Surface Dynamics of Coadsorbed CO and D₂O on Pt(100) in Ultrahigh Vacuum as Studied by Time-Resolved Infrared Reflection Absorption Spectroscopy

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Changes in the properties of CO adsorbed at saturation coverages on Pt(100) induced by subsequent coadsorption of fixed amounts of D₂O at 105 K in ultrahigh vacuum (UHV) were monitored by time-resolved infrared reflection absorption spectroscopy (tr-IRAS). The linear- and bridge-bonded CO stretching features were found to change in intensity and shift toward lower energies as a function of time at fixed CO and D₂O coverages. Also observed was the development of multiple features in both CO spectral regions depending on the amount of D₂O on the surface. These findings indicate that, under the conditions of these experiments, the interfacial dynamics are relatively slow, on the order of minutes, involving a gradual rearrangement of adsorbed CO and D₂O on the surface to yield surface solvated CO, as has been suggested in the literature (Kizhakevariam et al. *J. Chem. Phys.* **1994,** *100,* 6750). This factor should be considered when comparing, quantitatively, shifts induced by water coadsorption with CO on Pt single crystals in UHV with CO adsorption on the same surfaces in electrochemical environments.

Introduction

Considerable efforts have been devoted toward drawing reliable correlations between adsorption of species at metal−vacuum and metal−electrolyte interfaces. One of the most common strategies developed involves coadsorption of atoms and/or simple molecules with water on well-defined surfaces, primarily the low index faces of Pt.[1−11] Much of the focus has centered on the use of infrared reflection absorption spectroscopy (IRAS), a technique suitable for performing experiments in both types of environments, to monitor changes in the vibrational properties of carbon monoxide[3−7,9,10] or nitric oxide[11] induced by the presence of water on the surface. Indeed, the use of the stretching modes of CO as interfacial probes has revealed marked changes both in the intensity and position of such spectral features as a function of water coverage. Of special relevance to this work are experiments involving adsorption of water (or more precisely, D₂O) on single-crystal Pt surfaces covered by CO at saturation coverages. As reported by Weaver and co-workers for CO(sat)/Pt(111) surfaces in UHV, increasing the D₂O dosing brings about a general red shift in the peak position of CO adsorbed both on on-top and bridge sites to reach values more in line with those observed in electrochemical environments.[4,6,7] As will be shown in this work, however, such spectral changes at temperatures around 100 K occur over relatively long periods of time, on the order of minutes, indicating that care must be exercised when making comparisons of a quantitative character.

Experimental Section

All of the experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure, 4×10^{-11} Torr) described in a previous report.[12] As specified therein, the Pt(100) single crystal was mounted on a liquid-nitrogen-cooled cryostat. Prior to each coadsorption experiment, the Pt(100) crystal was annealed at 1100 K for several hours (including 5 min in an O₂ atmosphere), and XPS spectra were then recorded to check for impurities. Before each experiment, D₂O (Alfa Aesar, 99.95+% isotopic) was re-purified via two freeze/pump (5 min)/thaw cycles. Both CO and D₂O were delivered into the main chamber by back-filling. Partial pressures of CO and D₂O were monitored using a residual gas analyzer (RGA; Ametek Dycor 1000) during exposure.

The single crystal was initially cooled to 105 K, flash-annealed to 650 K to desorb adventitious adsorbates (mostly water and CO), and then cooled back to 105 K. At this stage, CO was admitted into the chamber until saturation coverage was attained. Following this step, IRAS spectra were collected (1024 scans/1024 background). D₂O was then admitted into the chamber, and the spectral collection continued. Since the response of the RGA to D₂O was not calibrated, the absolute exposures herein quoted may be in error by some constant factor, but the relative effects should be correct. Not surprisingly, the integrated area of the IRAS feature centered at 2530 cm⁻¹ was proportional to the exposure. Support for this view was provided by the plot shown in Figure 1 (see top abscissa and right ordinate), where the data were extracted from the spectral curves shown therein obtained for D₂O exposures of 0.009, 0.01, 0.05, and 0.3 L (curves a through d, respectively).

Time-resolved (tr) IRAS spectra were recorded during D₂O dosing (32 or 128 scans, denoted by an asterisk in the captions) and after the D₂O valve had been closed (1024 scans). Shorter

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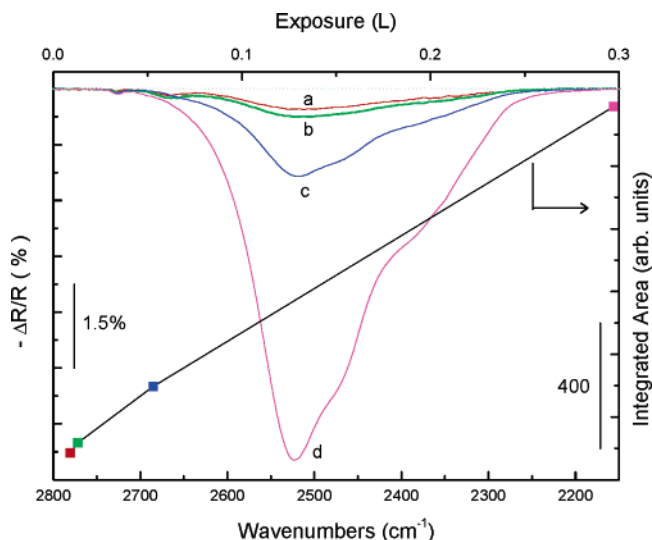[†] Department of Chemistry.
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Figure 1. Bottom, left ordinate: Steady-state IRAS spectra in the OD stretching region for CO(sat)/Pt(100) exposed to D_2O at 105 K in UHV. Curves a through d were collected for D_2O exposures (uncorrected, see text) of 0.009 (red), 0.01 (green), 0.05 (blue), and 0.3 L (magenta), respectively. Top, right ordinate gives values of the integrated area based on the curves under the spectral feature in question (see squares), where the line simply connects all the experimental points at various following the color code specified.
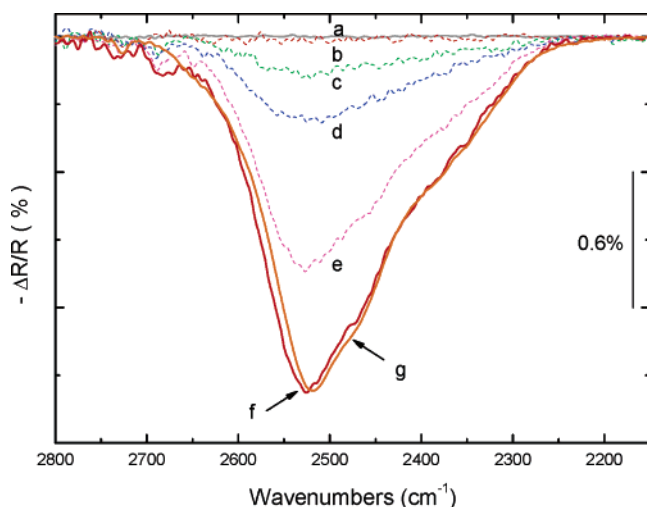

Figure 2. Series of tr-IRAS spectra in the OD stretching region for CO(sat)/Pt(100) (spectrum a), during (dashed spectra, b−e, corresponding to 29 s, 1 min 24 s, 1 min 49 s, and 2 min 29 s after the D_2O valve was opened, respectively), and after 0.05 L D_2O exposure (solid spectra, f & g, corresponding to 3 min 14 s and 44 min 39 s after the D_2O valve was opened, respectively).

(to increase time resolution) and longer (to improve signal quality) scans were required to monitor spectral changes during D_2O exposure along with the dynamics associated with the D_2O/ CO/Pt(100) surface, respectively. Water overtones and CO_2 peaks were subtracted from the data using the appropriate module in GRAMS/32 AI 6.00 (Galactic Industries Corp.). Baselines were corrected manually in Origin 7.0.

Results and Discussion

Shown in Figure 2 are selected spectra from a series of tr-IRAS in the OD stretching region, i.e., 2250−2800 cm^{-1}, during (128 scans, dashed lines, curves b through e) and after 0.05 L D_2O exposure (128 and 1024 scans, solid lines, curves f and g), where the features observed are consistent with the buildup

of D_2O on a CO saturated (CO exposure: 5.1 L) Pt(100) surface. Curve a in this figure was recorded just prior to opening the D_2O leak valve. No significant changes in the overall shape, intensity, or position of the prominent band centered at ca. 2530 cm^{-1} were found in the spectrum recorded immediately after closing the D_2O dosing valve at ca. 3 min and that collected ca. 40 min later (compare curves f and g, Figure 2). This observation affords unambiguous evidence that the coverage of D_2O remains constant while monitoring the interfacial dynamics. This is an important consideration, as all of the changes observed for the spectra obtained (see below) can be solely attributed to interfacial dynamics involving the two coadsorbates on the Pt(100) surface.

Panels A through D in Figure 3 display series of tr-IRAS spectra for CO(sat)/Pt(100) before (thick solid line), during (dotted lines), and after (thin solid lines) dosing of D_2O to four different total exposures, i.e., 0.009 L, panels A; 0.01 L, B; 0.05 L, C; 0.3 L, D, at 105 K, where each time represents that at which the spectral acquisition was initiated.

Cursory inspection of these curves shows rather drastic spectral modifications after the exposure to D_2O is completed (see thin solid lines), which underscores the dynamic character of the interface. Furthermore, ca. 30 min are required for the interface to reach equilibrium at constant temperature regardless of the D_2O exposure (or coverage), although very slight changes both in intensity and position were observed after this time, the collection was interrupted ca. 10 min later. Generally, most of the CO peaks show a red shift, overall broadening, and intensity changes, as time elapses. In particular, the linear-bonded CO feature found at ca. 2100 cm^{-1} under strict dry conditions evolves into at least two peaks for all D_2O coverages explored. A similar phenomenon was observed by Weaver et al. for CO-(sat)/Pt(111) (without consideration of possible dynamic effects) upon increasing D_2O exposure, except that in their case only a single peak was found for the highest D_2O coverage (see, for example, Figure 3A in ref 7).[4,6,7] Furthermore, the bridge-peak, centered at 1942 cm^{-1} for the dry surface undergoes an initial loss in intensity, which is later regained, surpassing that of the original peak, and splits into two features for the two highest D_2O coverages examined (panels C and D, Figure 3).

More detailed inspection of the results shown in this figure revealed a number of other interesting aspects. For the two smallest D_2O exposures (panels A and B, Figure 3), the position of the peak centered at 2091 cm^{-1} that emerged after about 2.5 and 7 min, respectively, remains virtually unchanged over the length of time examined. In contrast, the second component undergoes significant broadening and a shift in position from (apparently) 2100 down to 2050 cm^{-1}. After steady state is reached, the spectrum shows two peaks in the linear region (2091 and 2056 cm^{-1}) and one peak in the bridge region (ca. 1892 cm^{-1}).

A different dynamic behavior was observed in very similar independent experiments for higher D_2O exposures (panels C and D) on CO(sat)/Pt(100). More specifically, the clearly identifiable peak at 2091 cm^{-1} in panel A, Figure 3 was not observed in this case throughout the entire series both for 0.05 and 0.3 L D_2O exposures. As will be addressed in a forthcoming communication, the splitting of the CO stretching band observed for the two lowest coverages is consistent with differences in the hydration rates of CO adsorbed onto Pt(100) (5 × 20) and on unreconstructed Pt(100) (1 × 1) sites on the surface. After ca. 14 min, the linearly adsorbed CO feature for these higher D_2O exposures appears to contain at least two overlapping peaks (centered near 2040 and 2020 cm^{-1}) that weaken and red shift
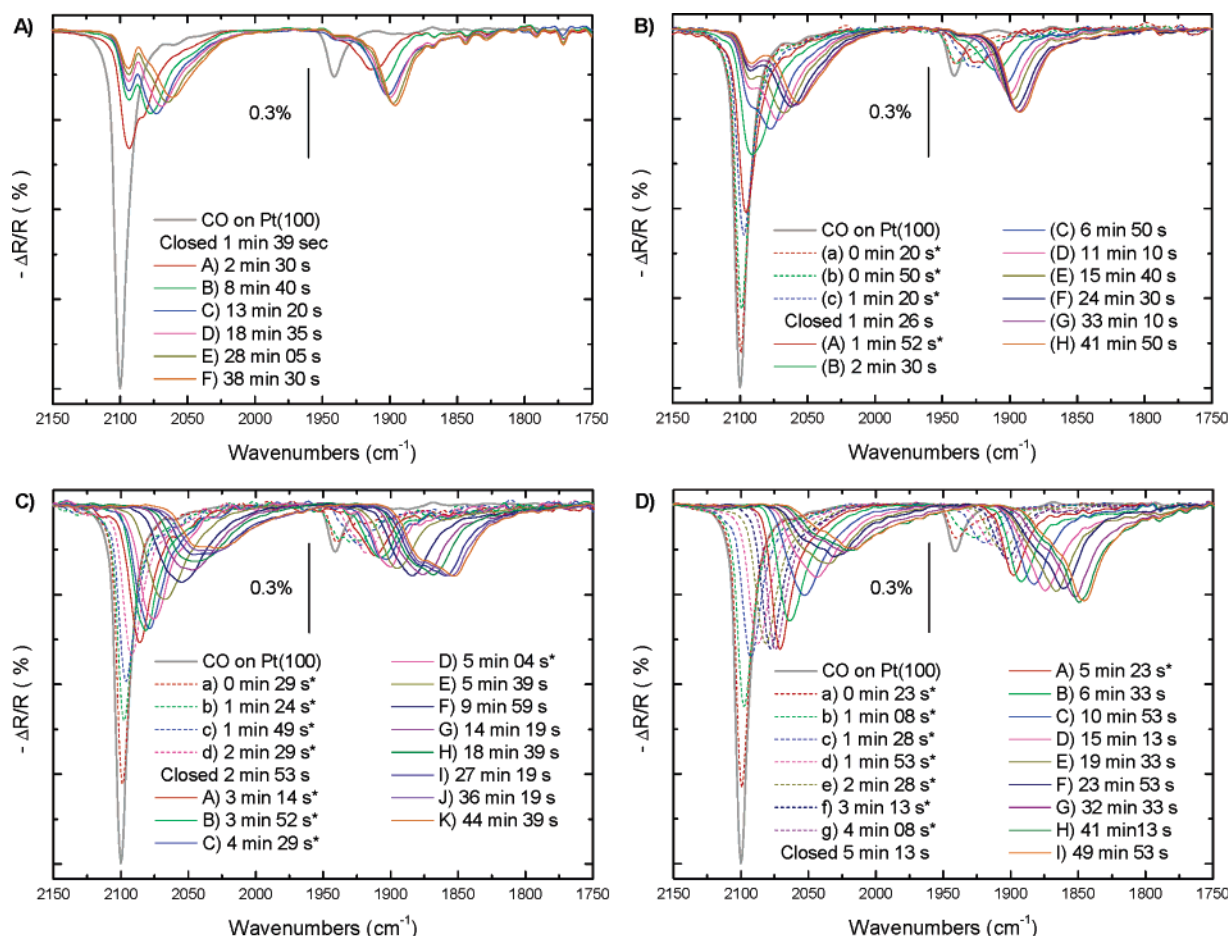
Figure 3. Time-resolved IRAS spectra for CO(sat)/Pt(100) at 105 K before (thick solid line), during (dashed lines), and after subsequent exposure to D_2O (thin solid lines). Acquisition of each spectrum was initiated at the times specified in the inset using the opening of the D_2O valve as a reference, i.e., $t = 0$. Panel A, 0.009 L; panel B, 0.01 L; panel C, 0.05 L; panel D, 0.3 L.

with time. In contrast to the spectrum observed for small D_2O exposures (panels A and B) which exhibits a fairly symmetric feature in the CO bridge region, the corresponding feature develops into at least two clear peaks centered in the range $1840-1880$ cm^{-1} (panels C and D) as the D_2O exposure is increased.

Most importantly, experiments in which D_2O/CO(sat)/Pt(100) surfaces that had achieved steady state were heated to ca. 225 K led, as expected, to the complete desorption of D_2O, as judged by the disappearance of features in the OD stretching region (inset, Figure 4). Inspection of the resulting spectra, recorded at 105 K (Figure 4), revealed for the higher D_2O exposures (0.05 and 0.3 L, curves c and d, respectively) features with very similar positions and intensities to those observed prior to D_2O adsorption. The differences in the spectrum for the smallest D_2O coverage (curve b) may well reflect a change in the occupancy of the two sites rather than a change in the absolute coverage. It must be noted, however, that heating the D_2O/CO(sat)/Pt-(100) layer to this temperature range ($217-235$ K) could lead to the disappearance of the CO bridge peak and an increase in the intensity of the linearly adsorbed CO peak.[13] On this basis, it can be ascertained that the dynamics for D_2O/CO(sat.)/Pt-(100) presented here occur at fixed CO and D_2O coverages.

Spectra collected for CO(sat)/Pt(100) immediately after D_2O valve closure (panel A, Figure 5) to those collected ca. 40 min later (steady state, panel B, Figure 5) for three different D_2O exposures, namely, 0.01, 0.05, and 0.3 L (curves b through d, in these panels, respectively), were found to be vastly different. Regardless of the time of acquisition, the linear and bridge CO
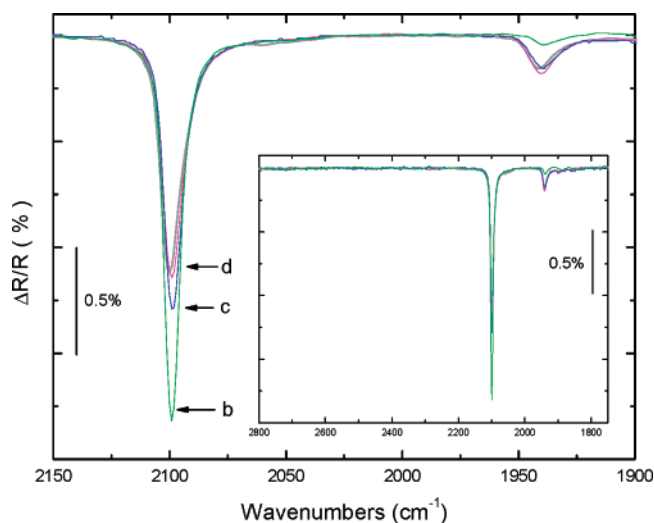

Figure 4. IRAS spectra for CO(sat)/Pt(100) surfaces recorded at 105 K after desorption of D_2O at 225 K at the D_2O exposures indicated (see text for details; b, green, 0.01 L; c, blue, 0.05 L; d, magenta, 0.3 L). A reference spectrum for CO(sat)/Pt(100) at 105 K (gray) is presented for comparison. Inset: same as in the main figure but over a wider energy range.

peaks red shifted while undergoing intensity redistribution as the exposure was increased. A listing of the positions and intensities of the features observed is given in the right halves of Tables A and B in the Supporting Information. Also shown in the left halves of those tables are data reported by Weaver
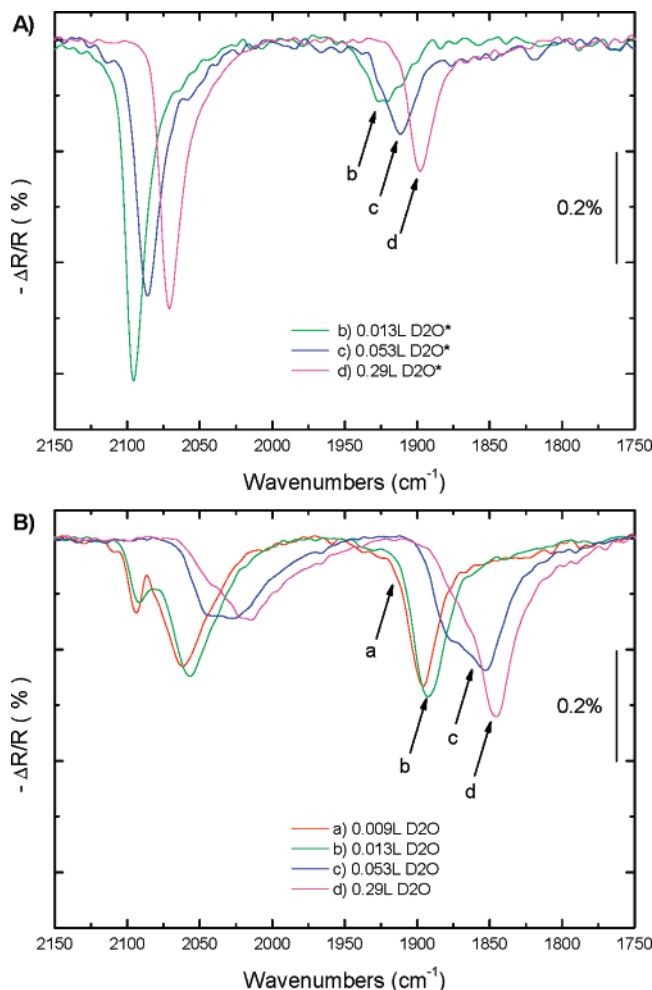
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Figure 5. Comparison of the IRAS spectra of CO(sat)/Pt(100) collected immediately after closing the D_2O dosing valve (panel A) and after allowing the interface to achieve steady state (panel B) for the final exposures (a, red, 0.009 L; b, green, 0.01 L; c, blue, 0.05 L; d, magenta, 0.3 L) indicated.

and co-workers for similar experiments for CO saturation coverages on Pt(111) following exposure to various amounts of D_2O at 110 K.[7] Unlike the data collected in this work, the times at which the spectra were recorded following D_2O exposure were not specified in the cited work. Also complicating direct comparisons is the slightly different temperature used in our studies (105 K) compared to those in ref 7 (110 K), e.g., one would expect the rates of the interfacial process to increase with temperature. In fact, in a subsequent communication for experiments performed at 90 K for D_2O coadsorption on CO-(0.65 ML, sat)/Pt(111),[6] Weaver and co-workers report values which were not as red shifted as those at the higher temperature. Nevertheless, inspection of the intensities and positions values of the peaks listed in the table reveals that for Pt(111) and Pt(100) both the linear and bridge features undergo red shifts, with the linear peak decreasing in intensity as the exposure to D_2O is increased.

It is also of interest to compare our steady-state values for the positions of the two CO features with those found in electrochemical environments. For the largest D_2O exposure examined in this work, i.e., 0.3 L, the linear and bridge peaks are centered at 2017 and 1845 cm^{-1}, respectively, whereas the values observed in situ for saturation coverage CO on Pt(100) in 0.1 M $HClO_4$ reported by Weaver[14] are at 2048 and 1872 cm^{-1} at 0.0 V vs NHE, respectively, i.e., blue shifted with respect to ours by ca. 30 cm^{-1} (at 0.35 V vs NHE, the hardly

noticeable bridge peak was very broad, and the linear peak was Stark shifted to 2062 cm^{-1}). This would imply that the UHV-electrochemistry correction, i.e., work function and surface potential, required for Pt(100) would not only be smaller but also opposite to that reported by Weaver for analogous experiments involving Pt(111). For that low index face of Pt, the corresponding values were 2089 and 1850 cm^{-1} for UHV,[6] and 2063 and 1843 cm^{-1} for 0.35 V vs NHE and 2059 and 1830 cm^{-1} for 0.0 V vs NHE in situ in the same electrolyte.[15] Unfortunately, the lack of temporal information in the literature and the fact the results reported therein are for Pt(111) and not for Pt(100) complicate further attempts to establish closer links between our set of data and theirs. It seems nevertheless quite possible that dynamics effects of the type illustrated in this work could also occur for Pt(111). It should be noted at the outset that Kitamura et al.[16] have reported changes in the in situ IRAS spectrum of CO(sat)/Pt(100) in 0.5 M H_2SO_4 following a potential step from 0.0 to 0.03 V vs Ag/AgCl, which occurred over periods of time on the order of several tens of micro-seconds. Such observations appear unrelated to the effects described herein and are, in all likelihood, related to the IR drop associated with the thin layer cell arrangement involved in in situ external reflection IRAS.

In summary, the vibrational features of CO adsorbed on Pt(100) surfaces at saturation coverages exposed subsequently to various amounts of water at 105 K in UHV can be conveniently monitored by tr-IRAS. As evidenced from the results, these features undergo changes in both positions and shapes to reach steady state after ca. 30 min, whereas the actual coverages of both CO and water remain constant. These findings underscore the dynamic character of CO surface hydration, a behavior that must be considered when attempting to compare data collected in UHV and electrochemical environments for the same system.

Supporting Information Available: Tables listing positions and relative intensities of the linear stretching feature for CO adsorbed on Pt(111) and Pt(100) for various subsequent D_2O exposures. This material is available free of charge via the Internet at http://pubs.acs.org.

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