

# Modeling the Metal-Solution Interface under Ultrahigh Vacuum: Vibrational Studies of the Coadsorption of Water and Carbon Monoxide on Rh(100)

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The coadsorption of D<sub>2</sub>O and CO on Rh(100) under ultrahigh vacuum has been investigated by using infrared reflection absorption spectroscopy. The results show that the presence of D<sub>2</sub>O induces partial displacement of the CO molecules from linear to bridged configurations. The resulting spectra are very similar to those observed at equivalent CO coverages in an electrochemical environment. The spectral data indicate that the coadsorption of D<sub>2</sub>O and CO results in the formation of CO islands of varying coverage and the aggregation of both CO and D<sub>2</sub>O islands on Rh(100) at temperatures below D<sub>2</sub>O desorption.

## I. Introduction

Over the last 10 years, there have been a growing number of studies concerned with the modeling of the electrochemical double layer under ultrahigh vacuum (UHV) conditions.<sup>1-4</sup> A common goal in these studies is that the information obtained by utilizing the powerful UHV surface science techniques will result in a better understanding of molecular phenomena at the solid-electrolyte interface.

In this respect a number of UHV vibrational studies of the coadsorption of water and CO on well-defined Pt(111) and Rh(111) have appeared.<sup>4-7</sup> These structures have shown promising results in comparison with the corresponding vibrational spectra obtained for the analogous electrochemical systems.<sup>8-12</sup> Vibrational spectroscopy has been frequently utilized in these UHV studies since it provides a common link with the corresponding electrochemical studies regarding the structure of the adsorbed overlayer.

In this paper we describe the results obtained by using infrared absorption reflection spectroscopy (IRAS) for the coadsorption of water and CO on a well-defined Rh(100) surface in UHV. The selection of the present system is due largely to the substantial spectral differences observed between our recent IRAS studies of CO adsorption on Rh(100)<sup>13</sup> and the corresponding in situ IRAS studies of the adsorption of CO on Rh(100) electrodes in aqueous media.<sup>12,14</sup> Under UHV conditions, IR data show that both the linear and bridged CO species are present (bands

at 2010–2086 cm<sup>-1</sup> and 1895–1965 cm<sup>-1</sup>, respectively) at all CO coverages. The linear CO band is the dominant feature at low and high coverages, while comparable absorption intensities are observed for these two bands at moderate coverages.<sup>13</sup> In contrast, the corresponding IR spectra obtained under electrochemical environment reveal that while CO bands with similar peak frequencies are observed, the bridged CO band is the dominant spectral feature at all CO coverages.<sup>12,14</sup> Thus, these results clearly suggest that the presence of water significantly modifies the adsorption properties of Rh(100) for CO. The present study demonstrates that marked changes in the CO surface coordination geometry indeed take place on the Rh(100) surface upon coadsorption with water. The IR spectra show marked similarities to those found at equivalent CO coverages under aqueous electrochemical environments.<sup>12,14</sup>

## II. Experimental Section

The spectrometer optics and the vacuum system employed in this work are described elsewhere.<sup>13,15</sup> Typically, the base pressure while recording experimental data was  $\sim 3 \times 10^{-10}$  Torr. The Rh(100) sample (area  $\approx 1$  cm<sup>2</sup>) was heated resistively by tantalum leads spot-welded to the rear of the crystal. Temperature measurement was made by a chromel–alumel thermocouple spot-welded to the back side of the sample. Sample cleaning was accomplished by heating the sample to 1200 K in  $10^{-6}$  Torr of O<sub>2</sub> followed by annealing under vacuum to 1400 K to remove traces of the oxide. Surface cleanliness was verified by Auger electron spectroscopy (AES) and the surface order by low-energy electron diffraction (LEED).

The IRAS experiments utilized a Mattson Cygnus 100 spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. All IRAS spectra reported here were obtained at an angle of incidence of 85° with the spectrometer operating at 4-cm<sup>-1</sup> resolution. A typical spectrum was acquired by adding 500 interferometer scans (4 min). This sum spectrum was then ratioed against a stored background spectrum of the clean surface. Research purity CO and the water vapor above a freeze–pump–thaw cycled sample of ultrapure D<sub>2</sub>O (99.8 atom %) were introduced into the UHV chamber with the sample temperature maintained at 90 K.

In this report, the CO coverage ( $\theta_{\text{CO}}$ ) can be determined from the CO exposure. The relation between coverages and exposures was established from a series of temperature program desorption (TPD) experiments.<sup>13</sup> In general, 1.5 L (1 L =  $10^{-6}$  Torr s) of CO produced a coverage of  $\sim 0.35$  monolayer (ML) and a 5.5-L

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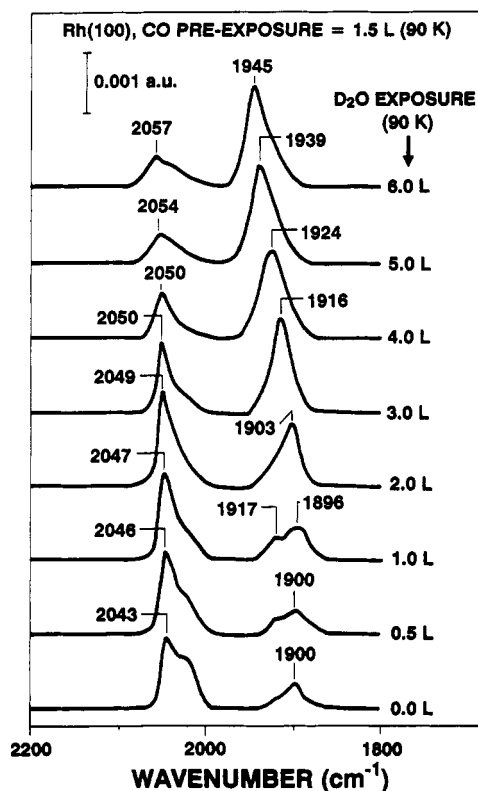
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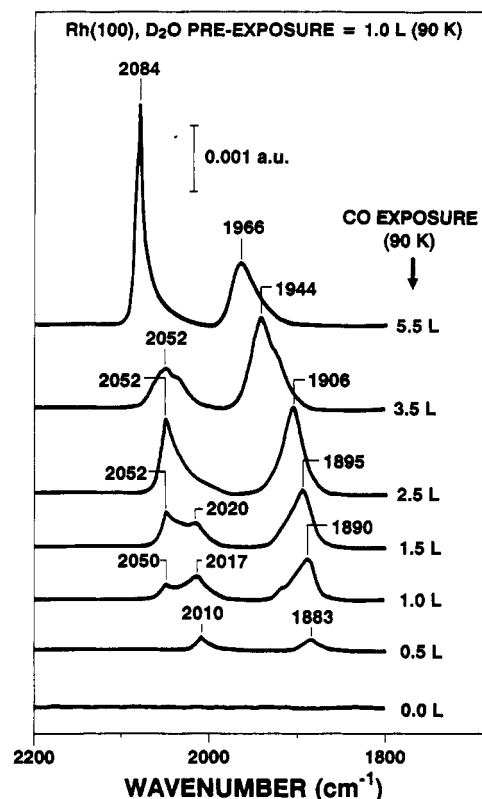
**Figure 1.** IRAS spectra of CO and D<sub>2</sub>O coadsorbed on Rh(100) at 90 K. After a CO exposure of 1.5 L, several D<sub>2</sub>O dosages were added stepwise as indicated.

exposure resulted in saturation coverage (0.75 ML). The coverage of D<sub>2</sub>O can be determined by assuming that the sticking coefficient of D<sub>2</sub>O on Rh(100) at 90 K is close to unity so that 1-L exposure would produce a coverage of  $\sim 1$  ML.

### III. Results and Discussion

Detailed IRAS studies of CO adsorption on clean Rh(100) can be found in ref 13, while recent high resolution electron energy loss spectroscopy (HREELS) studies reported for this system are discussed in ref 16. Briefly stated, IRAS spectra for CO adsorbed on Rh(100) at 90 K display both linear and bridged CO bands at 2010–2086  $\text{cm}^{-1}$  and 1895–1965  $\text{cm}^{-1}$ , respectively. The peak frequency for both IR bands increases as a function of increasing coverage, which can be attributed to dipole coupling interactions. At CO coverages below 0.5 monolayer (ML), the linear CO band is in general about 2–5 times more intense than the bridged CO band. At moderate CO coverages ( $0.5 \text{ ML} < \theta_{\text{CO}} < 0.7 \text{ ML}$ ), both CO bands have comparable adsorption intensities. At saturation CO coverage (0.75 ML), the linear to bridged IR integrated absorption intensity ratio is approximately 1.6/1.

Figure 1 shows the effects of increasing D<sub>2</sub>O exposure on the IR spectrum of 1.5 L ( $\theta_{\text{CO}} = 3.5 \text{ ML}$ ) of CO adsorbed on Rh(100) at 90 K. As mentioned earlier, CO adsorption on Rh(100) results in the formation of both linear and bridged CO species as indicated by IR bands centered at 2043 and 1900  $\text{cm}^{-1}$ , respectively. The low frequency shoulder accompanying the linear CO band (Figure 1, bottom spectrum) is due primarily to the presence of a second CO domain with a distinctly different coverage than that of the primary peak at 2043  $\text{cm}^{-1}$ .<sup>13</sup> At low D<sub>2</sub>O exposures ( $< 2 \text{ L}$ ), small changes in both the peak



**Figure 2.** IRAS spectra of CO and D<sub>2</sub>O coadsorbed on Rh(100) at 90 K. After a D<sub>2</sub>O exposure of 1.0 L, several CO dosages were added stepwise as indicated.

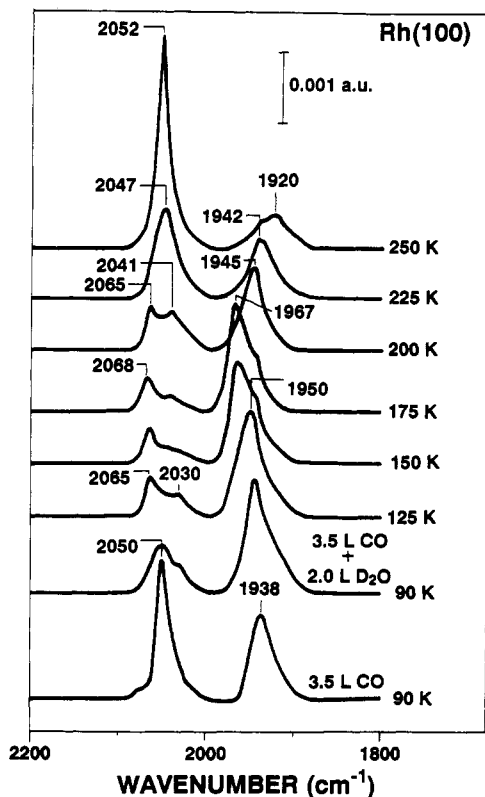
frequency and the relative absorption intensity of the linear and bridged CO bands are observed. However, a slight inhomogeneous band broadening is seen for the bridged CO band. In addition, a gradual attenuation of the low frequency shoulder of the linear CO band is observed, indicating that the CO adlayer is perturbed by the D<sub>2</sub>O molecules.

At higher D<sub>2</sub>O exposures ( $> 2 \text{ L}$ ), the inhomogeneous broadening of the bridged CO band is more apparent along with a marked increase in the peak frequency. Also a significant increase in absorption intensity clearly indicates an increase in the number of bridge-bound species. With this increase in bridge-bound intensity is a concomitant decrease in the absorption intensity of the linear band. A similar observation of the displacement from a linear configuration to a 3-fold bridge-bound configuration for CO coadsorbed with water on Rh(111) has been reported.<sup>4,7</sup> Taken together these results suggest that CO molecules undergo a translation from the linear configuration in the absence of D<sub>2</sub>O to the bridged-bound configuration in the presence of D<sub>2</sub>O. A slight increase in peak frequency is observed in Figure 1 for the linear CO band with increasing D<sub>2</sub>O exposures. This result, along with the increase in the peak width of both the linear and bridged CO bands, is consistent with the formation of CO domains with widely varying coverages.<sup>17</sup>

The effect of reversing the order of CO and D<sub>2</sub>O adsorption also was studied and the resulting spectra are displayed in Figure 2. Here a Rh(100) surface predosed with 1 L of D<sub>2</sub>O at 90 K was exposed to an increasing amount of CO. In contrast to CO adsorption on clean Rh(100) described earlier, the bridging configuration is seen as the preferred adsorption site at low to moderate CO exposures ( $< 4 \text{ L}$ ) on the D<sub>2</sub>O/Rh(100) surface. The

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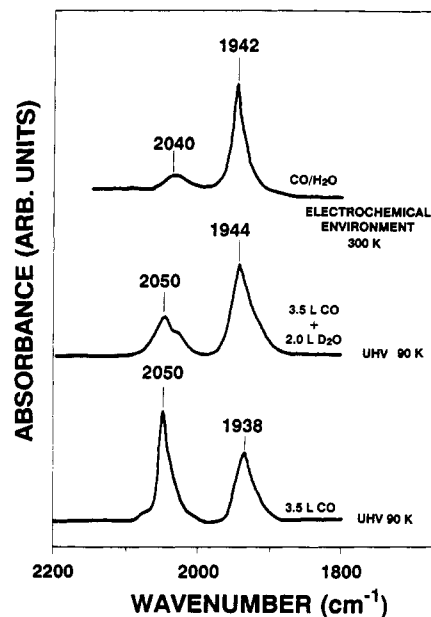


**Figure 3.** IRAS spectra of a Rh(100) surface exposed to 3.5 L of CO followed by 2 L of D<sub>2</sub>O at 90 K and subsequently warmed to temperatures indicated.

spectra displayed in Figure 2 resemble closely those shown in Figure 1 with the exception of the 5.5-L CO exposure in Figure 2 (top spectrum). For this exposure a sharp, intense linear CO band at 2084 cm<sup>-1</sup> and a broad bridged CO band at 1966 cm<sup>-1</sup> are observed. This spectrum closely resembles that observed for a saturated CO layer on clean Rh(100), suggesting the displacement of D<sub>2</sub>O by CO from the Rh(100) surface. The D<sub>2</sub>O molecules, rather than desorbing, may simply condense onto the adsorbed CO layer. These results are consistent with the lack of a change in the CO vibrational features upon exposure of a saturated CO layer on Rh(100) to varying amounts of D<sub>2</sub>O. CO island formation with varying CO densities, similar to that observed in Figure 1, is apparent from the multiplicity of the linear band and the broad bridged band of Figure 2.

Also of interest is the behavior of the CO and D<sub>2</sub>O layer(s) toward annealing following the adsorption step. Figure 3 shows IR spectra obtained by initially exposing the Rh(100) surface to 3.5 L of CO (corresponding to a CO coverage of about 0.6 ML) followed by a 2-L exposure of D<sub>2</sub>O at 90 K. The sample was then warmed to the temperature indicated. As shown in Figure 3, the presence of D<sub>2</sub>O displaces a portion of the linear CO species to the bridge-bound configuration. In addition, substantial inhomogeneous broadening of the bridged CO band and the development of a low frequency shoulder in the linear CO band are also observed, consistent with the results of Figures 1 and 2.

Two distinct regions of change are observed upon warming the sample. From 90 to 175 K, the absorption intensity of the bridged CO band continues to increase at the expense of the linear CO band. In addition, the peak frequency of the bridged CO band continues to shift to a higher wavenumber, consistent with an increase in the population of the bridge-bound species. It is noteworthy that the linear CO band initially broadens and gradually shifts toward a higher frequency. This shift is accompanied



**Figure 4.** IRAS spectra of a Rh(100) surface exposed to 3.5 L of CO followed by 2 L of D<sub>2</sub>O at 90 K in UHV (lower and middle spectra, respectively). The upper IR spectrum (extracted from ref 14) obtained for 0.75 ML of CO adsorbed on a Rh(100) electrode in 0.1 M HClO<sub>4</sub> at an electrode potential of +0.3 V vs SCE (saturated calomel electrode) at 300 K.

by the appearance of a low frequency component, consistent with the formation of a second CO domain with a different and distinct coverage from that corresponding to the feature at ~2065 cm<sup>-1</sup>. The low-frequency shoulder at ~2041 cm<sup>-1</sup> is attenuated gradually with increasing temperature, implying a relatively lower stability of this CO type compared to that with a frequency at ~2065 cm<sup>-1</sup>.

Above 175 K the bridged CO band shifts abruptly to a lower wavenumber with a gradual decrease in absorption intensity upon warming to 250 K. Concomitantly, the linear CO band grows and sharpens, indicating an increase in the number of linear-bound species. A comparison with the peak temperature for water desorption on Rh(100) from previous temperature programmed desorption studies<sup>18</sup> shows that this transition almost certainly corresponds to the desorption of the D<sub>2</sub>O layer. That is, the top spectrum in Figure 3 corresponds to that observed for CO adsorbed on clean Rh(100) at 250 K.<sup>13</sup>

As mentioned in the Introduction, the IR spectra obtained from the coadsorption of CO and water on Rh(100) in the present study display remarkable resemblance to the IR spectra obtained recently for CO adsorption on Rh(100) electrodes in aqueous media.<sup>12,14</sup> This is further illustrated in Figure 4 where the middle and the upper spectra represent IR spectra obtained for the coadsorption of 3.5 L of CO and 2.0 L of D<sub>2</sub>O on a clean Rh(100) surface at 90 K in UHV and that obtained for high coverage of CO ( $\theta_{\text{CO}} = 0.75$  ML) adsorbed on a Rh(100) electrode in an electrochemical environment, respectively. The latter spectrum is extracted from ref 14. For comparison purposes, the IR spectrum for the adsorption of 3.5 L of CO on Rh(100) at 90 K in UHV is also shown in Figure 4 (lower spectrum).

The above results, therefore, demonstrate the remarkable similarities between the IR spectra of coadsorbed water and CO on Rh(100) and IR spectra obtained recently for CO adsorption on Rh(100) electrodes.<sup>12,14</sup> Although

the origin and mechanism of the D<sub>2</sub>O induced partial displacement of CO from the linear to bridging configurations cannot be precisely defined at this point, the present data indicate that nucleation of CO and D<sub>2</sub>O domains takes place on Rh(100) at temperatures below D<sub>2</sub>O desorption. This nucleation process possibly involves either the formation of CO domains of varying size or domains with varying coverage as suggested by the multiplicity of the linear CO band and the broadness of the bridged CO band.

In summary, the present IRAS studies of the coadsorption of water and carbon monoxide on Rh(100) demonstrate a striking similarity between the IR spectra acquired at UHV conditions and the corresponding spectra obtained in an electrochemical environment. A direct comparison

between the present model experiments and in situ measurements in an electrochemical cell is complicated by the marked difference in sample temperature and by the difference in the solvent phases (solid versus liquid water). However, the present results are encouraging regarding the possible use of ultrahigh vacuum techniques to model the metal-solution interface.

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