiments shows that the chemisorbed hydrocarbon is *less* tightly bound than chemisorbed water by 2 to 6 kcal/mole.

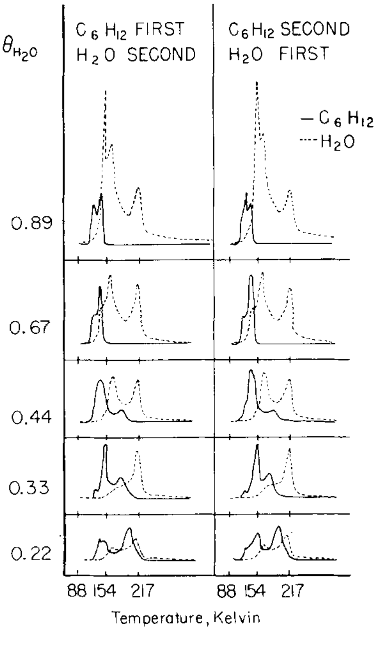


FIG. 3. Thermal desorption spectra of cyclohexane (solid lines) and water (dashed lines) following exposure to both adsorbates at <88 K. The abscissae are linear in time.

Figure 3 shows the results of a series of TDS experiments in which water and cyclohexane are coadsorbed, alternating the exposure sequence. For both sequences, the exposure of cyclohexane is held constant while the exposure of water is varied.

The desorption spectra of H_2O in the coadsorption experiments are shown by the dashed lines of Fig. 3. By comparison of Fig. 3 with Fig. 1, the H_2O TD spectra are not markedly influenced by the coadsorbed cyclohexane, even at coverages where water and cyclohexane desorb simultaneously ($\theta_{H_2O} < 0.33$). The integrated area under the H_2O desorption peaks is constant for a given exposure, independent of the coadsorbed cyclohexane, for either adsorption sequence. Therefore, the cyclohexane does not significantly alter either the adsorption or desorption kinetics of H_2O.

In the absence of H_2O, the cyclohexane exposure ($\varepsilon = 1.1$ L, $\theta'_{\mathrm{cycl}} = 1.1$) is sufficient to fill the first chemisorbed state at 200 K, and also the smaller feature at 169 K, but it is insufficient to significantly populate the multilayer state. This is displayed in Fig. 2, curve c. However, even at a very small coverage of H_2O ($\theta_{H_2O} < 0.22$), the cyclohexane begins to show evidence of the multilayer state (ca. 136 K) and a new weakly bound state at about 150 K (Fig. 3). As the water exposure increases, the new weakly bound cyclohexane state grows continuously in intensity at the expense of the two higher temperature states. This new state probably represents cyclohexane on top of the water bilayer. At $\theta_{H_2O} > 0.56$, the normal cyclohexane multilayer state grows at the expense of the weakly bound state, and no trace of the two higher temperature states remain. The total area of the cyclohexane desorption peaks remains constant throughout, indicating that the water does not either displace the cyclohexane from the surface into the gas phase or prevent its adsorption. However, water does strongly alter the state of the adsorbed hydrocarbon.

The shapes of the cyclohexane desorption spectra are significantly altered in the water coadsorption experiments, i.e., a new weakly bound state appears and the relative intensities of the existing clean-surface states change. The shapes of the water desorption spectra, however, are not affected by the coadsorbed cyclohexane. For H_2O on Ru(001), it is well known that the shape of the TD spectrum is related to desorption from well-ordered, three-dimensional hydrogen-bonded islands (*6–8*), and so we suggest that these clusters also form in the presence of cyclohexane. We propose that the adsorbed water condenses into islands at the metal surface (due to the strong attractive hydrogen-bond interactions), and the cyclohexane can only adsorb at those areas where the water is absent. As the water coverage grows, the cyclohexane is displaced from the chemisorption sites to more weakly bound sites above other adsorbate molecules, either water or cyclohexane. It appears to be slightly more favorable for this displaced cyclohexane to occupy positions above the chemisorbed water bilayer than above the chemisorbed cyclohexane layer. Finally, as the water multilayer grows, the cyclohexane is further displaced to the normal cyclohexane multilayer (Fig. 3). The fact that these events are independent of the order of adsorption indicates that what we observe is a true equilibrium situation, and is not limited by the kinetics of diffusion or displacement, on the time scale of our experiments (ca. 10 to 30 min between adsorption and desorption). [It is possible, of course, that experiments done under different conditions (such as on a faster time scale or under adsorption–desorption equilibrium) would be kinetically limited.] Other experimental data showed that water can effectively displace the chemisorbed cylohexane into the multilayer states even at cyclohexane coverages as high as $\theta'_{\mathrm{cycl}} \approx 3$.

Based upon these data, it is clear that water displaces cyclohexane from sites close to the metal surface. This must be because a water bilayer on ruthenium is thermodynamically more favorable than a cyclohexane layer. From our TDS data, we estimate that the difference in binding energies per molecule is at least 2 kcal/mole. However, there is an important additional effect to consider. The *number* of bonds formed per unit surface area (or, equivalently, per unit of surface metal atoms) will influence the total enthalpy change when one adsorbate is replaced by another. For water, the absolute coverage in the bilayer is $\theta_{H_2O} = 0.67$ (*7–9*) i.e., there are 0.67 moles of H_2O molecules per mole of surface ruthenium atoms. Half of the water molecules are bonded directly to the metal surface with a chemisorption bond strength of ca. 12.9 to 15.3 kcal/mole, based upon our data, and the other half are hydrogen-bonded to the first layer with no direct water–metal interaction. The strength of a single O—H---O hydrogen bond in ice is estimated at 4 to 6 kcal/mole (*16*), so each molecule in the second layer is bound by roughly 8 to 12 kcal/mole (two hydrogen bonds per molecule) to the first-layer molecules. The average binding energy of a water molecule anywhere in the bilayer is then 10.5 to 13.7 kcal/mole, so that the chemisorption energy for a complete water bilayer is (0.67) × (10.5 to 13.7 kcal) = 7.0 to 9.2 kcal per mole of surface Ru atoms.

In the case of cyclohexane, absolute coverage data are not available, but we can estimate the absolute coverage in the first monolayer. The approximate size of the molecule (*17*) indicates that it can exclude an area equivalent to 5.5 Ru surface atoms, as shown in Fig. 4. If we assume perfect

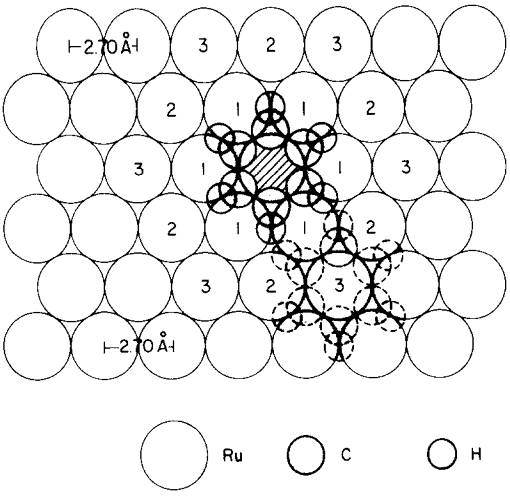


FIG. 4. Cyclohexane adsorbed on Ru(001). A cyclohexane molecule (fully outlined) adsorbs with its molecular plane parallel to the surface, centered above a Ru atom (hatched). The six surrounding Ru atoms (labeled 1) are blocked from further adsorption due to the size of the cyclohexane ring, which is drawn approximately to scale. Second-nearest-neighbor Ru atoms (labeled 2) are most probably blocked due to repulsion which would occur between adjacent equatorial hydrogens of neighboring molecules. Third-nearest neighbors (labeled 3) may also be blocked for this reason, i.e., the lower right molecule would probably *not* adsorb at the site where it is shown. Monte Carlo simulations of a randomly filled lattice predict that $\theta_{\text{cycl}} =$ 0.15 when first- and second-nearest neighbors are blocked. Simulations including third-nearest-neighbor exclusion predict $\theta_{\text{cycl}} = 0.10$ in the first layer (18).

and non-site-specific packing, then, based only on the molecule's size, the maximum absolute coverage in the first filled layer is $\theta_{\text{cycl}} = 0.18$. However, this does not take into account the known site and orientation of the molecule (*3, 4, 11*), as well as statistical imperfections in the adsorbate layer which may be significant if the molecule is immobile after adsorption (*18*). Both effects will lead to lower coverages. It is known that cyclohexane adsorbs in the chair configuration with the center of the molecular ring above a single Ru atom, and with three of the axial C—H bonds penetrating the surrounding threefold hollow sites (*3, 4, 11*). The sites occupied and probably excluded by adsorbed molecules are illustrated in Fig. 4. Monte Carlo simulations of a randomly filled, site-specific layer show that $\theta_{\text{cycl}} = 0.15$ or 0.10 in the first complete layer, depending upon whether only first and second-nearest neighbor Ru sites, or first through third-nearest-neighbor sites are blocked by an adsorbed molecule, respectively (see Fig. 4) (*18*). The randomly filled, site-specific layer with site blocking up to and including the third-nearest neighbor certainly places the *lower* limit on the true absolute coverage in the first layer ($\theta_{\text{cycl}} = 0.10$). On the other hand, the perfectly filled adlayer with no adsorption site specificity must represent the *upper* limit of the true coverage ($\theta_{\text{cycl}} = 0.18$). We conclude, therefore, that the chemisorbed cyclohexane layer has an absolute coverage between $\theta_{\text{cycl}} = 0.10$ and $\theta_{\text{cycl}} = 0.18$.

Our TDS data show that the cyclohexane–Ru chemisorption bond energy is 9.1 to 10.8 kcal per mole of adsorbed cyclohexane, which corresponds to (0.10 to 0.18) × (9.1 to 10.8 kcal) = 0.9 to 1.9 kcal per mole of Ru surface atoms for the complete layer. This means that replacing a layer of chemisorbed cyclohexane with a bilayer of water molecules is energetically favored by 5.1 to 8.3 kcal per mole of surface metal atoms.

We note that the contribution of entropy to the total free energy change is relatively small in this process. Based upon the entropy changes which occur upon sublimation of bulk ice and cyclohexane, the entropy term decreases (relative to the gas phase) by no more than 1 kcal per mole of Ru atoms at 100 K when an adsorbed (condensed) layer of C_6H_{12} is replaced by H_2O. This is small in comparison with the enthalpy changes calculated above. A decrease in entropy for this exchange process is supported also by the difference in preexponential desorption rate factors for H_2O and C_6H_{12}, which suggest that adsorbed water is more highly constrained (higher preexponential factor) than adsorbed cyclohexane, within the context of transition state theory.

With respect to understanding the role

which water plays in catalytic formation of cyclohex*ene* over ruthenium, these results demonstrate that water can compete very strongly with a cyclic hydrocarbon for ruthenium adsorption sites, and therefore provide a broad rationale for the observation that water can influence the pathway of reactions involving cyclic hydrocarbons (*2*). The original hypothesis of Don and Scholten, that water weakens the strength of the cyclohexene–metal bond, is certainly a plausible one on the basis of our data (*2*), although we anticipate that the π-bond of cyclohexene will lead to more complex chemistry than we have observed with cyclohexane. More specific conclusions will be based upon experiments with the entire family of cyclic C_6 hydrocarbons which are currently underway in our laboratory.

In summary, we observe that water can displace cyclohexane from chemisorption sites close to a Ru(001) surface. In so doing, TDS data indicate that water forms three-dimensional hydrogen-bonded clusters which are two layers deep, much as it would on the clean surface. When this bilayer partially covers the surface, cyclohexane is forced into a weakly bound state (possibly cyclohexane on water). As the water multilayer forms, the cyclohexane is forced into the cyclohexane multilayer. The displacement of cyclohexane by water is apparently driven by the slight difference in binding energies [water being more strongly bound than cyclohexane by at least 2 kcal per mole of adsorbate on Ru(001)] combined with the large difference in packing densities. We estimate that replacement of a chemisorbed cyclohexane layer with a water bilayer is energetically favored by about 5 to 8 kcal per mole of surface Ru atoms.

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REFERENCES

1. Hartog, F., U.S. Patent 3,391,206 (1968).

2. Don, J. A., Scholten, J. J. F., *Faraday Discuss. Chem. Soc.* **71,** 145 (1981).

3. Madey, T. E., and Yates, J. T., Jr., *Surf. Sci.* **76,** 397 (1978).

4. Hoffmann, F. M., Felter, T. E., Thiel, P. A., and Weinberg, W. H., *Surf. Sci.* **130,** 173 (1983).

5. Madey, T. E., and Yates, J. T., Jr., *Chem. Phys. Lett.* **51,** 77 (1977).

6. Thiel, P. A., Hoffmann, F. M., and Weinberg, W. H., *J. Chem. Phys.* **75,** 5556 (1981).

7. Doering, D. L., and Madey, T. E., *Surf. Sci.* **123** 305 (1982).

8. Thiel, P. A., DePaola, R. A., and Hoffmann, F. M., *J. Chem. Phys.* **80,** 5326 (1984).

9. Williams, E. D., and Doering, D. L., *J. Vac. Sci. Technol.* **A1** 1181 (1983).

10. Kretzschmar, K., Sass, J. K., Bradshaw, A. M., and Holloway, S., *Surf. Sci.* **115,** 183 (1982).

11. Hoffmann, F. M., and Upton, T. H., *J. Phys. Chem.* **88,** 6209 (1984).

12. Williams, E. D., and Weinberg, W. H., *Surf. Sci.* **82,** 93 (1979).

13. Thiel, P. A., and Anderegg, J. W., *Rev. Sci. Instrum.* **55,** 1669 (1984).

14. Goodman, D. W., Madey, T. E., Ono, D. M., and Yates, J. T., Jr., *J. Catal.* **50,** 279 (1977).

15. Herz, H., Conrad, H., and Küppers, J., *J. Phys. E* **12,** 369 (1979).

16. Eisenberg, D., and Kauzmann, W., "The Structure and Properties of Water." Oxford Univ. Press, New York, 1969.

17. Gavezzotti, A., Simonetta, M., Van Hove, M. A., Somorjai, G. A., *Surf. Sci.* **154,** 109 (1985).

18. Sanders, D., private communication.