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## Temperature-Resolved Surface Infrared Spectroscopy of CO on Rh(111) and (2 × 1)-O/Rh(111)

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## Temperature-resolved surface infrared spectroscopy of CO on Rh(111) and (2 × 1)-O/Rh(111)

Special Collection: [Celebrating the Early Career Professionals Contributing to the Advancement of Thin Films, Surfaces, Interfaces, and Plasmas](#)

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**Note:** This paper is a part of the Special Topic Collection: Celebrating the Early Career Professionals Contributing to the Advancement of Thin Films, Surfaces, Interfaces, and Plasmas.

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## ABSTRACT

Heterogeneously catalyzed reactions over transition metal surfaces are pillars of chemical industry and account for a significant fraction of the global energy demand. CO oxidation provides insight into the relative reactivity of various oxygenaceous surface phases, and it is necessary to first understand where it binds to the surface and the nature of the local environment to develop robust mechanistic pictures of the reaction. Surface IR spectroscopy is a quantitative technique that also provides information about the binding sites and chemical environments of the adsorbed CO molecules. Here, we report results from a study of CO sticking to clean Rh(111) and (2 × 1)-O/Rh(111) that shows that the intensity of the IR absorption was not linear with coverage and is an important consideration for further studies of the catalytic surface.

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## I. INTRODUCTION

The oxidation of small molecules over metal surfaces is of widespread importance in heterogeneous catalysis.<sup>1–3</sup> In particular, the oxidation of carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>) has attracted much interest, because it is relevant to industrial and consumer processes (e.g., catalytic converter in automobiles) and also because it allows for the study of the *surface* species because of the lack of molecular complexity.<sup>4,5</sup> CO oxidation has been studied using a variety of techniques including molecular beam-surface reactive scattering,<sup>6–8</sup> temperature programmed desorption/reaction (TPD/TPR) to monitor the production of CO<sub>2</sub>,<sup>9–13</sup> x-ray photoelectron spectroscopy (XPS) to speciate the surface species through the reaction via elemental analysis, and reflection-absorption infrared spectroscopy (RAIRS), which provides molecular information about the surface adsorbates.<sup>14–17</sup> Together, a picture has emerged about the surface-catalyzed oxidation of CO on a variety of different metal surfaces, but as key details are discovered, there is an emerging consensus that this seemingly “simple” reaction is far more complicated than was thought even a few years ago.<sup>7,18,19</sup> In particular, recent discoveries showing that surface oxide reactivity is strongly correlated to

geometry<sup>20</sup> and that terrace and steps proffer very different catalytic activities,<sup>7,21</sup> has spurred us to study the different oxygenaceous phases on Rh(111), where we have developed robust approaches for preparing three distinct phases.<sup>22–24</sup> Here, we present results showing that even CO adsorption to clean Rh(111) has complexities that must be considered in order to properly use RAIRS to determine the species present and their coverages.

The IR absorption spectrum of adsorbed CO is sensitive to the binding site and, thus, has been used to qualitatively probe the state of the surface through the sensitivity of the main CO stretch frequency to metals.<sup>25,26</sup> Although CO spectroscopy is well-developed, there have been only a handful of IR studies of CO on Rh(111)<sup>16,27,28</sup> and even fewer investigating CO on oxygenated Rh(111) surfaces.<sup>16,29</sup> We have determined the chemical significance of various oxygen phases on different Rh surfaces,<sup>9,10,22–24</sup> and here, we have studied CO adsorption on Rh(111) and (2 × 1)-O/Rh(111). Studying CO oxidation on different Rh surfaces provides atomic level information regarding oxidation reactions, progressing the understanding of various surface phases relevant to many Rh catalyzed processes.

O<sub>2</sub> readily dissociates on Rh(111) to form adsorbed oxygen (O<sub>ad</sub>), and adsorption is kinetically limited to an oxygen coverage

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( $\theta_{\text{O}}$ ) of 0.5 monolayers (ML, 1 ML =  $1.6 \times 10^{15}$  atoms  $\text{cm}^{-2}$ ).<sup>9,30,31</sup> CO does not dissociate on Rh(111) and chemisorbs as an intact molecule. CO preferentially adsorbs on atop sites and arranges in a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-CO}$  adlayer with a CO coverage ( $\theta_{\text{CO}}$ ) of 0.33 ML CO. Upon continued exposure, CO adsorbs to bridge sites as well and reaches  $\theta_{\text{CO}} = 0.75$  ML in a  $(2 \times 2)\text{-3CO}$  structure.<sup>4,16,32</sup> The CO stretch for CO in atop sites has an absorption peak calculated and observed between 2015 and 2100  $\text{cm}^{-1}$ , depending on  $\theta_{\text{CO}}$ .<sup>16,27</sup> On oxygenated surfaces, CO remains bound atop, while O occupies the hollow sites,<sup>16</sup> and the CO stretch was observed to increase by 25  $\text{cm}^{-1}$  to 2085  $\text{cm}^{-1}$ .<sup>16</sup> However, it is important to note that the previous IR measurements were typically made at low-temperatures ( $T_{\text{exp}} < 200$  K), and it does not seem that the behavior of the IR spectra with respect to temperature has been investigated.

In this paper, RAIRS and TPD were employed simultaneously to determine both the CO coverage on the surface and the binding sites and chemical environment for CO on Rh(111). The combination of TPD and RAIRS provides the chemical species and their local environment over a range of surface temperatures and adsorbate coverages. With the behavior of CO on clean Rh(111) established, the adsorption of CO to an oxygenated Rh(111) surface, the  $(2 \times 1)\text{-O}$  structure, was studied over a range of temperatures during a TPD experiment. In both cases, we observed that the IR peak shifts in accordance with previous measurements, but the intensity varies and is most intense, on a per-molecule basis, at low coverages. This suggests that the intensity of the absorption for the CO stretch does not linearly depend on  $\theta_{\text{CO}}$ , meaning that the correlation of  $\theta_{\text{CO}}$  to the RAIRS signal requires more than a simple application of the Beers law to the IR spectra.

## II. EXPERIMENT

All experiments were performed in an ultra-high vacuum (UHV) system described previously.<sup>24</sup> The system is comprised of two connected chambers, a preparation chamber (base pressure of  $1 \times 10^{-10}$  Torr) and a scanning tunneling microscope (STM) chamber (base pressure of  $< 2 \times 10^{-11}$  Torr). The preparation chamber was equipped with multiple surface science techniques including a Specs ErLEED 150 with 3000D controller (LEED), a PHI 10-155 Meitner-Auger Electron Spectrometer (MAES), and a Hiden HAL 3F 301 RC quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD) analysis. RAIRS measurements were made with a Bruker FT-IR Invenio R spectrometer and an external liquid nitrogen cooled MCT (mercury-cadmium-telluride) detector which increased sensitivity to around 800  $\text{cm}^{-1}$ . The IR light was p-polarized and traveled through enclosures purged with dry,  $\text{CO}_2$  free air (Parker, Spectra30, FT-IR Purge Gas Generator). The RAIRS spectra are an average of 36 scans were taken with a resolution of 4  $\text{cm}^{-1}$  and new background spectra were taken at the start of each experiment. In some of the spectra on Rh(111), a small spurious background absorption peak, likely from adsorbed CO from the chamber background, was present when the IR background was obtained. This resulted in a negative peak in the absorbance spectra around 2025  $\text{cm}^{-1}$  that appeared after CO exposure began and remained even after CO was desorbed. The small intensity and far-red shift indicated that this was only a small amount of CO. When present, this was removed from the spectra

by taking CO stretch portion of the spectrum at high temperatures, where the surface was clear of CO, inverting it, and adding it to all the spectra collected in that trial. This peak was never observed on the oxidized surface.

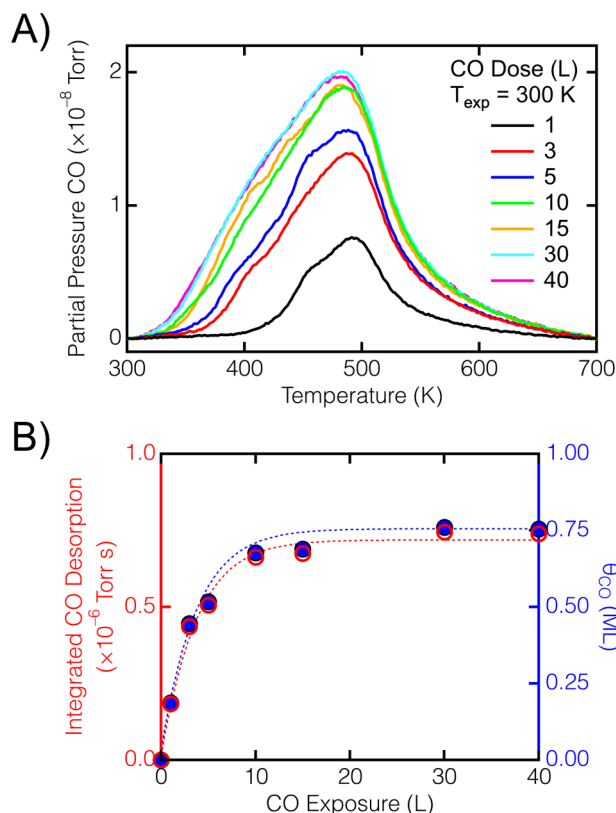
The Rh(111) crystal (Surface Preparation Labs, Zaandam, The Netherlands) sample was a 10 mm diameter, 3 mm thick, disk and was mounted on an exchangeable tantalum (Ta) sample plate with a type-K thermocouple welded to the side of the crystal. The crystal could be cooled with liquid nitrogen loop to 100 K and heated using electron beam heating to 1400 K. The surface was cleaned with repeated cycles of  $\text{Ar}^+$  sputtering and annealing at 1300 K until the surface cleanliness was verified with a clean  $(1 \times 1)$  LEED pattern and  $\text{O}_2$  TPD free of  $\text{CO}_2$ .

The Rh(111) sample was dosed with CO with a pressure of  $1 \times 10^{-6}$  Torr at an exposure temperature ( $T_{\text{exp}}$ ) of 300 K. For the oxidized surface, the Rh(111) was first dosed with  $\text{O}_2$  by backfilling to  $1 \times 10^{-6}$  Torr for 60 s at  $T_{\text{exp}} = 300$  K to yield a saturated surface with the adsorbed O ( $\text{O}_{\text{ad}}$ ) in a  $(2 \times 1)\text{-O}$  adlayer and  $\theta_{\text{O}} = 0.5$  ML. (ML, 1 ML =  $1.6 \times 10^{15}$  atoms  $\text{cm}^{-2}$ ).<sup>9</sup> After oxygen preparation, the surface was then separately dosed with CO at  $1 \times 10^{-6}$  Torr at  $T_{\text{exp}} = 300$  K. Spectra were obtained both during CO exposure to measure uptake and during the TPD experiment to complement the QMS desorption measurements. Spectra between 850 and 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  were collected every 10 s. For the TPD experiments, QMS and RAIRS spectra were collected synchronously. The TPD was run from 100 to 600 K with a ramp rate of 0.4  $\text{K s}^{-1}$ . CO oxidation on Rh(111) was complete by 600 K. The Rh(111) crystal was then annealed to 1250 K in between experiments to restore surface cleanliness and order, as verified with LEED.

## III. RESULTS AND DISCUSSION

In order to use the IR spectra to quantify  $\theta_{\text{CO}}$ , it was first necessary to establish  $\theta_{\text{CO}}$  as a function of CO exposure at  $T_{\text{exp}} = 300$  K. Figure 1(a) shows the TPD spectra taken after several CO exposures, clearly demonstrating the surface saturation after  $\approx 15$  Langmuir (L) CO exposure. The TPD spectra were background subtracted [as shown in Fig. 1(a)] and then integrated to obtain  $\theta_{\text{CO}}$  using the known saturation coverage of CO on Rh(111) of  $\theta_{\text{CO}} = 0.75$  ML CO,<sup>32</sup> the CO uptake is shown in Fig. 1(b) with the integrated TPD desorption in red on the left and the calculated  $\theta_{\text{CO}}$  in blue on the left plotted with respect to the CO exposure in L.

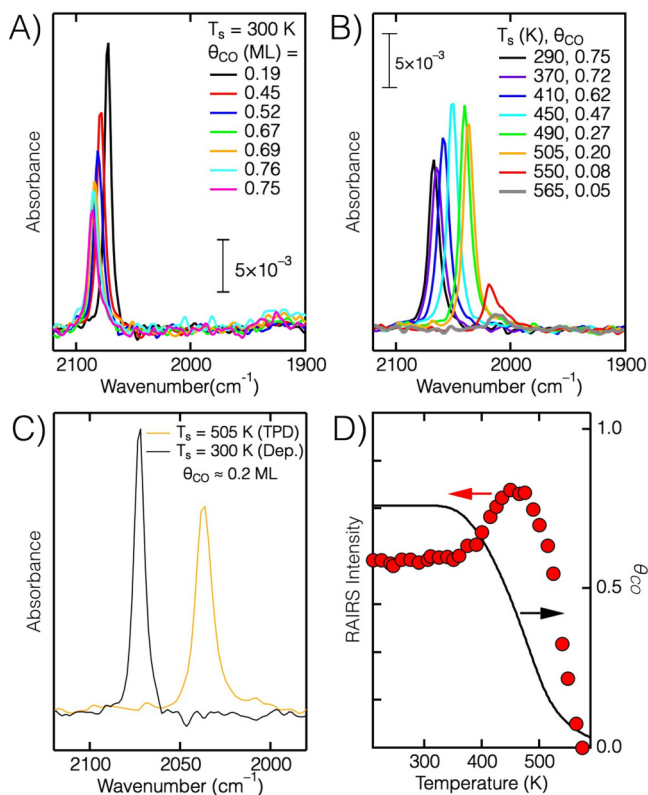
With the uptake quantified, the correlation between the RAIRS and  $\theta_{\text{CO}}$  could be determined. Figure 2(a) shows RAIRS obtained after each of the CO exposures at  $T_{\text{exp}} = 300$  K, in Fig. 1(a). Curiously, the highest peak was observed at 2072.2  $\text{cm}^{-1}$  after a 1 L CO exposure,  $\theta_{\text{CO}} = 0.19$  ML, and continued exposure saw the peak steadily blueshift to 2084.2  $\text{cm}^{-1}$ , broaden slightly, and diminish in amplitude. As coverage was determined from the TPD spectra, it is not the case that the reduced RAIRS intensity was from CO desorbing at 300 K for the longer CO exposures. Instead, it is more likely that the increased coverage decreased the per-molecule IR absorption cross section as the electron density available from the metal decreased, and the C-O bond strength increased, as suggested by the blue shift in the CO stretching absorption feature. The net result is that this seemingly anomalous behavior is indicative of a shift of electron density from the



**FIG. 1.** (a) TPD spectra of  $m/z = 28$  ( $\text{CO}^+$ ) after exposing the Rh(111) surface to varying amounts of CO at  $T_{\text{exp}} = 300$  K. Initial coverages are  $\theta_{\text{CO}} = 0.19$  ML (1 L), 0.45 ML (3 L), 0.52 ML (5 L), 0.67 ML (10 L), 0.69 ML (15 L), 0.76 ML (30 L), and 0.75 ML (40 L). The heating rate was  $4 \text{ K s}^{-1}$  for TPD. (b) Integrated TPD area showing the uptake of CO at varying exposures and correlation between integrated desorption (red open circles, left) and  $\theta_{\text{CO}}$  (blue filled circles, right).

CO–metal bond to the CO molecule. Although this could be rationalized by “back-bonding” where the metal contributed electron density to the  $2\pi^*$  antibonding orbital in CO, the situation is probably more complex, but the result the same.<sup>33–35</sup> Above  $\theta_{\text{CO}} \approx 0.6$  ML, this effect diminished and the peak intensity remained constant, while still modestly blue-shifting.

The convoluted relationship between absorption frequency and peak intensity was also present when surface temperature ( $T_s$ ) increased concomitantly with a decrease in  $\theta_{\text{CO}}$ , as shown in the RAIRS collected during the TPD experiment in Fig. 2(b) after a 30 L CO dose at  $T_{\text{exp}} = 300$  K and  $\theta_{\text{CO,initial}} = 0.75$  ML. With increasing  $T_s$ , and thus decreasing  $\theta_{\text{CO}}$ , the C–O stretch frequency red-shifted, suggesting strong CO–metal bond and weakening C–O bond, while the intensity does not appear to decrease linearly with  $\theta_{\text{CO}}$ . The observation of a pronounced increase in intensity for the absorbance of the C–O stretch was robust, as it was observed with isothermal uptake at  $T_{\text{exp}} = 300$  K and during the TPD experiment where  $T_s \approx 500$  K; the spectra for similar  $\theta_{\text{CO}}$  for the two different paths are shown in Fig. 2(c). Although we are unable to state

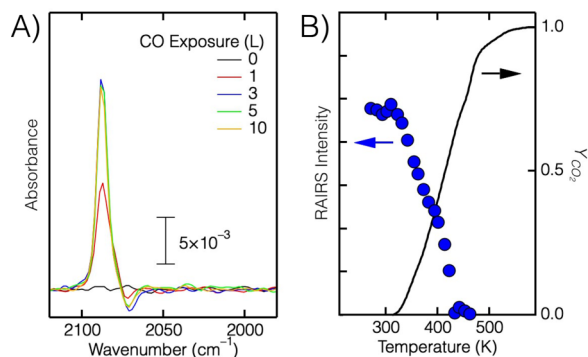


**FIG. 2.** CO on Rh(111) (a) IR spectra of varying doses taken after the CO exposures shown in Fig. 1 at  $T_s = 300$  K. (b) Sequence of the IR scans taken through TPD experiment with  $\theta_{\text{CO, initial}} = 0.75$  ML. These show the decreased intensity and red shift in the CO absorption peak as temperature increased and  $\theta_{\text{CO}}$  decreased. (c) The difference in IR spectra for similar coverages ( $\theta_{\text{CO}} \approx 0.2$  ML) collected after a 1 L CO dose at 300 K (black) and during the TPD experiment when  $\theta_{\text{CO}}$  has decreased from 0.76 ML (yellow), collected at 505 K. All RAIRS plots have the same vertical range. (d) RAIRS intensity (left)  $\theta_{\text{CO, initial}} = 0.75$  ML during TPD experiment (red circles) and  $\theta_{\text{CO}}$  from TPD data (right, solid line).

definitely why the absorption frequencies differ, it is reasonable to assume that the shift is caused by the difference in  $T_s$  for the two spectra. This effect is also evident in Fig. 2(d) for a 30 L CO dose at  $T_{\text{exp}} = 300$  K, and  $\theta_{\text{CO, initial}} = 0.75$  ML, where the black trace (right axis) is the integrated intensity of the C–O stretch peak (between 2072 and 2086  $\text{cm}^{-1}$ ) in the RAIRS data. As shown, despite a roughly 50% decrease in  $\theta_{\text{CO}}$ , the integrated intensity of the CO stretch peak actually increased. With additional desorption the RAIRS signal did diminish, but at the point where  $\theta_{\text{CO}}$  was down to 25% or so of the original value. It is important to note that  $\theta_{\text{CO}}$  from the TPD measurement was an upper limit, and most likely exceeded the actual  $\theta_{\text{CO}}$  at any moment because the QMS was measuring the partial pressure and there was some lag due to the pumping speed for CO in the UHV chamber.

On the  $(2 \times 1)$ -O adlayer at 300 K or below, CO also adsorbed intact and inserted into the adlayer forming a  $(2 \times 2)$ -2O + CO

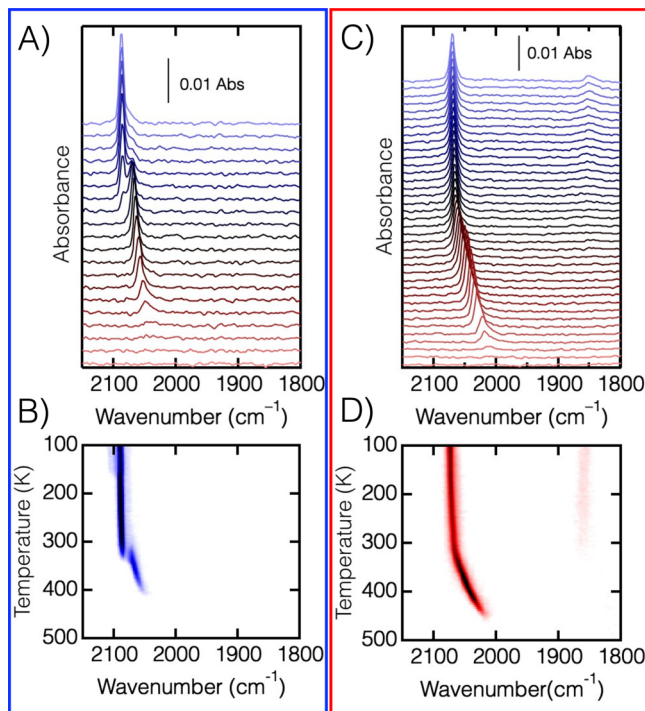




**FIG. 3.** CO on  $(2 \times 1)$ -O/Rh(111). (a) RAIRS taken during CO exposure for  $T_{exp} = 300$  K showing single C–O stretch absorption peak that rapidly saturated. (b) IRRAS intensity (left) for CO on  $(2 \times 1)$ -O during TPD experiment (blue circles) and  $\text{YCO}_2$  from TPD data (right), the integral of the  $\text{CO}_2$  desorption peak.

adlayer.<sup>27,29</sup> Although at higher temperatures CO would be oxidized, removing  $\text{O}_{ad}$ , for  $T_s < 300$  K, the reaction was not significant.<sup>9</sup> RAIRS taken after exposure of  $(2 \times 1)$ -O to CO is shown in Fig. 3(a), and only a single absorption peak, corresponding to a C–O stretching mode, was observed at  $2088 \text{ cm}^{-1}$ . Unlike CO on Rh(111), there was no shift in the peak location and the intensity monotonically increased with exposure, and rapidly saturated. This straightforward relationship between CO exposure and RAIRS intensity suggests that the factors that gave CO on Rh(111) the complex behaviors were not present on the oxygenated surface, likely because, although still metallic,  $\text{O}_{ad}$  reduced the availability of electron density to the CO, and contributions to CO–Rh orbitals aside from the surface–adsorbate bond did not occur.

However, IR spectra collected during the TPD experiment showed a transition not present for CO/Rh(111). As shown in Figs. 4(a) and 4(b) around 300 K (the CO exposure temperature) the absorption peak shifted from  $2088$  to  $2068 \text{ cm}^{-1}$ , the same frequency observed for CO on clean Rh(111). In addition, there was no absorption corresponding to CO binding at bridge sites, which was evident on Rh(111) in Figs. 4(c) and 4(d) around  $1850 \text{ cm}^{-1}$ . This shift occurred at the onset of CO oxidation to  $\text{CO}_2$ , as indicated by the appearance of  $\text{CO}_2$  in the TPD, shown in Fig. 3(b) (right axis, black trace). After a narrow window of coexistence, only the  $2068 \text{ cm}^{-1}$  peak was observed, and then as  $T_s$  increased, the RAIRS intensity steadily decreased, as shown in Fig. 3(b), left axis. The fact that the shift in IR absorption and desorption of  $\text{CO}_2$  occurred simultaneously indicated that the reactive CO fingerprint was the  $2068 \text{ cm}^{-1}$  mode. However, it is unclear at this point if this was due to a shift in binding site or from another factor. Figure 4 compares how the IR spectra of oxygenated to clean Rh(111) evolved with  $T_s$  and  $\theta_{CO}$ . As previously discussed, on Rh(111), CO desorption caused an increase in the RAIRS intensity although  $\theta_{CO}$  decreased, shown in Figs. 4(c) and 4(d). On the oxygenated surface, shown in Figs. 4(a) and 4(b), the RAIRS peak was unchanged until the transition to  $2068 \text{ cm}^{-1}$  near 300 K, and thereafter followed the same path as CO on Rh(111) without  $\text{O}_{ad}$ . However, instead of merely desorbing, the CO was being oxidized to  $\text{CO}_2$ . This suggests



**FIG. 4.** (a) (top) IR spectra taken during TPD experiment for an initial preparation of 30 L CO exposure at  $T_{exp} = 300$  K on  $(2 \times 1)$ -O/Rh(111). The transition from a single peak at  $2088$ – $2068 \text{ cm}^{-1}$ , with a limited coexistence around 300 K. (b) 2D plot to highlight the peak shift. (c) IR spectra for 0.75 ML CO on Rh(111) during TPD ramp and (d) 2D plot to highlight smooth shift in maxima.

that CO oxidation occurred along the desorption pathway, as the chemical state was the same, as indicated by the C–O absorption peak location. However, the steady decrease in RAIRS intensity with  $\theta_{CO}$  shows that RAIRS intensity was proportional to the CO coverage on the oxygenated surface.

#### IV. SUMMARY AND CONCLUSION

The intensity and location of the C–O stretch from the surface IR spectra of CO on Rh(111) and  $(2 \times 1)$ -O/Rh(111) clearly depended on the surface temperature. On clean Rh(111), CO deposited at 300 K yielded a sharp C–O absorption peak between  $2072$  and  $2086 \text{ cm}^{-1}$ , characteristic of adsorption on Rh atop sites, and a significantly smaller, broad peak near  $1850 \text{ cm}^{-1}$  corresponding to binding on Rh bridge sites. Upon heating in a TPD experiment, the atop C–O stretch first increased in intensity, before decreasing and redshifting as  $\theta_{CO}$  decreased. Alternatively, RAIRS of CO on  $(2 \times 1)$ -O/Rh(111) gave only the atop C–O stretch feature initially at  $2088.5 \text{ cm}^{-1}$ , which shifted to  $\approx 2070 \text{ cm}^{-1}$  with heating and the progress of CO oxidation until it too diminished in intensity and redshifted as seen on clean Rh(111). These results show that quantitative RAIRS requires more than only peak intensity. Furthermore, because the CO chemical environment was the same whether  $\text{O}_{ad}$  was present or not, CO oxidation occurs along the desorption

pathway. These results show the subtle interplay between coverage and temperature for CO oxidation on rhodium surfaces.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Elizabeth A. Jamka:** Conceptualization (equal); Investigation (lead); Writing – original draft (lead). **Maxwell Z. Gillum:** Investigation (supporting); Writing – review & editing (supporting). **Christina N. Grytshyn-Giger:** Investigation (supporting); Writing – review & editing (supporting). **Faith J. Lewis:** Investigation (supporting); Writing – review & editing (supporting). **Daniel R. Killelea:** Conceptualization (equal); Funding acquisition (lead); Supervision (lead); Writing – review & editing (equal).

### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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